

CONVECTION IN LIQUID METAL BATTERIES - COMPARING RESULTS FROM OpenFOAM, Semtex, AND SFEMaNS

PAOLO PERSONNETTAZ¹, TANJA KLOPPER², SABRINA BÉNARD³, NORBERT WEBER⁴, TOM WEIER⁵

¹Helmholtz-Zentrum Dresden - Rossendorf, Bautzner Landstr. 400, 01328 Dresden, Germany, p.personnetta@hzdr.de

²Helmholtz-Zentrum Dresden - Rossendorf, Bautzner Landstr. 400, 01328 Dresden, Germany, t.klopper@hzdr.de

³Ecole Normale Supérieure Paris-Saclay, 4 avenue des Sciences, 91190, Gif-sur-Yvette, France, sabrina.benard@limsi.fr

⁴Helmholtz-Zentrum Dresden - Rossendorf, Bautzner Landstr. 400, 01328 Dresden, Germany, norbert.weber@hzdr.de

⁵Helmholtz-Zentrum Dresden - Rossendorf, Bautzner Landstr. 400, 01328 Dresden, Germany, t.weier@hzdr.de

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Switching the energy supply from today's dominant fossil sources to mainly variable renewable energies (wind and solar) means a fundamental change. It will entail the transformation from a centralised energy system to distributed generation that needs flexibility options to balance supply and demand across time and space. Transmission grid expansions can only partially account for the resulting variations in supply. Therefore, large-scale stationary storage will gain importance in future energy landscapes.

Among the candidates to meet the growing demand for stationary storage are liquid metal batteries (LMBs) [1]. Their active materials as well as the electrolyte are in the liquid state. The cell interior consists of two layers of liquid metals interspaced by a molten salt electrolyte in stable density stratification (Fig. 1 top left). This conceptually very simple and self-assembling structure has the unique advantage to allow for an easy scale-up at the cell level: single-cell cross sections can potentially reach several square-meters. Such cell sizes enable highly favourable and otherwise unattainable ratios of active to construction material because of the cubic scaling (volume) of the former and the quadratic scaling (surface) of the latter. The total costs should therefore largely be determined by those of the active materials.

While mass transport in most modern battery systems is typically dominated by diffusion and migration in micrometer-scale

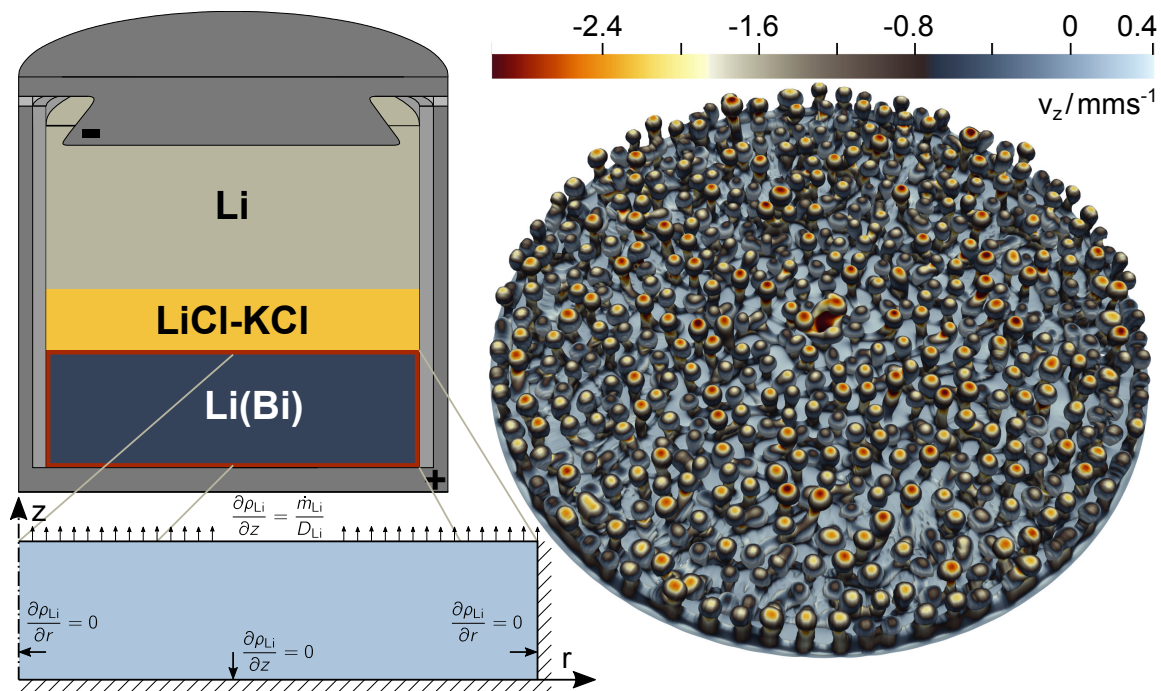


Figure 1: Sketch of a liquid metal battery and of the computational domain (left). Plumes (density iso-contours) of Li-depleted Li(Bi) alloy sinking down during charge. Their surface is colored by vertical velocity (right, view from below).

liquid layers and solids, convection - with exception of redox-flow batteries - rarely plays a role. This is in stark contrast to LMBs where the fully liquid interior fluid flow can be driven by various mechanisms and has a strong influence on cell performance and operational safety [2]. Electric currents, magnetic fields, and heat and mass transfer are tightly coupled with the cells' electrochemistry.

The talk will focus on the influence of solutal convection in the positive electrode on the cycling behaviour of a cell. We consider a Li-Bi battery, a cell chemistry for that ample experimental material is available in the literature, see, e.g. [3]. While this is true for the electrochemical characteristics, detailed experimental information on the flow in these batteries is largely missing. To compensate at least partially for this deficiency, we employ three different codes and compare their results.

In the discharged state, the positive electrode consists of a Li(Bi) alloy. When charging the cell, low density Li is removed from the top of the positive electrode. This increases locally the density of the alloy and Li-depleted fluid starts to sink down in plumes. Rapidly, solutal convection drives a flow in the whole cathode and intensely mixes the remaining alloy [4, 5]. While stabilising thermal gradients can occur, densities of the positive electrode's metal (Bi in our case) are typically an order of magnitude larger than the negative electrode metal (Li here) ones. In comparison, thermal expansion coefficients are quite small and due to the good thermal conductivity of metals, temperature differences tend to be smoothed out quickly. Thus, compositional (i.e. solutal) gradients should dominate over thermal ones and constitute the primary cause or inhibitor of motion in the positive electrode [2].

The OpenFOAM solver is based on `buoyantBoussinesqPimpleFOAM` extended by the concentration convection-diffusion equation and by a variable density depending on temperature as well as composition. Mass transfer through the electrolyte-positive electrode interface is captured by an electrochemically consistent mass flux boundary condition.

Onset of solutal convection from an initially well mixed state is studied in 2D (Fig. 1 bottom left) for different charging currents. The results are compared to computations done with the spectral element solver Semtex [6] and with the mixed spectral and finite element code SFEMaNS [7]. Both programs are available under the GNU General Public License. While different onset times are to be expected due to the various numerical approaches, growth rates obtained with all three solver match very well. Development of the plumes that are the immediate consequences of the instability is quite consistent across the codes, as well as the formation of larger vortical structures at later stages.

Computations in 3D allow for a more realistic description of the flow and a better understanding of mixing. Due to the limited computational resources available to us we undertook these investigations with the more specialised and fast code Semtex only. Even with this code, care had to be taken to sufficiently resolve the fine plume structures (Fig. 1 right) in the early phases of flow development especially near the cells rim.

Properly capturing flow development and mixing in the positive electrode of a typical liquid metal battery allows for a correct description of the cell's cycling behaviour.

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