

Model-Based Electrolyte Design for Rechargeable Zinc Ion Batteries

Niklas Borchers^{1,2}, Birger Horstmann^{1,2}

, Institute of Engineering Thermodynamics

²Helmholtz Institute Ulm (HIU), Computational Electrochemistry

Helmholtzstraße 11, DE-89081 Ulm - GERMANY

niklas.borchers@dlr.de

Materials for next-generation batteries are optimized and characterized in terms of energy- and power density. Nevertheless, the growing market for stationary energy storage needs affordable and safe cell chemistries. Zinc-metal electrodes are highly successful in primary alkaline and zinc-air batteries due to their high specific energy and the abundance of zinc and have a remarkably high voltage in aqueous electrolytes. As used in commercialized zinc systems, traditional alkaline electrolytes show a Zn/ZnO conversion reaction at the anode. While Zn^{2+} transport in the electrolyte and its insertion process is broadly addressed¹, neither its specific interaction with different electrolytes nor the influence of the electrolyte on cathodic and anodic reactions is well studied. Furthermore, the limited electrochemical stability window of aqueous electrolytes leads to hydrogen evolution at the anode and H^+ insertion at the cathode. All in all, the electrolyte is not an inert, idealistic charge carrier but significantly contributes to cell behaviour and performance. Within zinc-air batteries, we have performed model-based optimization studies of pH adjusted electrolytes^{2,3}.

To get a deeper understanding of this interplay in zinc-ion batteries, we have developed a model based on equilibrium thermodynamics of the electrolytes speciation interacting with a dynamic cell model. Consistent with simulations for primary alkaline cells, our model for a Zn/MnO₂ cell chemistry includes H^+ insertion into the cathode, forming MnOOH. Switching to near-neutral electrolytes, the electrolyte speciation and zinc solubility also allow

a zinc transport and insertion mechanism⁴, which we investigate and study not only for ZnSO₄ but also for newly proposed electrolytes such as Zn(OTf)₂.

In our contribution, we discuss the origin for varying cell performance in the most common electrolytes, compare the electrode capacities by different charge storage processes and investigate the likelihood of hydrogen evolution based on electrolyte choice and rate behaviour. This work is supported by the German Federal Ministry for Education and Research (BMBF) via the project ZIB (03XP0204F).

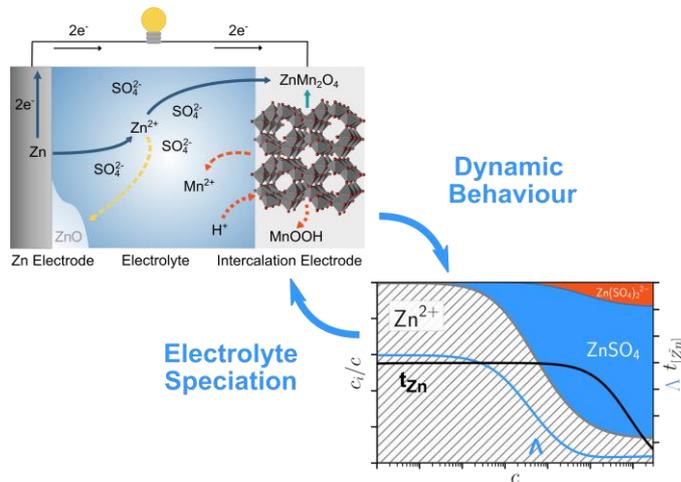


Figure 1: Schematic interplay of the dynamic cell model and the equilibrium speciation of the electrolyte. Cell schematic in the upper left adapted from [1].

References:

- [1] N. Borchers, S. Clark, B. Horstmann, K. Jayasayee, M. Juel, and P. Stevens, "Innovative zinc-based batteries," *J. Power Sources*, 2020, doi: 10.1016/j.jpowsour.2020.229309.
- [2] S. Clark, A. Latz, and B. Horstmann, "Rational Development of Neutral Aqueous Electrolytes for Zinc-Air Batteries," *ChemSusChem*, vol. 10, no. 23, pp. 4735–4747, Dec. 2017, doi: 10.1002/cssc.201701468.
- [3] S. Clark *et al.*, "Designing Aqueous Organic Electrolytes for Zinc–Air Batteries: Method, Simulation, and Validation," *Adv. Energy Mater.*, vol. 10, no. 10, p. 1903470, Mar. 2020, doi: 10.1002/aenm.201903470.
- [4] W. Sun *et al.*, "Zn/MnO₂ Battery Chemistry with H⁺ and Zn²⁺ Coinsertion," *J. Am. Chem. Soc.*, vol. 139, no. 29, pp. 9775–9778, 2017, doi: 10.1021/jacs.7b04471.