

Unprecedented Water-Assisted Chemical Route Towards the Oxygen Evolution Reaction at the Hydrated (110) Ruthenium Oxide Surface: heterogeneous catalysis via DFT-MD & metadynamics simulations

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The biggest (or one of the biggest) issue that the world human population faces in this century is the urgent need for clean and renewable technologies.

Herein, spin-polarized Density Functional Theory Molecular Dynamics (DFT-MD) simulations, coupled with advanced enhanced sampling methods in the well-tempered metadynamics framework, are applied to gain a global understanding of RuO₂ aqueous interface in catalyzing the Oxygen Evolution Reaction (OER), and hence possibly help in the design of novel catalysts in the context of photochemical water oxidation. Notwithstanding RuO₂ is one of the most active catalyst toward OER, a plethora of fundamental details on its catalytic properties are still elusive, severely limiting its large-scale deployment.

An atomistic understanding of structural, electronic and mechanical properties bulk rutile RuO₂ and explicit solvent effects on (110)-RuO₂ facet are provided in the context of (photo)electrochemical conditions.

We focus on the comprehension of the mechanistic interplay between surface wettability, interfacial water dynamics and surface chemical activity. Moreover, we provide a dependence of physical and chemical properties, such as surface electric field and work function, from different degrees of surface wettability of the (110)-RuO₂ facet.

Furthermore, the present study quantitatively assesses the kinetics, thermodynamics and the involved energies behind the OER at the (110)-RuO₂ catalyst surface revealing plausible pathways composing the reaction network of the O₂ evolution in both gas-phase and explicit solvent model. Albeit a unique efficient pathway has been identified in the gas-phase OER, a lowest-energy-requiring reaction route is possible when (110)-RuO₂ is in contact with liquid water.

By estimating the free-energy surfaces associated to these processes, we reveal an unprecedented water-assisted OER mechanism which involves a crucial proton-transfer-step assisted by the

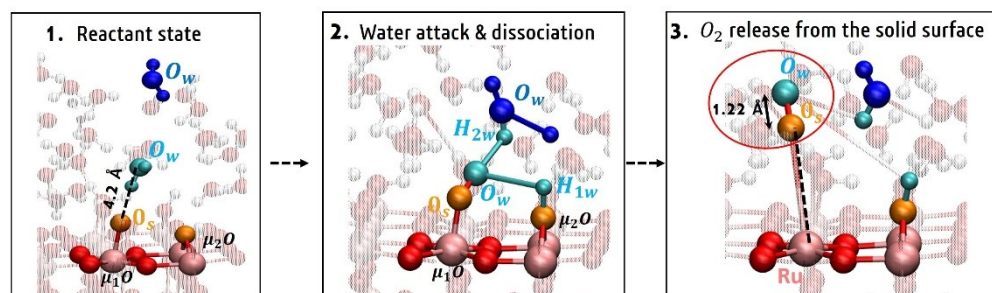


Fig. Water-assisted OER mechanism at the (110)-RuO₂ facet in explicit solvent model.

local water environment making the OER a spontaneous process, i.e. no overpotential is required.

These findings pave the way toward the systematic usage of those techniques for the fine assessment of the activity of catalysts, fully including the entropic contributions due to finite-temperature and explicit-solvent effects. The proposed study will be embedded into the “Solar light to chemical energy conversion” priority research program at the University of Zurich, *LightChEC* consortium (www.lightchec.uzh.ch).