Computational electrocatalysis: methods and fundamental applications on CO2 reduction and formic acid oxidation
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Propositions
accompanying the thesis
Computational Electrocatalysis: Methods and Fundamental Applications on CO$_2$ Reduction and Formic Acid Oxidation

1) Over-binding functionals (PBE, PW91) and under-binding functionals (RPBE, PBE+D3, RPBE+D3 BEEF-vdW, optPBE) provide different magnitudes of solvation energy of *OH on different near-surface alloys of Pt. The average difference between the two groups is ~0.15 eV, therefore extrapolation of solvation energies from one group to the other should be avoided.
Chapter 2

2) Using tabulated half-cell standard equilibrium potentials provides a simple and accurate method to calculate free energies of solution-phase charged species which are otherwise challenging to perform with DFT.
Chapter 3

3) Errors in the calculated formation energies of gas-phase molecules using DFT-GGA functionals can be corrected following an algorithm based on group additivity. By using this scheme, the mean absolute errors (MAEs) of calculated formation energies of CO$_2$ and CO reduction reactions are reduced by one order of magnitude.
Chapter 4

4) Pd$_{ML}$Pt(111) is a promising bimetallic surface for formic acid oxidation to CO$_2$ and CO$_2$ reduction to formic acid. This material catalyzes these reactions almost reversibly at low overpotentials, and combines the robustness of Pt and the tolerance toward CO poisoning of Pd.
Chapter 5 and 6

5) Plotting the DFT-calculated adsorption free energy as a function of coverage and electrochemical potential enables a direct comparison with experimentally measured cyclic voltammograms by providing information on the identity and the relevant coverage of the species adsorbed on the surface at a particular potential.
Chapter 5

6) High coverage of strongly adsorbed formate helps prevent CO poisoning on Pd$_{ML}$Pt(111) at oxidizing potentials by blocking the ensemble sites needed for its formation.
Chapter 6

7) The opening of the poisoning path during CO$_2$ reduction is related to the adsorption of *COOH at less negative potentials on Pt(111) than on Pd$_{ML}$Pt(111).
Chapter 6

8) Humans are a time machine that only moves forward.

9) To err is human; to edit, divine.
(Grammarly adaptation of Alexander Pope's quote)