

# Anderson-Newns Hamiltonian Molecular Dynamics Approach to Understanding Electrochemical Double Layer Effects in Hydrogen Electrocatalysis

by Jon Wilson

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Zoom: <https://udel.zoom.us/j/93326475676> , Password: platinum

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Today, green hydrogen is at the cusp of widespread adoption. However, to meet critical CO<sub>2</sub> emission reduction targets sooner, faster scale up of green hydrogen infrastructure is needed. To that end, progress in device design is needed to reduce the material costs in fuel cell and electrolyzer production. The development of hydroxide exchange membrane fuel cells (HEMFCs) and electrolyzers (HEMELs) is a promising route towards lower device costs. However, design challenges remain in the way of commercialization. The hydrogen oxidation (HOR) and evolution reaction (HER) kinetics are much slower at high pH. Several theories have been proposed to explain pH-dependent kinetics, however, debate is ongoing. Changes in interfacial electrostatic potential and the type of supporting electrolyte ions greatly affect HOR and HER kinetics, but such effects are not well understood. Here, we employ molecular dynamics simulation of the electrochemical interface to gain mechanistic insights into HOR/HER kinetic trends. These mechanistic insights are expected to inform design strategies for the development of efficient HOR/HER electrocatalysts beyond the traditional approach of using thermodynamic descriptors.

To clarify how interfacial properties are related to kinetic trends in HOR and HER, we developed a composite model to simulate the rate limiting Volmer reaction step in the electronically-adiabatic charge transfer regime. We embed an Anderson-Newns Hamiltonian electronic model for the H<sup>+</sup>/H redox event into classical molecular dynamics simulation of the Pt (111) – aqueous electrified interface. Moreover, we incorporate controlled-potential electrodes within this framework for the first time. With this approach, we calculate the redox solvent reorganization energy by sampling the slow solvent fluctuations– these time and length scales are otherwise inaccessible with current density functional theory simulation techniques.

First, we show how the HOR/HER solvent reorganization energy is not sensitive to interfacial electric fields as was previously thought. Instead, changes in the interfacial electrostatic potential affect the redox activation barrier by changing the local electrochemical potential of interfacial H<sup>+</sup>. Second, we demonstrate that slower HOR/HER redox kinetics in Cs<sup>+</sup>-containing electrolyte versus Na<sup>+</sup>-containing electrolyte are governed by increased solvent reorganization energy in the Cs<sup>+</sup> case as well as an increased entropic barrier as approaches the surface. Cs<sup>+</sup> electrostatically adsorbs at a relatively high coverage compared to Na<sup>+</sup>. Thus, a large fraction of the interfacial waters participate in the solvation of surface Cs<sup>+</sup>. Consequently, the motion of solvated H<sup>+</sup> is constrained by the nearby bulky solvated Cs<sup>+</sup>, lowering the configurational entropy. Additionally, near the surface, Cs<sup>+</sup> translation contributes to the collective reorganization process for H<sup>+</sup>, resulting in increased solvent reorganization energy and slow redox kinetics.