

Transport Theory of Ionic Liquids: Modelling and Simulations

Max Schammer^{*1,2,3}, Birger Horstmann^{1,2}, and Arnulf Latz^{1,2,3}

¹*Helmholtz Institute Ulm, Helmholtzstraße 11, 89081 Ulm*

²*German Aerospace Center, Pfaffenwaldring 38, 70569 Stuttgart*

³*University of Ulm, Albert-Einstein-Allee 47, 89081 Ulm*

**Presenting author, email: max.schammer@dlr.de, Tel.: +49 73150 34319*

Theoretical studies and simulations are efficient means for the evaluation of materials and for improving the design of electrochemical devices [1]. Here, we present a thermodynamically consistent transport theory of ionic liquids. This novel transport theory is based on a continuum framework and rigorous physical assumptions. The focus lies on the systematic derivation of a set of fully coupled transport equations for the ions, charge and heat based on the development of modeling methodologies for lithium-ion batteries [2].

Our transport theory describes the bulk phase of ionic liquid electrolytes at length scales where electro-neutrality can safely be assumed. This allows for the characterization of dynamic and kinetic effects of ionic liquids in electrochemical devices. In addition, we incorporate interactions into our transport theory which become dominant at length scales at the order of nanometers. Therefore, the theory also describes the characteristic effects of ionic liquids at electrified interfaces.

Upon this framework we model a zinc ion battery with a mixture of ionic liquid and water as electrolyte. This setup is described experimentally in Ref. [3]. The battery comprises a zinc anode and a Prussian blue analogue cathode in combination with a choline-acetate-water mixture, [Ch]OAc+30% wt water. [Ch]OAc, is a biodegradable, biocompatible, and inexpensive ionic liquid. The battery is simulated along one dimension and good agreement with the experimental observations described in Ref. [8] is found.

For the understanding of microscopic structures, we integrate the hardcore particle nature of the medium into our transport theory. In the vicinity of an electrified interphase, we find a quasi-crystalline structure with crowding and overscreening for a neat ionic liquid [4]. Recently, we examined the influence of a minor additive species (Ag[TFSA]) on the interfacial structure of the neat ionic liquid Pyr[TFSA] in a joint experimental/theoretical study [5]. Our theory predicts the minimal minor salt concentration which is needed to destroy the layered structure. The theoretical predictions are in good agreement with experimental observations.

This work was supported by the Federal Ministry of Education and Research (BMBF) via the project “Zinc/Air Battery with Advanced Materials for Storage of Renewable Energies and Grid Balancing” (LUZI).

- [1] Clark, S., Latz, A., & Horstmann, B. (2018). A Review of Model-Based Design Tools for Metal-Air Batteries. *Batteries*, 4(1), 1–26.
- [2] Latz, A., & Zausch, J. (2015). Multiscale modeling of lithium ion batteries: thermal aspects. *Beilstein Journal of Nanotechnology*, 6(1), 987–1007.
- [3] Liu, Z., Pulletikurthi, G., & Endres, F. (2016). A Prussian Blue/Zinc Secondary Battery with a Bio-Ionic Liquid–Water Mixture as Electrolyte. *ACS Applied Materials & Interfaces*, 8(19), 12158–12164.
- [4] Bazant, M. Z., Storey, B. D., & Kornyshev, A. A. (2011). Double Layer in Ionic Liquids: Overscreening versus Crowding. *Physical Review Letters*, 106(4), 46102.
- [5] Hoffmann, V., Pulletikurthi, G., Carstens, T., Lahiri, A., Borodin, A., Schammer, M., Horstmann, B., Latz, A., Endres, F. (2018). Influence of a Silver salt on the Nanostructure of a Au(111)/Ionic Liquid Interface: an Atomic Force Microscopy Study and Theoretical Concepts. *Phys. Chem. Chem. Phys.*