Pulsed discharge of printed secondary Zn-MnO$_2$ batteries for IoT and wearable devices

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Abstract. This paper reports the manufacturing and testing via pulsed discharging of printed secondary Zn-MnO$_2$ batteries with ionic liquid gel polymer electrolyte (GPE) for IoT and wearable devices. Printed cells under constant current discharge conditions demonstrated average DC internal resistances of 175-225 $\Omega$/cm$^2$. Printed cells under pulsed discharge current demonstrated decreasing internal resistances with increasing cycle number, reaching an average plateau of 125 $\Omega$/cm$^2$ after 50 cycles and remaining beyond 650 cycles. This work improves upon manufacturing methods reported at PowerMEMS 2015 and investigates system-level compatibility with IoT and wearable devices.

1. Introduction
As devices for the Internet of Things continue to develop, there is a need for safe and inexpensive energy storage to power them [1]. These devices generally operate in two regimes: a long period of low-current draw (e.g. sleep mode), or a short, high-current pulse (e.g. radio transmission) [2].

While battery performance under constant current discharge is a well-understood metric, performance under pulsed discharging, especially for smaller footprint batteries (on the order of 1 cm$^2$), must be better characterized. Of particular importance is the cell internal resistance, which is proportional to the ohmic (IR) drop observed upon pulse discharging. The magnitude of this drop must be minimized in order to maintain an adequate voltage to power device electronics and avoid brownouts as well as to maximize useable cell capacity (Fig. 1).

This work improves upon a previously presented layer-by-layer manufacturing process in order to decrease cell internal resistance and characterizes fully printed cell performance under a pulsed discharging regime [3].

2. Experimental Methods
Cells utilize a Zn-MnO$_2$ chemistry with an ionic liquid-based gel polymer electrolyte. The gel polymer electrolyte functions as both a mechanical separator layer as well as an ion permeable layer to facilitate ion transport between the cathode and anode. The ionic liquid [BMIM][OTf] with the dissolved salt Zn(OTf)$_2$ was used as the electrochemically functional electrolyte. This system has been proven to be rechargeable, as has been previously reported [3, 4].
Figure 1. Constant current capacity vs. pulsed current capacity. Due to ohmic drops exceeding the device voltage limit, effective cell capacity and runtime are diminished.

Table 1. Compositions of electrode and electrolyte inks after drying. All materials were measured in wt%.

| Cathode   | Anode   | Electrolyte                              |
|-----------|---------|------------------------------------------|
| 91% MnO$_2$ | 91% Zn  | 75% 0.5M ZnOtf in [BMIM][Otf]            |
| 2.57% Acetylene Black | 2.57% Acetylene Black | –                                      |
| 6.43% PVDF-HFP | 6.43% PVDF-HFP | 25% PVDF-HFP                            |

Separate inks were made for the cathode, anode, and gel polymer electrolyte, whose compositions are presented in Table 1. The electrode ink compositions were chosen to minimize printed film resistivity. Cells were manufactured using a layer-by-layer additive process. All casting steps took place in ambient at room temperature, and drying steps took place in air or under vacuum at 80°C. After the cells were fully dried, they were removed from the substrate and sealed in stainless steel 2032 coin cells (MTI Corp) for testing. The ink preparation and manufacturing processes were followed as previously reported [3].

Cells were tested on a Bio-Logic BCS 805/810 battery tester. Constant current discharge tests were performed from 1.0-1.8V with 125μA charge/discharge current. For pulsed discharge tests, a 1mA discharge pulse was applied to the cell 5 times for 4ms each, resting 1s between pulses. After discharging, the cell was charged to 1.8V at 125μA and then allowed to rest for 5 minutes before repeating (Fig. 2). To measure cell solution resistance, EIS measurements were also taken.

3. Results & Discussion

3.1. Effect of Drying Environment on Internal Resistance

EIS results indicate drying the GPE under vacuum produces cells with lower solution resistance compared to cells dried in air (Fig. 3). This is further supported by DCIR measurements during cycling, as cells dried under vacuum exhibit lower DC internal resistance at rest (Fig. 4). Scanning electron micrographs comparing GPE microstructures indicate variations in porosity as
well as polymer micelle radius (Fig. 5), which could be responsible for this observed difference in internal resistance. The difference in microstructure may affect electrolyte uptake, which could affect ion transport through the separator layer. Further investigation is necessary to characterize the impact of polymer microstructure on cell internal resistance.

3.2. Pulsed Discharging Performance

Figure 6 presents the change in cell internal resistance as a function of cycle life for cells cycled under constant current discharge and pulsed discharge. Cells cycled under pulsed discharge displayed constant internal resistance with increasing cycle number while cells cycled under constant current displayed steadily increasing internal resistance until failure. Furthermore, under pulsed discharging cells, cells cycled repeatable with no loss in performance for over 650 cycles, after which the test was stopped (Fig. 7). This increase in cycle life and plateau in DCIR may be due to the lower magnitude of charge being passed per cycle as well as the shorter time scale for each cycle, inhibiting the number of charge transfer reactions that can occur. Future testing will seek to combine constant current and pulsed discharging to better simulate IoT device operation.
4. Conclusion

Fully printed cells were manufactured in different atmospheres and tested via constant current and pulsed discharge. The resulting GPE microstructures as a result of drying atmosphere and their effects on cell internal resistance were investigated. GPEs dried under vacuum demonstrated lower solution resistance and cell internal resistance. Cells tested under pulsed discharging exhibited lower and more stable DCIR than cells tested under constant current discharge. Under pulsed discharging, cells were able to provide a 1mA, 4ms pulse current for over 650 tested cycles. Future testing will incorporate both discharging regimes into a single test.

References
[1] Swan M 2012 J. Sens. Actuator Netw. 1 217-253
[2] MacKenzie J D and Ho C 2015 Proc. of the IEEE 103 535-553
[3] Kim B, Winslow R, Lin I, Gurrungan K, Evans J and Wright P 2015 J. Phys.: Conf. Series 660
[4] Kumar GG and Sampath S 2003 Solid State Ionics 160 289-300