Effect of adsorbates on Pt (100) surface

Jia-Xin Zhu[1], Jia-Bo Le[1], Katharina Doblhoff-Dier[2], Marc T.M. Koper[2], Jun Cheng[1]

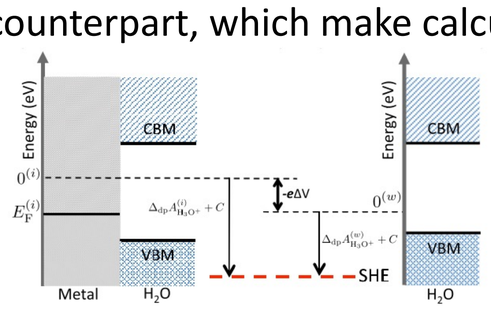
1. College of Chemistry and Chemical Engineering, Xiamen University, 361005 Xiamen, China
2. Leiden Institute of Chemistry, Leiden University, 2300 RA Leiden, The Netherlands

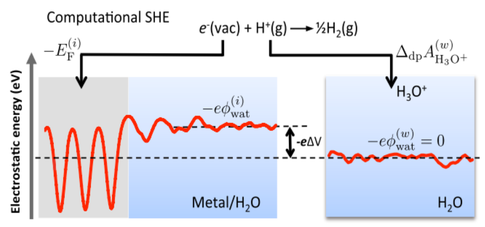
Introduction

In electrochemical reactions, the structure of electric double layer (EDL) strongly influences thermodynamics and kinetics of reactions. Platinum is one of the most active and wildly used catalyst in electrocatalytic reaction, so it is meaningful to model the EDL on its surface. However, Pt (100) doesn't have visible EDL region, which means that there always exist adsorbates on this surface. How will adsorbates influence the surface properties?

Computational standard hydrogen electrode

Computational standard hydrogen electrode (SHE) developed by Cheng and Sprik [1] enables a direct comparison of the computed electrochemical energy levels to experiments either in bulk liquid water or at electrode/water interfaces. Le et al. [2] transfer the deprotonation free energy of interfacial water to bulk water's counterpart, which make calculation for metal possible.





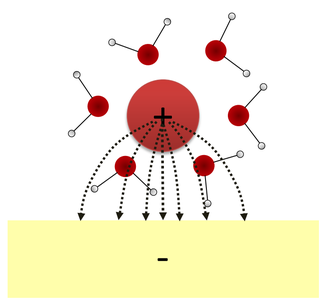
Outlook

Co-adsorption region

With deconvoluted CV of Pt(100), the co-adsorption of hydrogen and hydroxide around potential of total zero charge (pztc) has been presumed by many researchers [3] [4]. Mixture of adsorbates introduces some new questions, such as interaction between H* and OH*, impact on HB network.

Electric field analysis

The average electric field in x and y direction will be cancelled within a statistical average (if time is long enough). However, the local electric field in xy plane can not be ignored in the real system, especially when ions move slowly. We plan to extract the potential variation[5] and do three-dimensional electric field analysis.

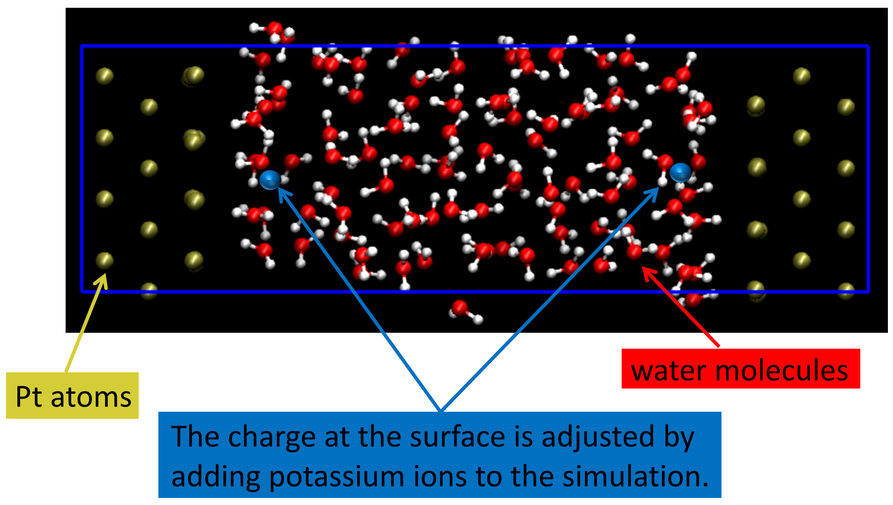


Reference

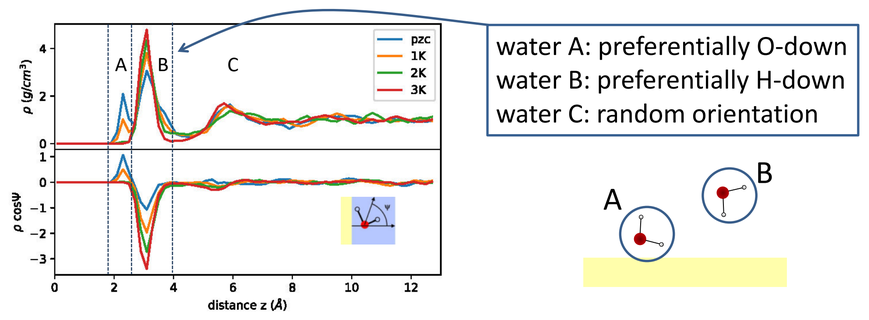
[1] Cheng, Jun, and Michiel Sprik. *Physical Chemistry Chemical Physics* 14.32, 11245-11267 (2012)
[2] Le J, Iannuzzi M, Cuesta A, et al. *Phys. Rev. Lett.* 119.1, 016801 (2017)
[3] Garcia-Araez, Nuria, Victor Climent, and Juan M. Feliu. *Journal of Electroanalytical Chemistry* 649.1-2, 69-82 (2010)
[4] Janik, Michael J., Ian T. McCrum, and Marc TM Koper. *Journal of Catalysis* 367, 332-337 (2018)
[5] Ando, Yasunobu, Yoshihiro Gohda, and Shinji Tsuneyuki. *Chemical Physics Letters* 556, 9-12 (2013)

Models of clean surfaces

Construct models with explicit water molecules and do the simulation with molecular dynamics based on density functional theory (DFTMD). Electrode potential is calculated with computational SHE.
Adjust the electrode potential by adding ions.

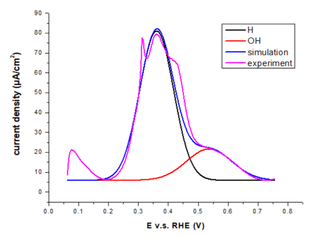


On a clean Pt(100) surface, the water structure changes strongly with changing surface charge.



Models of surfaces with adsorbates

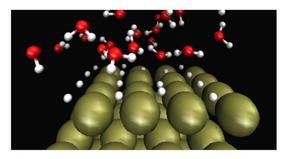
Experiments suggest, however, that there are adsorbates on the Pt(100) surface at the potential of zero charge.



Integrate to obtain for coverage

Potential (V v.s. RHE)	θ_H	θ_{OH}
0.23	0.99 (saturate)	9.00E-06
0.42 (pztc)	0.15	0.017
0.73	6.40E-09	0.28 (saturate)

- Study the influence of adsorbates on the EDL
- How does de/adsorption happen?
- What happens to the hydrogen bonding (HB) network?



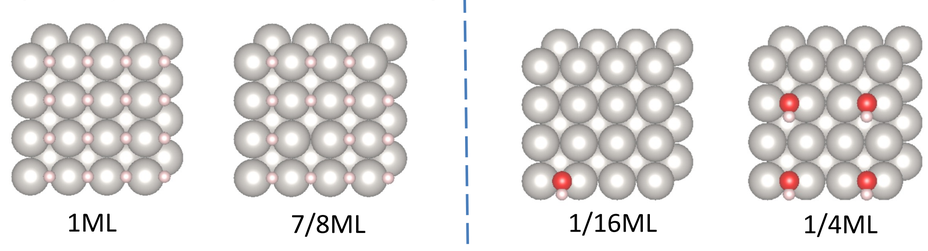
model surfaces with adsorbates

hydrogen

- More hydrophobic surfaces
- High mobility
- H transfer on surfaces (nearly-full covered surface)

hydroxide

- more hydrophilic surfaces
- High immobility
- promote HB formation



capacitance