Integrated modeling of multistep reactions at photo-electrochemical interfaces by combining DFT and non-linear state-space modeling

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Direct conversion of solar energy into storable fuels is the holy grail in the field of sustainable energy. Photo-electrochemical (PEC) cells can perform direct splitting of water to generate hydrogen and oxygen. A commercial breakthrough for this promising technology has not been achieved yet due to efficiency and stability issues of the photo-electrodes. A PEC has a semiconductor photo-anode where oxygen evolution reaction (OER) occurs and a cathode where hydrogen evolution reaction (HER) occurs. Under illumination, electron hole pairs are generated in the semiconductor electrode. In that, holes move towards the electrolyte interface where they oxidize water to form oxygen gas. Meanwhile electrons, under the influence of applied potential, move through the external circuit towards the counter electrode where they reduce water to form hydrogen gas. Among the two process, OER is a more complicated process which involved four charge transfer reactions with four different adsorbed intermediate species. Hence in this study we focus on OER to identify the performance limiting processes in PEC.

We present a new approach, which combines density functional theory (DFT) and state-space modeling to investigate the kinetics of water oxidation at PEC interfaces. A method to relate the kinetics of multistep reactions at the interface to electrochemical impedance is developed. We start with hematite (Fe_2O_3) as our model system. The OER mechanism proposed by Norskov is chosen as our first electrochemical model to develop the state space model (SSM). The free energy change (ΔG) of each electrochemical step in OER on Fe_2O_3 are calculated using DFT. The reaction rates for the four charge transfer reactions in OER are calculated based on Gerischer model of semiconductor-electrolyte interface, using above mentioned DFT results and other constant parameters from literature. With the help of these rate constants and micro-kinetic equations, mass conservation and charge balance equations are formulated. A state-space model of OER at the interface is developed using the resulting set of equations. A schematic representation of the model is given in fig. 1.
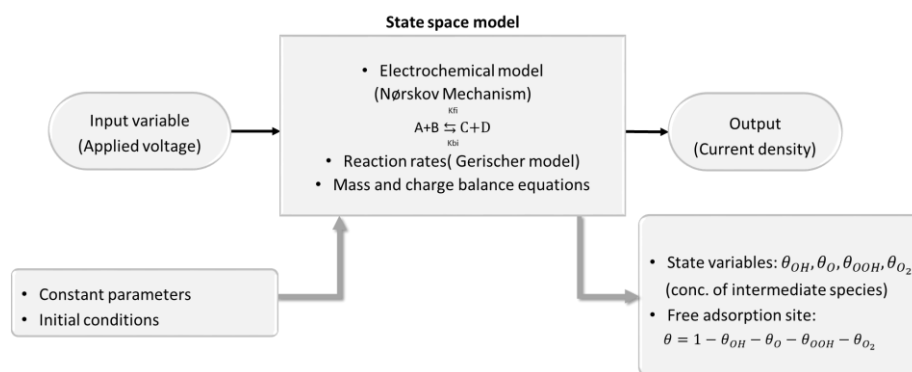

Figure 1 Schematic representation of state space model. Here applied voltage is the input variable, current is the output and the fractional coverage ratio of reaction intermediates at the interface are the state variables.

From the state-space model, electrochemical data, such as electrochemical impedance spectrum, species coverage plot and current-voltage plots are simulated. In our group we perform experiments on hematite electrode and experimentally calculated impedance spectra and current plots are available. This experimental plots can be compared with simulated plots and by using system identification technique, extrinsic values of rate constants can be estimated. Thus the limiting steps in OER can be identified. The model can be extended to study OER on systems other than hematite, with the help of corresponding DFT results and other system related parameters.

Keywords: *Photoelectrochemical cell, oxygen evolution reaction, electrode-electrolyte interface, electron transfer, state-space modeling.*