Generating Hydrogen from Seawater Electrolysis

Building Clean Energy Science in Guam

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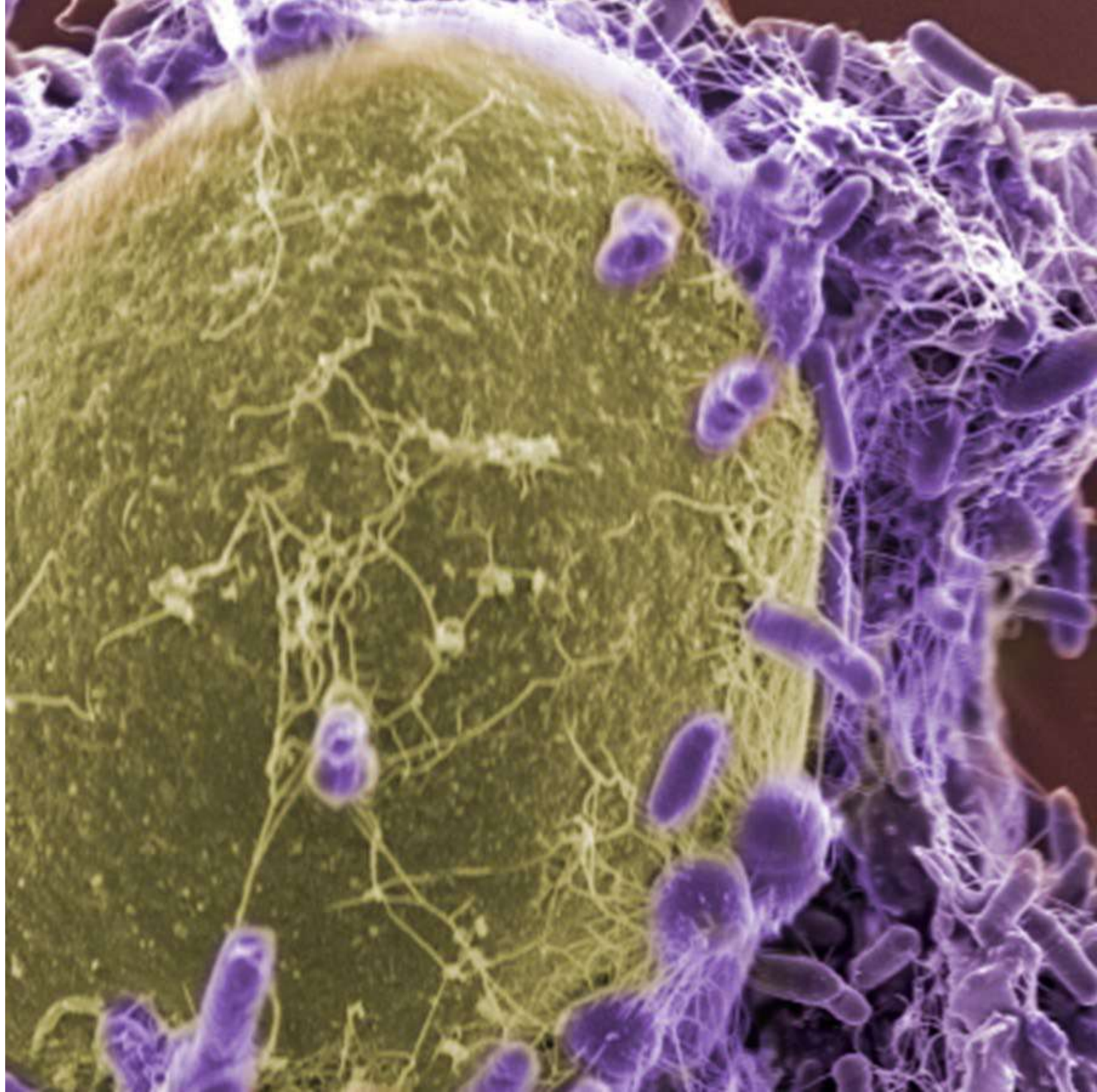
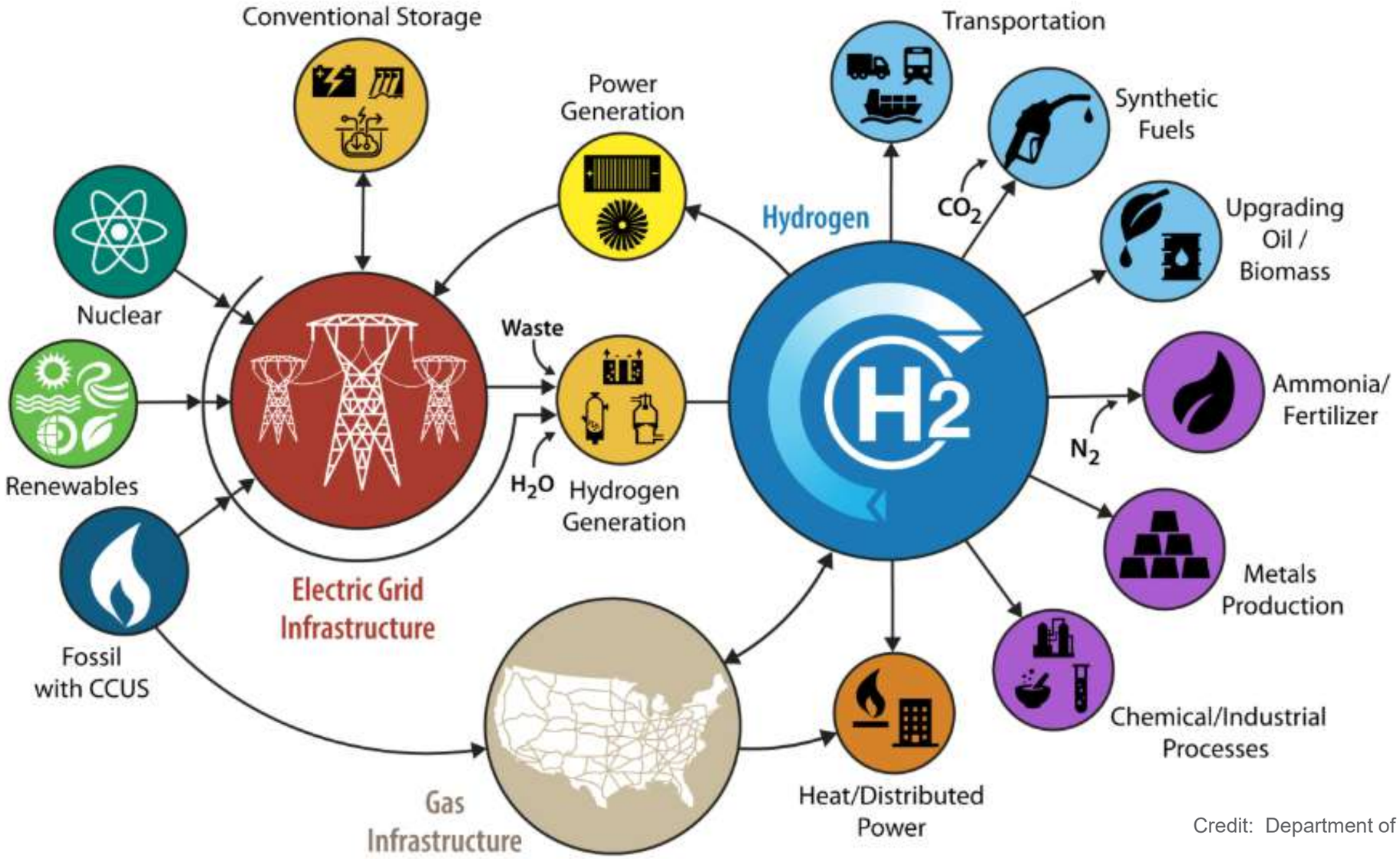
October 22, 2025

PNNL is operated by Battelle for the U.S. Department of Energy



Green Hydrogen is gaining traction as a clean energy alternative

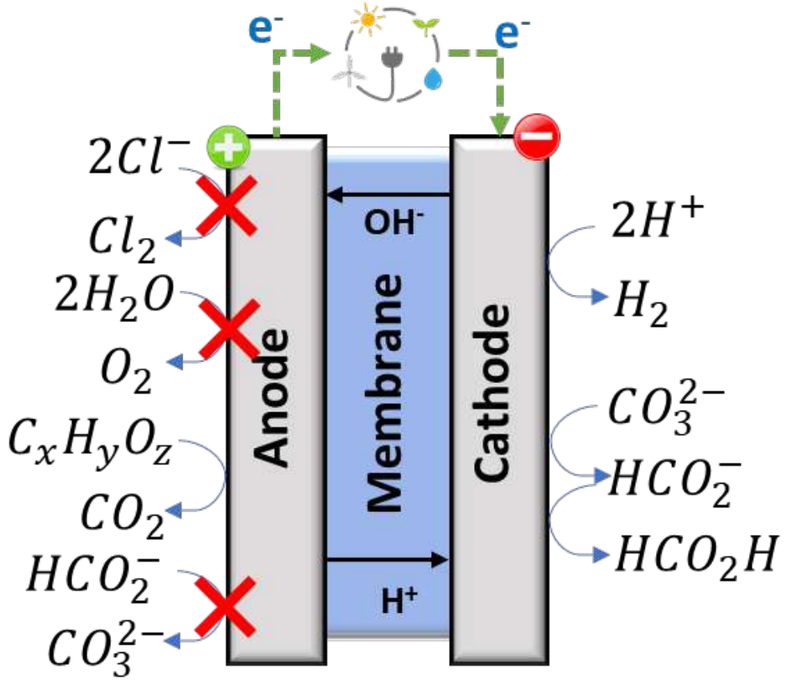


Credit: Department of Energy H2@Scale

UOG's BES-RENEW Program

Build scientific and technical expertise in under-represented groups leveraging DOE national laboratories and user facilities through hands-on experience.

- Fundamental understanding and foundation for "green" hydrogen production
- "Controlling reactor pathways under non-ideal conditions of seawater electrolysis."



Funded by the Department of Energy Office of Science

Basic Energy Science - Reaching a New Energy Sciences Workforce (BES-RENEW)

BES-RENEW Project

Controlling reaction pathways under the non-ideal conditions of seawater electrolysis

Objective

- To perform fundamental research aiming at understanding the complexity of electrode/liquid interfaces and controlling reaction pathways for the electrochemical evolution of hydrogen (H_2) and oxygen (O_2), and the prevalent side reactions, under the conditions of seawater electrolysis.

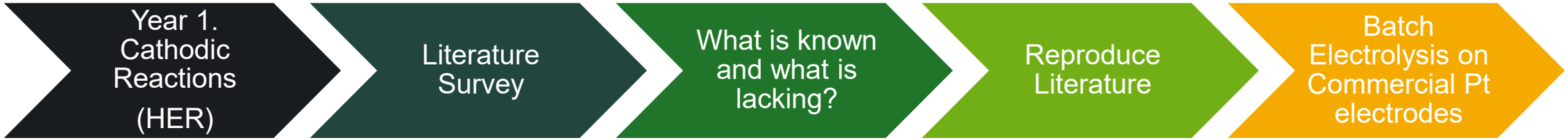
Approach/Tasks

- **Task 1.** Cathodic transformations (H_2 evolution reaction [HER], Electrochemical reduction [ECR])
- **Task 2.** Anodic transformations (O_2 evolution reaction [OER], Chlorine evolution reaction [CER], and electrocatalytic oxidation [ECO] of organic compounds)
- **Task 3.** Theory (Structural Dynamic and reactivity; reaction mechanism of HER, ECR, OER, and CER)
- **Task 4.** Recruitment and Inclusion Plan

Desired outcomes

- Understand how to control the electrochemical reactions across a wide range of potentials and electrode materials in non-ideal systems (such as seawater).
- Understand how the EDL's molecular organization, influenced by electrostatic fields and electrolyte environment, can be controlled to promote the targeted electrochemical reactions.
- Identify the electronic and structural features of (electro)catalysts that allow for efficient and stable ECO of organic compounds and ECR of dissolved CO_2-derived species in seawater.

FY23: Faculty and students were introduced to electrochemistry in seawater for the first time



- UOG researchers learned fundamentals of the hydrogen evolution reaction (HER) in seawater:
  - Performed experiments in rotating-disk electrode
  - Performed experiments in different batch cells and learned to interpret electrokinetic data
  - Evaluated the effect of NaCl concentration on the HER performance

FY24: Expand knowledge and learn about the different oxidation reactions and learned data analytics

- Four new students will learn the fundamentals of the oxidation reactions in seawater:
  - Performed experiments in different batch cells and learn to interpret electrokinetic data for different electrocatalytic oxidation (ECO) reactions
    - ✓ O_2 evolution reaction (OER)
    - ✓ Cl_2 evolution reaction (CER)
    - ✓ Full electrocatalytic oxidation (FECO) of organic compounds
  - Learn how to synthesize and characterize electrodes
  - Learn how to perform Flow electrolysis
  - Evaluated the effect of organic compounds on the oxidation performance
  - Learn how to model research data and develop visualization capabilities
    - ✓ Density Functional Theory simulations using CP2K software package

FY25: new UOG faculty and students will continue learning experience, including art of writing publications/journals

- FY25, new UOG researchers will learn the fundamentals of the oxidation reactions in seawater:
  - Continue performing experiments in different batch cells and the following:
    - ✓ Interpret electrokinetic data for different electrocatalytic oxidation (ECO) reactions (OER, CIER, FECO)
    - ✓ Evaluate the effect of organic compounds on the oxidation performance
  - Continue to learn data analytics and computational methods
  - Develop publication/journal writing and dissemination of research

Guam Seawater was sampled from 5 sites

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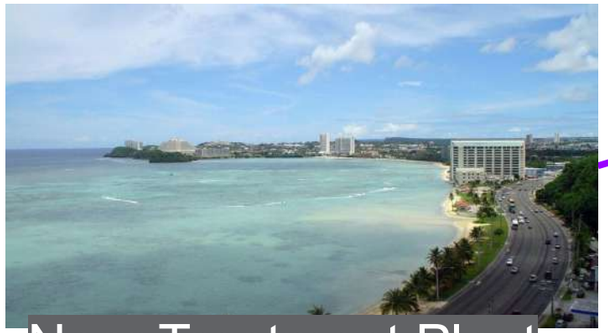
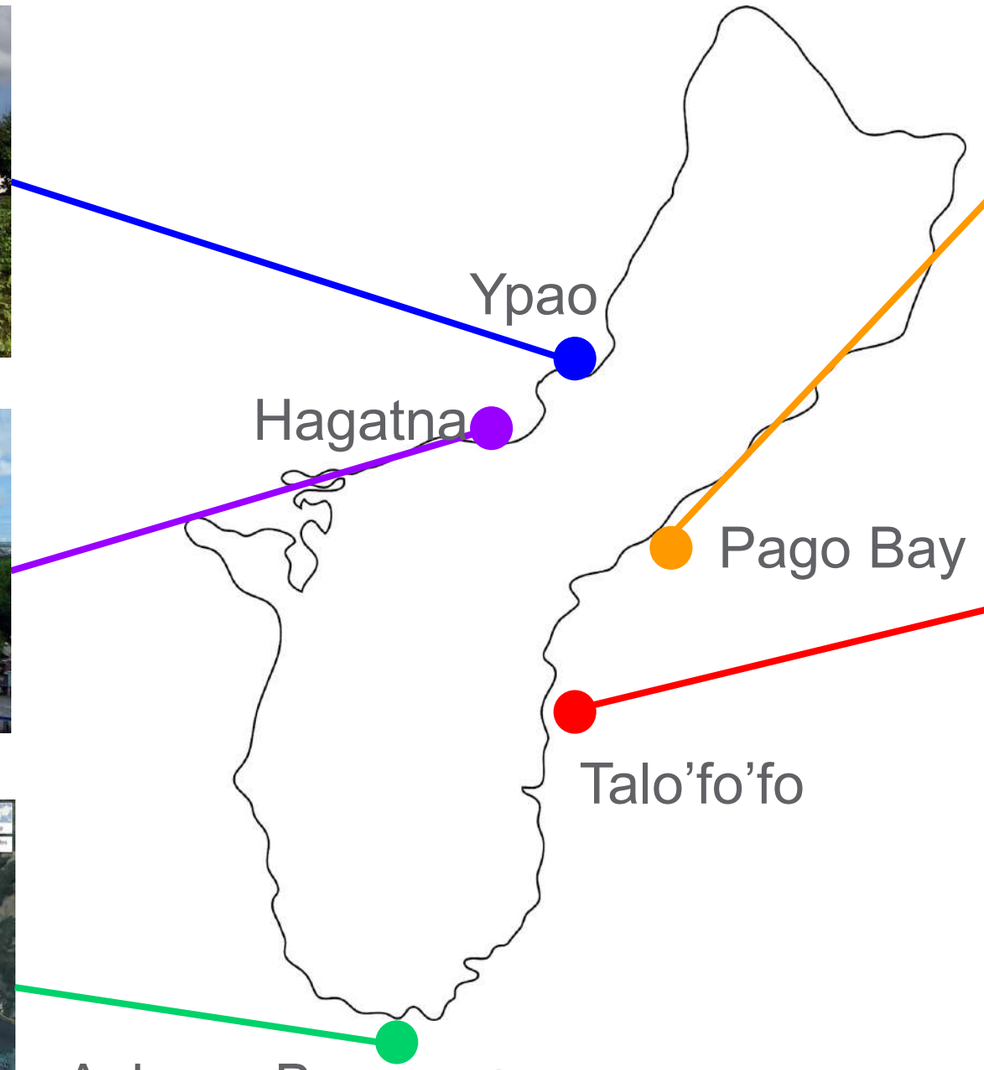
Popular Beach



Near Treatment Plant

Southern Bay



Marine Lab Research Station

Southern Rural Beach

IC, ICP, GC, LC, COD, & Conductivity were assessed

Gaining Priceless Knowledge and Experience

- Training/mentoring by PNNL researchers
  - On-campus within DOE national lab facilities
  - UOG electrochemistry lab
- Developed fundamental understanding of reductive reactions at the cathode as well as of oxidative reactions at the anode during water electrolysis in weakly buffered, complex, environments containing organic compounds like seawater

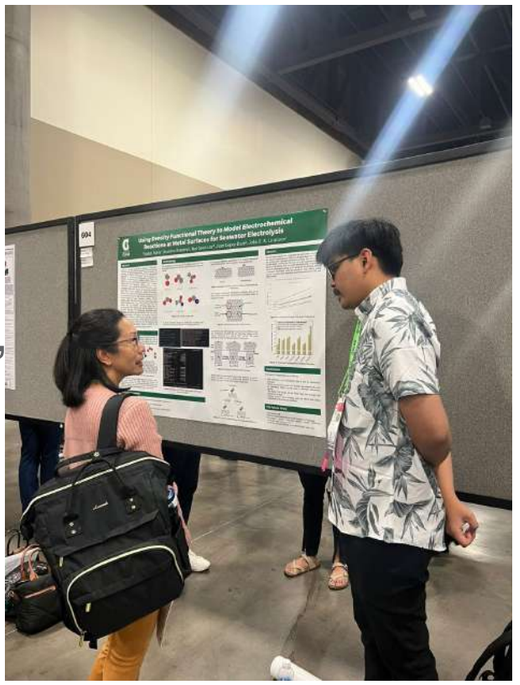
FY23 Student Researchers

FY24 Student Researchers

FY25 Student Researchers

Planned Future Collaboration Interests

- 3-year BES-RENEW program ending FY25; discuss with SC on plans to continue learning electrochemistry, data analytics, and modeling (Optional years 4 and 5)
- UOG developed an Electrochemistry program
  - New instruments and equipment (Nuclear Magnetic Spectroscopy, Potentiostat, Gas Chromatography Analyzer)
  - Electrochemistry 101 course starts Spring 2024
  - Migrated methods and procedures learned at PNNL in the performance of electrochemical water electrolysis experiments at UOG.
  - Goal is for Guam to become the Electrochemistry Hub for all Micronesia



UOG students present at Fall 2024 SACNAS

Future collaborations can focus on controlling reaction pathways of biomass and waste streams and algae to generate biofuels, H_2 gas, and liquid organic hydrogen carriers in seawater

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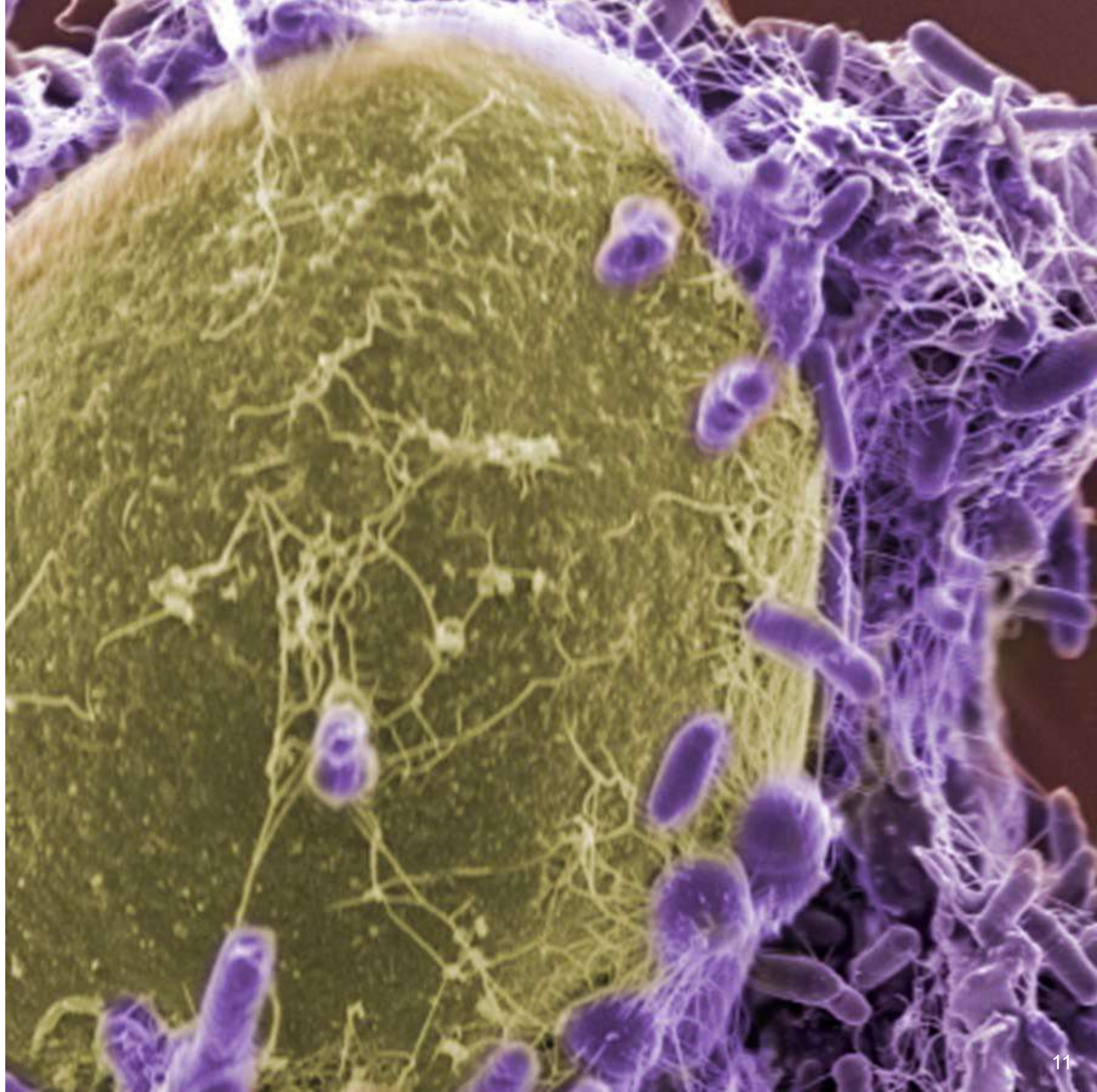
Thank you



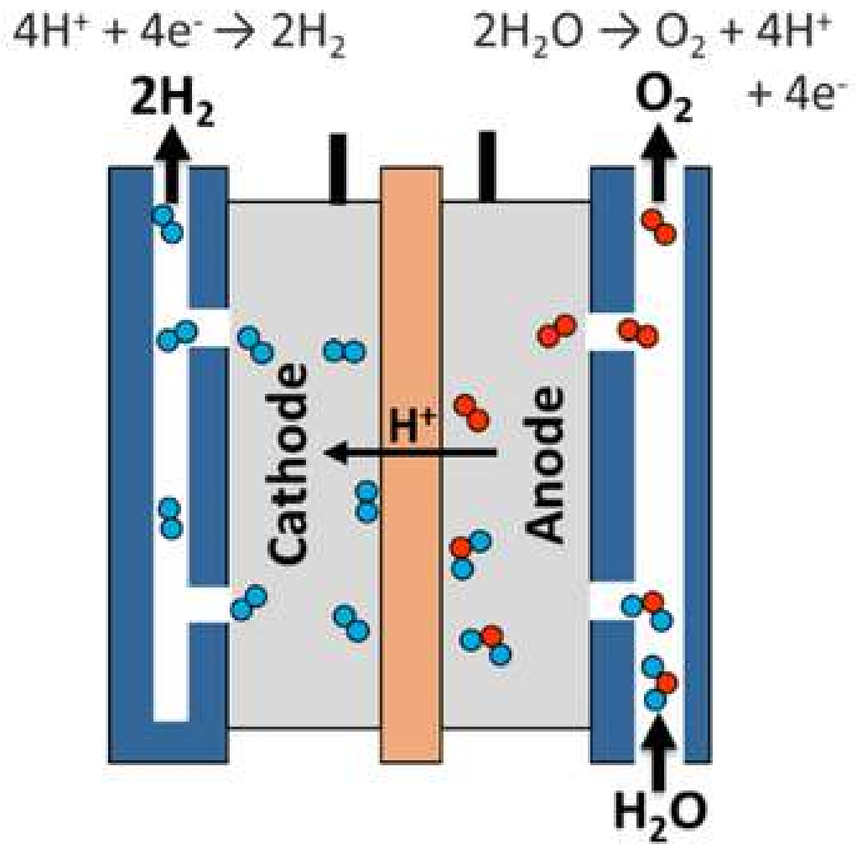
Water Electrolysis

- Hydrogen (H_2) not present in pure state
- Synthesis of hydrogen from water requires a lot of energy
- Electrolysis is the process of using electricity to split water into hydrogen and oxygen
- Electrolysis of water is energy intensive typically requiring an overpotential of >1.5 V versus standard reduction potential of 1.23 V

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^0_{ox} = -1.23\,V\ vs\ RHE$$

$$4H^+ + 4e^- \rightarrow 2H_2 \qquad E^0_{red} = 0\,V\ vs\ RHE$$

$$2H_2O \rightarrow O_2 + 2H_2 \qquad \Delta E = -1.23\,V\ vs\ RHE$$



Seawater Electrolysis

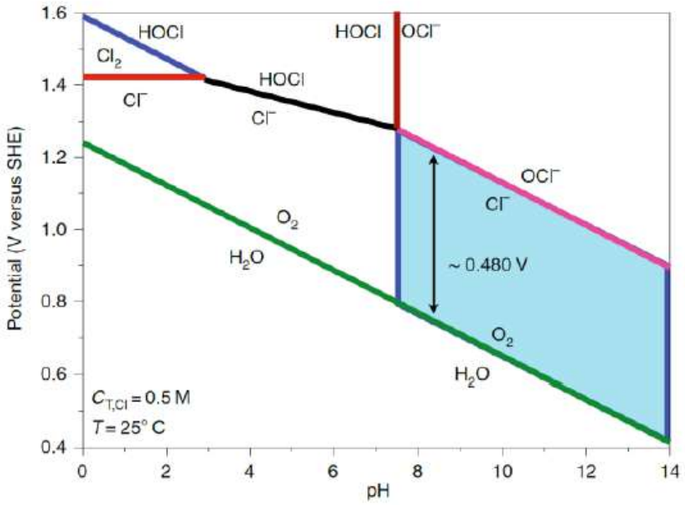
- Seawater as a major reservoir of H_2
- Challenges
  - Chlorine Chemistry
    - Strongly influenced by pH (Hypochlorite)
    - Kinetically favorable
    - Most studies leverage OER/CER design criteria that exploit the thermodynamic potential between the two catalytic processes
  - Influence of organic matter
    - Organics may protect the electrode surface
- Understanding pathways for hydrogen and oxygen evolution reactions and the influence that organic compound have at the EDL may help us drive desired electrochemical reactions
- Controlling of the composition of the interface will steer the selectivity of the electrolysis away from chlorine (hypochlorite) evolution and increase the selectivity towards energy carriers such as H_2

$$2H_2O + 2e^- \rightleftarrows 2OH^- + H_2$$

$$4OH^- \rightleftarrows 2H_2O + O_2 + 4e^-$$

$$2Cl^- \rightleftarrows Cl_2 + 2e^-$$

$$Cl^- + 2OH^- \rightleftarrows ClO^- + H_2O + 2e^-$$



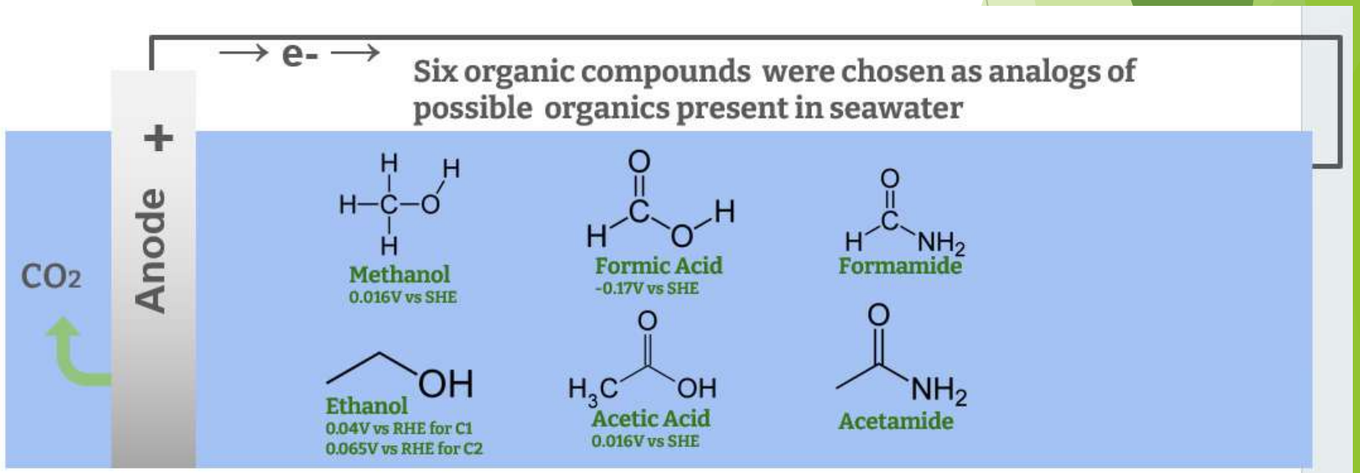
DOI: 10.1002/cssc.201501581

DOI: 10.1016/j.apcatb.2021.121060
DOI: 10.1016/j.apcatb.2020.119277

Summer 2:
Anodic Transformations

- Investigate the oxygen (OER) and chlorine evolution reaction (CER) and the effect that organic compounds has on OER and CER
  - Organic Compound Experiments
  - Guam Seawater Experiments
  - Theoretical Assessment of Electrochemical Processes

Summer 2024 BES-RENEW interns.



Electrochemical Oxidation Behavior of Organic compounds in Model Seawater (0.6 M NaCl)

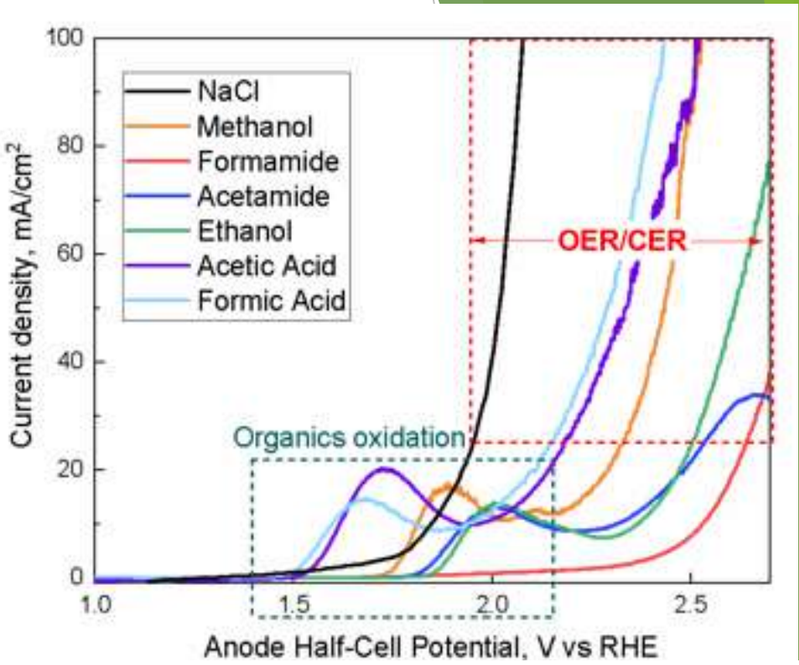
- **Objective**
  - **Investigate the effect of organics compounds on oxidation performance**

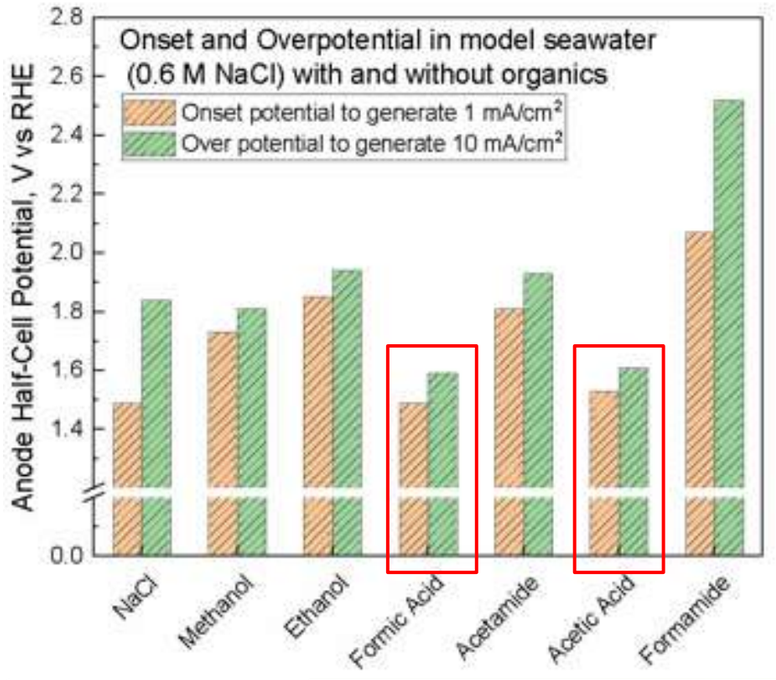
Electrolyte: 0.6 M NaCl + 500 ppm organic concentration

Organic Compounds: Methanol, Ethanol, Formic Acid, Acetic Acid, Formamide, Acetamide

Electrodes:

- Reference Electrode: Ag/AgCl
- Working Electrode: Pt Mesh (3 cm^2)
- Counter Electrode: Platinized Titanium Mesh



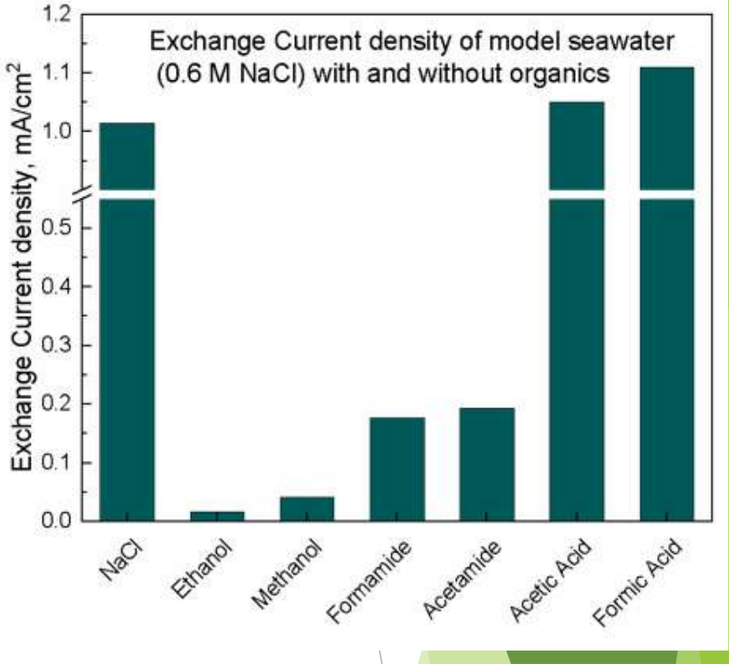


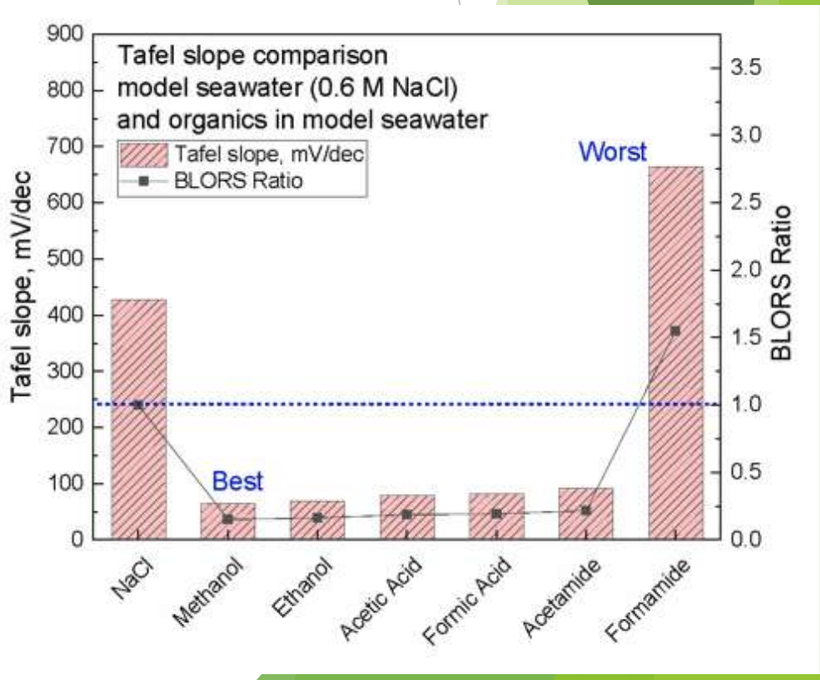
The organic acids formic acid and acetic acid reduced the onset potentials for oxidation below that of model seawater (NaCl).

Electrochemical Oxidation Behavior of Organic compounds in Model Seawater (0.6 M NaCl)

- Presence of organic compounds decreased the Tafel slopes
- Presence of some organic compounds increased exchange current densities
- Increase in organics concentration showed increase in oxidation current and also shifted the onset and overpotential for electrochemical oxidation to lower values

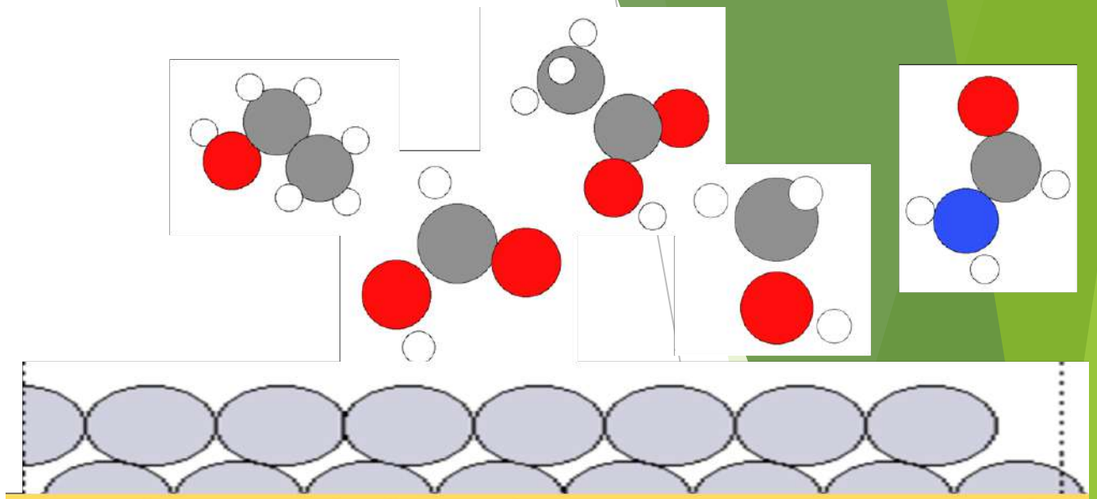
$$BLORS\ Ratio = Tafel\ slope\ ratio\ of \frac{Organics}{clean\ electriolyte}$$



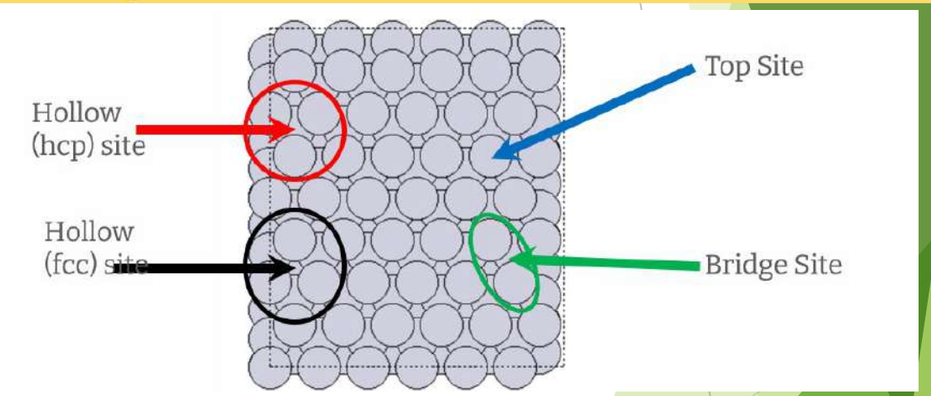


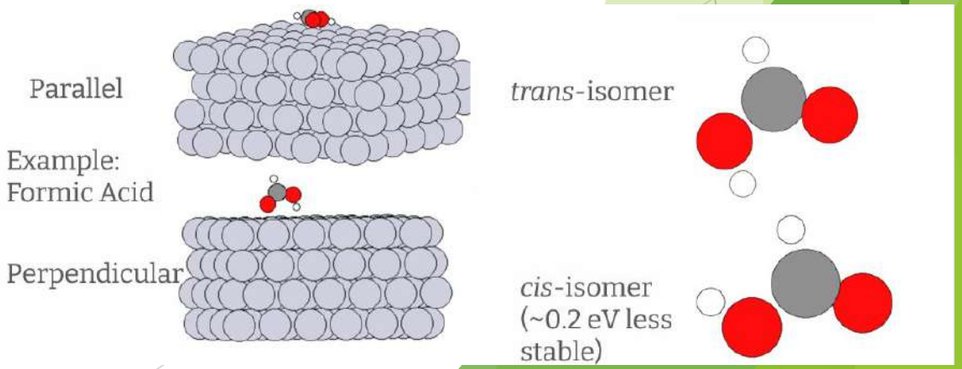
Computational Modeling of Organic Compounds on the Platinum Electrode Surface

- Objective
  - Investigate the adsorption of the six organic compounds utilized in the Model Seawater studies *in silico*
  - Impact that the different orientations, isomers, and placement of the molecules on the Pt(111) surface has on the computed binding energies



The platinum slab (Pt(111) surface) was used as a model for the anode in the DFT computations.





Computational Modeling of Organic Compounds on the Platinum Electrode Surface

- Site, structure, and orientation plays a role in the observed adsorption energies
- Methyl groups within the molecule strongly influences adsorption energies
- Amides interact more strongly with the Pt(111) surface when compared to the other organic compounds investigated