Title: **Contribution to the Modeling of Electrochemical Systems:**
                Multi-Ion Model in Presence of Gas Evolution

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Accurate simulation of electrochemical processes requires modeling of many complex phenomena. A typical example is the gas evolution due to electrode reactions. The aim of this thesis is to improve an existing multi-ion electrochemical model, which already considers the contribution of diffusion, convection, migration and homogeneous reactions, by modeling the macroscopic effects of the gas produced in the electrode side reactions. From a macroscopic perspective, the presence of gas can influence the electrochemical process in a positive way because it has a stirring effect and refreshes the electrolyte at electrode or it can deteriorate the conductivity of the bulk solution and reduce the active electrode area due to part-wise coverage. The change in electrical conductivity is introduced in the electrochemical model by adapting the apparent diffusion coefficients (Bruggemann relation), whereas the partial coverage of active electrode area is considered in the boundary condition imposed on electrode by correcting the reaction current density. The gas flux at an electrode is obtained by solving the electrochemical model, and then the distribution of gas in the electrolyte is calculated using the fluid flow model. In the fluid flow model, the gas is considered as a second phase to be distinguished from the bulk liquid. The gas fraction is calculated using the two-fluid model, which is based on an Eulerian description of the fluid flow (the two phases are characterized by their volume fraction, implying that the phases are homogenized at a macroscopic scale). The electrochemical and two-phase flow models are solved interactively as the electrochemistry influences gas evolution and vice-versa.

Both the electrochemical and two-fluid models are discretized using Residual Distribution Schemes (RDS) with distribution matrices given by the Lax-Wendroff scheme for the fluid flow models and the PSI scheme for the convection term in the electrochemical model. As far as known from literature, this thesis is the first effort to employ RDS for the discretization of the incompressible single-pressure two-fluid flow model. The complexity of the two-fluid model is not only caused by the large number of equations and by the formulation of the contributions that build these equations, but also by the well-posedness of the model. In order to find a consistent and robust discretization for the incompressible two-fluid flow model, different formulations of the equations and numerical discretization approach have been investigated. Consistent boundary conditions are assigned to each discretized system of equations. The two-phase flow solver implemented in this work gives similar solutions to those reported in literature and converges on complex geometries, but only for a small ratio between the phase densities. If physically consistent material properties of the phases are considered in the simulations, the ratio between liquid and gas phases is more than 1000 for real systems, the two-phase flow solver converges only on very simple geometries with similar flow conditions for both phases, e.g. the parallel plate channel with mixture inlet conditions. Most of the effort allocated to this research has been devoted to the development of two-phase flow solver, but no consistent and robust discretization approach for the

incompressible two-fluid models has been found. In order to facilitate the convergence of the two-phase solver to a solution that can be used for the coupling with the electrochemical solver, it was opted to include artificial diffusion in the equations assigned to the void fraction unknowns, which may influence the accuracy of the two-phase flow solution.

The coupling procedure assumes steady-state calculations each time the electrochemical or two-phase flow solvers are employed. The gas flux calculated by the electrochemical solver is transferred to the two-phase flow solver as boundary conditions for the void fraction and gas velocity unknowns. In return, the void fraction and liquid velocity calculated by the two-phase solver are used to evaluate the migration, diffusion, convection and the electrode reactions in the electrochemical solver. The coupling procedure is original and has to our knowledge not been reported in literature so far. The coupling procedure performs well if the amount of gas generated at the electrode is not too large (relatively small current densities along the cathode). Because of the vertical component of the electrolyte flow next to the cathode, the current density decreases on the downstream side of the cathode. For large values of void fractions, the current density along the electrode decreases more because of its dependency on the void fraction values, as given by the Bruggemann correction applied to the electrolyte conductivity. The bottleneck for the present coupling procedure seems to be the vertical component of the liquid velocity, which develops next to the electrode when a large amount of gas is evolving at the electrode. The large flux of gas is blocking the convection of electrolyte at the cathode and the coupling procedure drops into an infinitely loop oscillating between two states: the electrochemical solver will determine either a large amount of gas, when no vertical component of liquid velocity is developing in the flow, or the electrode reactions (thus also the gas evolution) are blocked by the large vertical component of liquid velocity. Although there are no experimental data or numerical simulations reported in the literature for the test case considered in this work, the results obtained using the present coupling procedure seems to be physically consistent with the model that is used. On the other hand it is believed that certainly for what the gas evolution concerns, relevant physical data based on experiments is missing.