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Computational electrocatalysis: methods and fundamental applications on CO2 reduction and formic acid oxidation

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SUMMARY & FUTURE PERSPECTIVES

This dissertation focused on computational methods based on first principles calculations using the Density Functional Theory (DFT) framework. Emphasis was laid on affordable methods that can provide a tradeoff between computational expense and accuracy. Specifically, we investigated solvation effects near the surface of the electrode, used thermodynamic cycles to compute solution-phase energies and also proposed a workflow to detect gas-phase errors on the free energies of target molecules. We used these simple methods to study complex adsorption processes at the $Pd_{ML}Pt(111)$ electrode surface. DFT and experimental studies were crucial to guide the investigation forward

Summary

Chapter 2 was dedicated to understanding the role of different DFT functionals with and without van der Waals (vdW) interactions, on the solvation energy of *OH adsorbed on near-surface alloys (NSAs) of Pt-M-Pt (111), where M = Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au. From this study, we obtained a dataset of solvation energies per functional, and found that (i) adsorbate stabilization due to water solvation is weaker when including vdW interactions, (ii) extrapolating solvation energies within functionals that include vdW interactions is safe, and (iii) while extrapolating solvation energies obtained with PW91 to PBE and vice versa is OK, it is not advisable to extrapolate from RPBE to neither PBE nor PW91. We concluded that it is important to assess solvation energy specifically for the system under study, and that it is safe to use solvation energies calculated with other functional as long as it belongs to the same group.

Accurate and affordable methods are necessary to describe ions both in the bulk solution (far away from the electrode surface) and at the metal-electrode interface, to predict catalytic activities, influenced by not only the reaction intermediates but also by their interaction with the adsorbed ions from the electrolyte. In *Chapter 3*, we presented a simple-to-use method to determine solution-phase free energies of any ion in solution using simple electrochemical thermodynamic cycles. This solution-phase reference method does not require intensive computational models of solvation to obtain the free energy of the solvated ion, avoids periodic calculations of charged species by linking neutral gas-phase or solid-state species to the charged ones through experimentally measured equilibrium potentials, and offers solution-phase energies of the ions that lie at the same potential scale. This allows for comparisons across different ions/adsorbates. We examined the adsorption potentials of various ions on Pt(111) and Au(111), and were able to reproduce the trend between the ions measured experimentally.

DFT methods based on the generalized gradient approximation (GGA) provide accurate energetics and describe well the electronic and geometric structures of

bulk metals. However, gas-phase molecules require more sophisticated and expensive calculations, often based on hybrid functionals. A clear problem is that hybrid functionals are not suitable for metals, and GGA functionals are not particularly accurate for molecules. Therefore, *Chapter 4* was dedicated to providing an inexpensive solution for this dilemma, where we can model adsorption processes when a metal surface is in contact with gas-phase species, as it is the case in electro(catalysis). We presented a systematic, semiempirical method to correct errors in the gas-phase energies of four GGA functionals commonly used in catalysis, namely PBE, PW91, RPBE and BEEF-vdW. This method was applied to a dataset of 27 gases and we found that it lowers the maximum and mean absolute errors by one order of magnitude. We identified an intrinsic limitation of DFT for the description of CO and CO_2 across all studied functionals, as the energy difference between the formation energies of these species is constant, and implementation of this method significantly decreased the errors of the calculated onset potentials when used to model electrocatalytic CO_2 reduction on Au, Ag and Cu electrodes. Therefore, with this method we can identify and correct errors in gas-phase molecules leading to predictive electrocatalysis models.

The simple and affordable DFT methods proposed in *Chapters 2-4* were implemented in the remaining chapters of this thesis, where we investigated the adsorption processes on the $Pd_{ML}Pt(111)$ surface, one of the most active catalysts for the oxidation of formic acid and the carbon dioxide reduction reaction, in a comparative fashion with Pt(111).

To elucidate the mechanisms of reactions catalyzed by $Pd_{ML}Pt(111)$ during electrochemical conditions, under applied potentials, it is important to study the adsorption processes happening at the electrode surface. In *Chapter 5* we combined experimental measurements with density functional simulations to investigate the adsorption processes corresponding to various peaks in the blank cyclic voltammogram of $Pd_{ML}Pt(111)$ in perchloric acid, and compared with Pt(111) at the same conditions. We found that the peak named H_I is significantly influenced by cations while the peak H_{II} is greatly influenced by anions. We ascribed the peaks in the region between 0.05 to 0.35 V vs RHE to be first the replacement of adsorbed hydrogen with adsorbed hydroxyl, that is the peak at 0.25 V vs RHE, and second the exchange of the H/OH adlayer to adsorbed perchlorate at 0.306 V vs RHE. The peak at later potentials between 0.60 and 0.90 V vs RHE was ascribed to a perchlorate/ hydroxide adlayer or the replacement of perchlorate with a higher coverage of adsorbed hydroxide, and this peak is suppressed by strong binding anions. The detailed information gained in this chapter is important to understand the catalytic properties of palladium-based electrodes.

There has been some debate on whether adsorbed formate plays a role as an active intermediate or spectator species during the formic acid oxidation reaction. Although recent works agree on the role of adsorbed formate being that of spectator and not an intermediate, its role as spectator remains elusive. Furthermore, during carbon dioxide reduction, the $Pd_{ML}Pt(111)$ catalyst produces formate at a low overpotential while Pt(111) is passivated with CO. *Chapter 6* was devoted to gaining knowledge on the particular question of how $Pd_{ML}Pt(111)$ prevents CO poisoning during CO_2 reduction and HCOOH oxidation by combining experiments on well-defined single-crystal electrodes of $Pd_{ML}Pt(111)$ and Pt(111), and density functional theory calculations. We found that the coverage at which formate adsorbs during the oxidation reaction dictates

whether or not CO forms, high coverages of 1/3 ML prevent CO formation on $Pd_{ML}Pt(111)$ by blocking the sites necessary for COOH (CO precursor), while coverages of 1/4 ML on Pt(111) allows COOH formation and subsequent electrode poisoning. During the reduction reaction the nature of the adsorbed hydrogen on the surface plays an important role on the mechanism of formation of formic acid from carbon dioxide. We find that this hydrogen on $Pd_{ML}Pt(111)$ is more negatively charged than that on Pt(111), and suggest that the reaction proceeds via nucleophilic attack. The knowledge gained in this study can help in catalyst design where CO poisoning is to be avoided.

Future Perspectives

From the work conducted in this thesis various other questions emerged or were left unanswered, and those questions could be the beginning of future projects.

- Chapter 2: Similar to the investigation conducted in this chapter, we were curious to know how solvation energies varied for the *OOH adsorbate on the same surface alloys studied and to verify if the trend found for *OH is similar or not to *OOH. For example, the unanswered question here is whether the solvation energies for the *OOH are significantly different when calculated with the different DFT functionals with and without van der Waals (vdW) interactions? Since *OOH is similar to *OH we could expect similar trends.

- Chapter 3: The investigation from this chapter can be extended through a screening investigation of adsorption energies of various anions on various transition metals (TM), but to follow the line of the work in this thesis, the investigation would be for palladium overlayers on different TM surface (Pd_{ML}(hkl)/TM(hkl)), and one could investigate the effect of adsorbing anions on the electronic-structure properties, like d-band centers and work functions.

- Chapter 4: Future work from this chapter is the implementation of a machine-learning algorithm that can follow the proposed workflow, and be able to run calculations, get the free energies, pinpoint the errors in formation energies of gas-phase molecules and produce error corrections. This can have great potential in scientific software automation and development.

- Chapters 5 and 6: There are still various questions that emerged from this work. One of them was to know whether a clean monolayer of palladium is formed on the Pt(111) surface, to know whether defects form during the experiments, or whether the surface contained segregated Pt atoms. We conducted preliminary DFT investigations at very early stages of this project where we calculated the adsorption energies of *OH on intermetallic $Pt_1Pd_2(111)$/Pt(111), that is 1/3 ML of Pt on Pd. Although we found the energetics of the *OH to be favorable, we believed that it would be kinetically forbidden to have such exchange of atoms. Further research would be of great interest to understanding Pd/Pt alloy behavior. From Chapter 6, one interesting question that appeared and is left unanswered is to obtain an electronic-structure explanation as to why *COOH binds more strongly on Pt(111). The hypothesis proposed is that *COOH forms a

more covalent interaction with the Pt(111) surface than with Pd(111). If that is true, stronger overlap between the orbitals of the metal and the adsorbate should be observed on Pt(111) than on Pd(111).