

# Simulating zinc-ion batteries

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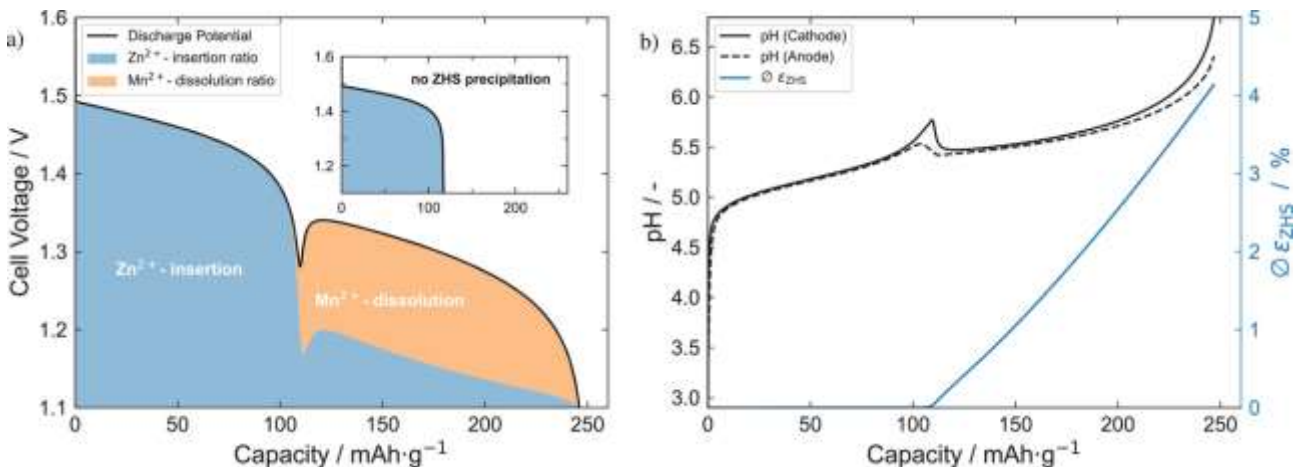
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The best studied candidate for efficient zinc-ion batteries (ZIB) are manganese-oxide ( $\text{MnO}_2$ ) cathodes [1]. ZIBs with aqueous neutral electrolytes exhibit two distinct phases during charge and discharge. Experiments have revealed that the second discharge phase goes hand-in-hand with the precipitation of zinc-hydroxide sulfate (ZHS) at the cathode [2]. Besides the most desired zinc insertion, the proposed working mechanisms of the  $\text{MnO}_2$  cathodes are the (co-)insertion of protons into the cathode and the reversible dissolution of the  $\text{MnO}_2$  itself, both having similar effects on the local pH evolution eventually leading to ZHS precipitation. Our work uses a continuum full-cell model supported by DFT calculation to investigate the implications and details of the experimentally observed properties and deduced claims [3]. We model speciation in the aqueous electrolytes and predict electrolyte pH. We combine this approach with DFT calculations of the cathode structure with inserted zinc and proton to give a detailed picture of ZIB's cycling behaviour. Our cell simulations investigate the interplay of the various proposed reactions [3]. We find that the precipitation of ZHS stabilizes electrolyte pH accelerating  $\text{MnO}_2$  dissolution in the second discharge phase. This understanding for the cycling mechanism allows us to propose operating strategies for mitigating the shape-changing  $\text{MnO}_2$  dissolution [3]. Finally, we compare the discharge behavior of various electrolytes [4].



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(2) Godeffroy, L.; Aguilar, I.; Médard, J.; Larcher, D.; Tarascon, J. M.; Kanoufi, F. *Adv Energy Mater* 2022, 12 (30), 2200722. DOI: 10.1002/AENM.202200722.

(3) Herrmann, N. J.; Euchner, H.; Groß, A.; Horstmann, B. *Advanced Energy Materials* 2024, 14(1), 2302553.

(4) Herrmann, N. J.; Euchner, H.; Groß, A.; Horstmann, B. submitted to *Energy Storage Materials* 2024.