Simulating the cycling mechanism of zinc-ion batteries with MnO_2 cathodes

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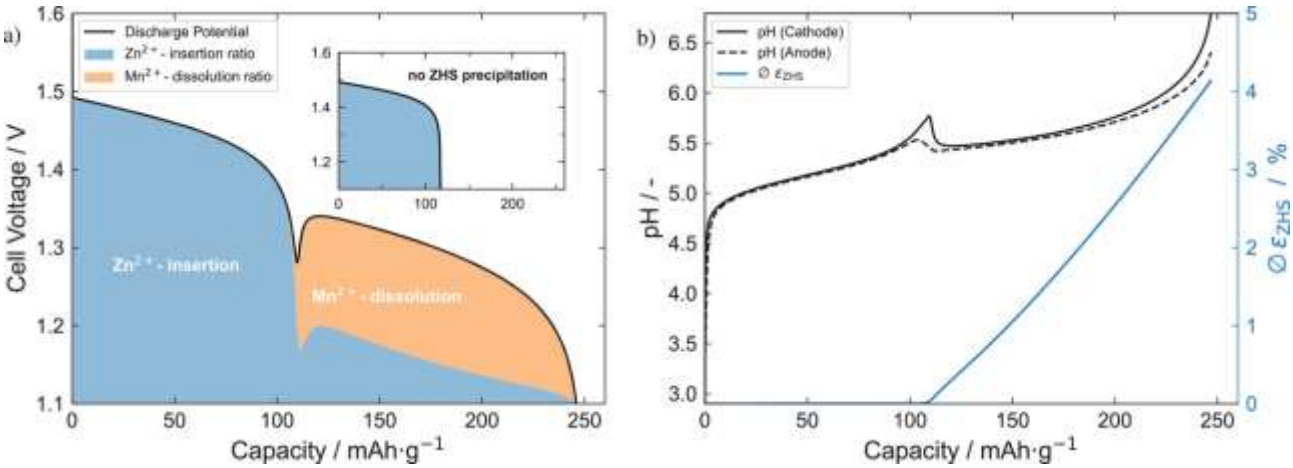
The best studied candidate for efficient zinc-ion batteries (ZIB) are manganese-oxide (MnO_2) cathodes [1]. ZIBs with aqueous neutral electrolytes exhibit two distinct phases during charge and discharge. Experiments have revealed that the second discharge phase goes hand-in-hand with the precipitation of zinc-hydroxide sulfate (ZHS) at the cathode [2]. Besides the most desired zinc insertion, the proposed working mechanisms of the MnO_2 cathodes are the (co-)-insertion of protons into the cathode and the reversible dissolution of the 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 MnO2 dissolution in the second discharge phase. This understanding for the cycling mechanism allows us to propose operating strategies for mitigating the shape-changing MnO_2 dissolution [3]. Finally, we compare the discharge behavior of various electrolytes [4].



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