Interfacial Studies of the HOR/HER Mechanism on Pt in Alkaline Electrolytes

By Nicholas J Oliveira

Advisor: Prof. Yushan Yan

Committee: Prof. Dongxia Liu, Prof. Raul Lobo, Prof. Ajay Prasad

Friday, May 17th, 2024 at 9:00 am EST in Colburn 366

Zoom: https://udel.zoom.us/j/2685589261?omn=94236577629, Password: Platinum

---

Growing global climate concerns have motivated the transition to renewable energy, which when coupled with electrochemically produced green hydrogen can reduce greenhouse gas emissions across a variety of economic sectors, from transportation industrial processes. This is achieved by virtue of the electrochemical device which operates at ambient temperatures and pressures and does not react through combustion, increasing process efficiency over typical thermal methods. Thus, a hydrogen-based economy using hydrogen fuel cells and electrolyzers in tandem with renewables has the potential to transition our society toward our net zero emissions goal.

However, current state of the art acid based electrolyzers and fuel cells are prohibitively expensive due to their high precious metal requirements, leading researchers to develop alkaline based alternatives. Despite their advantages, the typically fast hydrogen electrocatalysis in acidic environment becomes prohibitively slow in alkaline, also necessitating high precious metal loadings to overcome severe overpotential losses and making these devices economically infeasible. In order to facilitate better catalyst design, the underlying parameters influencing the reaction mechanism must be understood.

To understand the two orders of magnitude activity decrease in alkaline, we systematically analyze the leading hypotheses with electrochemical and spectroscopic techniques. Through the use of crown ethers, we demonstrate that alkali metal cations specifically adsorb on platinum in base, but do not influence reactivity through modulation of adsorbed hydroxide's binding energy. Rather adsorbed crown ethers and benzyl tri alkyl ammonium cations enable a higher degree of hydrogen bonding amongst interfacial water and allow for facile proton and hydroxide shuttling between the surface and the bulk. Establishing water structural entropy as the alkaline hydrogen electrocatalysis activity descriptor enables rational catalyst design to lower fuel cell and electrolyzer overpotentials to become economically viable.