



Rechargeability and economic aspects of alkaline zinc–manganese dioxide cells for electrical storage and load leveling



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HIGHLIGHTS

- Zn–MnO₂ battery was cycled at shallow DOD for more than 3000 cycles.
- Relatively low delivered cost of less than \$150 per kWh.
- Mathematical model developed to understand the capacity fade mechanisms.
- Resistive film formation on the surface of MnO₂ particle during cycling.
- Change in SOC during cycling was used to measure capacity loss.

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ABSTRACT

Batteries based on manganese dioxide (MnO₂) cathodes are good candidates for grid-scale electrical energy storage, as MnO₂ is low-cost, relatively energy dense, safe, water-compatible, and non-toxic. Alkaline Zn–MnO₂ 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–MnO₂ 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 MnO₂ 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–MnO₂ batteries based on the experiments reported here.

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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

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irreversible products associated with MnO_2 cycling [1]. It is also known that if a Zn anode is used then it can interact with the manganese dioxide cathode and cause additional irreversible capacity loss due to the formation of hetaerolite (ZnMn_2O_4) during cycling [2,3]. Zn metal anodes 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 $\epsilon\text{-MnO}_2$) 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 $\text{Mn}(\text{OH})_2$, 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%–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 MnO_2 electrode. Some studies in the literature have attempted to retain the electrochemically active $\gamma\text{-MnO}_2$ 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 MnO_2 cathodes at various DODs and C-rates and identify conditions leading to long cycle life while using commercially available MnO_2 . 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 MnO_2 . The Zn– MnO_2 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– MnO_2 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 h. 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. MnO_2 electrodes

The MnO_2 cathodes were made with 65 wt% MnO_2 (EMD Trolox, USA), 30 wt% KS44 graphite (Timcal, USA), and 5 wt% T3859 Teflon. The MnO_2 electrode sheet was made in the same manner as the Zn electrode sheet. Two pieces of rolled MnO_2 electrode sheet were pressed on either side of an expanded Ni plated steel mesh current collector. The MnO_2 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, MnO_2 and Cd electrodes used had identical width and height.

2.4. Separators and cell assembly

MnO_2 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

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