DIRECT WRITE DISPENSER PRINTING OF ZINC MICROBATTERIES

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Abstract: The need for energy dense microbatteries with miniature dimensions has prompted the development of unconventional materials, cell geometries, and processing methods. This work will highlight our materials investigations, deposition methods, and device performance of a printed zinc-manganese dioxide polymer microbattery. We have developed a direct write dispenser printing method with the ability to fabricate energy storage devices and precisely deposit and pattern these components onto any substrates. The use of a unique ionic liquid swelled into a gel electrolyte with solid-like mechanical strength and liquid-like charge transport properties has enabled this simple fabrication process by eliminating any liquid components that may require hermetic packaging. Initial microbattery tests and cycle behavior are discussed, and after an initial activation of the cathode material, a cell discharge capacity and energy density of 1.05 mAh/cm\textsuperscript{2} and 0.37 mW-hr/cm\textsuperscript{2} were measured, respectively.

Keywords: microbattery, dispenser printing, direct write, gel electrolyte, zinc battery

INTRODUCTION

Although research efforts in developing microbatteries, especially for autonomous wireless sensor platforms, have been promising, the successful implementation of these energy storage components has continued to be stymied by the need for new processing paradigms, materials and geometric configurations \cite{1}. We present a simple, solutions-based process for integrating rechargeable zinc-metal oxide microbatteries directly onto microdevice substrates. With the development of electrochemical materials compatible with this process, we have fabricated and tested an initial prototype.

Typically microbatteries are defined as energy storage reservoirs occupying less than a few square millimeters of a substrate and capable of supplying milliwatt-hour energy and milliwatt power densities. For microdevice applications requiring substantial energy storage capacities, processing methods capable of depositing thick films of electrode materials within small footprint areas are necessary. We have developed a direct-write dispenser printing process with the ability to additively pattern a wide range of solutions, suspensions, and slurries (more generally known as “inks”) into films with lateral and vertical precision between 10-200 µm. As an additive process, dispenser printing offers an easy method to deposit materials with minimal fabrication steps, energy inputs, and negligible waste generation. This versatile tool has been used to fabricate a variety of devices including electrochemical capacitors \cite{2}, thermoelectric energy harvesters \cite{3}, and the magnetic proof masses on the ends of MEMS-cantilever current sensors \cite{4}.

The most common rechargeable battery chemistries are lithium-ion and zinc alkaline systems, and microbattery prototypes using both chemistries have been demonstrated with similar output performances \cite{5,6}. We have modified the electrolyte/separator of a zinc-metal oxide battery, replacing the traditionally used alkaline liquid component with a room temperature ionic liquid electrolyte swelled into a polymer to form a gel. Ionic liquids are a novel class of solvents that are molten salts at room temperature with interesting properties including high ionic conductivity, large electrochemical and temperature stabilities, and negligible vapor pressures \cite{7}. Because of these characteristics, gel electrolytes incorporating ionic liquids have ion transport properties a few orders of magnitude greater than other polymeric or solid-state electrolyte systems \cite{8} and are structurally robust, able to maintain physical separation between the electrodes even under compression. Furthermore, the gel uniquely does not dry out or “sweat” since the ionic liquids are non-volatile.

Dispenser printed microbatteries composed of zinc and manganese dioxide slurry electrodes sandwiching an ionic liquid gel electrolyte were fabricated. This work will detail the materials development, printing fabrication process, resulting microbattery device performance, and prospects of this system.

EXPERIMENTAL

Electrode films were deposited as slurries composed of powders, additives, a common polymer binder, and a removable solvent that tailors the
viscosity of the ink. The polymer binder and solvent used were poly(vinylidene fluoride-hexafluoropropylene), (PVDF-HFP from Kynar Flex 2801), and n-methyl-2-pyrrolidone (NMP from Sigma Aldrich), respectively. The zinc electrode was composed of 95 wt. % zinc powder (Alfa-Aesar) and 5 wt. % PVDF-HFP. Manganese dioxide (MnO$_2$) electrodes contained 90 wt. % activated MnO$_2$ powder (Alfa Aesar), 6 wt. % acetylene black conductive filler (Alfa Aesar), and 4 wt. % PVDF-HFP. The gel electrolyte was composed of a 1:1 mixture of PVDF-HFP and 0.5 M solution of zinc trifluoromethanesulfonate (Zn$^+$Tf$^-$) salt dissolved in 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIM$^+$Tf$^-$) ionic liquid. These inks were printed into designated patterns, and multiple films were deposited in a successive fashion to form a stacked microbattery configuration as shown in Figure 1.

Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) experiments were conducted with a Gamry Reference 600 Potentiostat/Galvanostat/ZRA. All AC impedance measurements were performed potentiostatically with a DC voltage of 0V and an AC voltage of 5mV within a frequency range of 10mHz – 10kHz. Viscosity measurements were taken using a Brookfield LVDV III+ Cone–Plate rheometer. All galvanostatic and cycling measurements were conducted using a custom potentiostat/galvanostat [9]. All cycled cells were tested in the ambient at room temperature without encapsulation. Measurements are normalized according to the substrate footprint area occupied, (not the surface areas of the electrodes), as this usually is the most restrictive parameter in designing microbatteries for microdevices.

RESULTS AND DISCUSSION

Ionic liquid electrolyte

The ionic liquids electrolyte electrochemical properties were optimized with respect to its zinc salt concentration between 0 – 0.75 M. Cyclic voltammetry was used to determine the electrochemical potential stability of the electrolyte solutions. For all concentrations, the electrolytes showed negligible current densities and therefore were stable between 0 and 3 V with respect to zinc (Fig. 2). This potential range is sufficient for the battery’s operating voltage between 1 – 2 V. As illustrated in Fig. 3, the increased addition of salt to
the ionic liquids resulted in a decrease in ionic conductivity associated with a corresponding viscosity increase measured in the solution. The magnitude of the zinc dissolution (Zn → Zn^{2+} + 2e^-) and converse deposition reactions with respect to electrolyte concentration were determined by comparing current densities measured using cyclic voltammetry. While the current density showed an increasing trend with higher zinc salt concentrations in the ionic liquid, the cells no longer exhibited reversible Zn/Zn^{2+} behavior above 0.5 M (Fig. 4). From these properties, it was determined that a 0.5 M zinc salt concentration in BMIM^+Tf^- has the most desirable electrochemical and physical properties and was used as our battery’s liquid electrolyte solution.

**Ionic liquid gel electrolyte**

PVDF-HFP co-polymers are often used in electrochemical systems because of their ability to remain a structurally robust material while absorbing large volumes of liquid when used as a gel. Our previous work has shown that the gel electrolyte ionic conductivity is negligibly diminished compared to the neat liquid property, and therefore favorable for battery electrolytes which require good charge transport for high power performance [10]. The gel is composed of crystalline junctions providing mechanical strength dispersed in amorphous regions swelled with liquid. As shown in Fig. 5, the “grains” in the gel are observed to expand in volume as more liquid is incorporated. Using the ionic liquid electrolyte developed in the previous section, an increase of more than 350 % in grain volume could be observed in the PVDF-HFP, and an optimal gel composition of 1:1 polymer to ionic liquid electrolyte weight ratio was employed because of its high ionic conductivity (~ 3 mS/cm) and mechanical integrity maintained even under substantial compression and temperatures.

**Microbattery testing**

A microbattery was dispenser printed using the process schematically illustrated in Figure 1. The cell occupied 0.49 cm² and for various samples the electrode dimensions ranged between 50 - 80 µm while electrolyte thicknesses of 15 - 30 µm were measured. The zinc slurry served as both the electrode and its own current collector, while a nickel foil substrate was used as the current collector of the manganese dioxide electrode. This simulates a pre-deposited metallic film on a substrate through deposition processes used in patterning neighboring components. We are also currently developing a nickel current collector slurry so that conceivably, the microbattery will be printable on any substrate.

The microbattery was cycled using galvanostatic constant current algorithms. Representative charge and discharge potentials with respect to capacity are shown in Fig. 6 for the third and eleventh cycle. Initial cycles of many microbattery samples have often exhibited variable and sometimes erratic charge and discharge behavior, which may be attributed to phase Fig. 5: Gel electrolyte “grains” swell and increase in size with added liquid.

![Fig. 5: Gel electrolyte “grains” swell and increase in size with added liquid.](image)

Fig. 7: Initial cycle behavior shows activation of MnO_2 electrode between cycle 7-9, resulting in an increase in discharge capacity. I = 0.1 mA/cm²

Fig. 6: Battery constant current charge and discharge between 1.2 – 1.9 V for third and eleventh cycle. Activation of the MnO_2 electrode causes a capacity increase I = 0.1 mA/cm².
changes in the MnO₂ electrode. Within the first few cycles, manganese dioxide undergoes an activation process either due to an interfacial surface film formation and/or the crystalline material becoming amorphous. The eleventh cycle displays a knee at 1.5 V during charge, which may indicate a phase change occurring at this potential, and a higher film resistance is detected by the vertical potential drop when switching between charge and discharge. The activation of the MnO₂ electrode has led to more than a two-fold increase in energy storage capacity of the cell. Further studies on this phenomenon will be conducted. After from the first ten cycles shown in Fig. 7, the discharge capacity performance stabilized at 1.05 mA·hr/cm² within the first 25 cycles with a corresponding areal energy density of 0.37 mW·hr/cm².

Future studies will include the determination of the microbattery’s power performance, further understanding of the electrolyte compatibility with both electrodes, and the effects of processing parameters on electrochemical performance. Long term cycle and materials stability as a result of the environment and use conditions will also be investigated.

CONCLUSION
A printed zinc-manganese dioxide microbattery with an ionic liquid gel electrolyte was fabricated. Ionic liquids were used because of their unique properties, including negligible vapor pressure, high electrochemical and temperature stability, and good ion transport. This was swelled into a polymer to form a gel electrolyte with the mechanical strength to provide physical separation between the electrodes even under compression, yet maintained good electrochemical and charge transport properties through the film. Manganese dioxide exhibited compatibility with the gel electrolyte, and when cycled in a full battery structure, exhibited an activation behavior within the initial 10 cycles that led to increased capacity. Future experiments investigating this phenomenon as well as device performance are underway. A cell discharge capacity and energy density of 1.05 mAh/cm² and 0.37 mW·hr/cm², respectively, were measured.

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REFERENCES