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D3.1. MODA: Modelling DAta providing a description for simulated photoelectrochemical materials and devices

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Executive Summary

This deliverable contains a template with an overview of the simulations as well as the main aspects of the different models involved within the project FotoH2, with a focus on the physics of the models (together with user case definition and information on the solvers and post-processing). A chain of two models (models 1 and 2) is defined to study the user case (photocurrent vs. voltage characteristics of a polymer electrolyte membrane photoelectrolyser based on semiconducting oxide electrodes under different illumination conditions).

Model 1 deals with the application of the density functional theory to binary and ternary oxide semiconductor materials. This analysis focusses on the optoelectronic properties of pure and doped oxides. Model 2 applies a continuum approach to obtain relevant parameters of the photo-electrochemical device (cell design, fluid dynamics, heat exchange, reaction rates, etc.).

The rationale for using the chain of models 1 and 2 is the following. The user case demands a continuum model that comprises conservation of species and charge, transport phenomena, and electrochemical thermodynamics and kinetics. For most of the macroscopic properties, materials relations and data are available. The key elements in the device are the photoelectrodes that act as light absorbers and sustain the electrochemical reactions. Electronic structure (and particularly corresponding optical properties) determine to a great extent the behaviour of the electrode materials. Related literature data for ternary oxides is scarce and thus model 1 should provide valuable input for model 2. Model 1 aims at screening different semiconductor ternary oxides for selecting candidate materials with convenient electronic properties for the intended application. Density Functional Theory (DFT) calculation methodologies will provide a convenient means for obtaining band structure information of oxide semiconductors, leading to an estimation of their electronic and optical properties.

1 Overview of the simulation

OVERVIEW of the SIMULATION			
1	**User Case**	Photocurrent vs. voltage characteristics of a polymer electrolyte membrane photoelectrolyser based on semiconducting oxide electrodes under different illumination conditions	
2	**Chain of Models**	**Model 1**	Ab initio electronic models: Electronic density functional model.
		Model 2	Continuum model (Computational Fluid Dynamics -CFD, Heat flow, electrochemical reactions)
		data mining methodology	
3	**Publication Peer-Reviewing the data**		
4	**Access conditions**	The program Vienna Ab Initio Simulation Package (VASP) is commercially distributed by the University of Wien (www.vasp.at). For the simulations of the continuum model commercial software COMSOL (www.comsol.com) and/or ANSYS (FLUENT) (www.ansys.com) will be employed. The use of the open source CFD software OpenFoam (www.openfoam.com) is not discarded. The models and post-processed data will be distributed among project partners. External user may be given access upon contacting the owners (partners contributing to the development of the models) and after approval by the consortium.	

5	**Workflow and its rationale**	As shown in the workflow (figure 1), in model 1, activities will regard the application of the density functional theory to binary and ternary oxide semiconductor materials. This analysis focusses on the optoelectronic properties of pure and doped oxides. Model 2 will apply a continuum approach to obtain relevant parameters of the photo-electrochemical device (cell design, fluid dynamics, heat exchange, reaction rates etc.). The rationale is discussed below: The user case demands a continuum model that comprises conservation of species and charge, transport phenomena, and electrochemical thermodynamics and kinetics. For most of the macroscopic properties, materials relations and data are available. The key elements in the device are the photoelectrodes that act as light absorbers and sustain the electrochemical reactions. Electronic structure (and particularly corresponding optical properties) determine to a great extent the behaviour of the electrode materials. Related literature data for ternary oxides is scarce and thus model 1 should provide valuable input for model 2. Model 1 aims at screening different semiconductor ternary oxides for selecting candidate materials with convenient electronic properties for the intended application. Density Functional Theory (DFT) calculation methodologies will provide a convenient means for obtaining band structure information of oxide semiconductors, leading to estimation of their electronic and optical properties.

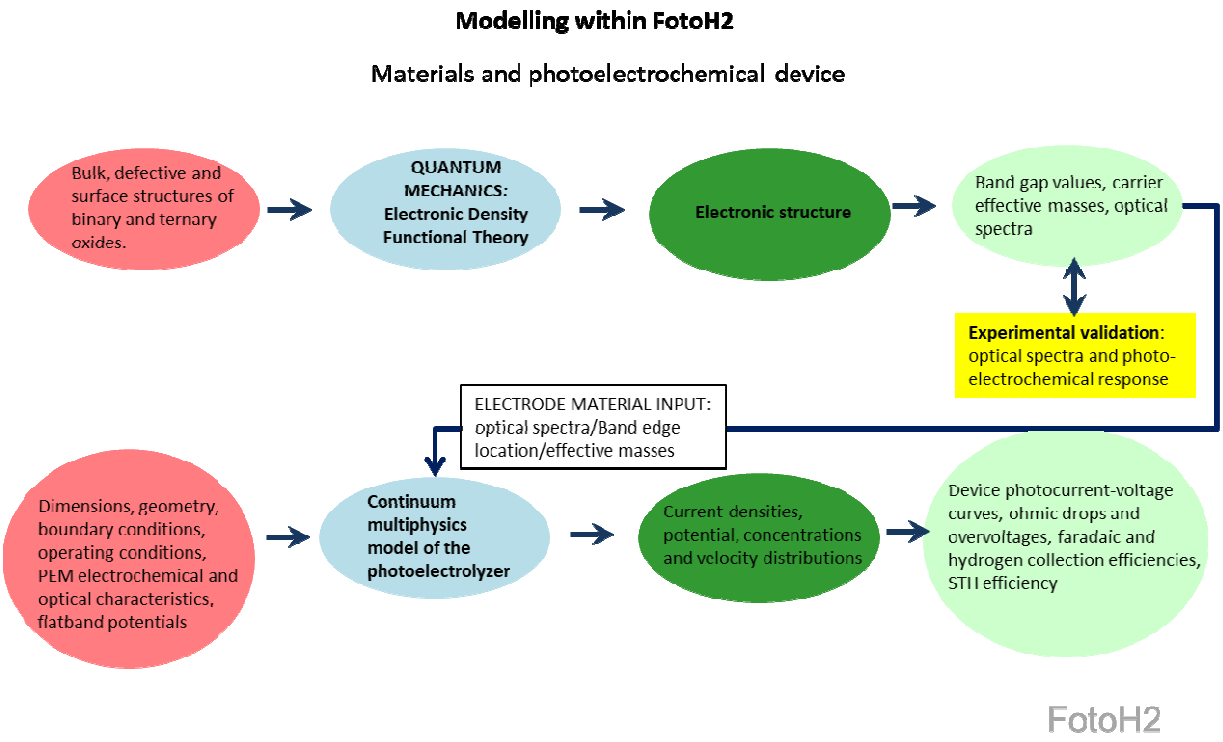

Figure 1. Worklow for modelling within project FotoH2

2 Simulation with model 1

1	Aspect of the User Case/System to be Simulated	
1.1	**Aspect of the User Case to be simulated**	Electronic properties of semiconductor oxides: band structure and related information.
1.2	**Material**	Binary and ternary semiconductor oxides (pure as well as doped).
1.3	**Geometry**	Unit cells for the bulk 3D material. Slabs for 2D models (surfaces).
1.4	**Time Lapse**	*N/A*
1.5	**Manufacturing process or in-service conditions**	
1.6	**Publication on this data**	

2	Generic Physics Of The Model Equation		
2.0	**Model type and name**	Ab initio electronic model	
2.1	**Model entity**	Electrons	
2.2	**ModelPhysics/ Chemistry equation PE**	**Equation**	Kohn-Sham equations.
		Physical quantities	Kohn-Sham wavefunctions, electronic density, energy eigenvalues.
2.3	**Materials relations**	**Relation**	Hubbard on-site d-electron interaction correction to DFT Kohn-Sham electronic energy levels (in GGA+U calculations). Range-separated hybrid functional (HSE06) (in hybrid-functional calculations).
		Physical quantities/ descriptors for each MR	Effective interaction parameters (U) in GGA+U calculations. Amount of exact exchange in hybrid functional calculations.
2.4	**Physics formulation of the conditions**		
2.5	**Simulated input**		

3	Solver and Computational translation of the specifications		
3.1	**Numerical Solver**	Self-consistent eigensolver.	
3.2	**Software tool**	VASP (www.vasp.at)	
3.3	**Time step**	*N/A*	
3.4	**Computational Representation**	**Physics Equation, Material Relations, Material**	Electronic wavefunction expressed using Projector-Augmented Wave basis sets (plane waves with appropriate pseudopotentials).
3.5	**Computational boundary conditions**	Periodic boundary conditions.	
3.6	**additional Solver Parameters**	• Convergence of density • Convergence of eigenstates • Convergence of forces on atoms	

4	POST PROCESSING	
4.1	**The processed output**	• Bandgap values and band edge energies. • Electron and hole effective masses. • Optical properties (absorption coefficients vs photon energy curves)
4.2	**Methodologies**	• Bandgap (direct/indirect) values and band gap energies from band structure (E vs k graphs). • Carrier effective masses from parabolic fit and curvatures of bands - numerical partial derivatives of E(n,k) vs k. • Optical properties from the frequency-dependent dielectric function (obtained by the VASP solver using linear response theory).
4.3	**Margin of Error**	Up to 30% due to inherited error of parent DFT calculations.

3 Simulation with model 2

1	Aspect of the User Case/System to be Simulated	
1.1	**Aspect of the User Case to be simulated**	The behavior of an individual photoelectrochemical tandem cell including mass and momentum transport as well as the electrochemical reactions.
1.2	**Material**	Oxide photoelectrodes and polymer electrolyte membrane, water, hydrogen and oxygen.
1.3	**Geometry**	A 1D simplified representation of the photoelectrodes, polymer electrolyte membrane (including water flow channels) and porous hydrophobic photocathode substrate.
1.4	**Time Lapse**	*N/A.* Focus on (quasi)steady-state conditions
1.5	**Manufacturing process or in-service conditions**	The device will be simulated under different types of illumination (including a standardized one, 1 sun) with the application of a bias.
1.6	**Publication on this data**	

2	Generic Physics Of The Model Equation		
2.0	**Model type and name**	Tightly coupled continuum models consisting of a drift-diffusion model for the photoelectrodes, electrochemical reaction models, and CFD approach for the rest of components.	
2.1	**Model entity**	Finite volumes	
2.2	**ModelPhysics/ Chemistry equation PE**	**Equations**	1. Continuity and drift-diffusion equations for the charge carriers in the photoelectrodes 2. Microkinetic LMA equations for interfacial charge transfer (including modified Arrhenius formulation incorporating the effect of the interfacial electric potential difference) 3. Navier-Stokes equations for incompressible convective flow. 4. General convection-diffusion equation (conservation form) for a. Mass/species b. Energy c. Charge

		Physical quantities	1. Charge carrier mobilities, absorption coefficient, bulk recombination constant. 2. Rate constants (transfer and recombination), symmetry factors, activation energies. 3. Density, velocity, viscosity 4. a. Mass concentration, density, velocity, diffusivity b. Density, enthalpy/heat capacity, temperature, thermal conductivity. c. Electric potential, electrical conductivity.
2.3	**Materials relations**	**Relation**	1. PEM properties: conductivity, osmotic drag coefficient, water diffusivity, hydrogen and oxygen permeabilities. 2. Hydrophobic porous support (gas diffusion layer): Darcy modification of Navier-Stokes equations. 3. Nernst equation for the equilibrium potential.
		Physical quantities/ descriptors for each MR	1. Membrane water content, oxygen and hydrogen permeabilities. 2. Porous layer porosity and permeability. 3. Thermodynamic magnitudes for water splitting reaction.
2.4	**Physics formulation of the conditions**		
2.5	**Simulated input**	From Model 1: • Bandgap values and band edge energies. • Electron and hole effective masses. • Optical properties (absorption coefficients vs photon energy curves)	

3	**Solver and Computational translation of the specifications**		
3.1	**Numerical Solver**	Finite Volumes	
3.2	**Software tool**	COMSOL (www.comsol.com) ANSYS Fluent (www.ansys.com/Products/Fluids/ANSYS-Fluent) OpenFoam (http://www.openfoam.com/)	
3.3	**Time step**	N/A: focus on the steady-state.	
3.4	**Computational Representation**	**Physics Equation, Material Relations, Material**	The governing equations are converted by control volume balances into non-linear algebraic equations (discretization) that are then solved numerically using the Newton's method (linearization). The materials relations are parametrized. The material is specified for each of the layers in the geometrical model representing the device.

3.5	**Computational boundary conditions**	Translation of physical boundary conditions: continuity of mass, temperature and electric charge fluxes among the various components.
3.6	**additional Solver Parameters**	Residuals must attain a value lower than the set tolerance. Residuals include velocity, energy, hydrogen species, oxygen species, water species, electrical potential, and water content