An overview on electrochemical simulation with OpenFOAM

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Modelling electrochemical devices, such as fuel cells, batteries or electrolysers asks typically for coupling electrochemistry with flow simulation and mass transfer. While solvers for mass transfer and fluid dynamics are well established in the open-source CFD library OpenFOAM, electrochemistry simulations are a rather young field of application. The presentation shall give therefore an overview on different approaches on how to simulate potential and current distributions as well as the cell voltage of electrochemical devices using OpenFOAM.

In case that only the terminal voltage – but not the current distribution – is of interest, the latter can simply be computed without solving a differential equation. For this purpose, the reversible cell voltage is first computed from the Gibbs free energy or using tabulated standard potentials. Thereafter, the Nernst equation is applied to include the concentration dependence of the electrochemically active species on the cell potential. Finally, voltage losses are subtracted thus giving the correct cell voltage of the battery or fuel cell. In this context, the ohmic losses are typically computed using an area specific resistance, while charge-transfer overpotentials are computed by solving the Butler-Volmer equation numerically, or the Tafel equation analytically.

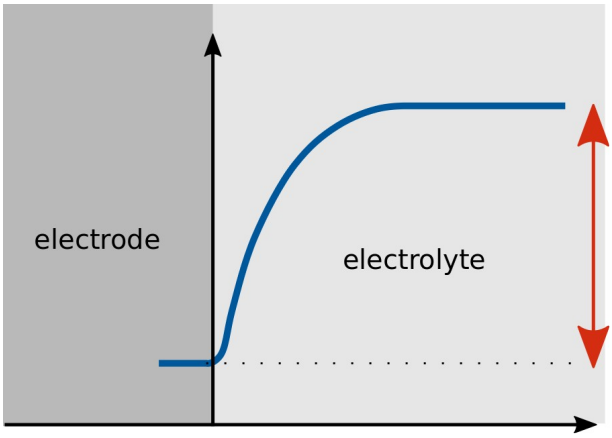

Figure 1: Potential change over the electrochemical double layer.

In case that not only the cell potential at the contacts of the battery is needed, but the complete current distribution inside the cell, the simple approach described above cannot be applied any more. Then, a Laplace or Poisson equation for the electric potential in the cell needs to be solved. In doing so, the change of the electric potential over the electrochemical double layer needs to be

accounted for (Fig. 1). Modelling complete cells on a macroscopic scale, the potential change over the double layer is typically not resolved, but approximated by a discrete jump of the electric potential at the electrode-electrolyte interface (Fig. 2).

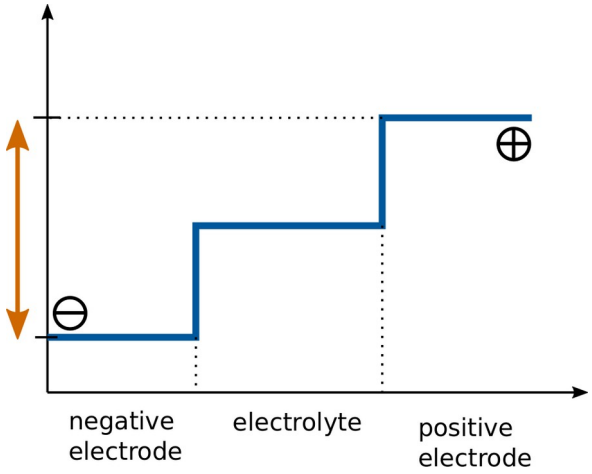

Figure 2: Jumps of the electrochemical potential over the double layer in a battery.

This jump can be computed from the Nernst equation, and depends therefore on the local concentration of the active species. Various options exist to implement the jump numerically: via different meshes and appropriate boundary conditions, using cyclic boundary conditions for implicit coupling and by implementing the jump directly into the Laplace operator. Similarly, charge-transfer overpotentials – obtained again from the Butler-Volmer or Tafel-equation can directly be implemented into the potential jump. When solving the Laplace equation, Ohmic losses are simply accounted for by setting an appropriate conductivity of the electrodes and electrolyte. Finally, the current distribution can be obtained by Ohms law.

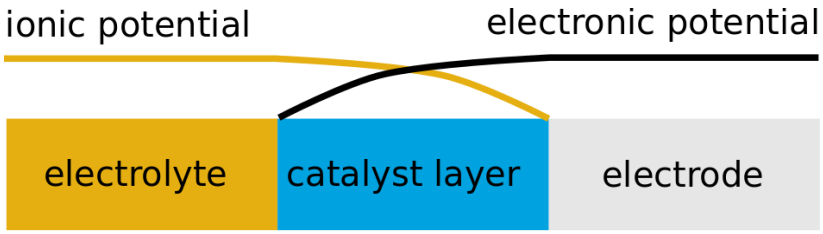

Figure 3: Schematic illustration of the ionic and electronic potential change over the catalyst layer of a fuel cell.

In certain electrochemical devices the transition from electronic to ionic conduction happens in a comparably thick layer (Fig. 3). For example, in fuel cells the reaction occurs within a catalyst layer of finite thickness, which consists of a mixture of electronically conducting and ionically conducting material, interspersed by a catalyst. Hence, the transition from ionic to electronic conduction cannot be a sharp jump, but is rather gradually. In such cases, it is most appropriate to define a single electronic potential as well as an ionic one. Both will then be coupled via a volumetric current source within the catalyst layer.

The presentation shall give an overview on all these different approaches, discussing their advantages and challenges. Moreover, possible problems and pitfalls will be discussed. The implementation of the described techniques will be illustrated by a number of different technical examples. This includes, e.g., the simulation of air-breathing fuel cells, where buoyancy, mass transfer and electrochemistry need to be coupled. Further, the coupling of

magnetohydrodynamically driven flow with electrochemistry will be illuminated using the example of liquid metal batteries.

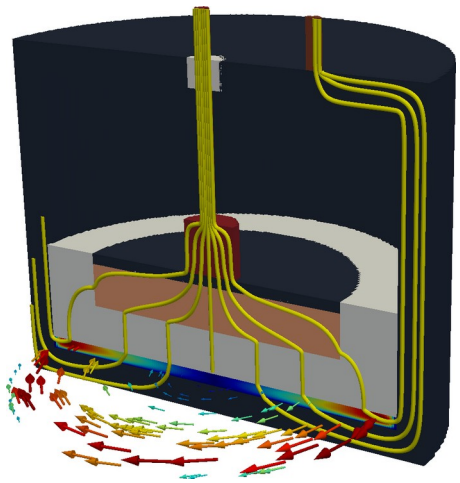

Figure 4: Exemplary current distribution and flow in a liquid metal battery.

References

Ashour, R.; Kelley, D.; Salas, A.; Starace, M.; Weber, N.; Weier, T.
Competing forces in liquid metal electrodes and batteries
Journal of Power Sources 378(2018) 301-310

A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, second ed., Wiley, New York, 2001.

S.B. Beale, H.-W. Choi, J.G. Pharoah, H.K. Roth, H. Jasak, D.H. Jeon
Open-source computational model of a solid oxide fuel cell
Comput. Phys. Commun. 200(2016) 15-26

A.N. Colli, H.H. Girault
Compact and general strategy for solving current and potential distribution in electrochemical cells composed of massive monopolar and bipolar electrodes
J. Electrochem. Soc. 164 (11) (2017) E3465-E3472

A. Colli, J. Bisang
Current and potential distribution in electrochemical reactors with activated or resistive electrodes. A multiregion and open source approach
Electrochim. Acta 290 (2018) 676-685

J. Newman, K.E. Thomas-Alyea, Electrochemical Systems, John Wiley & Sons, 2004.

Personnettaz, P.; Landgraf, S.; Nimtz, M.; Weber, N.; Weier, T.
Mass transport induced asymmetry in charge/discharge behavior of liquid metal batteries
Electrochemistry Communications 105(2019) 106496

Personnettaz, P.; Beckstein, P.; Landgraf, S.; Köllner, T.; Nimtz, M.; Weber, N.; Weier, T.
Thermally driven convection in Li||Bi liquid metal batteries
Journal of Power Sources 401(2018) 362-374

K.J. Vetter, Electrochemical Kinetics Theoretical Aspects, Elsevier Science, Burlington, 1967.

Weber, N.; Nimtz, M.; Personnettaz, P.; Weier, T.; Sadoway, D.
Numerical simulation of mass transfer enhancement in liquid metal batteries by means of electro-vortex flow
Journal of Power Sources Advances 1(2020) 100004

Weber, N.; Landgraf, S.; Mushtaq, K.; Nimtz, M.; Personnettaz, P.; Weier, T.; Zhao, J.; Sadoway, D.
Modeling discontinuous potential distributions using the finite volume method, and application to liquid metal batteries
Electrochimica Acta 318(2019) 857-864

Weber, N.; Nimtz, M.; Personnettaz, P.; Salas, A.; Weier, T.
Electromagnetically driven convection suitable for mass transfer enhancement in liquid metal batteries
Applied Thermal Engineering 143(2018) 293-301

Weber, N.; Beckstein, P.; Galindo, V.; Starace, M.; Weier, T.
Electro-vortex flow simulation using coupled meshes
Computers and Fluids 168(2018) 101-109