# Development and manufacture of printable next-generation gel polymer ionic liquid electrolyte for Zn/MnO$_2$ batteries

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**Abstract.** While much energy storage research focuses on the performance of individual components, such as the electrolyte or a single electrode, few investigate the electrochemical system as a whole. This research reports on the design, composition, and performance of a Zn/MnO$_2$ battery as affected by the manufacturing method and next-generation gel polymer electrolyte composed of the ionic liquid [BMIM][Otf], ZnOtf salt, and PVDF-HFP polymer binder. Materials and manufacturing tests are discussed with a focus on water concentration, surface features as produced by printing processes, and the effect of including a gel polymer phase. Cells produced for this research generated open circuit voltages from 1.0 to 1.3 V. A dry [BMIM][Otf] electrolyte was found to have 87.3 ppm of H$_2$O, while an electrolyte produced in ambient conditions contained 12400 ppm of H$_2$O. Cells produced in a dry, Ar environment had an average discharge capacity of 0.0137 mAh/cm$^2$, while one produced in an ambient environment exhibited a discharge capacity at 0.05 mAh/cm$^2$. Surface features varied significantly by printing method, where a doctor blade produced the most consistent features. The preliminary results herein suggest that water, surface roughness, and the gel polymer play important roles in affecting the performance of printed energy storage.

## 1. Introduction

With the strain on global electrical grids increasing year after year, there is an imperative need to develop and install reliable, long-lasting energy storage solutions. The utilization of new materials such as ionic liquid electrolytes [1] and gel polymers [2] with additive manufacturing techniques [3] exhibit the potential for creating flexible, rechargeable energy storage solutions can fit many geometries and scales. In order to succeed at that goal, it is imperative that the parameters that influence system performance, from electrochemical to production, be well-modeled and understood.

Energy storage research is often conducted on a single component. These experiments test performance separate from full cells, thus leaving a knowledge gap in understanding how one part can affect the system as a whole. For instance, much research surrounding ionic liquid-based electrolytes explores proof of concept functionality among various material options instead of determining robustness with respect to many parameters. Such qualities are important to know for manufacturing control to attain consistent device performance.

Printed electrochemical energy storage composed of a manganese dioxide ($MnO_2$) slurry cathode, zinc (Zn) foil anode, and an ionic liquid gel polymer electrolyte were produced with several different compositions, environments, and manufacturing methods. This work details the variability between processes and the identification of the influential parameters as determined through cell discharge capacity.

## 2. Experimental

Cathode ink composed of 9 g of $MnO_2$ powder, 0.5 g of carbon black, 6.6 g of modified styrene-butadiene copolymer (PSBR), and 4 g of DI water was deposited via flexographic printing, doctor blade casting, and dispenser printing to create cathode films. The ink was mixed in a ball milling machine for 120 min at 30 Hz to evenly disperse the components. Zinc foil with a purity of 99.95%+ and thickness of 50 $\mu$m was purchased from Goodfellow Corp. and used as the anode.

The electrolyte was composed of 0.2 g of zinc trifluoromethanesulfonate (ZnOtf) (purchased from Sigma-Aldrich) dissolved in 3 g of 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][Otf]) ionic liquid (IL) (purchased from EMD Chemical). A Mettler Toldeo DL39 Karl Fischer coulometer was used to determine the amount of water present in each electrolyte composition. Electrolytes were produced in a dry, Ar-filled glovebox and in ambient laboratory conditions.

The gel polymer was produced by mixing 1 g of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) polymer to 5 g of n-methylpyrrollidone (NMP) organic solvent. 1 g of the electrolyte was dispensed into the gel polymer mixture to yield the gel polymer electrolyte with a ratio of 1 g of electrolyte to 1 g of PVDF-HFP polymer.

Coin cells (CR2330) with a 1.27 cm diameter punched cathode disc and a 1.43 cm diameter punched anode disc were assembled in a dry, Ar-filled glovebox. A 26 $\mu$m thick Celgard separator insulated the electrodes from each other while still allowing for ions to conduct between interfaces. Electrolyte was dispensed onto both sides of the separator to provide a good interface with the electrodes. These cells were charged and discharged, from 1.0 V to 1.8 V, 100 times on a commercial Maccor tester.

Sandwich cells were produced in ambient conditions by casting gel polymer electrolyte with a doctor blade on cathode and anode strips that were cut to have a width of 1 cm. The electrodes with gel polymer electrolyte were dried at 80 °C for 6 h to form a solid electrolyte film. After drying, the electrodes were stacked orthogonally to produce a cell with an active area of 1 $cm^2$. These cells were cycled, from 1.0 V to 1.8 V, for 48 h on a custom galvanostat/potentiostat [4].

An Olympus LEXT OLS4000 laser confocal microscope was used to retrieve 643 $\mu m^2$ area primary surface profiles of cathodes produced via flexographic printing, dispenser printing, and doctor blade casting. Matlab was used to run a Fast Fourier Transform (FFT) with a cutoff wavelength of 80 $\mu$m to produce the waviness profile. Thus the roughness profile was calculated by subtracting the waviness profile from the primary profile.

## 3. Results and Discussion
### 3.1. Water Saturation
[BMIM][Otf] is known to be hygroscopic, but it is currently unknown how environmentally sensitive [BMIM][Otf]-based electrolytes are [5]. Water absorbed from the environment has the
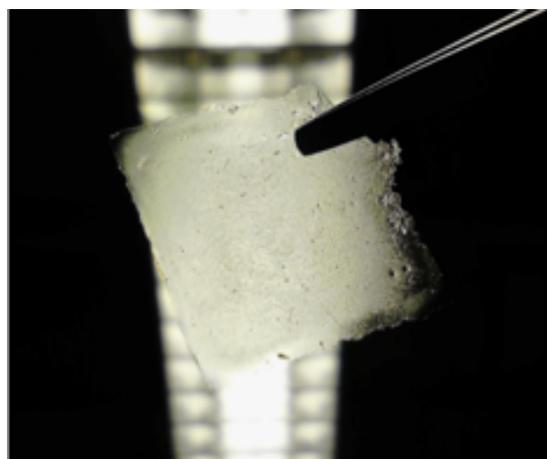
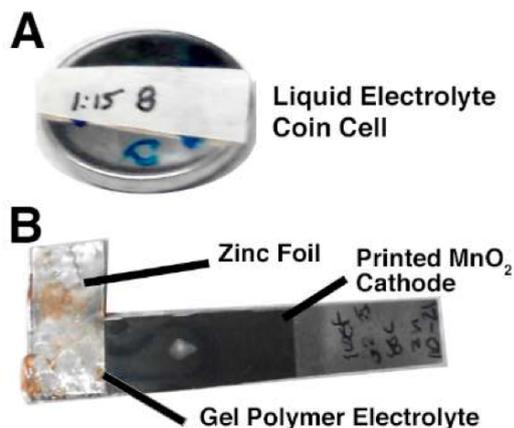**Figure 1.** Gel polymer ionic liquid electrolyte.



**Figure 2.** Test cell form factors. A) Coin cell containing liquid electrolyte (no PVDF-HFP gel component); B) Sandwich cell.

potential to take part in the reactions of the battery and may affect the discharge performance of the battery cells, thus it is important to determine how cells respond to the presence of water at various concentrations.

The compositions produced and their respective water contents are shown in Table 1. The saturated sample produced in the ambient laboratory environment was exposed to air with an average relative humidity of 50%. All cells produced had open circuit voltages between 1.0 V and 1.3 V. Cells of each electrolyte composition were produced and cycled 100 times to determine their average discharge capacity normalized per unit area, as shown in Figure 3.

As expected, the addition of the ZnOtf salt to the ionic liquid increased the water content from 37.5 ppm of $H_2O$ to 87.3 ppm of $H_2O$. Interestingly, the electrolyte was able to hold up to 12,400 ppm of $H_2O$ and, as indicated in Figure 3, the cell produced with that electrolyte had the highest discharge capacity. These results indicate that exposure to a humid environment can have a strong effect on the composition of battery cells produced. While the trend over this subset of data indicates that water has a beneficial effect on cell discharge capacity, it is unknown whether a humid manufacturing environment will affect other aspects of the cell such as cycle life or thermal stability. Further experiments are required to answer these questions and to determine if any optimum composition exists.
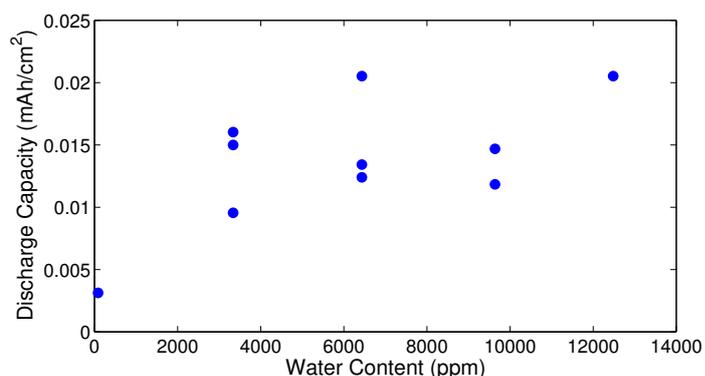


**Figure 3.** Discharge capacity of coin cells without a gel polymer. Each cell was cycled 100 times.

**Table 1.** Amount of water present in neat [BMIM][Otf] and several electrolyte samples.

| Sample Label | Composition | Water Content (ppm) |
| --- | --- | --- |
| Neat IL | Neat [BMIM][Otf] in dry Ar only | 37.5 |
| Dry | Electrolyte with all components dried in Ar | 87.3 |
| Saturated | Electrolyte produced in ambient environment | 12400 |
| 1:3 Mixture | 1 g of Dry mixed with 3 g of Saturated | 9640 |
| 2:2 Mixture | 2 g of Dry mixed with 2 g of Saturated | 6430 |
| 3:1 Mixture | 3 g of Dry mixed with 1 g of Saturated | 3340 |

*3.2. Surface Roughness*

With many printing options available, it is important to determine how surface characteristics are influenced manufacturing method. Roughness and waviness are common metrics used to quantify such features. The Figures 4 and 5 show the average line roughness and average line waviness for a 643 $\mu$m$^2$ sample for each manufacturing method. The dispenser printer has both the least uniform roughness and waviness across the sample area, with variation on the order of 2.5 $\mu$m for average line roughness and 50 $\mu$m from highest to lowest average line waviness. While flexographc printing and doctor blade casting appear approximately equivalent in terms of surface roughness, the flexographic printer exhibits a greater degree of non-uniformity than the doctor blade cast with two distinct troughs and peaks ranging from approximately -5.99 $\mu$m to 6.88 $\mu$m. This may be the result of viscous fingering, a phenomenon where surface features are formed on the printer as air is pressed between the rollers with the ink.
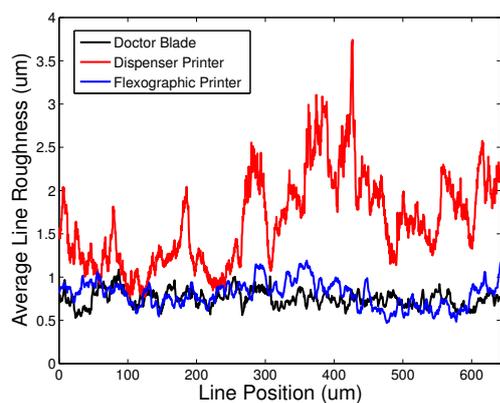


**Figure 4.** Comparison of resulting cathode average line roughness ($R_a$) as produced by doctor blade, dispenser printer, and flexographic printer.
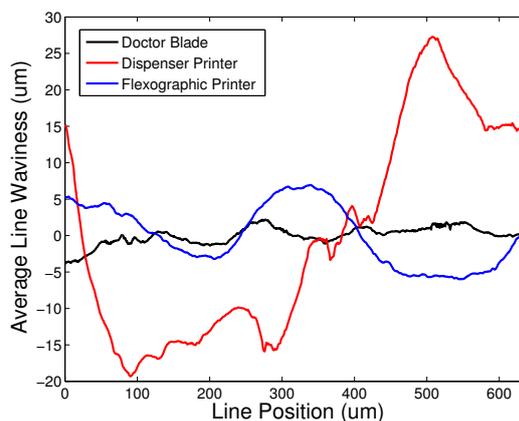


**Figure 5.** Comparison of resulting cathode average line waviness ($W_a$) with a zero average as produced by doctor blade, dispenser printer, and flexographic printer.

*3.3. Gel Polymer Performance*

Each of the samples in Figure 6 utilized a doctor blade cast cathode. The sandwich and ambient coin cells were cycled with the custom galvanostat/potentiostat, while the coin cell produced in

Ar was cycled on a Maccor. All cells used the same cycling procedure with a charge to 1.8 V with constant 0.1 mA current, hold at a constant 1.8 V for 3 minutes, 20 seconds, discharge to 1.0 V with constant 0.1 mA, then rest for 5 minutes. The coin cells, neither of which contained any gel polymer component, have an expected drop in performance after the first cycle. Interestingly, the sandwich cell improves in performance as the cycles continue, although not smoothly, from 0.024 mAh/cm$^2$ to 0.077 mAh/cm$^2$. This phenomenon has been seen in other work with similar materials and composition [3].

The effect seems to be connected to the inclusion of the gel polymer component, although the specific mechanism related to the materials has cannot yet be determined from this initial investigation. Further experiments will be conducted with a focus on interfacial interactions.
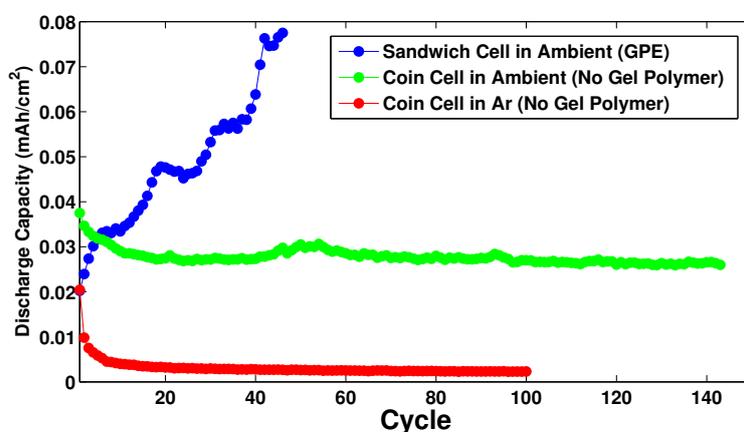


**Figure 6.** Comparison of performance of a sandwich cell produced with a gel polymer electrolyte in ambient laboratory conditions, a coin cell produced with a liquid electrolyte (no gel polymer) in ambient laboratory conditions, and a coin cell produced with a liquid electrolyte in an Ar atmosphere.

## 4. Conclusion
The printed Zn/MnO$_2$ battery with an ionic liquid-based gel polymer electrolyte was successfully fabricated and tested to determine parameters that most influence performance. A greater amount of water dissolved into the electrolyte seems to improve cell performance, although the current subset of data does not yet indicate an optimum composition. Doctor blade casting exhibited the most consistent roughness and waviness, while dispenser printing exhibited the most variability with the highest range. Both doctor blade casting and flexographic printing may be improved with process controls. The gel polymer component seems to provide a boon to cell performance, causing the discharge capacity to increase with number of cycles. Future experiments investigating these phenomena and the underlying mechanisms are underway.

## 5. Acknowledgements

## References
[1] Kuboki T, Okuyama T, Ohsaki T and Takami N 2005 *Journal of power sources* **146** 766–769
[2] Kumar G G and Sampath S 2003 *Journal of The Electrochemical Society* **150** A608–A615
[3] Ho C, Evans J and Wright P 2010 *Journal of Micromechanics and Microengineering* **20** 104009
[4] Steingart D A, Redfern A, Ho C, Wright P and Evans J 2006 *ECS Transactions* **1** 17–22
[5] Cao Y, Chen Y, Sun X, Zhang Z and Mu T 2012 *Physical Chemistry Chemical Physics* **14** 12252