

Ab initio molecular dynamics simulation of the platinum/water interface: Further insights into structure and electrocatalysis

Rasmus Kronberg, Nico Holmberg and Kari Laasonen

Research Group of Computational Chemistry, Department of Chemistry and Materials Science, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland

Understanding solid/water interfaces at an atomistic level has gained significant interest over the last decade¹. For example, complex surface processes occurring at electrode/electrolyte interfaces play a key part in numerous energy conversion devices, such as electrolyzers and fuel cells. A comprehensive and detailed characterization of such interfaces is, however, unfeasible by experimental measurements which are typically conducted at a macroscopic level. Fortunately, experimental results can be complemented by electronic structure calculations based on density functional theory, consequently providing a refined picture of the fundamental structure-activity relationships of electrochemical interfaces².

Herein we present a systematic DFT-MD study of the platinum/water interface using the three most common unreconstructed platinum low-index crystal facets as model electrodes. The aim of the work is to investigate the dynamics of the Pt/water interface at realistic electrochemical conditions by properly accounting for the equilibrium hydrogen coverage, a sufficient solvation layer as well as the electrode potential. Additionally, the hydrogen evolution reaction is revisited by calculation of the activation barriers of the Volmer-Tafel and Volmer-Heyrovský pathways on each studied Pt-surface. The obtained results are compared with previous experimental and theoretical studies between which notable discrepancies still exists, e.g. regarding the equilibrium hydrogen coverage and the magnitude of the HER activation barriers which are both overestimated by computational approaches^{3,4}.

The calculations are conducted at the DFT/GGA level of theory using the CP2K quantum chemistry code. The RPBE exchange-correlation functional with D3 dispersion corrections is applied. Especially regarding the structural features of the Pt/water interface we expect improved results by employing the RPBE-D3 functional, as previous comprehensive studies of electrochemically relevant interfaces^{5,6} have widely applied the unrevised PBE exchange-correlation functional, which is well known to yield overstructured results⁷. Recent studies have indeed shown that the RPBE-D3 functional is ideal for the description of both metal/water interfaces as well as bulk water and water clusters⁸.

References

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