Numerical Challenges with Convection in Concentrated Solution Theories and Their Application to 3D Simulations of Zinc-Air Batteries

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ABSTRACT

We distinguish two approaches for the modeling of reactive flows in incompressible, multi-component, multi-phase systems. The standard approach requires a divergence free velocity field. It is used in most of the fields in computational fluid dynamics. However, it is only correct for one-component systems. For dilute solutions, in which the solvent is the dominant species, it is only approximately correct. $\nabla \cdot \boldsymbol{v} = 0$ is no longer valid if the concentrations become larger, if the solvent takes part in reactions, or if solvent free electrolytes are modeled. For such cases, the partial molar volumes of all species have to be taken into account. This has a consequence for the convection velocity, which becomes dependent on the change of the fluid composition. It can change or even dominate the overall behavior of the modeled system.

Our extended approach for concentrated solutions takes those effects into account. We consider the partial molar volumes of all constituents and the phase changes to determine the velocity field. It shows that the new set of equations is very stiff and can produce numerical instabilities. For that reason, the governing equations are no longer unconditionally stable. Conventional algorithms, such as implicit Runge-Kutta, BDF, or the SIMPLE-algorithm fail to solve this issue. We analyse this behavior and show the limitations of a fully coupled implicit system. We develop a method, which can solve the system of equations, without limitations on the time step size. To this aim, we decouple the system of equations into two parts. Part one contains the concentrations and the electric potentials. Part two involves the volume fractions and the liquid pressure. We alternately solve both of them in a partially implicit manner within one time step until convergence. By that we introduce a controllable inaccuracy, but solve the system of equations fast. The error is constantly monitored to ensure reasonable results. The linearized systems of equations are solved with a preconditioned algebraic multigrid solver which utilizes BiCGSTAB as coarsest level solver.

We apply this algorithm in three-dimensional, meso-scale simulations of zinc-air batteries with aqueous electrolytes. Such cells are attractive candidates for next-generation energy storage, because they offer high energy densities and are cheap to produce. Up to now, only primary cells have been commercialized and further research is required to enter the rechargeable battery market. A promising improvement is the change of an aqueous electrolyte to near neutral electrolytes or ionic liquids [1]. To model this type of fluids, we apply our new approach of an incompressible medium. We adopt a thermo-dynamically consistent bulk theory [2, 3] and extend an already developed one dimensional model [4]. The phases are averaged over the whole domain by local volume averaging [5].

According to tomographies [6,7], zinc-air cells have a very inhomogeneous anode structure and a non-uniform zinc utilization. One dimensional models can predict the cell voltage of such a battery type. However, they are not sufficient to describe the local effects of such inhomogeneities. Thus, we make use of three dimensional simulations to understand the intimate correlation between electrode structure, electrolyte composition, multi-phase coexistence, and zinc passivation. For that, we keep track of six species, incorporate passivation effects and consider shape changes of the electrodes.

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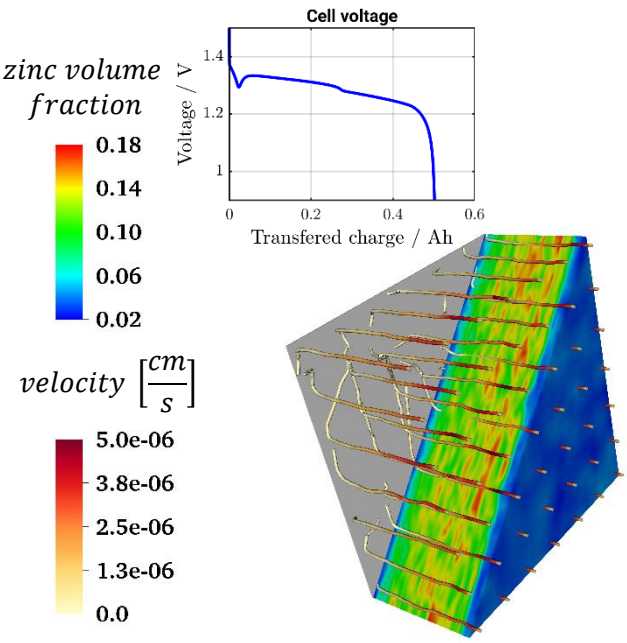

Figure 1: Cross section of a zinc-air cell simulation. The volume fraction of zinc is plotted in color scale. The streamlines represent the fluid velocity with a color-coded speed. The anode current collector is displayed in gray. The plot in the top shows the cell voltage over the transferred charge.