Layer-by-layer fully printed Zn-MnO$_2$ batteries with improved internal resistance and cycle life

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Abstract. This research created direct layer-by-layer printed zinc-based secondary batteries with an ionic liquid-based gel polymer electrolyte to power micro- and meso-scale devices. The effects of additive printing methods on cell discharge capacity, cycle life, and internal resistance are discussed. Fully printed cells have demonstrated average discharge capacities of 0.548 mAh/cm$^2$, energy densities of 8.20 mWh/cm$^3$, and specific energies of 2.46 mWh/g with some cells achieving over 1000 cycles without catastrophic failure. Layer-by-layer printed devices exhibited decreased DC internal resistance and longer cycle life over previous mechanically assembled cells.

1. Introduction

As ionic liquids have grown in use, investigations have been carried out on their applicability in rechargeable batteries [1]. In particular, advancements in zinc-based chemistries with ionic liquid electrolytes have proven the feasibility of creating rechargeable zinc cells through additive manufacturing methods to power micro- and meso-scale devices [2, 3, 4].

Previous work has investigated the feasibility of using gel polymer electrolytes based on the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][Otf]) and the salt zinc trifluoromethanesulfonate (ZnOtf) in Zn-MnO$_2$ secondary battery systems by mechanically assembling cells, but has not investigated the effects of layer-by-layer printing on cell performance [5, 6, 7]. This work improves upon past prototypes by characterizing the effects of fully printing cells and by utilizing a direct layer-by-layer printing process to improve cell performance and cycle life.

2. Experimental Methods

Individual inks were made for the cathode, anode, and electrolyte, the compositions of which are listed in Table 1. The cathode is composed of an MnO$_2$- and carbon-based ink developed for this work. The anode is composed of either zinc foil, for half printed cells, or a Zn and carbon ink similar to the cathode ink, for fully printed cells. The gel polymer electrolyte is composed of PVDF-HFP permeated with the ionic liquid and salt solution ([BMIM][Otf] and ZnOtf). For all inks, PVDF-HFP was first dissolved in NMP to create a gel. Once the gel was
fully homogenized, the respective active materials and fillers were added, and additional NMP was added to tune the rheology (for the cathode and anode inks). The inks were thoroughly mixed and sonicated to ensure adequate homogenization and particle dispersion.

Cells were manufactured using stencil printing and doctor blade coating. A 100 µm thick PET sheet with 1 cm² square holes was used as the stencil. To fabricate cells, the cathodes were first stencil cast into 1 cm² squares on stainless steel foil and dried in a gravity oven at 80°C. The GPE was cast with a doctor blade over the cathodes in multiple passes with increasing blade offset distances, drying partially between layers. Once the GPE was fully dried, the anode was either stencil cast directly on top of the GPE and dried (for fully printed cells), or 1 cm² squares of zinc foil were placed on top (for half printed cells). Throughout the casting process, the cells were maintained at approximately 80°C by adhering the substrate to an aluminum block, which acted as a thermal sink and maintained film temperatures constant. After the entire cell was dried, the cells were peeled from the foil, cut out with a razor blade, and sealed in stainless steel 2032 coin cells (MTI Corp) (Figure 1). Half printed cells were manufactured with thick (200 µm) GPE layers, and fully printed cells were manufactured with both thick and thin (70 µm) GPE layers.

Table 1. Compositions of electrode and electrolyte inks. All materials were measured in wt% with additional NMP added to tune rheology.

| Cathode      | Anode      | Electrolyte                      |
|--------------|------------|----------------------------------|
| 86% MnO₂     | 84% Zn     | 67% ZnOtf:[BMIM][Otf] (1:6.5 mass ratio) |
| 6% Acetylene Black | 7% Acetylene Black | –                                |
| 8% PVDF-HFP  | 9% PVDF-HFP| 33% PVDF-HFP                     |

Figure 1. Left: front view of fully printed cell. Layers from back to front: printed MnO₂ cathode, gel polymer electrolyte, printed Zn anode; Right: side view of fully printed cell.
Mechanically assembled cells were manufactured by stencil printing the cathode in 1 cm\(^2\) squares, casting the GPE in flat circular disks about 500 \(\mu\)m thick, cutting out 1 cm\(^2\) squares of zinc foil, and arranging them in a sandwich structure in a coin cell, with additional electrolyte added at the interfaces for wetting.

The cells were cycled on a Neware battery tester with a constant current charging profile and were cycled from 1.0-1.8V (Table 2). Cell performance data was collected from the Neware testing software. SEM images were taken with a Hitachi TM-1000 Tabletop Scanning Electron Microscope. Samples were prepared by cutting cells in half with a razor blade and mounting them on 90\(^\circ\) stages to examine the cross section.

| Table 2. Cycling profile for a single step |
|------------------------------------------|
| Step Name                  | Parameters                     |
| 1  Constant Current Charge   | 125 \(\mu\)A from 1.0-1.8V     |
| 2  Constant Current Discharge | -125 \(\mu\)A from 1.8-1.0V    |
| 3  Rest                      | 3 minutes                      |

3. Results & Discussion

3.1. Interfacial Cohesion of Printed Components

SEM images of fully printed cells with thick and thin GPE layers illustrate the interfacial cohesion between printed components (Figure 2). The interfaces between the electrodes and GPE are continuous and free from any delamination. As a consequence of the processing parameters, the polymer structure in each additional layer is allowed to mix with the previous layer, forming a continuous structure with minimal interfacial discontinuities and improving cell performance.

![Figure 2. Cross sections of fully printed cells with thick and thin GPEs. Left: fully printed, thick GPE cell; bottom: fully printed, thin GPE cell](image)

3.2. Discharge Capacity

Figure 3 presents the discharge capacities of the first 100 cycles for all cells. Figure 4 presents the discharge capacities of the first 250 cycles for both fully printed cells. The mechanically
assembled and half printed cells were cycled until failure, but testing was terminated before the fully printed cells reached failure.

![Figure 3](image1.png)  
**Figure 3.** Discharge capacities of first 100 cycles for all cells. Only mechanically assembled and half printed cells were cycled until failure.

![Figure 4](image2.png)  
**Figure 4.** Discharge capacities of first 250 cycles for fully printed cells. Cells were cycled until tests were terminated.

Both fully printed cells demonstrated higher discharge capacities compared to the mechanically assembled cell for the same number of cycles, while the half printed cell demonstrated an equal discharge capacity in the same period. The fully printed, thin GPE cell exhibited the highest discharge capacity of all cells. Averaged over the data collected, the cell had a discharge capacity of 0.548 mAh/cm², energy density of 8.20 mWh/cm³, and specific energy of 2.46 mWh/g. However, the half printed cell sustained a more stable discharge capacity over its lifetime compared to the fully printed cells.

The half printed and mechanically assembled cells exhibited continuously decaying discharge capacities, but the fully printed cells experienced a “break in” period where the discharge capacity initially increased before decaying. Further work is needed to provide confirmation, but this is likely due to the concentration of zinc at the electrolyte interface in the printed anode increasing with initial replating cycles, as opposed to the bulk zinc foil anode which already provided the highest concentration of zinc possible. The faster rate of decay in discharge capacity for the fully printed cells compared to the other two may also be a result of the composite nature of the printed zinc anode.

### 3.3. Cycle Life

While all half printed and fully printed cells demonstrated improved cycle life compared to mechanically assembled cells, fully printed cells exhibited about an order of magnitude improvement in cycle life (Figures 3 and 4). Previously, mechanically assembled cell failure was consistently accompanied by delamination between the cathode and electrolyte layers, but the interfacial cohesion between those two components in printed cells prevents delamination from occurring. Fully printed cells may have longer cycle lives than half printed cells due to similar interfacial cohesion issues at the anode, but additional experiments are necessary to confirm.

Figure 5 presents the full cycle life of a fully printed, thick GPE cell. Testing was terminated beyond 1000 cycles. While the discharge capacity decayed to a level too low for useful work, the cell did not reach a point where it was no longer able to cycle, in contrast to mechanically assembled and half printed cells.
Figure 5. Cycle life of fully printed, thick GPE cell. Cycle life exceed 1000 cycles without cell failure.

Figure 6. Average internal resistances of all cells at rest.

3.4. Internal Resistance

Figure 6 presents the average DC internal resistances of all cells while at rest between testing cycles. The internal resistances of half printed and fully printed cells are lower than the internal resistance of mechanically assembled cells. While the internal resistance of fully printed thick GPE cells is the highest among all printed cells, the mechanically assembled and half printed cells contained a zinc foil anode, which has lower resistance than the printed zinc anode. However, the fully printed thin GPE cells exhibited the lowest internal resistance of all printed cells, which may be attributed primarily to the difference in GPE thickness between cells as well as improved interfacial cohesion (Figure 2). This lower internal resistance therefore corresponds to higher discharge capacity, as the lower resistive losses due to the thinner GPE layer result in better cell performance (Figure 3).

4. Conclusion

Layer-by-layer fully printed Zn-MnO$_2$ secondary cells with an ionic liquid-based gel polymer electrolyte were successfully manufactured and cycled. Fully printed cells showed significant improvements in discharge capacity, cycle life, and internal resistance over previously mechanically assembled cells. These improvements are in large part due to the increased interfacial cohesion between layers afforded by direct layer-by-layer printing. Future experiments will optimize ink compositions and process parameters to improve performance metrics and will scale up printing to produce larger cells.

References

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