
Multi Material Electrocatalysis (MultECat II)

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Project Funding Scheme: Category A (Dr. Rüdiger Müller); Start: 1 JAN 2021

Short Summary: Electrocatalysis is crucial for our future society and sustainable economy. Thermodynamic modeling and numerical simulation will help to increase their efficiency, scalability and reduce cost. Results of MultECat will be extended to non-equilibrium, a large set of samples calculated, and data provided within the NFDI.

Extended Synopsis of the Proposal

Background The strategic importance of technologies based on electrocatalytic reactions is underlined in the recently approved National Hydrogen Strategy of the German Federal Government. It grants hydrogen, and in particular “green hydrogen” created with renewable energies, a strategic role in the decarbonization of the economy. Hydrogen serves as energy carrier, energy storage option, sector coupling technology, precursor for the chemical industry and can reduce CO₂ in various industrial processes. The creation of hydrogen from electrical energy in electrolyzers and the reverse process – the recovery of electrical energy from hydrogen in fuel cells – are seen as indispensable technologies whose development shall be supported by R&D investments and market incentives. Both technologies rely on electro-catalytic reactions. Production and utilization of hydrogen are just examples for this class of reactions, other electro-catalytic reactions occur in post lithium batteries, material synthesis and other fields.

The main driving forces for the development of electrocatalytic technologies are (i) the synthesis of new electrode and electrolyte materials (e.g. ionic liquids and perovskites) (ii) the fabrication of nano-structured and composite electro-catalytic surfaces (multi-material catalysts) and (iii) material and operational optimization. Central goal for large scale electro-catalysis is cost reduction by reducing the use of expensive raw materials like Pt and Pd. For instance, the Berlin based cluster of excellence UniSysCat searches for substitutions of these materials.

Investigations of electro-catalytic reactions on new materials are carried out by a number of experimental techniques, e.g. RRDE (Rotating Ring Disc Electrode), CV (Cyclic Voltammetry), STM (Scanning Tunneling Microscopy), SEM (Scanning Electrochemical Microscopy), AFM (Atomic Force Microscopy), EIS (Electrochemical Impedance Spectroscopy).

In order to interpret experimental results, and to understand, predict and optimize electro-catalytic systems, mathematical models have to be used. Modeling results can be expressed as analytic expressions or need to be obtained via numerical simulation. Research more and more focuses on the interplay between mass transport, reactions and electric field on the nanoscale, resolving double layer effects [12, 13, 11, 10]. Most approaches, however, assume homogeneous interfaces and do not take into account variations in the surface spatial structure, although it leads to variations in electrochemical activity.

WIAS research group 3 “Numerical mathematics and Scientific Computing” represented by PI J. Fuhrmann contributes to the numerical modeling and simulation of electrochemical systems. This includes the derivation of a thermodynamically consistent finite volume method [5] for the electrolyte models [7, 3], implementations in Julia and C++, as well as convergence investigations for different thermodynamically consistent flux expressions [2].

WIAS research group 7 “Thermodynamic Modeling and Analysis of Phase Transitions” rep-

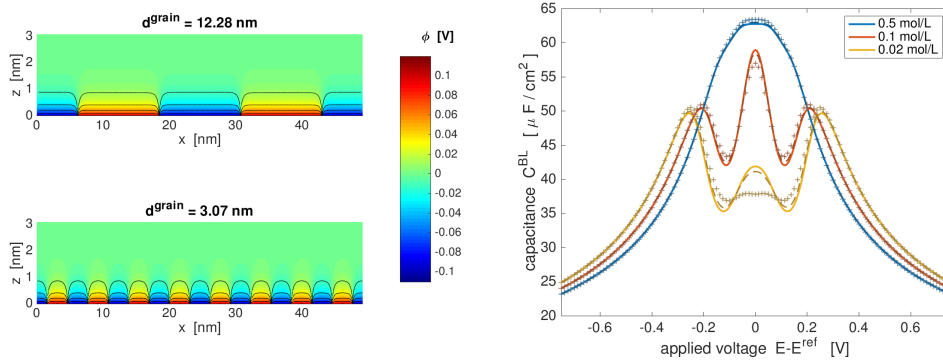


Figure 1: Left: profile of the electrostatic potential for a bi-crystalline interface with different grain sizes. Right: double layer capacity curves for different electrolyte concentrations. Solid lines (—) refer to the weighted sum of the grain contributions., (+) and dashed (- -) lines mark data obtained from numerical simulations for small and large grain sizes, respectively.

resented by PI M. Landstorfer is active in the development of mathematical models for electrochemical systems. A seminal result is a comprehensive electrolyte model which provides an accurate description of the electrochemical double layer and yields broad accordance to experimental data of single crystal electrodes. Based on this, thermodynamically consistent boundary conditions for electrochemical reactions at electrode surfaces have been developed [8, 7, 6, 4].

Recently published work [1], supported by MATH+ within the project MultECat, provides first results on modeling, simulation and validation of electrochemical interfaces on polycrystalline materials (see Fig. 1). A methodology to handle realistic multi-material surfaces was developed, allowing for a their stochastic description. Results on Debye–Hückel theory, concentration dependent susceptibilities, and electrolyte transport are in the final stage of publication.

Goals of the Project and Methodologies Our recent results on modeling multi-material metal-electrolyte interfaces are confined to the case of thermodynamic equilibrium without charge transfer reactions. This experimentally validated model framework is our starting point for non-equilibrium thermodynamic modeling of electron transfer reactions at multi-material electrodes coupled to charge transport. It accounts for the polycrystalline interface structure, catalyst surface phase transitions, finite ion sizes, solvation, concentration dependent susceptibility.

A pioneering aspect for heterogeneous interfaces is the transition from surface patch labeling towards a description on the basis of work function values of multi-material electrodes. This allows additionally for a statistical distribution across the surface. Further we intend to extend averaging methods as developed in [1] by periodic and statistical homogenization approaches. These efforts shall result in rate equations for polycrystalline interfaces and their respective coupling to the bulk processes.

Many electrocatalysts, in particular platinum free electrocatalysts for water splitting, have semiconductor properties, therefore we intend to extend the electrode models to the case of semiconductor-electrolyte interfaces.

Thermodynamically consistent discretization approaches which allow to preserve qualitative features of the continuous systems of equations (second law of thermodynamics, mass conservation, positivity of concentrations) will be used to develop numerical simulation models for multi-material electrocatalytic systems. Preferably, models will be implemented in Julia.

Model adaptivity strategies shall provide efficient ways to handle the different temporal and spatial scales. In particular they shall be able to decide between spatial resolution of the electrode boundary layers and the lumping of the relevant processes into interface models.

Main Contributions The envisioned modeling framework will allow to set up analytical and numerical simulation models for multi-material electrocatalytic systems including features of electrochemical measurement processes, e.g. voltage cycling for CV or extraction of potential surfaces for STM. These simulation tools shall be used to create a series of prototypical synthetic measurement data, which can serve (i) as catalogue for experimentalists to (visually) compare their results to our modeling and simulation approach, (ii) as (labeled) training sets for machine learning tools, (iii) as database for parameter estimation. Data will be published using infrastructure developed by the NFDI4Cat consortium under the German National Research Data Initiative (NDFI) [9], provisionally allowing to access measurement data by other groups.

The project will result in extended bulk-surface models for electrochemical systems which provide an ample field for further investigation in analysis and numerics. Classical electrode theory based on the Butler-Volmer equation will be generalized. Upscaling and averaging methods for surface rate equations developed in the project are of potential interest in other applications.

Consistent coupling of charge transport to other physical processes and corresponding numerical methods are investigated in several other projects of the application area AA2.

Future Research and New Horizons The establishment of material models for heterogeneously structured electrocatalytically active surfaces provides the possibility of experimental comparison with polycrystalline or multi-material electrodes as they occur in electrochemical experimentation and in real world devices.

The ability to model and simulate processes at polycrystalline electrodes, and the communication pathway with experimentalists related to the publication of synthetic measurement data will be an excellent foundation for collaborative research projects in the field of electrochemistry based e.g. on grants available through the National Hydrogen Initiative.

In the future, it will be possible to apply the methodology to various electrolyte-interface systems and to set up inverse problems to interpret results of various measurement methods used to characterize real electrode surfaces. Upon experimental validation, the models can be used to optimize electrocatalytic processes. The inclusion of semiconducting electrodes will be a starting point to develop models and simulation methods for photocatalytic reactions. The methodological framework and the resulting models will provide many open questions regarding their mathematical and numerical analysis.

Publications

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Additional Aspects of the Proposal

Collaborations Internal cooperation (within MATH+): AA2 (A. Glitzky et al, P. Farrell et al, D. Hömberg et al): models and methods for Drift-Diffusion systems coupled to various physical processes; AA2: (M. Thomas et al): Bulk-Interface models; AA2: (S.Burger et al): development of outlook on photocatalysis.

External scientific cooperation (outside MATH+): Sebastian Matera (FU Berlin, UniSysCat), Peter Strasser (TU Berlin), Sonya Calnan (HZB Berlin), Timo Jacob (University Ulm, Institute of Electrochemistry), Michael Eikerling (Forschungszentrum Jülich), Peter Berg (University of Alberta), Boris Zaltzman (Ben Gurion University of the Negev).

External industrial cooperation (outside MATH+): Robert Bosch GmbH, Dr. Ulrich Sauter, Modeling of Electrochemical Components (CR/ARC CE-MEC).

Related Projects The project “Electrical Double Layers in Solid Oxide Cells” (DFG FU 316/14-1; PI J. Fuhrmann) focuses on high temperature solid electrolytes. The project “Kontinuumsbasierte Modellierung und Simulation elektrochemischer Prozesse für Metall-Luft-Batterien” (BMBF 03EK3051B; PI J.Fuhrmann, M. Landstorfer) focuses on homogeneous electrode models. The project “Coupled atomistic and nanofluidic simulations for electrocatalysis” (Joint PhD project with S. Matera in the Berlin International Graduate School for Natural Science and Engineering (BIG-NSE) linked to the UniSysCat excellence cluster) focuses on atomistic electrode models coupled to electrolytes.

Further Impact of the Project on MATH+ We see a good perspective for additional projects within the National Hydrogen Initiative. Methods and results of the project will be used in teaching activities at TU Berlin, which will be provided to a diverse group of students. Dr. Manuel Landstorfer intends to finish his habilitation during the project. We will participate in public outreach activities (e.g. Lange Nacht der Wissenschaften).

Position(s) of the PI(s) Both PIs have full permanent positions at Weierstrass Institute, J. Fuhrmann is deputy head of WIAS Research group 3.