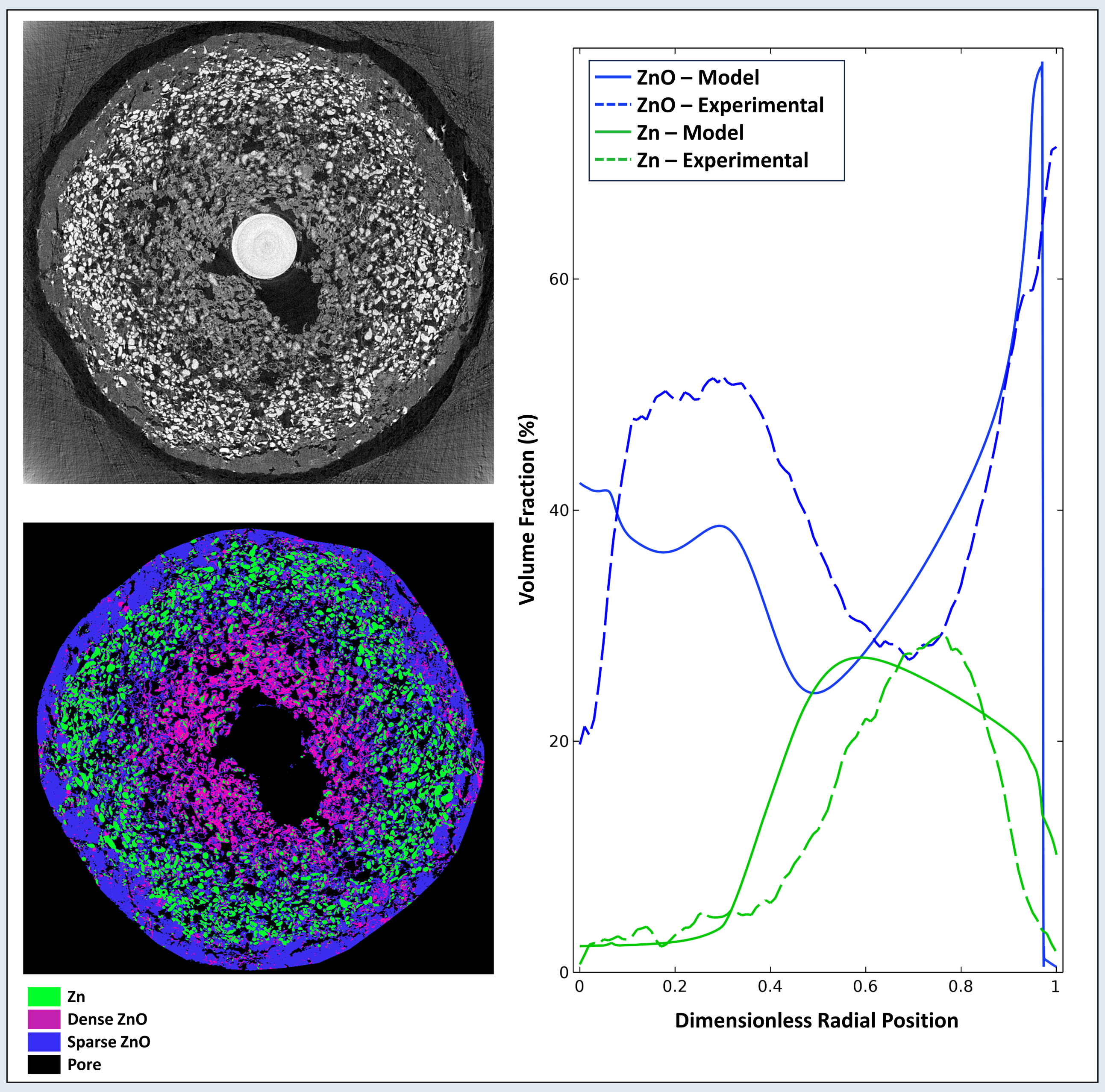

Modeling the Distribution of Active Phases in Alkaline Zn Anodes

Computational modeling can be used to simulate the discharge of alkaline Zn-MnO_2 batteries, predicting performance. The Zn anode contains many complex phenomena that have been captured in this model.

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Introduction

The discharge of an alkaline Zn anode involves the conversion of Zn metal to solid ZnO through the zincate ion. With the heterogeneous dissolution of Zn and mobility of zincate in the electrolyte, complex radial distributions of Zn and ZnO have been observed to occur in the anodes of commercial bobbin-type alkaline batteries. These distributions are highly dependent on the discharge rate and lead to phase distributions that are difficult to predict. The distribution of Zn and ZnO within these electrodes is relevant to battery performance, as localized pore closure and breakdown of the electronically conductive network can lead to premature cell failure. As a result, the ability to accurately model material distribution in Zn anodes is imperative in predicting battery performance. Early work from Mao and White sought to model the material distribution in Zn anodes, but only agrees with experimental observation under high-rate continuous discharge.[1]

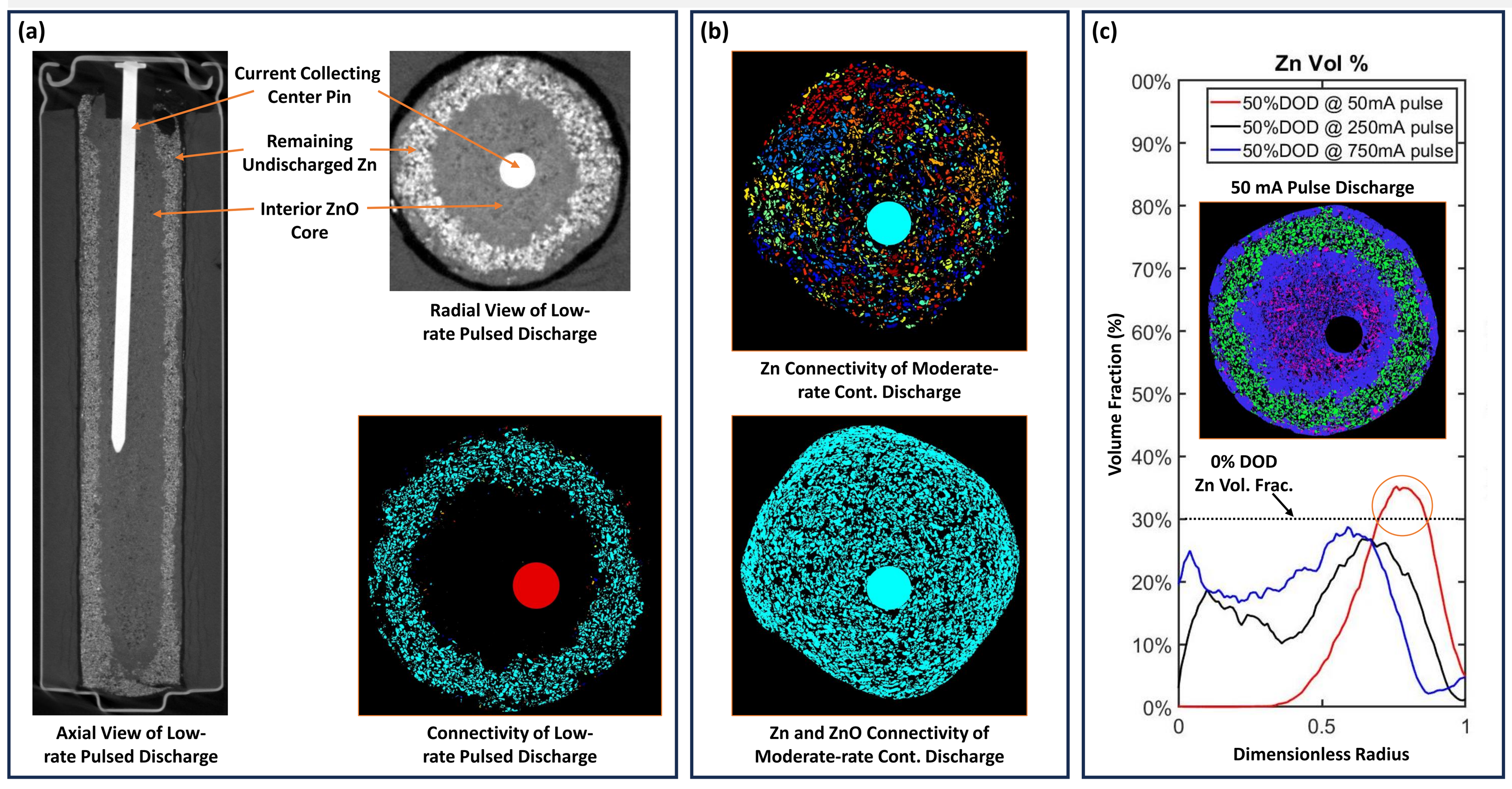

Figure 1: (a) Loss of Zn connection to current collector under low-rate pulsed conditions. (b) Maintenance of connectivity through ZnO bridging. (c) Concentrated region of Zn is evidence of granular flow.

Methodology

CT results show: 1. Zn particle-to-particle connections are lost under many discharge conditions and may rely on ZnO bridges to maintain electronic connectivity; 2. Substantial movement of the Zn particles during discharge.

Redefine anode electronic conductivity using percolation theory and resistors-in-series.[2]

$$\sigma_{anode} = \sigma_{perc} + \sigma_{bridge} \qquad \sigma_{perc} = \sigma_{Zn}\left(\frac{\varepsilon_{Zn} - \varepsilon_c}{1 - \varepsilon_c}\right)^2 \cdot (\varepsilon_{Zn} > \varepsilon_c) \qquad \sigma_{bridge} = \left(\frac{(\varepsilon_{Zn})^{1/3}}{\sigma_{Zn,eff}} + \frac{\max\left((\varepsilon_c)^{1/3} - (\varepsilon_{Zn})^{1/3}, eps\right)}{\sigma_{ZnO,eff}}\right)^{-1}$$

Incorporate granular flow of Zn and ZnO phases to more accurately match the phase distributions observed by CT experiments during low-rate discharge.[3]

$$\frac{\partial}{\partial r}\left(\frac{\partial u_r}{\partial r}\right) = \frac{1}{\nu_{Zn}}\left(u_r - \frac{\nu_{Zn}}{\varepsilon_{Zn}}\frac{\partial \varepsilon_{Zn}}{\partial r} - \frac{\nu_{Zn}}{r}\right)\frac{\partial u_r}{\partial r} + \frac{1}{\nu_{Zn}}\left(\frac{1}{2\varepsilon_{Zn}}\frac{\partial \varepsilon_{Zn}}{\partial r} + \frac{1}{2r}\right){u_r}^2 + \frac{u_r}{r^2} - \frac{F}{2\nu_{Zn}} \qquad \text{(Navier-Stokes eqn.)}$$

$$F \propto -\frac{\partial}{\partial r}\left(\frac{\partial \varepsilon_{ZnO}}{\partial t}\right)\varepsilon_{ZnO} \qquad \frac{\partial \varepsilon_{Zn}}{\partial t} + \nabla \cdot (\varepsilon_{Zn} u_r) = 0$$

Results

By redefining the anode's electronic conductivity and adding granular flow of the solid Zn and ZnO phases, the model was able to accurately predict the phase distributions of the anode under a range of discharge conditions. Figure 2 shows a substantial improvement in the model's ability to predict an inverted reaction zone under low-rate conditions, which was observed experimentally using *in situ* CT.

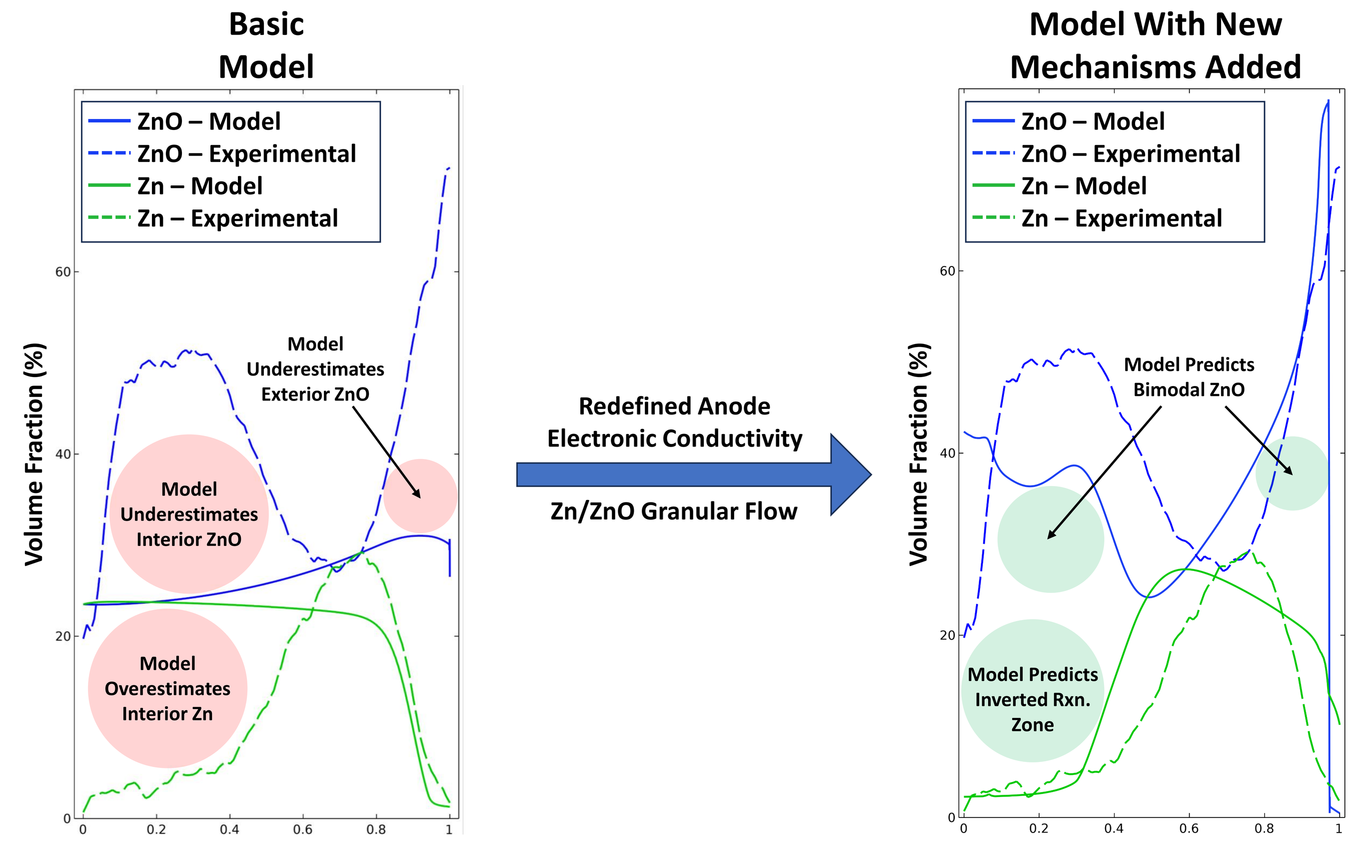

Figure 2: Model predictions without (left) and with (right) the new anode electronic conductivity and granular flow compared against quantitative CT results for low-rate continuous discharge.

REFERENCES

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