

The cause of the voltage “dip” during the high rate discharge of the primary alkaline MnO_2/Zn cells

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Abstract

The phenomena of the voltage “dip” during the high rate discharge of the primary alkaline MnO_2/Zn cells have been investigated. The “dip” was found anode related. Formation of the type II ZnO film during the high rate discharge was believed to be the cause of the “dip”. The majority of the potential “dip” results from the sharp increase of the Ohmic resistance of the zinc gel matrix; the diffusion overpotential across the ZnO film also contributes to the potential “dip”. The reactivation is believed to have resulted from the removing of the type II film.

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1. Introduction

Portable primary electrochemical cells have been used for many years. The most commonly used primary cells are primary alkaline manganese dioxide/zinc cells, due to their unique performance characteristics and favorable cost structure. Recent advancements in electronic devices such as digital cameras, MP3 players and high-tech toys require the traditional alkaline cells to function under high rate conditions. In order to achieve a high rate performance in the alkaline electrolyte, the surface area of the zinc anode is increased by suspending zinc powders in gel electrolyte. A few years ago, up to 9% or higher of mercury (by weight) was added in the zinc anode, either by surface or mass amalgamation, to prevent Zn corrosion, which is the main cause of cell leakage resulted by hydrogen generated from the corrosion process, when the increase of internal pressure is sufficient to burst the safety seal. Amalgamation is the most effective way to suppress zinc corrosion. However, due to environmental concerns, Hg

is now banned from use in cylindrical batteries including Zinc-carbon and alkaline primary cells in US and Europe. Instead, organic surfactants and inorganic inhibitors e.g. Bi, Al, Ca, Pb were used to reduce Zn corrosion [1]. Unfortunately, eliminating Hg from the Zn anode has a significant impact on the high rate discharge domain. The high rate performance of a zero-Hg, zero-Pb zinc anode with (or without) organic inhibitors still needs to be improved in the following areas: 1st, initial voltage “dip” [2]; 2nd, the voltage “dip” during the high rate discharge; 3rd, partial discharge gassing. In this study, the cause of the voltage “dip” during the high rate discharge is explained for the first time.

2. Experimental method

Zinc anodes were made by mixing Zn alloy powders with gel electrolyte using high-speed lab mixer. The Zn alloy used for the study containing 300 ppm Bismuth, 300 ppm Indium and 300 ppm Aluminum. The majority of particles are within 150–525 μm . Polyacrylic acid (0.6%) was used as gelling agent to make the gel electrolyte. 9 M KOH and 0.5 M ZnO was used as the electrolyte.

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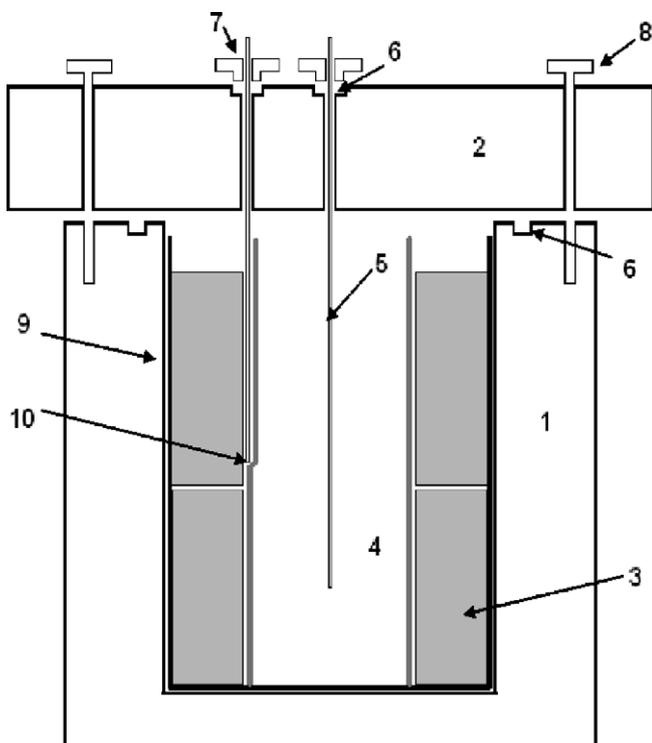


Fig. 1. Electrochemical cell used in the experiments. 1, cell holder made by solid Ni metal, also serving as cathode contact; 2, plastic top; 3, EMD cathode; 4, Zn gel; 5, In coated brass nail as anode current collector; 6, O-rings; 7, seal Zn wire reference electrode; 8, screws; 9, D-size can and 10, non-woven separator.

The zinc anode gel was housed in a D-size cell with bobbin cathode design. The counter cathode contained Electrolytic Manganese Dioxide (K60, EraChem) as electrochemical active reagent, graphite powder (MP11, NDG) as conductive filler and 9 M KOH solution as electrolyte. The cathode was made to have intimate contact with the metal can to ensure low Ohmic resistivity. A non-woven separator was placed between the cathode and the anode. The D-size cell was sealed in the fixture shown in Fig. 1. An indium coated brass nail was used as the anode current collector. A zinc reference electrode was made by sealing pure Zn wire in a Teflon tube; the reference electrode was placed at the cathode-separator interface.

All experiments were done at room temperature (298 ± 1 K).

The ac impedance measurements were conducted by means of an AutoLab impedance spectrometer. The dc discharge measurements were done with EG&G 170 potentiostat controlled by Q&R Smart Data.

3. Results and discussion

Fig. 2 shows the discharge curve of a D-size cell, under 1 A constant current discharge. A voltage “dip” can be clearly observed. The inset shows the enlargement of the voltage “dip”. The high rate voltage “dip” could be so severe as to disable commercial electronic devices prematurely by reaching the device “cut-off” voltage, which will

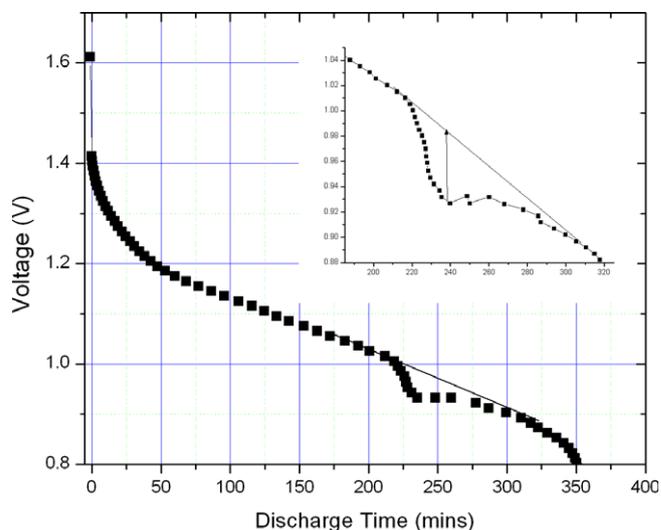


Fig. 2. 1 A constant current discharge curve for the D-size cell. The inset shows the enlargement of the voltage “dip”.

significantly reduce the service life of a battery. The present work reports the investigation of the phenomenon for the first time.

In order to identify whether the cell voltage “dip” is cathode or anode related, a D-size cell was discharged at 1 A in the fixture shown in Fig. 1, the potentials of the cathode and the anode during the discharge were monitored against the common Zn reference electrode. The potential profiles for the anode and the cathode are shown in Fig. 3. An anode potential “dip” can be clearly observed during the discharge, which corresponds very well to the cell voltage “dip”; while there is no evidence of dipping in the cathode discharge curve. Thus, the cell voltage “dip” can be solely associated to the Zn anode with confidence. In addition, preliminary data show that the “dip” is also related the type of the zinc alloy, the concentration of KOH, zinc particle size, packing density and anode additives, the details will be reported later.

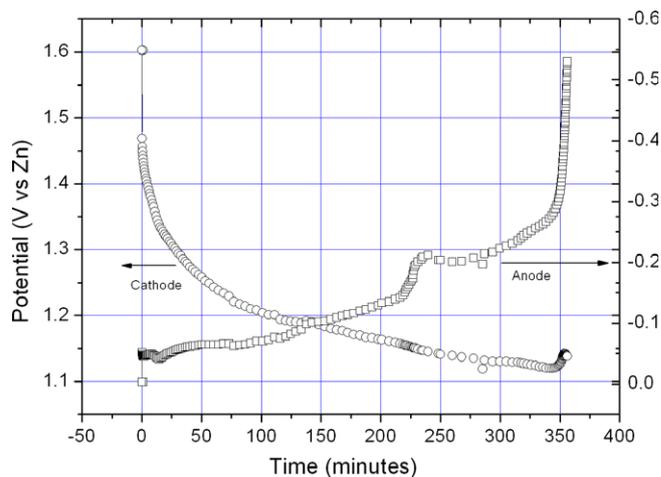


Fig. 3. Comparison of the discharge curves of a cathode and an anode in the same D-size cell.

The ac impedance was used to study the cause of the “dip”. The advantage of impedance spectroscopy is acquisition of multiple meaningful mechanistic information, which otherwise could not be obtained through traditional dc techniques. Numerical fitting of an impedance spectrum has proved useful to extract the information. A Randles equivalent circuit, which is shown in Fig. 4, was used to fit the impedance spectra. In the Randles circuit, R_s is the Ohmic resistance of the system. R_{ct} and C_{dl} represent the charge transfer resistance and the double layer capacitance, respectively. A finite Warburg component is used to represent the diffusion of charge carriers (OH^- ions) through a medium, since OH^- ions would diffuse from the bulk electrolyte and penetrate the entire thickness of diffusion layer, which was ZnO layer in this study. In the transition region between the semi-infinite and the true finite diffusion control, where $\omega \approx D/\delta^2$, D is the diffusion coefficient, the Nernst diffusion layer thickness, δ was comparable to the distance traveled by the diffusion species in the low frequency oscillating perturbations, then the impedance is given [3,4] as

$$Z_\omega = (1 - i)\sigma\omega^{-1/2} \tanh[\delta(i\omega/D)^{1/2}] \quad (1)$$

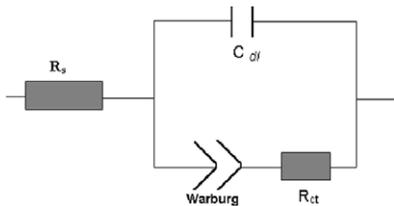
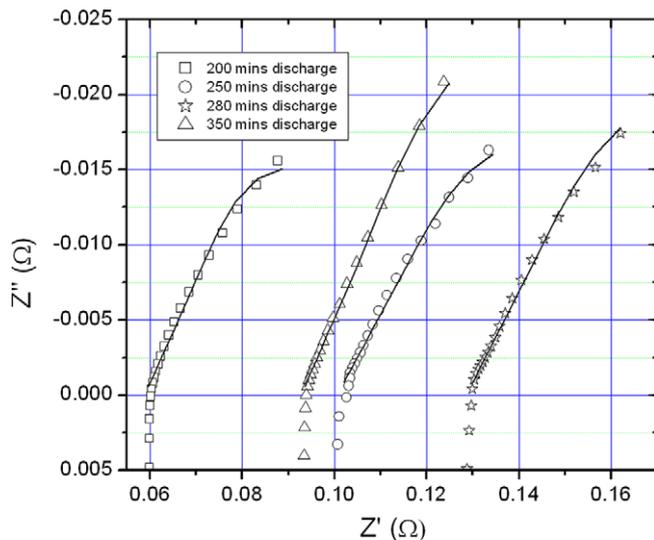


Fig. 4. Comparison of ac impedance spectrum (symbols) and fitting results (solid lines). The measurements were taken at various time during 1 A discharge and in the range of the “dip” happening. The numerical fittings were based on the Randles equivalent circuit shown in the low portion.

when

$$K = \sqrt{\frac{2\delta^2}{D}} \quad (2)$$

Then,

$$Z'_\omega(\text{real}) = \frac{\sigma}{\sqrt{\omega}} \frac{(\sinh K\sqrt{\omega} + \sin K\sqrt{\omega})}{(\cosh K\sqrt{\omega} + \cos K\sqrt{\omega})} \quad (3)$$

$$Z''_\omega(\text{imaginary}) = \frac{\sigma}{\sqrt{\omega}} \frac{(\sinh K\sqrt{\omega} - \sin K\sqrt{\omega})}{(\cosh K\sqrt{\omega} + \cos K\sqrt{\omega})} \quad (4)$$

Both σ and K can be obtained by means of the least-square fitting of the ac impedance results. Fig. 4 also shows the comparison of the impedance spectra (symbols) for the same D-size cell anode after various lengths of discharge during the period of the “dip” and the fitting results (lines) based on the Randles circuit. Fig. 5 illustrates the changes of the Ohmic resistance and K^2 during the period of the “dip”. It is obvious that the Ohmic resistance increase was corresponding to the “dip”, in other words, the “dip” was partially caused by the sudden increase of the “IR drop” of the zinc anode during the high rate discharge. In addition, the profile of K^2 matched well with that of the Ohmic resistance. Thus, the Zn potential “dip” could also result from the changes of the diffusion layer thickness and the diffusion coefficient.

The Zn oxidation reaction mechanism in the concentrated KOH electrolyte was first report by Powers et al. [5–7]. Two different types of ZnO were found forming on the surface of the Zn particles. The type I ZnO film is loose and flocculent and the type II film is dense and compact. The formation of the ZnO film is believed directly related to the local supersaturation of zincate ions and the local concentration of KOH [8]. The mechanism of ZnO formation during the oxidation has been widely studied [9–13]. Most of the previous studies were conducted on polished planar Zn electrodes, the investigation on porous powder

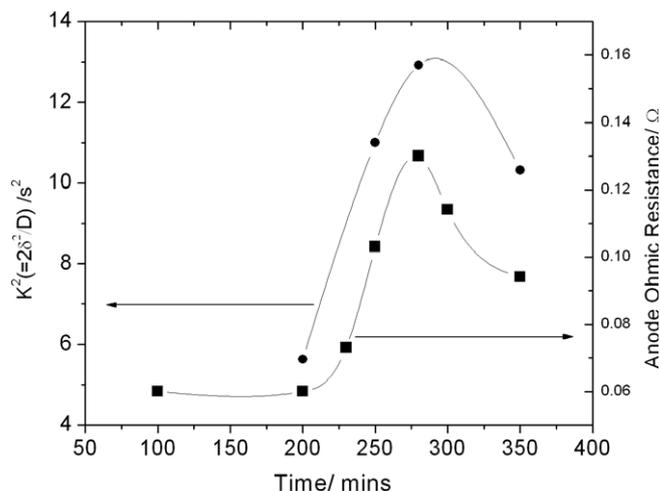


Fig. 5. The changes of K^2 value and Ohmic resistance during the period of the potential “dip”. $K^2 = 2\delta^2/D$, where D is the diffusion coefficient and δ is the diffusion layer thickness.

Zn electrode is limited [14,15]. The two types of ZnO were clearly observed forming on the discharged Zn anode in a commercial AA cell [14].

The ac impedance results indicate that the anode potential “dip” in the alkaline cells may result from the formation of the dense type II ZnO film during the high rate discharge. The Warburg responses (K^2) indicate that when the potential “dip” occurs the diffusion layer thickness increases and the diffusion coefficient decreases. The formation of the dense type II ZnO film shields the Zn particles by reducing the porosity, thus impeding the diffusion of OH^- ions toward Zn particles from the bulk electrolyte and the redistribution of H_2O away from the reaction sites. Thus the reaction kinetics are under diffusion control. The diffusion becomes more sluggish as the value of K^2 increases, which causes the potential “dip”. One of the significant differences between solid planar electrode and porous powder electrode is the conductivity of the latter electrode depends on the particle–particle contact. The formation of the type II ZnO film increases the contact resistance of the gel anode matrix. The IR drop also contributes to the potential “dip”. The experimental results in Fig. 5 prove the hypothesis by demonstrating the simultaneous Ohmic resistance increase with the K^2 increase during the high rate discharge. It is believed that after passivation, the main potential drop occurs across the passivating layer [11]. It is shown in the inset in Fig. 2 that the “dip” potential was about 80 mV, the contribution from the Ohmic resistance change (Fig. 5) was about 60 m Ω , the IR drop under 1 A discharge would be 60 mV. The diffusion resistance would contribute less than 20 mV to the potential “dip”.

As the 1 A discharge continued, the Ohmic resistance started to decrease, so did K^2 . Evidentially, the compact passive layer disappeared and the Zn surface became reactivated. The detailed mechanism of the reactivation is not clear yet, but two mechanisms were proposed to explain the phenomenon. Type II ZnO was found to be a catalyst inducing hydrogen evolution at potentials anodic to the Zn/ZnO equilibrium potential. The hydrogen bubbles forming on the surface of Zn particles could mechanically dislodge the passivating film to regain particle–particle contacts and to enhance the mass transfer in and out of

the Zn electrode, thus to cause reactivation of the anode [7]. As the type II film thickness increases, the film would become more dense, the internal stresses would develop in the course of film growth, when the stresses reach the threshold, the compact ZnO layer would be self-destructed by folding and buckling [8], the electrode would be reactivated.

The reason that the potential “dip” only happens at the high rate discharge may due to the fact that the dissolved zincate ions do not have sufficient time to diffuse away from the Zn anode, supersaturation is more likely to reach the point of inducing the type II film formation. In addition, the local pH would be significantly reduced as well.

4. Conclusion

The voltage “dip” during the high rate discharge of an alkaline MnO_2/Zn cell is caused by the formation of the compact type II ZnO film on the anode. Both IR drop and diffusion overpotential contribute to the potential “dip”, but IR drop is the main cause of the potential “dip”. The passive film eventually disappears from the Zn surface and the anode is reactivated.

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