Inherent Co-ion Influence on Electric Double Layer Structure and Electrochemical Reactivity in the Hydrogen Evolution Reaction

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The formation of an electric double layer is ubiquitous in electrolytes undergoing electrochemical reactions. Currently, models for the double layer rely on the assumptions of dilute electrolyte theory where ions in solution do not interact. Dilute electrolyte theory predicts that solely hydrated counterions, or ions opposing the surface charge, occupy the near surface region and impact reactivity. Since this theory does not account for conditions like high applied potentials and high ion concentrations, understanding the relationship between double layer structure and electrochemical reactivity is critical for opening new domains for electrochemical modulation.

Notably, our recent work shows that co-ions, or ions with the same charge as the surface, can also have a definitive influence on reactions, particularly under condition of high applied potential, even at bulk concentrations as low as 5 mM. The hydrogen evolution reaction was used as a model system to explore co-ion effects in electrocatalytic reactions. We systematically vary co-ion identity and track hydrogen evolution reactivity as a function of concentration. We highlight the universal nature of the co-ion influence on hydrogen evolution at large potentials of -1.9 V and reveal that its impact on hydrogen evolution can outsize that of the cation in many circumstances. In particular, we focus on the unique ability of the tetrafluoroborate co-ion to undergo dynamic ligand exchange between hydroxide and fluoride. This allows tetrafluoroborate to act as a hydroxide sink to stabilize the hydrogen evolution byproduct. Furthermore, we used X-ray absorption spectroscopy to probe the electrode-electrolyte interface of tetrafluoroborate solutions which reveals markers of clustering and a surprisingly unperturbed water structure in the electric double layer. Lastly, sum-frequency generation spectroscopy reveals how co-ions influence interfacial hydrogen bond networks, which can have a significant impact on aqueous electrochemistry. Our results highlight how co-ions influence double layer structures and have significant implications for tuning other aqueous reactions such as carbon dioxide and nitrate electroreduction.

Keywords: Electric double layer, electrolytes, co-ion, anion, hydrogen evolution reaction, interfaces, water structure, catalysis.

Acknowledgments: Work supported by the National Science Foundation (NSF). Work supported by the U.S. DOE Office of Science Graduate Student Research (SCGSR) program. The SCGSR program is administered by the Oak Ridge Institute for Science and Education for the DOE under contract number DE-SC0014664.