Center for Electrochemical Dynamics and Reactions on Surfaces (CEDARS)
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Class: 2022-2026

Mission Statement: *To reveal the formation of the transient intermediates of oxygen evolution reaction and hydrogen evolution reaction and how the catalyst evolves before, during, and after catalysis.*

Hydrogen produced from water electrolysis is abundant, clean, and secure. This method of producing hydrogen, however, is slow and requires energy beyond what is thermodynamically necessary. At present, the molecular factor(s) responsible for these limitations is not well known because the two electrochemical reactions of water splitting, the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), are complex cascades of electron-driven reactions with transient species forming and disappearing at each step along the catalytic process. Starting from the descriptions of proton transfer (PT) and electron transfer (ET) to surface bond formation and dissociation, the mission of this center is to reveal step-by-step the formation of the transient intermediates, what causes the chemical bonds to form, how a catalyst evolves before, during, and after catalysis, as a function of time and reaction conditions. A team with the capabilities to deconstruct the mechanism of OER and HER into the elementary steps has been put together to address this challenge. The intended work integrates high-precision growth of materials with studies of the short-lived transient intermediates by optical and X-ray scattering and spectroscopy, and first-principles modeling inclusive of beyond density functional theory (DFT) and grand canonical calculations. The plan requires a team interweaving across disciplines, from materials, chemical, to computational sciences.

Our team integrates investigators from universities and DOE laboratories (**Fig. 1**). The research is organized into three thrusts by the time and event sequence of the catalytic cycle. The research in Thrust 1 focused on determining how the water dissociation energies and dynamics on oxide catalysts containing 3d, 4d, and 5d metals. Identifying the electrochemical dynamics of the metal-oxygen bond as a function of electronic structure, surface composition, and excitation potential will reveal how the starting point of an electrochemical reaction varies between different catalysts. CEDARS will focus on metals, metal oxides, and oxynitrides prepared as single-crystal, epitaxial, or conformal films on photo-adsorbers that are oxides or III-V semiconductors. To resolve the molecular structure and formation dynamics of the intermediates, CEDARS will apply multi-modal, *in situ*, and time-resolved spectroscopy. Ultrafast optical spectroscopy and ultrafast X-ray absorption spectroscopy will in-tandem assign electronic orbitals to the optical transitions of charge-transfer intermediates and derive changes in the covalency and metal-oxygen bond distance.

Thrust 2 is concerned with resolving how the reaction kinetics are related to surface thermodynamics and the local environment of electric fields, diffusive motion of charge and ions, and chemical exchange, controllable by interfacial chemistry and device structure. The challenge implicit to this Thrust is the need to probe the interface holistically to find the reaction coordinate. CEDARS will harness two strategies: (a) Systematic tuning of the interfacial environment through reaction chemistries, spatial control, and select-area excitation and (b) Employing multi-modal and multi-dimensional probes to follow interacting intermediates through bond formation, utilizing the full electromagnetic spectrum and non-linear spectroscopy. The team will use these approaches in tandem to reveal surface dynamics related to bond formation. The approach and findings of Thrust 2 will allow the team to interrogate how the electronic and chemical states favor specific reaction pathways and how to tailor them for faster bond formation for better catalysis.

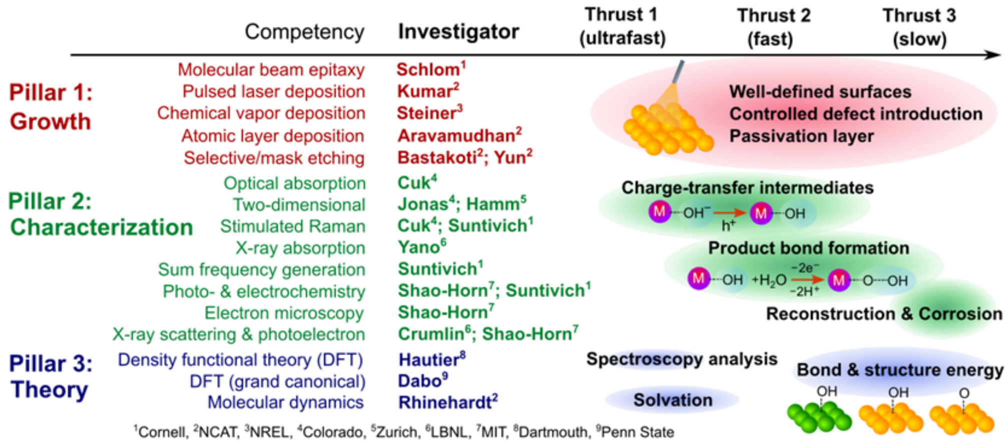

Fig.1: CEDARS team and intertwined three research thrusts.

The research in Thrust 3 is focused on establishing a connection between catalytic turnover, surface restructuring, and stability. CEDARS will detect how the underlying materials adapt during the formation of transient intermediates and the accompanying chemical bonds building on the intermediates and bond formation events that occur at a fast-time scale ($> 10^{-6}$ s). The surface changes that arise from M-O, O-O, and H-H bond distortions are small but can cumulatively initiate failure event such as corrosion. CEDARS will explore two strategies to limit the corrosion: (1) Applications of thin passivation layers to allow the subsurface electronic structure to interact with the reactive intermediate but sufficiently inert such that corrosion is suppressed (2) Use the time constants associated with the intermediates that lead to corrosion to inform alternative strategies for engineering stability, such as timing surface activation by electron flow. Comparing the electrochemical and spectroscopic studies from the fast-time domain through many catalytic cycles will allow CEDARS to holistically investigate surface reconstruction and its connection to corrosion. As detailed earlier, *operando* characterization will be performed and alongside online mass spectroscopy. High-throughput DFT calculations will be applied to survey the large space of possible compositions and structures to map possible local motifs of corrosion to the experimental spectroscopic signatures.

The research efforts are complemented by activities in Workforce development, Diversity, Equity & Inclusion, and training. The integrated research and education plan will allow CEDARS to imbue the next-generation workforce with a unique skillset to drive the effort of clean hydrogen production at terawatt scales through multidisciplinary, diverse research collaboration and exchange.

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