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## 일시 : 2024년 3월 28일 (목) 오후 4 : 30 장 소 : 이학관 331

### DFT-CES: eyes to see the unseen, buried electric double layer

Electrochemistry, the fundamental basis of sustainable energy conversion technologies, investigates the electric-chemical energy interconversion process at the electrode-electrolyte interface, where a characteristic liquid structure, namely an electric double layer (EDL) is known to be formed. Since the early 1900s, when the concept of EDL was theoretically formulated, unremitting efforts have been made to identify potential-dependent EDL structural changes, but only a few molecular details have been disclosed to date. One famous example is EDL capacitance, which is an indicative quantity of the EDL structural change, but no molecular theory of liquid structure has fully explained its characteristic features. To address this century-long debate by accurately modeling the electrified interface, we develop a first-principles-based multiscale method called a *density functional theory in classical explicit solvents (DFT-CES)*, which mean-field couples the DFT and the molecular dynamics for respective description of electrode and electrolyte.[1,2] Using DFT-CES, we find unprecedented liquid structural changes and phase transitions of the EDL, which originate capacitance peaks that have been observed from experiments (but never explained before).[3] Atom-level investigation on the EDL region, enabled by our DFT-CES simulations, further unravels a new mechanistic role of the cations in the EDL during electrochemical reactions - they are no more spectating the reaction but are coordinating to key intermediates for a *cation-coupled electron transfer*.[4] Our studies envisage a new perspective for developing better electrocatalysts by tailoring the electrochemical interface.


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[4] Shin, S.-J.; Choi, H.; Ringe, S.; Won, D.H.; Oh, H.S.; Kim, D.H.; Lee, T.; Nam D.-H.; Kim, H.; Choi, C.H. A Unifying Mechanism for Cation Effect Modulating $C_1$ and $C_2$ Productions from $CO_2$ Electroreduction *Nat. Commun.* **2022**, 13, 5488



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