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Abstract:

Title of Project: Coupled atomistic and nanofluidic simulations for electrocatalysis#

Co-supervisor 1: Sebastian Matera, FU Berlin

Co-supervisor 2: Rupert Klein, FU Berlin

Co-supervisor 3: Jürgen Fuhrmann, WIAS Berlin#

The interplay between bond making and breaking on electrocatalytic surfaces, electrostatics and the transport of chemical species to the surface can have a significant impact on the observed catalytic response and lead to non-trivial phenomena like sizable nanoscale variations of potential and concentration.

The theoretical modeling of this interplay beyond phenomenological approaches is currently underdeveloped in the field of electrocatalysis. The goal of the project is to develop a multiscale modeling approach and corresponding software, which allows to resolve the atomistic nature of surface chemistry. For this, kinetic Monte Carlo simulations of the surface chemistry shall be coupled with continuum level computational models for the treatment of nanofluidic transport near the surface and in the reactor. #

The project will be conducted in close collaboration with the MATH+ project by M. Landstorfer and J. Fuhrmann "Modeling of Multimaterial Electrocatalysis", in which the continuum nanofluidic models and solvers will be improved.#

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Extended description version of the project: #

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1. Overall goal of the project #

During the project, novel strategies for coupling kinetic Monte Carlo (kMC) for stochastic models of surface reactivity with continuum level simulations of transport and electrostatic fields will be developed for the theoretical investigation of nanoscale phenomena of electrocatalytic processes. For this, a kMC solver will be implemented, which can address nanostructured surfaces and lateral variation of external fields, such as concentration and electrostatic potential. This code will later be integrated with the continuum level solver which addresses double layer and nanofluidic effects, developed at WIAS and the partner MATH+ project. For this, a dynamic and non-local coupling approach shall be developed. The general purpose code will be used to address and disentangle issues like the impact of nanoscale transport, of double layer effects or the size and spacing of catalytic particles. It furthermore will serve as tool to scrutinize more approximate approaches such as meanfield microkinetics and nonequilibrium thermodynamic models which are at the foundation of the partner MATH+ project. This will be based on well-developed kinetic mechanisms for water splitting. In the long run, the developed methodology shall serve as a basis to investigate more complex situations.#

2. State of the art#

The prevalent approaches for modeling the interplay of chemical reaction events are based on meanfield microkinetic approaches. While successful for modeling macroscale phenomena, their ability to properly describe nanoscale effects is limited due to their intrinsic approximations neglecting fluctuations, local adsorbate ordering and assuming locally homogeneous fluid phase concentrations and potentials. In contrast, kMC is a stochastic method, which can fully account for all those effects and therefore has gained popularity during the last years. The price for the increased accuracy are often orders of magnitude higher computational costs and dedicated software optimization is crucial [1].#

Coupling of kMC with continuum level solvers (CLS) for transport modeling can be done directly, where kMC and CLS are coupled dynamically [2], or indirectly, where scale separation is exploited to achieve efficient strategies for problems where only macroscopic concentration gradients appear [3]. For electrocatalysis with possible nanoscale gradients, scale separation does not apply and direct coupling is more natural. For electrochemical problems, the computationally more demanding direct approaches are still in their very infancy. Consequently, existing studies concentrate on simplified geometries, mechanisms and transport models [2]. In order to tackle more complex problems, e.g. a nanoparticle on a flat surface, efficient coupling strategies and software tools need to be developed, which is the goal of the project.#

The additional accuracy gained from employing kMC is, of course, wasted if the transport model does not provide a comparable accuracy. Established continuum models for transport in electrochemical cells are not suited for our goals because of their inability to properly describe the

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small scale features and double layer effects in the vicinity of the catalytic surface. However, during the last years, models have been derived based on first principles of nonequilibrium thermodynamics, which overcome these limitations [4]. For these models, specialized numerical solvers have been developed, which obey conservation and thermodynamic principles [5,6]. #

[1] Hoffmann, M. J., Matera, S., & Reuter, K. (2014). *Computer Physics Communications*, 185(7), 2138-2150.#

[2] Röder, F., Braatz, R. D., & Krewer, U. (2019). *Computers & Chemical Engineering*, 121, 722-735.#

[3] Matera, S., Maestri, M., Cuoci, A., & Reuter, K. (2014). *ACS Catalysis*, 4(11), 4081-4092.#

[4] Landstorfer, M. and Guhlke, C. and Dreyer, W. (2016). *Electrochimica Acta* 19(15), 7075-7086#

[5] J. Fuhrmann (2016). *Fuel Cells* 6(16), 704-714#

[6] J. Fuhrmann, C. Guhlke, C. Merdon, A. Linke, and R. Müller (2019). arXiv:1901.06941 [physics.chem-ph] #

3. Specific aims and how they may be reached:#

During the first phase of the project, a general purpose kMC solver shall be developed. For this, we will rely on the design principles, which we already employed for the kmos lattice kMC code, such as exploitation of locality of reaction events and the code generator paradigm [1]. However, the new code shall allow for spatially varying reaction parameters and a general structure of the adsorption sites, which appear for nanoparticles in contact with an inhomogeneous fluid phase and cannot be simulated with the kmos code. After benchmarking against analytically solvable problems and the kmos code, the new code will be used to address first electrochemical problems and to scrutinize the advanced phenomenological models developed in the partner MATH+ project. #

In the second workpackage, the coupling strategy will be devised. This will be done on basis of operator splitting for the probabilistic formulation of the coupled problem, but we will also consider existing approaches [2,6]. A software interface between the kMC and the CLS shall be implemented. For the CLS, we plan to employ the thermodynamically consistent and conservative discretization developed by our partners [5,6]. We expect that these properties are beneficial for the robustness of the coupled solver against the stochastic noise in the kMC simulations. The coupling strategy will be tested for low dimensional, semi-analytically solvable models to test for the impact of the numerical parameters of the strategy and the influence of noise.#

Finally, the methodology shall be applied to investigate more complex and realistic problems. Particularly, water splitting by well defined, supported nanoparticles will be examined using existing models for the reaction mechanism, e.g. for the Oxygen Reduction/Evolution Reaction on Pt [7,8]. With our strategy, we will address issues like the impact on key observables by nanoscale field heterogeneities, the particle size and spacing and their interplay with different ion species and concentration.#

Besides the close collaboration with the MATH+ Cluster of Excellence via the project "Modeling of Multimaterial Electrocatalysis", we, of course, expect synergistic effects with S. Matera's UniSysCat projects. By both kind of projects, there is also a link to the experimental projects in UniSysCat. Further, the student will profit from the research environment provided by the CRC 1114 "Scaling Cascades in Complex Systems" and, especially, the collaboration with the project C01 lead by L. Delle Site, F. Höfling and R. Klein. Collaboration with U. Krewer (U Braunschweig) on kMC/continuum coupling is planned.#

[7] Quiroga, M. A., & Franco, A. A. (2015). *Journal of The Electrochemical Society*, 162(7), E73-E83.#

[8] Fortunelli, A., Goddard III, W. A., Sementa, L., & Barcaro, G. (2015). *Nanoscale*, 7(10), 4514-4521.#