Modeling the effect of electric potential at Ag(111)/water interface through neural network molecular dynamics

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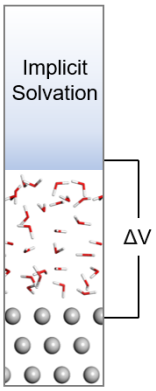
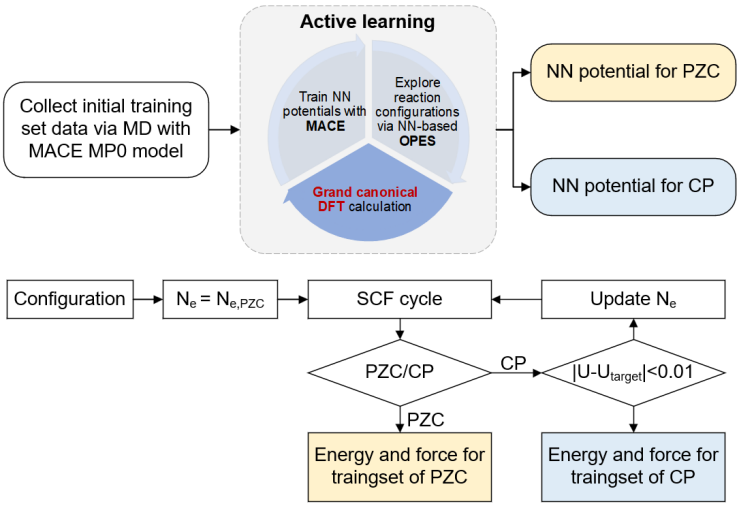
Introduction

We explore the influence of electric potential at the Ag(111)/H_2O electrochemical interface using state-of-the-art neural network (NN) potential molecular dynamics and enhanced sampling methods. With a hybrid explicit-implicit solvation model and constant potential algorithm in VASP[1,2], grand canonical DFT calculations were employed to provide the energies and forces for training the NN potential at a constant potential (CP) of -1.5 V vs. SHE. Our simulations show that electric potential significantly impacts the dynamics of interfacial water and CO_2 adsorption, compared to the potential of zero charge (PZC). This highlights the critical role of electric potential in capturing realistic interfacial behavior under operational conditions.

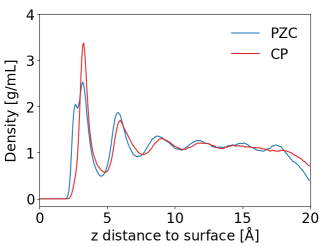


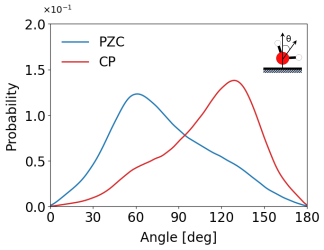
Workflow for building NN potentials

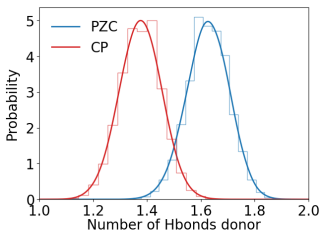


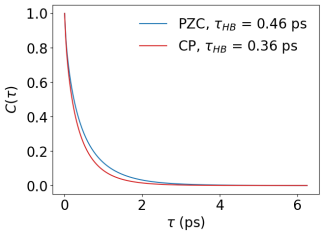
Dynamic behavior of interfacial water

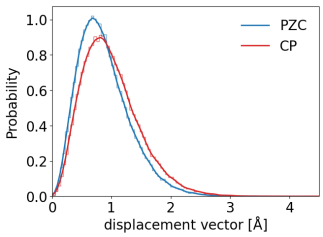
- The orientation of interfacial water forms “H-down” structure at applied potential, which is in agreement with AIMD simulations[3].
- The strength of hydrogen bond network become weak and the mobility of water increases at applied potential.

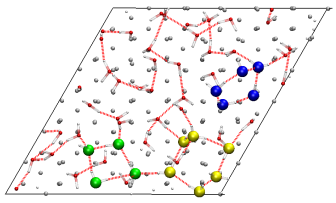








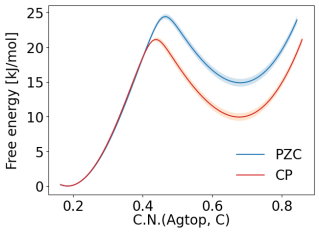


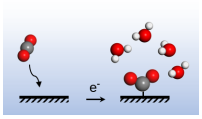


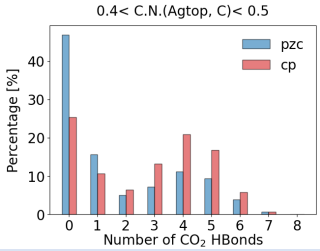
Interfacial water Hbond rings in CP condition

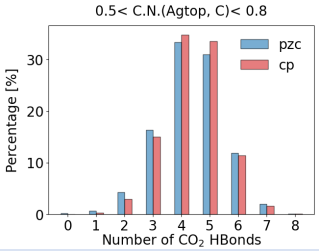
Potential effect on CO_2 adsorption process

- The transition state of CO_2 adsorption shifts at applied potential for the increased number of hydrogen bonds in CO_2.
- The barrier of CO_2 adsorption decreases at applied potential.









Conclusions

The applied constant potential at Ag(111)/H_2O interface significantly influences the orientation, hydrogen bond network, and the mobility of interfacial water, and in turn affects the CO_2 adsorption process. Our results also confirm the reliability of combing NNMD with grand canonical DFT calculation to simulate the electrochemical interface under realistic operating conditions.

References

(1) Xia, Z. et. al. Grand Canonical Ensemble Modeling of Electrochemical Interfaces Made Simple. J. Chem. Theory Comput. 2023, 19 (15), 5168–5175.

(2) Le, D. An Explicit-Implicit Hybrid Solvent Model for Grand Canonical Simulations of the Electrochemical Environment. March 27, 2023.

(3) Le, J.B. et. al. Molecular Origin of Negative Component of Helmholtz Capacitance at Electrified Pt(111)/Water Interface. Science Advances 2020, 6 (41), eabb1219.