Final Report

Project acronym: MuMo4PEC

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M-ERA.NET Call 2016

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2. Publishable project summary

Photo-electrochemical (PEC) solar fuel conversion is one of the most promising techniques to convert sunlight directly into the most versatile form of energy, a fuel. Unfortunately, efficiencies are low and performance needs to be increased. The main challenge in the field is the identification of the limiting processes at the solid–liquid interface. In this proposal, we develop for the first time a multiscale modeling approach for PEC interfaces to solve this challenge.

We worked on an innovative **multiscale modeling approach from atomistic to continuum level**. Next to deep insight into single processes at the solid–liquid interface, we simulated electrochemical data directly from an electrochemical model with kinetic parameters. This opens a new way to interpret experimental data without equivalent circuit fitting. Hence, with this proposal, we **bridged theory and experiment**. The **Fe_2O_3–water oxygen evolution reaction (OER) system** was chosen due to its abundance, low costs, and PEC properties, but also because of its benchmark character.

The following **main results** were obtained:

- A **four-level framework** of atomistic, molecular, coarse-grained, and continuum modeling was developed to simulate the hematite electrochemical interface. Lower scale models provide input for the higher scale models and thus realize the results obtained in each scale.
- **Atomistic modeling**: 1) calculation of free energies of the single reaction steps of OER for diverse systems (pure/doped/nanocluster hematite, other materials systems, different structures); 2) determination of electrochemical activity for diverse systems
- **Molecular dynamics modeling**: 1) development of a classical force-field for the solid-liquid interface of pure hematite; 2) extension of classical force field to doped hematite; 3) modeling of water diffusion on surface of hematite
- **Coarse-grained modeling**: 1) development of a kinetic Monte Carlo modeling code; 2) elucidation of time and voltage dependent surface coverages of various intermediates in OER at the hematite-water interface; 3) investigation of the impact of interaction of water with the hematite surface via explicit chemisorption.
- **Contiuum modeling**: 1) Development of a code for a 4th and a 10 th order model which allowed to compare modeled electrochemical data with experimental data; good agreement between experiment and modeling was obtained; 2) Set-up of a sensitivity analysis to identify the most sensitive parameters to impact electrochemical results.
- **Individual scales were connected**, e.g. atomistic/continuum and atomistic/MD/coarse grained, leading to a **multiscale modeling suite of the hematite-water interface** and to simulations of current-voltage curves and impedance data, i.e. data that can be directly compared to experiments.

The results ended up in **14 papers** where in most papers several scales of modeling were connected. The project was a stimulus for the COST Action No. 18234 where 3 of the 4 PIs of this project are actively involved. MoMo4PEC also prepared the project of a new PhD student on continuum modeling.

Conclusions

- A multiscale modeling approach of the hematite-water interface could be realized and is now a framework for other materials systems.
- Advances on single scales, e.g. force field for hematite, can be used for further identification of the limitations at electrochemical interfaces, in particular for OER.
- Connection of several modeling scales is possible; by combining modeling scales simulation results can be obtained that cannot be obtained by single scales. Hence, multiscale modeling is an essential step to realistic simulation of electrochemical interfaces
- Multiscale modeling allows for simulating data that can be directly compared to experimental data.
- This multiscale modeling approach is a new and innovative alternative to state-of-the-art equivalent circuit fitting for the analysis of impedance data.