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Impact of Double Layer on Electrochemical Kinetics Via Bottom up Multiscale Modeling Approach

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Abstract Text:

Electric double layers (EDLs) play a fundamental role in various electrochemical processes such as colloidal dispersions, surface charging, and charge-transfer reactions. Increasingly, the role of EDLs on reaction kinetics is being studied^[1], revealing their importance in predicting the intrinsic and electrolyte-dependent kinetics of electrochemical reactions. Despite the extensive history of EDL modeling, there remain challenges in predicting the impact of EDL structure on reaction kinetics. The characteristic length of EDL for non-dilute solutions (typically 10 – 100 nanometers) exceeds the grasp of regular *ab initio* molecular dynamics (AIMD) simulations. While continuum models offer a means to estimate the quasi-equilibrium structure of EDLs with substantially lower computational cost than molecular dynamics, conventional continuum models require parameter fitting^[2] due to their lack of appropriate expressions for microscopic interactions. Furthermore, the lack of a commonly accepted micro-kinetic model to evaluate the role of the EDL structure on the reaction kinetics prevents the optimization of the interface for improved reaction rates.

In this talk, we propose a novel modeling framework for analyzing micro-kinetics that accounts for the contributions of EDL structure by leveraging our recently developed continuum EDL model^[3] and density functional theory (DFT) calculations. Our previous work showed that the continuum model can accurately predict differential capacitance for EDL charging without necessitating parameter-fitting by incorporating microscopic interactions such as electron spillover, entropy due to solute size variation, and polarization of solvent and solute molecules^[3]. We refine the continuum EDL model to account for the interactions between adsorbate coverage and EDL structure. This model utilizes DFT results, i.e., free energies and charge distributions of the adsorbates at potential of zero charge, as input properties. The model calculates the adsorbates' coverage to minimize the total grand potential, while accounting for both the effect of electrostatic potential on the adsorbate free energy and the effect of adsorbate charge density on the electrostatic potential simultaneously. The transition state of the rate determining step is treated as an adsorbate species, with its coverage evaluated in the same manner as the other adsorbates, which is used to evaluate the reaction rate based on transition state theory. This model framework enables us to evaluate the intrinsic and electrolyte-dependent kinetic activity with reasonable computational resources. Finally, we apply this model to investigate the kinetics of hydrogen evolution and oxidation reactions (HER/HOR) having favorable comparisons with measured cation- and pH- dependent kinetics^[4]. The results suggest that the charge distribution of the transition state can significantly affect electrolyte-dependent kinetics of electrochemical reactions, highlighting the importance of further analyzing the effects of EDL structures on reaction kinetics.

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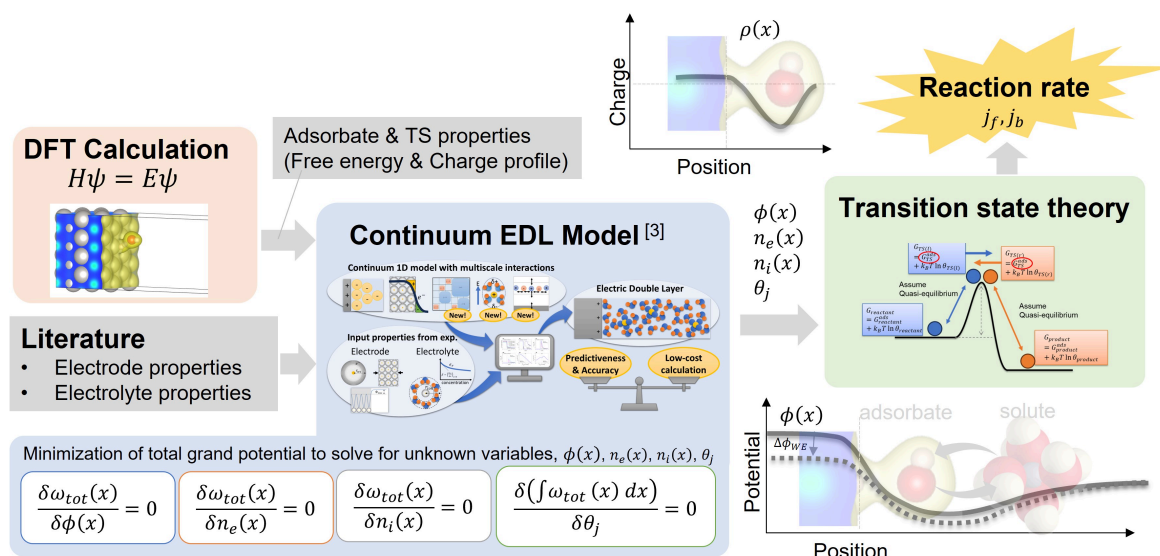
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[1] Shin, S.J., et al., *On the importance of the electric double layer structure in aqueous electrocatalysis*. Nat Commun, 2022. **13**(1): p. 174.

[2] Huang, J., *Density-Potential Functional Theory of Electrochemical Double Layers: Calibration on the Ag(111)-KPF(6) System and Parametric Analysis*. J Chem Theory Comput, 2023. **19**(3): p. 1003-1013.

[3] Shibata, M., S., et al., *Parameter-fitting-free Continuum Modeling of Electrical Double Layer in Aqueous Electrolyte*, Submitted.

[4] Huang, B., et al., *Cation- and pH-Dependent Hydrogen Evolution and Oxidation Reaction Kinetics*. JACS Au, 2021. **1**(10): p. 1674-1687.

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