Understanding the Electrochemical Interface from First-Principles DFT with Implicit Solvation Model

Abstract: Classical molecular dynamics (CMD) has been widely used to model the electrochemical interface as a conventional way, but it failed in aqueous solution system since the experimental observation exhibited large difference from CMD prediction. To have a deeper understanding on the aqueous electrochemical interface, we applied the First-Principles DFT calculation with implicit solvation model to investigate the cation-graphene interaction under electrochemical environment. The cation-graphene interaction was found to governed by the energetic competition of cation’s hydration energy, electrostatic attraction and repulsion. In addition, beyond classical picture, space charge transfer (SCT) effect was found at the interface that significantly dependent on the specific ion type and the contact distance of cation-graphene. Moreover, the SCT effect can be even enhanced under the confinement in sub-nanometer pore. Combining with experimental characterization, the observed electrochemical behavior of aqueous electrolyte can be well explained by the synergic effect of SCT and ion accessibility. Our work provides a deeper physical insight into the aqueous electrochemical interface beyond conventional model.

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