**Rechargeability and Economic Aspects of Alkaline Zinc-Manganese Dioxide Cells for
Electrical Storage and Load Leveling**

Nilesh D. Ingale, Joshua W. Gallaway, Michael Nyce, Alexander Couzis, Sanjoy Banerjee*

The CUNY Energy Institute, Department of Chemical Engineering, City College of the City

University of New York, New York, NY 10031, USA

* Corresponding author: Department of Chemical Engineering, City College of City University
of New York, 140th Street at Convent Avenue, New York, NY 10031. USA.

Tel.: +1 212 650 5728 Fax: +1 212 650 6660

Email: banerjee@che.ccny.cuny.edu

Abstract:

Batteries based on manganese dioxide (MnO_2) cathodes are good candidates for grid-scale electrical energy storage, as MnO_2 is low-cost, relatively energy dense, safe, water-compatible, and non-toxic. Alkaline Zn- MnO_2 cells, if cycled at reduced depth of discharge (DOD), have been found to achieve substantial cycle life with battery costs projected to be in the range of \$100 to 150 per kWh (delivered). Commercialization of rechargeable Zn- MnO_2 batteries has in the past been hampered due to poor cycle life. In view of this, the work reported here focuses on the long-term rechargeability of prismatic MnO_2 cathodes at reduced DOD when exposed to the effects of Zn anodes and with no additives or specialty materials. Over 3000 cycles is shown to be obtainable at 10% DOD with energy efficiency >80%. The causes of capacity fade during long-term cycling are also investigated and appear to be mainly due to the formation of irreversible manganese oxides in the cathode. Analysis of the data indicates that capacity loss is rapid in the first 250 cycles, followed by a regime of stability that can last for thousands of cycles. A model has been developed that captures the behavior of the cells investigated using measured state of charge (SOC) data as input. An approximate economic analysis is also presented to evaluate the economic viability of Zn- MnO_2 batteries based on the experiments reported here.

Keywords:- rechargeable zinc-manganese dioxide battery, cycle life, Zn- MnO_2 battery model, capacity fade model, film resistance

1. Introduction:

Batteries could be attractive candidates for grid-scale electrical energy storage, as they have high efficiency, can ramp to deliver power rapidly, and are modular, scalable and suitable for distributed siting. Alkaline zinc anode/manganese dioxide cathode batteries could potentially be low-cost, energy dense, safe, water-based, and non-toxic. They have many of the desirable attributes but currently have cycle life that is too limited for economical grid storage systems. Through an effort funded by the ARPA-E GRIDS (Grid-Scale Rampable Intermittent Dispatchable Storage) program, we have investigated the rechargeability of Zn-MnO₂ batteries designed for stationary applications in the grid. The goal of the GRIDS program was a battery investment cost in the range of \$100 to 150 per kWh (delivered) for electricity storage with 3000-5000 cycles capability at discharge rates up to C/3 to C/5. To this end, our approach was to focus on this inexpensive chemistry and investigate whether the targeted costs, cycle life and discharge rates could be achieved at relatively shallow depths of discharge (DOD). A preliminary analysis indicated that the manganese dioxide cathode DOD would need to be at least 10% for the cost targets to be achieved. Whether the desired cycle life and C rates could be achieved are the issues addressed here.

Rechargeable alkaline batteries have been available since the 1960s, but cycle life was limited to 20-30 cycles due to formation of irreversible products associated with MnO₂ cycling [1]. It is also known that if a Zn anode is used then it can interact with the manganese dioxide cathode and additional irreversible capacity loss due to the formation of hetaerolite (ZnMn₂O₄) during cycling [2,3]. Zn metal anodes, however, have attractive properties such as low equilibrium potential, compatibility with aqueous electrolytes, and low toxicity. However, Zn anodes, when discharged deeply, have cycle life limitations of their own due to redistribution of Zn active

material and formation of short-circuiting dendrites upon recharge [4,5]. All these issues, i.e., those associated with the cathode, those associated with the anode, and their possible interactions, have to be addressed in improving the cycle life of such zinc-manganese dioxide batteries.

To proceed, MnO_2 exists in various polymorphs, but $\gamma\text{-MnO}_2$ (or $\varepsilon\text{-MnO}_2$) is the most electrochemically active and has a configuration of Mn vacancies and associated protons that facilitates proton transfer and therefore electrochemical reactivity [6,7]. During discharge of MnO_2 , insertion of protons leads to formation of manganese oxyhydroxide (MnOOH), which then undergoes a dissolution-precipitation mechanism to form lower valent manganese compounds such as Mn(OH)_2 , Mn_2O_3 , and Mn_3O_4 [8–10]. Some of these oxides formed have poor rechargeability which is a detriment for secondary batteries. Several investigations have focused on improving Zn- MnO_2 rechargeability by adding dopants to MnO_2 such as CeO_2 , MgO , TiS_2 and/or Bi_2O_3 , Ba and Sr based compounds which hinder formation of the unwanted irreversible manganese oxides and maintain the stability of $\gamma\text{-MnO}_2$ during cycling [11–16]. Although additives have generally improved initial discharge capacity, cycle life has remained limited and capacity fade has been observed. As one example, a flat plate Zn- MnO_2 cell was developed in which the MnO_2 cathode was modified with BaSO_4 , which minimized the capacity fade during cycling [17]. With this, 25-30 cycles were obtained for a Zn- MnO_2 cell.

The strategy followed here to enhance cycle life was to take advantage of the relative inexpensiveness of MnO_2 and evaluate cathodes at 5% to 20% DOD while still realizing low costs by avoiding expensive battery materials like current collectors, separators and fasteners. The cathodes must however maintain their conductivity and porosity to allow access to the active material by the electrolyte on repeated charge and discharge, which is also a significant

challenge. The hypothesis underlying this strategy is that when the manganese dioxide cathode is only partially discharged through the first electron reduction step to MnOOH (less than half the first electron discharge), reversibility can be maintained through thousands of cycles [9,10]. Beyond $\frac{1}{2}$ to $\frac{3}{4}$ electrons there may be lattice dilation and recrystallization leading to irreversible capacity loss [10,18,19]. Furthermore if reversibility is to be maintained there can be no local deep discharge zones within the porous MnO₂ electrode. Some studies in the literature have attempted to retain the electrochemically active γ -MnO₂ structure by limiting Zn anode capacity and cycling at 100% DOD with respect to the Zn. In these cases, 50-100 cycles have been obtained [1,10,20,21]. In these studies, failure could have been due to rapid shape change of the Zn anode.

The main objective of the work reported here was to investigate the cycling behavior of MnO₂ cathodes at various DODs and C-rates and identify conditions leading to long cycle life while using commercially available MnO₂. More specifically, reasonable power and energy densities, typically C/3 discharge rates and 20 Wh L⁻¹, and cycle life of ~3000 cycles were targeted without addition of dopants or modifications to commercially available MnO₂. The Zn-MnO₂ batteries were constructed in a prismatic configuration rather than in a cylindrical configuration which may have had lower fabrication costs. However, the prismatic design allowed a more uniform current distribution and active material utilization due to elimination of curvature effects, which allowed a slim battery profile and thin cathodes of 1 mm thickness. A prismatic design also permits more flexibility during cell scale-up, allowing electrode thickness to be tailored to the application, although cylindrical configurations could afford a higher degree of standardization in manufacturing [22].

Also, the batteries were examined at various stages to delineate the causes of capacity fade during long-term cycling. When pairing cathodes with Zn anodes designed to be non-limiting, the major cause of capacity fade was formation of irreversible manganese oxides in the cathode. A limited set of experiments was also done with cadmium anodes. A series of SEM, EDS and XRD analyses confirmed this, both by spot-checking healthy batteries as well as performing post-mortem analyses on failed cells. A simplified mathematical model was developed to interpret the data with regard to the effects of discharge rate and DOD. This model was based on more detailed alkaline Zn-MnO₂ battery models in the literature [23–26]. An economic analysis is also presented to evaluate the economic viability of batteries based on the experiments reported here.

2. Experimental:

2.1 Zn electrodes:

The Zn electrodes were made using 85 wt% Zn powder (Umicore, USA), 10 wt% ZnO powder (Fischer Scientific, USA), and 5 wt% T3859 Teflon (DuPont, USA) as a binder. The Zn, ZnO, and Teflon were wet-mixed in a mixer with isopropanol to form a thick paste. This paste was then rolled to a predetermined thickness. The rolled sheet of Zn was dried at 60 °C for 2 hrs. The Zn electrode sheets were typically made to be 5.08 cm wide, 7.62 cm high and 0.05 cm thick. Pieces of this size were cut from the rolled Zn electrode sheet and were pressed at 4.83 kN cm⁻² on expanded Ni plated steel mesh, which was used as a current collector.

2.2 MnO₂ electrodes:

The MnO₂ cathodes were made with 65 wt% MnO₂ (EMD Tronox, USA), 30 wt% KS44 graphite (Timcal, USA), and 5 wt% T3859 Teflon. The MnO₂ electrode sheet was made in the

same manner as the Zn electrode sheet. Two pieces of rolled MnO₂ electrode sheet were pressed on either side of an expanded Ni plated steel mesh current collector. The MnO₂ electrode size was 5.08 cm wide, 7.62 cm high and 0.1 cm thick. Particle size distribution of the manganese dioxide powder was measured using a Horiba Partica Particle Size Distribution Analyzer LA-950V2.

2.3 Cd electrodes:

Sintered Cd electrodes were purchased from Jiangsu Highstar Battery Manufacturing Co., Ltd. (China). The Cd electrode had capacity of 0.028 Ah cm⁻². As used in the test cells, all Zn, MnO₂ and Cd electrodes used had identical width and height.

2.4 Separators and Cell Assembly:

MnO₂ electrodes were wrapped in one layer of polyolefin nonwoven membrane (FS 2192 SG by Freudenberg, Germany) and three layers of low cost cellophane separator. Battery grade cellophane (350P00) separator was purchased from Innovia Films Inc, USA. The Zn electrodes were wrapped in one layer of polyolefin nonwoven membrane. Electrode packs were assembled in one of two ways: one cathode with an anode on each side; or an analogous arrangement with two cathodes and three anodes. This pack was placed in a molded polysulfone cell container (approximately an LR40 size cell) with the empty space filled by polypropylene shims on either side of the pack, which held the electrode pack under a uniform compression. The electrolyte was potassium hydroxide (KOH) solution of 10, 30, or 45 wt% made with de-ionized water and pure KOH pellets purchased from Sigma-Aldrich, USA.

2.5 Zn-MnO₂ cell cycling method:

Cells were cycled using a multi-channel Arbin BT 2000. The cycling profile used constant-current/constant-voltage (CCCV) taper charging and constant current (CC) discharging, both to a desired capacity. The charge capacity included a 5% overcharge to account for coulombic inefficiencies. The voltage limit for CCCV charging was 1.65 V, and CV charging was halted when the desired capacity was reached or when the taper charging current dropped below 10% of the charging current. Discharge was continued until either the desired capacity was reached or a preset lower voltage limit of 1.1 V was reached. A typical charge-discharge cycle is shown in Figure 1.

DOD was based on the one electron theoretical capacity of MnO_2 ($308 \text{ mAh g-MnO}_2^{-1}$). Energy density was calculated from discharged capacity for the MnO_2 electrode and the combined mass of anodes, cathodes, current collector mesh and tabs, terminals, and separators used. Cells were assembled in the charged state.

2.6 Electrode and separator characterization:

SEM (scanning electron microscope) images were recorded with a Hitachi TM3000. X-ray diffraction (XRD) experiments were carried out with a Philips Panalytical XRD operating at 40 kV/40 mA with a Cu-K α filter. In all electrodes the graphite (002) reflection at 26.58° was used as an internal standard, and spectra were corrected to eliminate any displacement error.

Kozawa and Powers [27,28] have reported the equilibrium potential of MnO_2 as a function of SOC, discharging electrodes with an excess of graphite and porous coke to various values of SOC. As our MnO_2 was of a different manufacture and combined with graphite in a different amount, we performed a similar experiment. The MnO_2 equilibrium potential E_{eq} was determined as a function of state of charge (SOC) by pulse discharge in a three-electrode cell

using a Hg/HgO reference electrode (Koslow Industries). The MnO₂ electrode was discharged at a C/20 rate in increments of 5% DOD. After each pulse the current was interrupted and the open circuit potential (OCP) was recorded for 4 hrs, which was found to be sufficient to achieve a stable value. The resulting equilibrium potential curve is shown in Figure 2, and was in agreement with those of Kozawa and Powers.

2.7 Symmetric cell experiments:

Separator impedance was measured in a symmetric cell with the separator between two squares (2.54 cm X 2.54 cm) of pure zinc foil (Sigma-Aldrich, 99.9% pure) and electrolyte. AC impedance measurements were carried out in the frequency response mode with a VersaStat 4 potentiostat (Princeton Applied Research).

3. Results and Discussion:

3.1 Rechargeability of MnO₂ at 100% Cathode DOD

The one electron reduction of manganese dioxide takes place according to the reaction

In this step, proton insertion in the MnO₂ lattice and formation of Mn⁺³ takes place. This is a single phase reaction and is reversible if formation of any irreversible phases is avoided [8,9,18]. The reversibility of MnO₂ cycling depends on many factors such as: rate of cycling, depth of discharge, and the chemical environment of the MnO₂. This includes both the base electrolyte and species introduced by the anode during cycling. Figure 3 shows the capacity of prismatic MnO₂ batteries cycled at full one-electron DOD of the cathode, with both Zn and Cd anodes. Cycling rate was 15 mA g-MnO₂⁻¹ (C/20). With Zn anodes full DOD was defined as discharge to

1 V; with Cd anodes full DOD was discharge to 0.6 V. The rate of capacity loss was a strong function of both anode chemistry and base electrolyte concentration.

The Zn-MnO₂ cell capacity losses in Figure 3a reflected a loss in cathode capacity. This was assured by full discharge of the Zn or Cd anodes in a half cell configuration after 24 cycles. Resistance of the separators was also assessed, and showed no increase over the base separator resistance. Figure 3 illustrates that MnO₂ capacity loss at full DOD involved more than one phenomenon. With Cd anodes capacity loss was a dramatic function of KOH concentration. In 10% KOH, after an initial drop of 41 mAh g-MnO₂⁻¹ the loss was linear and gradual at 1.2 mAh g-MnO₂⁻¹ per cycle with 76% capacity remaining at cycle 24. At 30% and 45% KOH the losses were rapid, with only 31% and 20% capacity remaining at 24 cycles respectively. No Cd contamination of the cathodes was observed in any case, suggesting a Mn-dissolution mechanism. As KOH concentration increases, the solubility of the Mn⁺³ ion increases [9]. With zinc anodes capacity loss was a weaker function of electrolyte concentration: compared to cadmium, the Zn had less capacity loss at 45% KOH but more at 10% KOH. This implies a relationship between Mn⁺³ dissolution and dissolved Zn in the electrolyte. For example, dissolved Zn ions and low KOH concentrations result in low solubilities of Mn [9] and Zn [29]. With zinc anodes, capacity loss at full DOD was somewhat mitigated by a low electrolyte concentration of 10% KOH, but not as much as with the Cd anode. The dissolved Zn concentration was found to increase with increasing KOH concentration, as measured by EDTA titration after 24 cycles as shown in Table 1.

3.2 Effect of DOD on the rechargeability of Zn-MnO₂

Zn-MnO₂ cells were cycled at 10%, 20%, 50%, and 100% DOD for 24 cycles at a discharge rate of 15 mA g-MnO₂⁻¹ in 45 wt% KOH. The cells were then disassembled and examined to

quantify material changes that occur during early cycling. The amount of dissolved Zn in the electrolyte and the Mn/Zn mass ratio on the cathode surface are shown in Figure 4 as a function of DOD. As DOD increased the amount of dissolved Zn in the electrolyte increased, as did the mass fraction of Zn on the cathode surface.

The presence of dissolved Zn in the electrolyte lead to Zn incorporation in the cathode during shallow cycling. XRD analysis in Figure 5 shows the cycling products formed on the electrode surface after 24 cycles at various DOD. At 10% DOD the electrode had a similar composition as a new electrode, with the γ -(ϵ -)MnO₂ peaks showing some strain to lower angles. At higher DOD, reflections for the irreversible spinel products Mn₃O₄ or hausmannite (●) and ZnMn₂O₄ or hetaerolite (○) were predominant. Other spinel-like products were also possibly apparent, as in the work of Grey and co-workers [30]. Hausmannite and hetaerolite d-spacings differ by no more than 0.04 Å and thus these are marked together in Figure 5. In the 10% and 20% DOD cases the (112) reflection may indicate some hetaerolite in the 10% case and a mixture of hausmannite and hetaerolite in the 20% case. The EDS experiments show that some hetaerolite had formed in all cases due to a Zn signal from the MnO₂ particles.

3.3 Long-term cycling of prismatic Zn-MnO₂ cells

For long-term cycling an electrolyte concentration of 45 wt% KOH was selected, as the effect of KOH concentration was not pronounced above 30% (see Figure 3a). Increased KOH concentrations were also desirable for long-term cycling, as cellophane degrades in water and in low KOH concentration [31]. Table 2 details the cycling and cell capacity information for Zn-MnO₂ cells cycled at reduced DOD. Cells 1, 2, and 3 compared the effect of DOD at a constant discharge rate with respect to mass of MnO₂ active material. Cells 4 and 5 varied rate at a DOD of 10%. Cell 6 provided a representative duplicate of Cell 1.

Cycling results are shown in Figure 6, with energy efficiency in the upper panels (a,c) and discharge end voltage (DEV) in the lower panels (b,d). Cell 1, cycled at 10% DOD and C/2 rate, maintained an energy efficiency above 80% for 3004 cycles. Cell 3, with the same configuration and DOD lowered to 5%, maintained 86% energy efficiency beyond 4500 cycles and continued to cycle as of this writing. Cycling at 20% DOD as in Cell 2 resulted in a more rapid loss in efficiency and cell failure near cycle 500. Discharge end voltage (DEV) for cells at 10% DOD showed an initial rapid decrease in the first 300-400 cycles, followed by a shallower, more gradual decrease. At 5% DOD the decay in DEV was linear, remaining more above 1.25 V for 4500 cycles. At 20% DOD cell failure was preceded by a second rapid decrease in DEV. The initial decrease in DEV was more rapid in cases of higher DOD, with the exception of Cell 1 discussed below. An increase in DOD correspondingly increases the energy density of the battery.

Data in Figure 6 were representative of our more general results, and each cell had at least one and in most cases several repetitions. The comparison of Cell 1 and Cell 6 illustrated a variation that was occasionally observed. In case of cell 1, during initial cycling (cycles 1 to 200) the DEV decreased at a more rapid rate than expected, as did the CEV. At the 200th cycle the overcharge was increased from 5% to 7%. In Cell 1, as in other cases of this behavior, both DEV and CEV stabilized after this overcharge correction, and the cells showed no long-term ill effects. Cell 6 did not display this behavior and therefore had no correction in overcharge. Cell 1 exhibited more profound initial losses in both energy efficiency and DEV than did Cell 6, but after the Cell 1 overcharge correction both cells settled to the same long-term trend in both metrics.

An increase in cycling rate caused more rapid capacity fade. Comparing variations in rate at 10% DOD, Cell 4 was cycled at a 1C rate (30 mA g-MnO₂⁻¹) and achieved 1200 cycles with >75%

energy efficiency before performance began to fade. Cell (5) cycled at a 1.5C rate (48 mA g- MnO_2^{-1}) for somewhat less than 1000 cycles at 10% DOD with ~80% energy efficiency.

Commercial rechargeable manganese dioxide-zinc cells have been recently reported by Daniel-Ivad [32], using cylindrical form factors of AA and AAA size (LR6 and LR03). These cells used fundamentally different design principles than the work reported here: pelletized cathodes containing unspecified additives, gelled-zinc anodes, and proprietary separators. Most importantly these cells were anode-limited to protect their cathodes from over-discharge and were intended as a drop-in replacement for primary cells in portable electronics applications. By limiting DOD to 5% a cycle life of 4000 was achieved with these cylindrical cells. This is comparable, if somewhat lower, than performance presented here. However the prismatic cells in the current work were designed for scale-up and made exclusive use of low cost components. The results suggest that MnO_2 cathodes, paired with zinc anodes, could be an appropriate storage solution for large-scale, long cycle life applications, with no specialty materials required. This is further discussed in the section on economic analysis.

3.4 Degradation mechanisms for long term cycling of batteries

During cycling, decreases in efficiency and DEV are correlated, as apparent from Figure 6. The underlying cause for this impact on performance is two-fold: a) loss of active material, either through chemical change or physical isolation, and b) an increase in resistance within the electrodes, which causes a drop in cell voltage as cycling progresses. These mechanisms occurred chiefly in the cathodes, as these cells were designed for cathode limitation. Destructive physical analysis of the cells was performed to confirm this and account for increases in resistance due to the other cell components, e.g. the anode and separators. A semi-empirical

model was then developed to quantify capacity fade during extended cycling. This approach was based on analysis of long term 18650 Li-ion cell cycling reported by Popov and co-workers [33].

3.4.1 Physical analysis of Zn-MnO₂ cells

After cell cycling was completed, cathodes were removed, washed, and analyzed for material composition by SEM, EDS, and XRD. Figure 7 compares new cathodes with those of Cell 1 after completion of 3004 cycles. After cycling the MnO₂ particles, which began spatially well distributed, were connected by an adherent film deposited throughout the electrode. This film was concentrated on MnO₂ particle surfaces, but was also apparent on graphite in some locations. Comparison of the MnO₂ particles in panels (b) and (d) show a qualitative change in particle texture and the presence of a dappled film. The inset of Figure 7 shows the magnification of a MnO₂ particle on which a significant thickness of this film can be seen in profile. Zinc oxide rods were also found scattered in the electrode. Large-area EDS analysis of a new electrode showed an atomic distribution of 40.5% Mn, 40.3% C, 10.2% O, and 9% F, which was found in the Teflon binder. Similar area analysis after 3004 cycles showed a prevalence of zinc: 36.4% C, 29.6% Zn, 22.4% Mn, and 6.9% O with the remainder being F and K. Spot analysis showed the strongest zinc signals were from the ZnO rods and the film covering the MnO₂ particles. The Cell 1 results were representative of the other cells in Figure 6.

Figure 8 shows the surface XRD of a cathode in Cell 1 after 3004 cycles compared to a cathode cycled 24 times at 10% DOD, discussed in Section 3.2. Placement of the prominent spinel (211) reflection in Cell 1 shows that hausmannite and hetaerolite were formed during advanced cycling. The hausmannite/hetaerolite Bragg peaks were not distinguishable, but the Zn EDS results suggest that hetaerolite was present in the film formed on the MnO₂ particles. Reflections

of $\gamma\text{-MnO}_2$ remain in the 3004-cycled cell (marked with an arrow). This indicates that active material remains even after cell failure at high cycle life at 10% DOD. Hausmannite and hetaerolite have resistivities six orders of magnitude higher than $\gamma\text{-MnO}_2$ and therefore their extensive presence in an electrode can lead to a loss of conductivity and failure [30,34–36]. Based on these data we hypothesize that these spinels form pervasively as resistive films in the cathode at advanced cycle numbers. In the semi-empirical capacity fade model this phenomenon will be treated by addition of a film resistance on the active material designated as R_f .

To assure that cells at advanced cycle numbers did not fail due to a loss of anode capacity, the Zn electrodes were removed, washed, and discharged at a C/20 rate in a half cell configuration. In all cases, anode capacity was not limiting. As an example, anodes in Cell 1 retained over 50% of initial capacity, which was well above what was needed for battery cycling. Buildup of a ZnO layer between the anode and separator has previously been identified as a critical phenomenon for Zn-MnO₂ cycle life [18]. Cell separators were removed and tested for resistance in a symmetric cell arrangement [37]. The resistance for three layers of fresh cellophane was 2.87 ohm-cm². Upon cell failure at 3004 cycles, the resistance for the three layers in Cell 1 was 5.64 ohm-cm², a ~67% increase. This increase was treated empirically and assumed to evolve linearly during cycling, designated as separator resistance R_s .

3.4.2 Capacity fade analysis for Zn-MnO₂ cells

A mathematical model was used to interpret capacity fade in the cells. This model divided the cells into three regions, anode, separators, and cathode, and treated the anode and cathode as porous electrodes. The model is presented in more detail in the appendix, and was a simplified version of more extensive models discussed in the literature [23–26]. With a relatively small

number of input parameters focused on the cathode, the model predicted battery discharge behavior, and was then modified to quantify capacity fade and its impact in the cells. The key parameter in the model was the equilibrium potential of the MnO_2 electrode, E_{eq} , which is fundamentally a function of the relative concentrations of Mn^{+4} and Mn^{+3} ions in the active material [26]. The dependence of E_{eq} on MnO_2 SOC is shown in Figure 2. E_{eq} then was used to calculate the local cathode overpotential η as given in Equation (A-19). As the anode was non-limiting, the anode equilibrium potential for the anode was taken to be constant at -1.4 V vs Hg/HgO [23]. Table 3 lists the parameters used in the model. The cathodes were made from poly-dispersed EMD particles but the simple model treated these by use of an ‘effective’ particle with a diameter that was treated as a fitting parameter that was not changed for all the calculations.

Simulated discharge curves are shown in Figure 9, compared to experimental data at various discharge rates. The agreement was reasonable in all cases, and the model accurately predicted the reduction in discharge capacity as rate increased. The effective particle radius of the MnO_2 active material was taken to be 10 μm , which was the only averaged parameter used in matching the experimental curves. This was a reasonable assumption for mean particle size although the actual size was a wide distribution, as measured by particle size analysis.

To quantify the impact of capacity fade, the model was adapted to include the loss of active material and formation of irreversible oxides in the MnO_2 electrode, which had been detected in the physical analysis. The hausmannite and hetaerolite formed in the cathode during extended cycling had poor electronic conductivity, causing a drop in cell voltage during extended cycling. This was modeled as formation of a resistive film on the MnO_2 particles, and this film effected an addition contribution to the local MnO_2 surface overpotential η at every point in the cathode,

given by Equation (2) where i_n is the interfacial current density on the MnO_2 and ϕ_s and ϕ_l are the solid and liquid potentials at the interface.

$$\eta = \phi_s - \phi_l - E_{eq} - R_f i_n \quad (2)$$

It was assumed that as an MnO_2 electrode was discharged the active material maintained the same crystal structure following the reaction in Equation (1), and SOC was determined from the equilibrium potential of the MnO_2 electrode. During cycling the potential was recorded after each charge and discharge cycle during a 30 minutes rest period, as shown in Figure 1. Via a series of experiments on cells allowed to equilibrate for many hours it was found that open circuit potential (OCP) could be empirically predicted by a logarithmic function of the form

$$OCP = A \ln(t) + B \quad (3)$$

with constants A and B are dependent on cycle number. Thus OCP at each cycle number N was determined by extrapolation of the rest potential to a time of five hours after both the charged and discharged states, $OCP_{C,N}$ and $OCP_{D,N}$ respectively. This progressive change in OCP is plotted for several cells in Figure 10a.

Both $OCP_{C,N}$ and $OCP_{D,N}$ decreased with cycle number. In all cases $OCP_{D,N}$ dropped more rapidly than $OCP_{C,N}$ in the first 250 cycles. Using the equilibrium relationship in Figure 2 the SOC for the MnO_2 electrode at each cycle number N in the charged and discharged state were determined, $SOC_{C,N}$ and $SOC_{D,N}$ respectively. These values are plotted in Figure 10b. SOC is fundamentally defined by the ratio of manganese atoms in the crystal structure in the +4 oxidation state C_{Mn+4} relative to the total number of available manganese sites C_{Mn+4}^0 , given in Equation (4).

$$SOC = \frac{C_{Mn^{+4}}}{C_{Mn^{+4}}^0} \quad (4)$$

Cathode $SOC_{C,N}$ dropped linearly during cycling for all cells at 10% DOD, and this drop was more rapid under faster rates. Cell 1 demonstrated that even at 3000 cycles SOC in the charged state remained 0.9. $SOC_{D,N}$ dropped rapidly in the first 250 cycles from ~0.85 to 0.3. As the nominal DOD remained 10% in these cells, this indicated a loss of active material accompanied by a more gradual lowering of the SOC window. The loss of active material was not a function of rate, as Cells 4, 5, and 6 showed comparable behavior. Cell 1 lost active material more rapidly until an overcharge correction, discussed above. In all 10% DOD cells the loss of active material evinced by $SOC_{D,N}$ leveled off to a gradual value around cycle 500, and in some cases maintained this value for thousands of cycles. In Cell 2 at 20% DOD $SOC_{D,N}$ dropped more rapidly, after which a drop in $SOC_{C,N}$ was triggered until cell failure. In general cell failure was presaged by a downturn in $SOC_{C,N}$, which could be used as an indicator of cell health.

From the SOC values in Figure 10b, the manganese atom concentrations could be calculated at every cycle number and used as model inputs to calculate a predicted discharge curve. This was accomplished in a similar fashion as in the capacity fade analysis for lithium ion batteries reported by Popov and co-workers. [33,38]. The total capacity accessible at N^{th} cycle $Q_{total, N}$ is given by,

$$Q_{total, N} = Q_{th} - Q_{lost, N} \quad (5)$$

Where $Q_{lost, N}$ is lost capacity at any cycle number and Q_{th} is the total initial theoretical capacity for the MnO_2 electrode in the cell. The cycled capacity Q_{cycled} at any cycle number is

$$Q_{cycled} = \int_0^{t_D} I(t) dt \quad (6)$$

Where t_D is total discharge time and $I(t)$ is the discharge current. The cycled capacity can be calculated by knowing the change in SOC after charge and discharge as

$$Q_{cycled} = Q_{total,N} * (SOC_{C,N} - SOC_{D,N}) \quad (7)$$

From equations (7)-(9), the lost capacity at any cycle number can be calculated as

$$Q_{lost,N} = Q_{th} - \frac{\int_0^{t_D} I(t) dt}{(SOC_{C,N} - SOC_{D,N})} \quad (8)$$

As outlined above, the film resistance was caused by the formation of irreversible products (Mn_3O_4 and $ZnMn_2O_4$) on the surface of MnO_2 particles. Overall formation of these oxides is given by

By assuming the lost capacity was entirely converted to resistive manganese oxides, the film resistance was calculated at every cycle number. As hausmannite and hetaerolite were difficult to distinguish during physical analysis, we assumed the resistive film to be composed 50% of each oxide. Thus, for every 5 mol of MnO_2 deactivated, 1 mol of Mn_3O_4 and 1 mol of $ZnMn_2O_4$ were formed. From Faraday's law of electrolysis the film thickness was given as

$$\delta_{film} = \frac{Q_{lost} \times (2/5) \times M_{avg}}{a \times W_{MnO_2} \times F \times d_{avg}}$$

where the average quantities were calculated assuming that the film is composed of 50 wt% Mn_3O_4 (molecular weight, $M = 228.8 \text{ g mol}^{-1}$ and density, $d = 4.9 \text{ g cm}^{-3}$) and 50 wt% $ZnMn_2O_4$

(molecular weight, $M = 239.25 \text{ g mol}^{-1}$ and density, $d = 5.02 \text{ g cm}^{-3}$). The factor (2/5) comes from the reaction stoichiometry for the formation of Mn_3O_4 and ZnMn_2O_4 . The total specific surface area $a \text{ (cm}^2 \text{ g-MnO}_2^{-1}\text{)}$ was calculated knowing the amount of MnO_2 (W_{MnO_2}) present in the electrode. For EMD, $a = 30 \text{ m}^2 \text{ g}^{-1}$ [39]. The resistance of the film was given as

$$R_f = \frac{\delta_{film}}{\kappa_{avg}} \quad (11)$$

Where, κ_{avg} is the average conductivity of the film (κ for $\text{Mn}_3\text{O}_4 = 1 \times 10^{-7} \text{ S cm}^{-1}$ and κ for $\text{ZnMn}_2\text{O}_4 = 1 \times 10^{-8} \text{ S cm}^{-1}$) [36]. The progressive value of the film resistance for several cells is plotted in Figure 11.

The battery model, modified to account for capacity fade and conversion to a resistive film, could be used to predict discharge curves at a cycle N based on the extrapolated SOC values. The active material available at N^{th} cycle was calculated based on total available capacity as,

$$C_{Mn^{+4},N}^0 = C_{Mn^{+4}}^0 \left(\frac{Q_{total,N}}{Q_{th}} \right) \quad (12)$$

The change in initial SOC was incorporated by calculating the concentration of active Mn^{+4} ions at N^{th} cycle as using equation (4),

$$C_{Mn^{+4},N} = (SOC_{C,N}) C_{Mn^{+4}}^0 \quad (13)$$

The capacity fade was taken into account by adjusting initial SOC and R_f after each cycle. Anode effects were treated empirically by assuming the separator resistance R_s was a linear function with cycle number as shown in Equation (5).

$$R_s = 0.0001(\text{cycle number}) + 0.55 \quad (14)$$

This resistance was included to account for the increase in cell resistance caused by ZnO buildup and clogging at the separator by Equation (16).

$$E_{cell} = \phi_{s,x=L_{pos}+L_{sep}+L_{neg}} - \phi_{s,x=0} - R_s I \quad (15)$$

Where E_{cell} is the cell voltage (difference between the potentials at positive and negative electrode current collectors) at any time t .

Figure 12 shows the comparison of actual and simulated discharge curves for Cell 1 at several cycle numbers. For each cycle, the initial and final SOC values are accepted as inputs, as well as the empirical adjustment to the separator resistance R_s . By accounting for lost capacity and assuming that capacity was converted to resistive manganese oxides, the cell discharge behavior was predicted with reasonable agreement, especially at low cycle numbers. Deviations seen after long cycling are likely due to further physical alteration of the cathode, as we neglect effects such as porosity changes during cycling [40]. As each cycle was begun before full relaxation to OCP, the model accounted for this initial potential. Thus the voltage for cycles 2 and 150 were higher compared to that of cycle 1.

The dominant phenomenon affecting the discharge performance of MnO_2 cathodes during long-term shallow cycling was a loss in capacity, which was most profound in the first 250 cycles. By assuming this capacity was entirely converted to a resistive film within the cathode, discharge curves of Zn- MnO_2 cells could be approximated for any given cycle number, by using SOC values at that cycle as an input.

3.5 Economic Analysis

The economics of large-scale energy storage depends on specific cost per unit of energy stored (\$ per kWh) at a specified C-rate and cycle life of the energy storage system. Table 4 lists all major cell components for prismatic alkaline Zn-MnO₂ cells with cathode design principles as those reported in this paper. Material costs in 2014 USD are reported based on quotations from respective vendors. To estimate the cost per delivered kWh at a given DOD, we assumed a battery unit of 9 cells of 80 Ah cycled capacity each. Nominal cell voltage of 1.43 V results in a 12.8 V battery with a delivered energy of 1030 Wh. We assumed 351 cm² electrodes, sized to match an appropriate battery box. With this design a cell would have 6 anode plates and 5 cathode plates. As in this study cathodes were assumed to be wrapped in three layers of cellophane separator and anodes in one layer of pelon membrane. The \$ per kWh cost was calculated at different DOD values based on the MnO₂ cathode, as shown in Table 4. These costs included the battery casing, box, and top as well as the current collector tabs. At 10% DOD the cost of \$140 per kWh is well below the cost of many battery chemistries. At 20% DOD the cost is improved by a factor of 1.57, and falls below \$100 per kWh.

Battery cost is 1.5x more sensitive to cathode utilization than anode utilization. For the calculations in Table 4 zinc utilization was set at 25%, which is higher than that used in the experimental section of this work, but within the experience base to control shape change. The overall battery cost is relatively insensitive to zinc utilization above a value of ~25%. Our results have shown that while a 20% DOD cell achieved 500 cycles, a 10% DOD cell discharged at comparable current achieved over 3000 cycles. This is 6 times increase in cycle life. As this is greater than the factor of cost improvement of 1.57, in applications where energy density is not critical, 10% DOD could provide a lower capital cost per cycle than 20% DOD. There is a strong incentive to improve the cycle life at 20% DOD to ~3000 cycles without materially affecting the

cost of materials, which is the focus of our current work. Table 5 compares the lifetime investment cost of the Zn-MnO₂ battery with other electrochemical systems appropriate for large-scale electrical energy storage. All battery characteristics are taken from Chen and co-workers [41], but it should be noted that capital cost and cycle life estimates show wide variation depending on source [42–44]. The lifetime investment cost was calculated based on cycle life and DC round-trip energy efficiency as:

$$\text{Lifetime Investment Cost } (\text{¢/kWh per cycle}) = \frac{\text{capital cost } (\$/\text{kWh})}{\text{cycle life} \times \text{energy efficiency } (\%)} \quad (16)$$

Many of these technologies, such as Pb-acid, Ni-Cd, Na-S, V-redox, and the various types of Li-ion batteries, have been suggested for grid-scale storage applications. However, many of these technologies have drawbacks related to cycle life, complexity, toxicity, or safety. The Zn-MnO₂ batteries described in this paper compare favorably in all regards, including lifetime investment cost, which is estimated as ~5 ¢ per kWh per cycle, while having no toxic or flammable components. Thus the Zn-MnO₂ system is appropriate for broad market penetration for grid-scale energy storage or load leveling applications in comparison with other matured electrochemical systems.

4. Conclusion

Prismatic Zn-MnO₂ batteries have the potential for grid-scale storage applications, and owing to their low cost, low toxicity, and non-flammability could address the storage needs tied to renewable energy sources such as wind and solar. The design used in these studies did not use additives or specialty materials, and demonstrated that MnO₂ electrodes cycled at a C/2 rate to 10% DOD can achieve more than 3000 cycles with >80% energy efficiency and an energy

density of 20 Wh L⁻¹. Destructive physical analysis of cathodes that achieved high cycle life revealed the formation of irreversible manganese oxides such as Mn₃O₄ and ZnMn₂O₄. A mathematical Zn-MnO₂ model was adapted for capacity fade analysis, using a method similar to that reported by Popov and co-workers. Using SOC values at each cycle number N as inputs, the model indicated that capacity loss was rapid in the first 250 cycles, followed by a regime of stability, which lasted for thousands of cycles. Higher rates and higher values of DOD were observed to hasten capacity fade. At 20% DOD ~500 cycles was achievable using the same design principles, while 5% DOD extended cycle life dramatically. An economic analysis demonstrated that when paired with an appropriate Zn anode, a battery system based on cells such as these could achieve substantial cycle life with total fabricated battery costs near \$100 to 150 per kWh, depending on DOD.

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Appendix: Mathematical Model for Capacity Fade Analysis of Cells

Several detailed discharge models of Zn-MnO₂ batteries appear in the literature [23–26]. The simplified model presented here was adapted to model discharge in cathode-limited cells using a small number of parameters. Anode and cathode were treated individually with macrohomogeneous porous electrode models in which both ionic and electronic currents were calculated. In the separator region, the current was carried entirely by an ionic phase. A schematic representation of the three sections is shown in Figure 13.

The model assumed isothermal conditions and a concentrated binary electrolyte consisting of K^+ and OH^- ions. The three sections were coupled via their boundary conditions. Cell discharge curves were calculated by solving Equations (A-1)-(A-19) below using COMSOL Multiphysics 4.3b finite element package.

A.1 MnO_2 Electrode:

The cathode equations described a porous electrode comprised of spherical MnO_2 particles. The equilibrium potential defined the concentration of Mn^{+4} atoms in the particles. Mn^{+4} was reduced to Mn^{+3} by insertion of H^+ and electrons via Equation (1). The transport of H^+ within a MnO_2 particle is given in terms of concentration of Mn^{+4} ions per unit volume [26] and is governed by

$$\frac{\partial C_{Mn^{+4}}}{\partial t} = D_{H^+} \left[\frac{\partial^2 C_{Mn^{+4}}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{Mn^{+4}}}{\partial r} \right] \quad (A-1)$$

At the outer surface of the particle, the diffusion of H^+ ions is coupled with reaction rate and is given by imposing the following boundary condition

$$\text{At } r = R_p, \frac{i_n}{F} = -D_{H^+} \frac{\partial C_{Mn^{+4}}}{\partial r} \quad (A-2)$$

And at the center of the particle a no flux boundary condition is imposed

$$\text{At } r = 0, \frac{\partial C_{Mn^{+4}}}{\partial r} = 0 \quad (A-3)$$

The reaction current density at the MnO_2 solid-liquid interface is given by a Butler-Volmer expression as

$$i_n = i_0 \left\{ \exp \left(\frac{\alpha_a F \eta}{RT} \right) - \left(\frac{\alpha_c F \eta}{RT} \right) \right\} \quad (A-4)$$

where the exchange current density is given by

$$i_0 = i_0^0 \left(\frac{C_{Mn^{+4}}}{C_{Mn^{+4}}^0} \right) \left(\frac{C_{Mn^{+3}}}{C_{Mn^{+3}}^0} \right) \left(\frac{C_{OH^-}}{C_{OH^-}^0} \right) \quad (A-5)$$

The material balance for hydroxyl ions in the electrolyte is given by

$$\varepsilon \frac{\partial C_{OH^-}}{\partial t} = \varepsilon D_{OH^-} \frac{\partial^2 C_{OH^-}}{\partial x^2} + \frac{ai_n(1-t_+^0)}{F} \quad (A-6)$$

where, $D_{OH^-} = \varepsilon^{-1/2} D_{OH^-}^\infty$ (A-7)

A no flux boundary condition was used at the current collectors

At $x = 0$ and $x = L_{pos}$, $\frac{\partial C_{OH^-}}{\partial x} = 0$ (A-8)

The hydroxide diffusion coefficient in the electrolyte depends on the concentration of electrolyte as follows

$$D_{OH^-}^\infty = \exp \left[-10.46 - 0.411 \frac{C_{OH^-}^{1/2}}{1+C_{OH^-}^{1/2}} + 0.29182 C_{OH^-} - 0.091543 C_{OH^-}^{3/2} + 0.0059489 C_{OH^-}^2 \right] \quad (A-9)$$

The conservation of charge is given by adding the solid and liquid phase current densities

$$i_s + i_l = I \quad (A-10)$$

The solid phase potential is given by Ohm's law

$$i_s = -\sigma \frac{\partial \phi_s}{\partial x} \quad (A-11)$$

and the liquid phase potential is given by

$$i_l = -\kappa \frac{\partial \phi_l}{\partial x} - \frac{2\kappa RT}{F} (1 - t_+^0) \frac{\partial^2 \ln C_{OH^-}}{\partial x^2} \quad (A-12)$$

Where porosity is accounted for by

$$\kappa = \varepsilon^{-1/2} \kappa^\infty \quad (A-13)$$

The following boundary conditions are used at the current collector-positive electrode interface and at the negative electrode-current collector interface

$$i_s = I \quad (A-14)$$

$$i_s = 0 \quad (A-15)$$

The initial conditions are given as

$$\text{At } t = 0, C_{OH^-} = C_{OH^-}^0 \quad (A-16)$$

$$\text{At } t = 0, C_{Mn^{+4}} = C_{Mn^{+4}}^0 \quad (A-17)$$

In a similar manner to bulk diffusion coefficient, the variation of liquid phase conductivity, despite any porous structure, with electrolyte concentration is given by [23]

$$\kappa^\infty = C_{OH^-} \exp(5.5667 - 6.1538 C_{OH^-}^{1/2} + 13.408 C_{OH^-} - 1075.8 C_{OH^-}^{3/2}) \quad (A-18)$$

The MnO_2 surface overpotential η is given by

$$\eta = \phi_s - \phi_l - E_{eq} \quad (A-19)$$

A.2 Zn Electrode

The similar set of governing equations (A-4) and (A-6)-(A-19) were also written for porous Zn electrode. For the negative Zn electrode i_0 is taken as constant [23]. As the Zn electrode was not the limiting electrode and material utilization was low, precipitation of ZnO within the electrode pore space was neglected. This was experimentally justified by measurement of the remaining anode capacity after cell failure, which was always in great excess. ZnO precipitation and buildup during long term cycling was handled empirically by introducing an additional resistance accounting for the separator region in Equation (16).

A.3 Separator

The similar set of governing equations (A-6)-(A-19) were written for the separator region. Since there is no reaction occurring in the separator, $i_n = 0$. There is no solid phase and hence, $i_s = 0$. At all inner boundaries, $x = L_{neg}$ and $x = L_{neg} + L_{sep}$, the concentration flux is continuous.

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Nomenclature

a	Active surface area of manganese dioxide per unit volume (cm^{-1})
$C_{Mn^{+3}}^0$	Initial concentration of Mn^{+3} ions (mol cm^{-3})
$C_{Mn^{+4}}^0$	Initial concentration of Mn^{+4} ions (mol cm^{-3})
$C_{Mn^{+3}}$	Concentration of Mn^{+3} ions at time t (mol cm^{-3})
$C_{Mn^{+4}}$	Concentration of Mn^{+4} ions at time t (mol cm^{-3})
$C_{OH^-}^0$	Initial concentration of OH^- ions (mol cm^{-3})
C_{OH^-}	Concentration of OH^- ions at time t (mol cm^{-3})
D_{H^+}	Diffusion coefficient of H^+ ions ($\text{cm}^2 \text{s}^{-1}$)
D_{OH^-}	Diffusion coefficient of OH^- ions ($\text{cm}^2 \text{s}^{-1}$)
E_{cell}	Cell voltage (V)
E_{eq}	Equilibrium potential (V)
F	Faradays constant ($96,480 \text{ C mol}^{-1}$)
I	Applied current density (A cm^{-2})
i_0^0	Initial exchange current density (mA cm^{-2})
i_0	Exchange current density (mA cm^{-2})
i_l	Liquid phase current density (mA cm^{-2})
i_n	Reaction current density (mA cm^{-2})
i_s	Solid phase current density (mA cm^{-2})
L_{pos}	Thickness of positive (MnO_2) electrode (cm)
L_{neg}	Thickness of negative (Zn) electrode (cm)
L_{sep}	Thickness of separator (cm)
r	Radial co-ordinate in the MnO_2 particle (cm)
R	Universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)

R_f	Film resistance (ohm cm ²)
R_p	Radius of MnO ₂ particle (μm)
R_s	Separator resistance (ohm cm ²)
t	Time (sec)
T	Temperature (K)
t_+^0	Transference number for potassium (K ⁺) ions (-)
x	axial co-ordinate in the direction of electrode thickness (cm)

Greek letters

α_a	Anodic transfer coefficient (-)
α_c	Cathodic transfer coefficient (-)
δ_{film}	Film thickness (cm)
ε	Porosity for separator, positive and negative electrode (-)
η	Overpotential (V)
ϕ_l	Liquid phase potential (V)
ϕ_s	Solid phase potential (V)
κ	Liquid phase conductivity (S cm ⁻¹)
κ^∞	Bulk liquid phase conductivity (S cm ⁻¹)
σ	Solid phase conductivity (S cm ⁻¹)

List of tables:

Table 1 Dissolved Zn concentration in the electrolyte after 24 cycles at full DOD

Table 2 Zn-MnO₂ cell cycling capacity

Table 3 Parameters used in the model

Table 4 Zn-MnO₂ cost component analysis for a 1030 Wh battery (12.87 V, 9 cells)

Table 5 Comparison of electrochemical systems for large-scale energy storage applications.

Lifetime investment cost range was calculated from cycle life and capital cost ranges taken from ref [41].

Table 1

Conc. Electrolyte (wt% KOH)	Zn concentration (M)
10	0.2
30	0.36
45	0.54

Table 2

Cell Numbers	Cycling Condition	Build capacities		Cycled capacity	Discharge rate ^b	Energy density
		Anode	Cathode ^a			
1	10% DOD	21 Ah	1.9 Ah*	0.19 Ah	15 mA g-MnO ₂ ⁻¹ (C/2)	20 Wh L ⁻¹
2	20% DOD	21 Ah	1.9 Ah*	0.38 Ah	15 mA g-MnO ₂ ⁻¹ (C/4)	40 Wh L ⁻¹
3	5% DOD	14 Ah	3.6 Ah**	0.18 Ah	15 mA g-MnO ₂ ⁻¹ (1C)	10 Wh L ⁻¹
4	10% DOD (high rate 1)	14.5 Ah	3.6 Ah**	0.36 Ah	30 mA g-MnO ₂ ⁻¹ (1C)	20 Wh L ⁻¹
5	10% DOD (high rate 2)	14.2 Ah	3.6 Ah**	0.36 Ah	48 mA g-MnO ₂ ⁻¹ (1.5C)	20 Wh L ⁻¹
6	10% DOD (Repeat cell 1)	21 Ah	3.6 Ah**	0.36 Ah	15 mA g-MnO ₂ ⁻¹ (C/2)	20 Wh L ⁻¹

a Based on one-electron MnO₂ discharge

b C-rates based on the cycled capacity of the cell

*One cathode and two anodes configuration in the cell

**Two cathodes and three anodes configuration

Table 3

Variable	Value	
L_{pos} , cm	0.06	Measured
L_{neg} , cm	0.06	Measured
L_{sep} , cm	0.00254	Measured
$C_{Mn^{+4}}^0$, mol cm ⁻³	0.053	Measured
D_{H^+} , cm ² s ⁻¹	1×10^{-15}	[23,26]
R_p , μ m	10	Fitted
i_0^0 , mA cm ⁻²	2×10^{-7}	[23]
$C_{OH^-}^0$, mol cm ⁻³	6.91×10^{-3}	Measured
ε for Zn electrode	0.35	Measured
ε for MnO ₂ electrode	0.45	Measured
ε for separator	0.3	Known from vendor
a (cm ⁻¹)	1350	Measured

Table 4

Component	Cost per Quantity	10% Cathode DOD		15% Cathode DOD		20% Cathode DOD	
		Quantity Needed	Component Cost	Quantity Needed	Component Cost	Quantity Needed	Component Cost
Zn	\$4.1 kg ⁻¹	3.5 kg	\$14.35	3.5 kg	\$14.35	3.5 kg	\$14.35
ZnO	\$1.31 kg ⁻¹	0.35 kg	\$0.46	0.35 kg	\$0.46	0.35 kg	\$0.46
Current Collectors	\$2.13 m ⁻²	3.4 m ²	\$7.24	3.4 m ²	\$7.24	3.4 m ²	\$7.24
Separators	\$1.0 m ⁻²	3.1 m ²	\$3.10	3.1 m ²	\$3.10	3.1 m ²	\$3.10
MnO ₂	\$1.58 kg ⁻¹	23.9 kg	\$37.76	15.9 kg	\$25.12	12.0 kg	\$18.96
Graphite	\$5.68 kg ⁻¹	11.0 kg	\$62.48	7.4 kg	\$42.03	5.5 kg	\$31.24
Binder (Teflon)	\$2.0 kg ⁻¹	2.0 kg	\$4.00	1.4 kg	\$2.80	1.1 kg	\$2.20
Electrolyte (KOH)	\$1.97 kg ⁻¹	0.7 kg	\$1.38	0.7 kg	\$1.38	0.7 kg	\$1.38
Tabs	\$0.02 /item	99	\$1.98	99	\$1.98	99	\$1.98
Casing/Box /Top	\$10		\$10		\$10		\$10
Battery Material Cost:			\$142.75		\$108.46		\$90.91
Cost Delivered kWh at Specified DOD:			\$138.60 per kWh		\$105.30 per kWh		\$88.26 per kWh

Table 5

Electrochemical systems	Cycle life (Cycles)	Capital Cost (\$ per kWh)	Efficiency (% , average)	Lifetime investment cost (¢ per kWh per cycle)	Notes
Pb-acid	500-1000	200-400	75	27-107	Lead toxicity
Ni-Cd	2000-2500	800-1500	65	49-115	Cadmium toxicity
Na-S	2500	300-500	82.5	15-24	High temperature, Safety issues
V-redox	12,000	150-1000	80	2-10	Poor energy-to-volume ratio
Li-ion (various)	1000-10,000	600-2500	92.5	7-270	Safety issues
ZEBRA	2500	100-200	87.5	5-9	High temperature
Zn-Br	200	150-1000	67.5	11-74	Bromine toxicity
Zn-MnO₂	3200	140 (at 10% DOD) 90 (at 20% DOD)*	80-85	0.1⁺-5	Aqueous chemistry, non-toxic

*current testing indicates cycle life >550 at the time of writing

⁺Based on projected cycle life of 2000 at 20% DOD

List of figures:

Figure 1 A typical current-voltage profile at 2398th cycle for one of the cell cycled at 10% DOD and 2 hr rate (1) CC charge (2) CV charge (3) rest period after charge (4) CC discharge (5) rest period after discharge

Figure 2 Equilibrium potential for MnO₂ electrode vs SOC

Figure 3 Cycling performances of MnO₂ cathode batteries at full DOD. The effect of electrolyte concentration was as indicated. (a) With pasted Zn anodes, full DOD defined as discharge to 1 V. (b) With cadmium anodes, full DOD defined as discharge to 0.6 V.

Figure 4 Effect of DOD on the dissolved Zn concentration in the electrolyte and Mn/Zn mass ratio on the cathode surface, as measured by EDS. Error bars are standard deviation based on 3 experiments.

Figure 5 Surface XRD of the MnO₂ cathodes shown in Figure 4 after 24 cycles at various DOD. Reflections for: (●) Mn₃O₄ (○) ZnMn₂O₄ (▼) γ -(ϵ -)MnO₂ (▽) γ -MnO₂ (⊗) attributable to Mn₃O₄, ZnMn₂O₄, Mn₂O₃, Mn(OH)₂ (■) graphite (•) Teflon (◇) ZnO

Figure 6 Long-term cycling performance of Zn-MnO₂ cells at reduced DOD. (a and c) Energy efficiency of all cells (b and d) Discharge end voltage (DEV) for all cells. Cell failure is indicated by an X (1) 10% DOD and C/2 (2) 20% DOD and C/4 (3) 5% DOD and 1C (4) 10% DOD and 1C rate (5) 10% DOD and 1.5C (6) 10% DOD and C/2.

Figure 7 SEM images of MnO₂ electrode after cycling with Zn anode for 3004 cycles (a and b) Fresh MnO₂ electrode before cycling (c and d) MnO₂ electrode cycled with Zn anode for 3004 cycles. Magnified areas (indicated by white boxes) show the presence of adherent layer formed on the MnO₂ particle and presence of ZnO rods

Figure 8 Surface XRD spectra of MnO₂ cathodes cycled in Zn-MnO₂ batteries for 3004 and 24 cycles. Over time hausmannite and hetaerolite were formed. MnO₂ peaks remained but were reduced. Symbols are as in Figure 5.

Figure 9 Discharge curves from the model (solid lines) compared to experimental data (dotted lines) at various discharge rates in mA g-MnO₂⁻¹

Figure 10 Variation of OCP as a function of cycle number for Zn-MnO₂ cells discussed in Table 2 at various cycle numbers (a) OCP after charge and discharge (b) SOC after charge and discharge (the numbers in legend are cell numbers discussed in Table 2) The filled symbol indicates after charge and the hollow symbol indicates after discharge.

Figure 11 Film resistance (R_f) for different battery cycling conditions for cells shown in Table 2.

Figure 12 Comparison of experimental and simulated discharge curves for Cell 1, cycled at 10% DOD and 2 hr rate.

Figure 13 Schematic representation of the Zn-MnO₂ battery

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13