Mathematical Modeling of Primary Zn/MnO_2 Alkaline Batteries

Xiaotong. H. Chadderdon, Matthew. T. Wendling
Energizer Holdings, Inc., Westlake, OH, USA

INTRODUCTION: In this work, a mathematical model based on porous electrode theory was developed in COMSOL Multiphysics to simulate discharge of primary AA Zn/MnO_2 batteries. This model was applied to:

- Visualize and verify mechanisms that control battery behavior during discharge;
- Increase efficiency of R&D by screening and optimizing battery design concepts, thereby reducing the amount of samples built and tested.

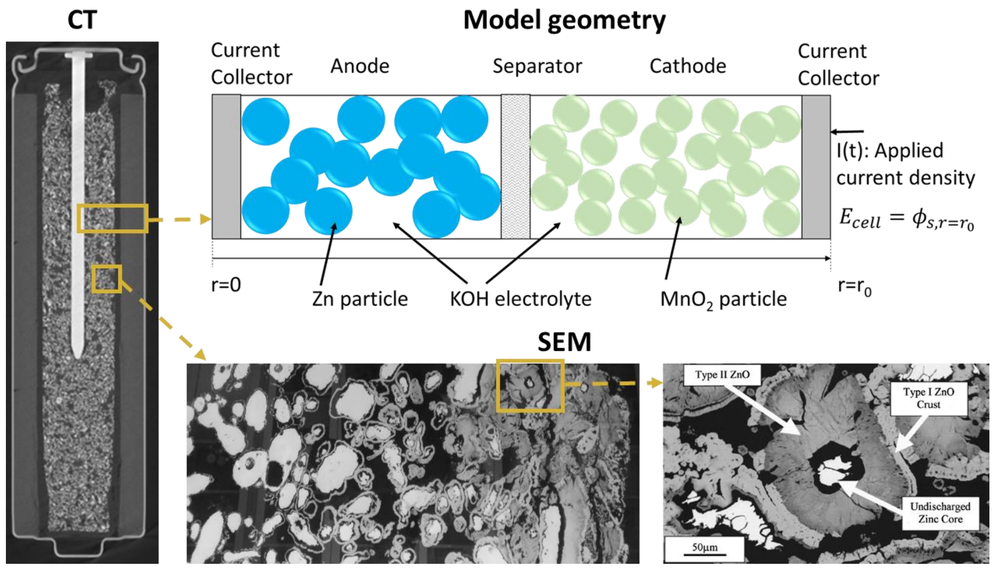

Figure 1. Schematic of a cylindrical AA Zn/MnO_2 cell

Anode: $Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^-$
$Zn(OH)_4^{2-} \rightarrow ZnO + 2OH^- + H_2O$
Cathode: $MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^-$
Overall: $Zn + 2MnO_2 + H_2O \rightarrow ZnO + 2MnOOH$

MODEL EQUATIONS: PDE interfaces were used to solve for 18 variables in a two step (stationery and time dependent) study.

Mass conservation	$\frac{\partial \epsilon C_i}{\partial t} + \frac{r_0}{r}\nabla \cdot \left(\frac{r}{r_0}\left(-D_{i,eff}\frac{\partial C_i}{\partial x} + \frac{t_i i_l}{z_i F} + C_i v\right)\right) = -\frac{s_i j_{a\ or\ c}}{nF} + R_i$
Charge conservation	$i_l = -\left(\kappa_{eff}\frac{\partial \phi_l}{\partial x} + \frac{\kappa_{eff}}{F}\left(\frac{s_1}{n} + \frac{t_1}{z_1}\right)\frac{\partial \mu_A}{\partial x} + \frac{\kappa_{eff}}{F}\left(\frac{s_2}{n} + \frac{t_2}{z_2}\right)\frac{\partial \mu_B}{\partial x}\right)$ $i_s = -\sigma_{eff}\frac{\partial \phi_s}{\partial x}$
Solid species conservation	$\frac{\partial \epsilon_a}{\partial t} = \frac{V_{Zn} j_a}{nF} - \frac{V_{ZnO} R_{ZnO}}{1-\epsilon^*_{ZnO}}$, $\frac{\partial \epsilon_{Zns}}{\partial t} = -\frac{V_{Zn} j_a}{nF}$ $\epsilon_{ZnO} = 1 - \epsilon_{Zns} - \epsilon_a$
ZnO precipitation	$R_{ZnO} = k_{f,T}\left(C_1\left(\frac{C_1}{c_{1eq}}\right)^{\xi} - \frac{1}{K}{C_2}^2\left(a_p + k_o \epsilon_{ZnO}\right)\right)$
Transfer current density	$j_{a\ or\ c} = \frac{r_0}{r}\nabla \cdot \left(\frac{r}{r_0} i_l\right) = -\frac{r_0}{r}\nabla \cdot \left(\frac{r}{r_0} i_s\right)$ $j_a = k_a\left(\left(\frac{C_{2,s}}{C_{2,ref}}\right)^3 exp\left(\frac{2\alpha_{aa}F\eta_a}{RT}\right) - \frac{C_{1,s}}{C_{1,ref}} exp\left(-\frac{2\alpha_{ac}F\eta_a}{RT}\right)\right)$ $j_c = k_c\left(\frac{C_2 CH_s}{C_{2,ref} CH_{ref}} exp\left(\frac{\alpha_{ca}F\eta_c}{RT}\right) - \frac{CH_m - CH_s}{CH_m - CH_{ref}} exp\left(-\frac{\alpha_{cc}F\eta_c}{RT}\right)\right)$ $\eta_{a\ or\ c} = \phi_s - \phi_l - \phi_{ref}$ $k_a = a_{a0}\left(\frac{\epsilon_{Zns}}{1-\epsilon_0}\right)^{\gamma} i_{a,ref}$, $k_c = a_{c0}\left(\frac{1-\epsilon_c}{1-\epsilon_{c0}}\right)^{\gamma} i_{c,ref}$
Mass conservation in microlayer	$\frac{\partial C_i}{\partial t} + \frac{\partial}{\partial y}\left(-D'_{i,eff}\frac{\partial C_i}{\partial y}\right) = \frac{2}{y}D'_{i,eff}\frac{\partial C_i}{\partial y}$
ZnO microlayer growth	$velo = \frac{V_{ZnO} R_{ZnO}}{(1-\epsilon^*_{ZnO}) a_{ZnO}}$

RESULTS: Simulated battery voltage is a function of discharge time, current, and intermittency. Local trends in internal properties show an accumulation of discharge reaction product near the separator interface and a depletion of reactant species both near the particle surface and near the separator interface.

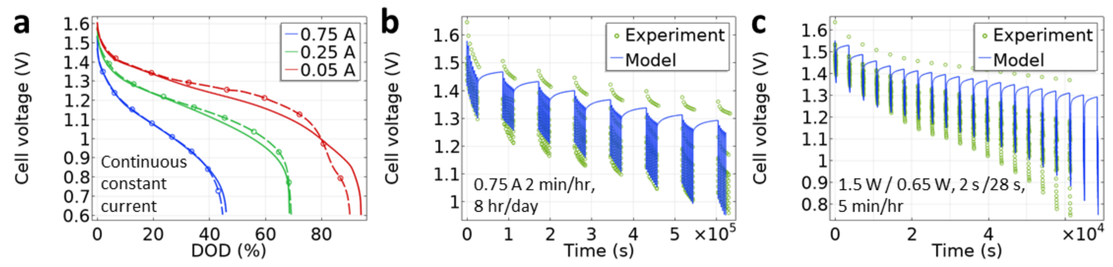

Figure 2. Modeled and experimental discharge behavior of Zn/MnO_2 cell under (**a**) continuous constant current, (**b**) ANSI pulsed constant current, and (**c**) ANSI pulsed constant power conditions.

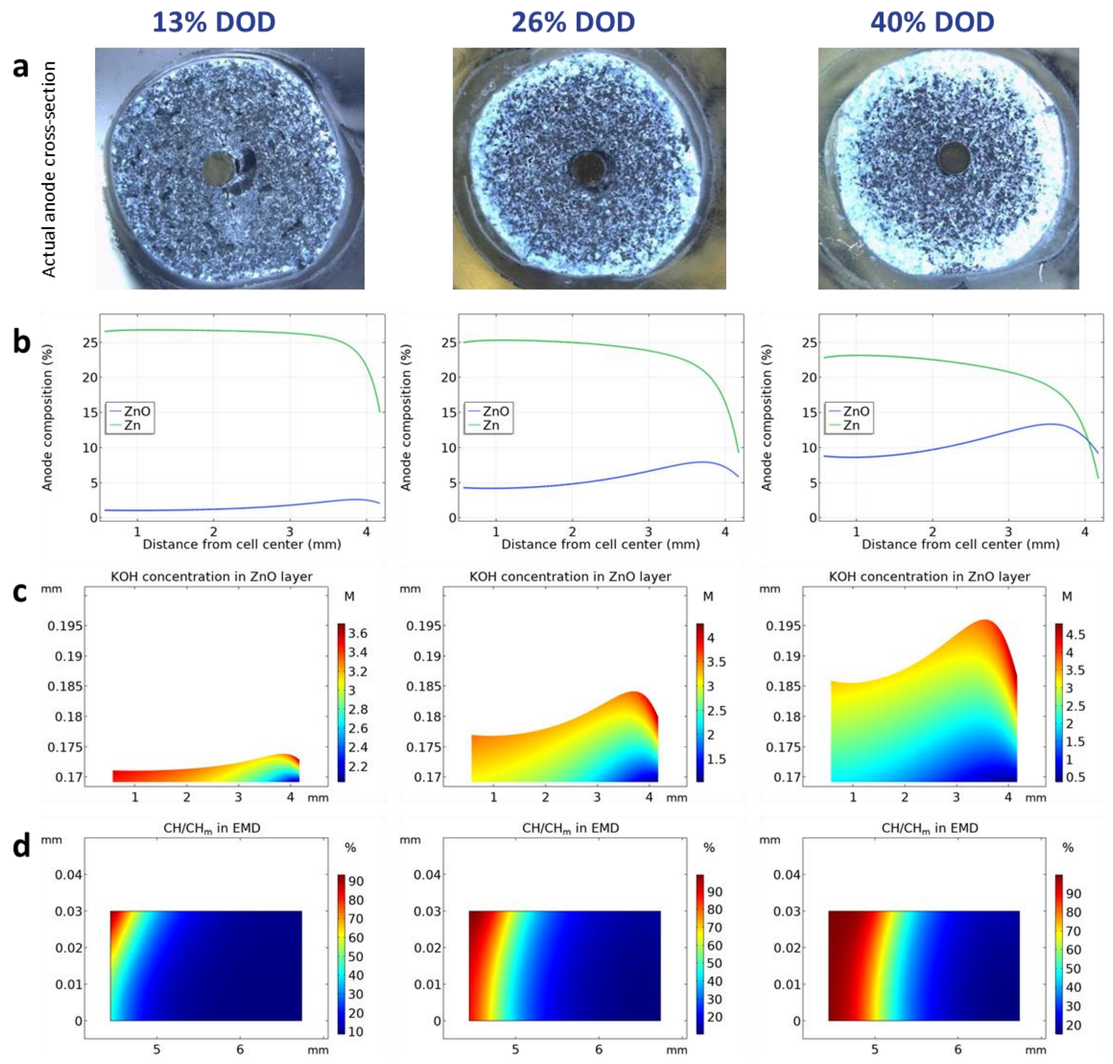

Figure 3. Internal cell properties at various depths-of-discharge (DODs) during 0.75 A discharge, including (**a**) actual anode cross-section, modeled (**b**) anode volume composition, (**c**) KOH concentration across ZnO microlayer and thickness of that layer, and (**d**) CH/CH_m in MnO_2 particle as a function of position at 13% (left), 26% (middle) and 40% (right) DODs.

CONCLUSIONS: The predicted battery performance shows good agreement with experiments under various conditions. These results provide battery engineers better understanding of limiting mechanisms that would otherwise be costly and laborious to explore. Further experiments to refine parameters are planned to increase the fidelity of the model.

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