

Three Dimensional Direct Writing of MnO₂ Battery Cathodes

Christopher Apblett^a, Krista Hawthorne^b, Eric Branson^a, Adam Cook^a, Kyle Fenton^b, and Paul Clem^a

^aSandia National Laboratories
1515 Eubank SE
MS 1349
Albuquerque, NM 87185-1349

^bUniversity of New Mexico
247 Farris Engineering Center
Albuquerque, NM 87131

Abstract:

Thin film printed batteries offer an attractive option for low cost, high energy density storage for the next generation of portable electronics. To meet the rate requirements of these devices, however, requires a high surface area of the battery electrode. This has the unintended consequence of having high self discharge rates for the battery system, resulting in short shelf lives for thin, printed batteries. An alternative approach is to use reserve cell systems, where the electrolyte is only introduced when the battery is put into service. A design for a printed, reserve cell zinc-air battery is introduced, and the manufacture by print-casting of the cathode is demonstrated. The structural hydrophobicity and electrochemical activity of a manganese dioxide oxygen reduction catalyst are demonstrated to be retained in the cast structures.

Background:

As electronic devices shrink and their capabilities expand, an ever increasing demand is placed on the power supply for higher capacity and higher rate capability. However, shrinking device dimensions have the opposite effect on most battery systems. Smaller batteries have less active material in them simply because they are smaller in volume, but also, the percentage of volume relegated to inactive materials within the battery increases as the battery size decreases¹. Additionally, the rate demand on a battery during peak power is formidable, and is limited by the physical area separating the anode and cathode.² One possible solution to this rate limitation is to produce very thin, flat batteries with a minimum of packaging surrounding each cell, but retaining a high surface area to support high rate demand. A number of ultrathin batteries have been fabricated,^{3,4} but rate and self discharge continue to be a challenge. Printing of battery materials has also been demonstrated previously, by printing the zinc anode of an alkaline battery using zinc powder in a solvent as the ink.⁵ Other groups have also been printing battery materials, and have demonstrated function of one or more components of various types of battery systems in thin film form.⁶

One of the challenges, however, for printed batteries is the design limitations inherent in thin film form factors. The rate of self discharge for batteries is related to the area of the separator between the anode and cathode, with higher printed area leading to a higher self discharge. However, larger area is also needed in order to support higher currents without polarization during discharge. For printed batteries which can deliver very high surface areas, the problem of self discharge becomes significant, and the shelf life of these batteries is problematic. However, reserve cell batteries, where the electrolyte is

removed from the separator until a mechanical event introduces the electrolyte, have excellent shelf life, as there is essentially no self discharge until the electrolyte is introduced and the battery becomes active.

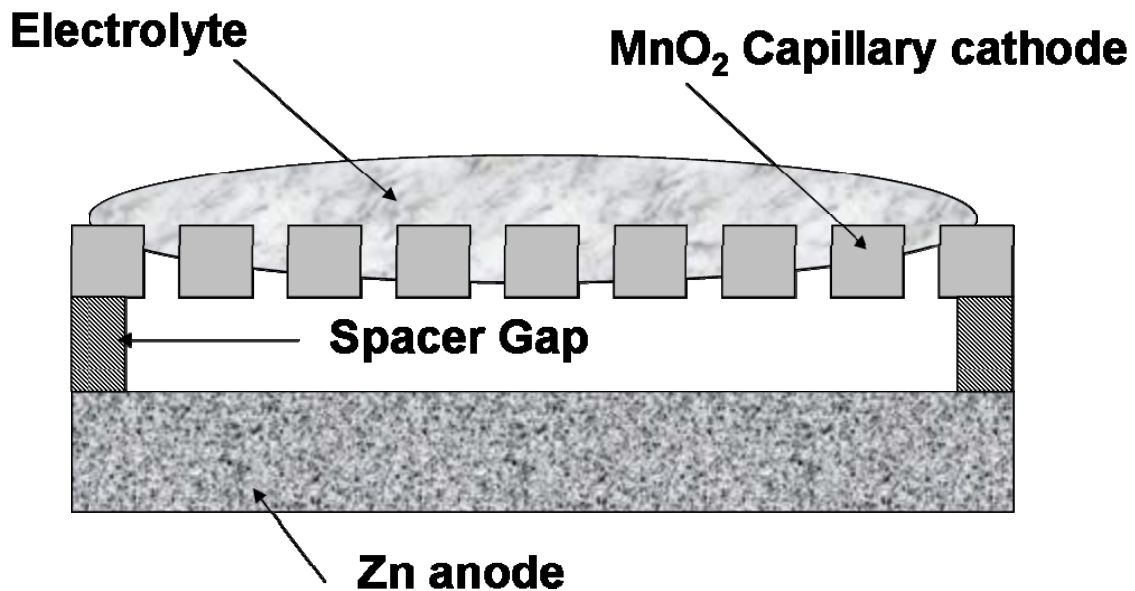


Figure 1: Schematic of a zinc-air reserve printed cell. Key to realizing this technology is a manganese dioxide cathode that can span the spacer gap, be hydrophobic to the electrolyte, and be catalytically active.

One of the highest energy density batteries currently in use is the zinc-air cell, which oxidizes zinc metal and reduces oxygen to form zinc oxide as part of a complex set of reactions in an alkaline aqueous electrolyte. Other than the attractive energy density, this system also lends itself well to being prepared as a reserve cell, since the alkaline media can be removed from the system, and stored elsewhere in the cell. One of the places to store that electrolyte would be over the cathode catalyst, which for zinc-air cell is often manganese dioxide, MnO_2 , as shown schematically in Figure 1. This configuration has the advantage that the electrolyte is kept in reserve, and also helps to reduce the oxygen diffusion into the cell prior to activation. To keep the alkaline media as a reservoir on top of manganese dioxide catalyst, the catalyst would need to be hydrophobic, so that the electrolyte will not seep into the battery over time and activate the cell. Conversely, for good performance, the cathode catalyst needs to be well wetted by the electrolyte, or a high series resistance of the cathode catalyst/electrolyte interface will rob the cell of power. To resolve these two disparate demands for the cathode, this work discusses the development of a printed, structurally hydrophobic electrode that is non-wetting initially, but once the liquid is forced into the structure through an externally applied pressure, the electrolyte wets the cathode catalyst, and battery performance is retained. Structured hydrophobic surfaces have been shown before in silicon⁷, but this represents the first time an active battery material has been structured to demonstrate hydrophobic properties, but yet retain electrochemical accessibility.

Experimental:

Initial work on printed structurally hydrophobic MnO_2 was performed using commercial grade polyvinyl butyrol (PVB, Sigma) and commercially available MnO_2 that was subsequently treated using the Ikeda method.⁸ Ink formulations for this were 5% MnO_2 , 90% graphite, 5% PVB, with a total solids content of 50% in ethanol (Sigma). Casting of structures was done in DI water using a constant pressure cast head (EFD, Inc) using a 100 μm diameter tip. Casting was done on a gantry system using slides and motors from Parker, and utilizing a Galil based software control system. Subsequent inks exchanged the PVB binder for polyvinylidene fluoride (PVDF) for electrochemical compatibility with approximately the same mass ratio in the ink, and exchanged the alcohol solvent system for n-methyl pyrrolidone (NMP, Sigma). Final electrochemical test coupons were cast using 87% MnO_2 and 8% graphite powder, with the balance PVDF. Electrochemical tests were performed in a standard three electrode configuration using a Bioanalytical Systems test rig, and driven using an Epsilon potentiostat, platinum counterelectrodes, and a saturated potassium chloride/silver/silver chloride reference electrode. Samples were prepared on commercial grade nickel foil (Alfa-Aesar) with a polymeric coating on the back of the foil to prevent the nickel from being oxidized and reduced during voltammetry. Sweep rates for cyclic voltammetry were 10mV/sec, unless otherwise noted. Electrolytes for these tests were 1N potassium hydroxide (KOH, Sigma) in DI water, unless otherwise noted. Tests in the absence of oxygen were performed with a nitrogen sparge (TriGas, 99.95%) and with an oxygen sparge for the oxygen reduction test (Trigas, 99.98%).

Results:

In the initial formulations of the inks, the published results for use of phase separation methods for solvated polymers were followed.⁹ This involved the use of PVB as a binder, and produced good structural members with high aspect ratio. However, this binder was found to have two significant drawbacks. First, the binder is electroactive in the window between zinc oxidation (at roughly 0V vs. saturated Ag/AgCl in an alkaline solution) and oxygen reduction (about 1.2V under the same conditions), meaning that the binder itself can be oxidized and/or reduced while the battery is running. The second is that the binder is slowly oxidized and solvated by the alkaline electrolyte over time. Because of these issues, the binder was changed to PVDF, which is not electrochemically active in the Zn- O_2 voltage window, and is stable against alkaline media. PVDF is not very soluble in alcohols, however, and so the solvent system was changed to NMP, which was known to solvate PVDF, but would still provide the phase separation necessary to have fast solidification when cast underwater.

The cast cathode electrodes had to have three properties; they had to have a high (yet controllable) surface area and reasonable structural stability, they had to be structurally hydrophobic to alkaline media, yet still wet sufficiently to allow for battery operation, and they had to demonstrate good electrochemical activity under polarization. For the first criterion, a simple mesh electrode was printed under water, and then removed and allowed to dry. It was then cleaved from the printing substrate using a razor edge, and was still structural after that time. Likewise, the second criterion is for hydrophobicity, and a small mesh electrode was printed 3 layers deep to test this. The MnO_2 ink is normally reasonably hydrophilic up to a binder loading of 10 weight percent, at which is

becomes slightly hydrophobic. The current formulation is at 5 wt.%, and therefore is expected to be hydrophilic in the planar form, with a wetting angle of roughly 45 degrees. When cast as a mesh, however, it is expected to increase in hydrophobicity due to the structure of the electrode. This effect has been demonstrated before for a number of materials.¹⁰ A drop of alkaline media is shown on the electrode in Figure 2, and is indeed hydrophobic, with a wetting angle of ~100 degrees.

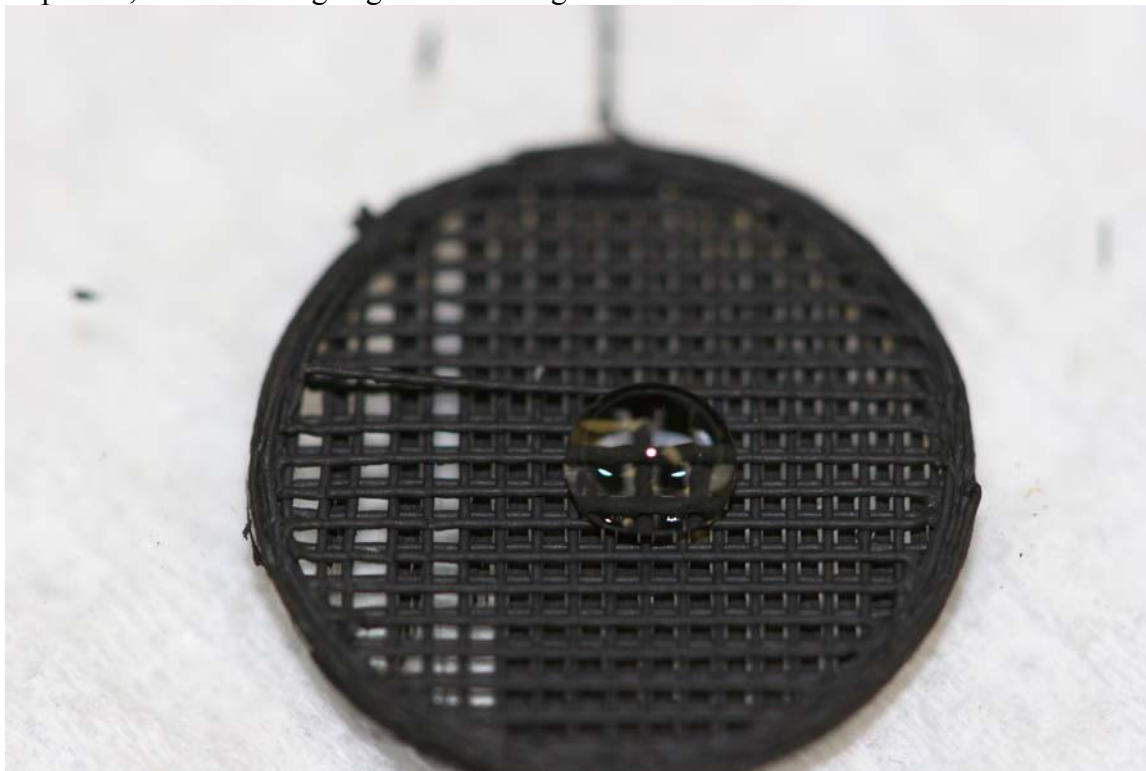


Figure 2: A cast MnO₂ cathode with a drop of electrolyte sitting above it. The pitch of the cast structure is roughly 100um, and the lattice is 3 layers deep. The droplet will wet when mechanically pushed through the lattice.

For electrochemical performance, samples were prepared in three states; either a nickel blank with a polymer coating over the electrode, or with one side of the nickel coated with the manganese dioxide ink, and the opposite side coated with a non-reactive polymer. This sample was tested both in the absence and presence of oxygen to observe the activity of the electrode to oxygen reduction. These results are shown in Figure 3. As can be seen from the data, the nickel blank shows no electrochemical activity at all, while the MnO₂ coated electrode in the absence of oxygen shows a capacitive effect (which would be expected given a thick coating and the presence of the binder leading to a resistive and capacitive effect). In the presence of oxygen, however, the onset of a reductive wave is seen above 450mV vs. Ag/AgCl, which coincides with the expected potential for oxygen reduction on MnO₂ under alkaline conditions.¹¹ While the size of the reductive wave is small, it is clearly indicative that the electrode is active at the correct potential and is reducing the oxygen present in the electrolyte.

Conclusions and Further Work:

We have demonstrated the function of a free standing, electrochemically active MnO_2 cathode for a zinc-air reserve cell that is capable of providing a hydrophobic surface for the alkaline media of the cell, but can be wetted after activation of the cell to provide electrochemical activity for the reduction of oxygen. Wetting of the printed electrode had an initial contact angle in excess of 100 degrees, and was structural as a free standing lattice. The electrode showed electrochemical activity to oxygen reduction in alkaline media. Initial currents were low, but improvements can be made to the electrode. The ultimate performance of the electrode will be limited, however, by the tradeoffs for control of the hydrophobicity for wetting, the rheology for casting, and the conductivity and electrochemical activity of the electrode.

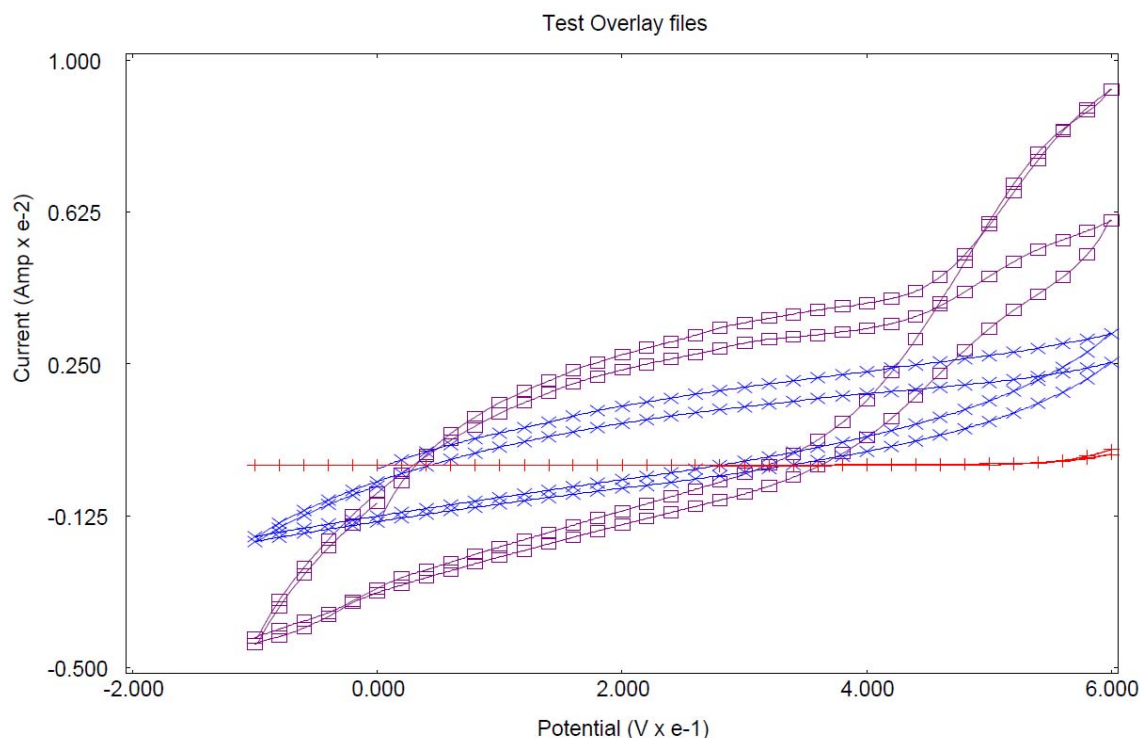


Figure 3: Cyclic voltammograms of printed MnO_2 electrodes. (+) background scan of base nickel electrode protected by polymer. (x) electrode with printed MnO_2 on nickel, but no oxygen in the media. () electrode with printed MnO_2 on nickel, in the presence of oxygen. Note the reductive peak at $\sim 450\text{mV}$. Conditions: 25C, 1N KOH in DI, Ag/AgCl ref, Pt counter, 10mV/sec, nitrogen sparge.

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