Modeling Interplay Between Catalyst Performance and Microenvironment in CO_2 Electrolyzers

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MATERIAL MEASUREMENT LABORATORY

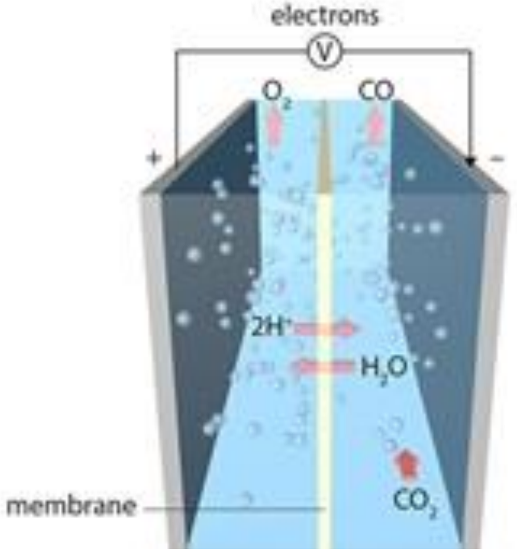
Broad Outlook: Electrochemical CO_2 Reduction to Replace Fossil Fuels

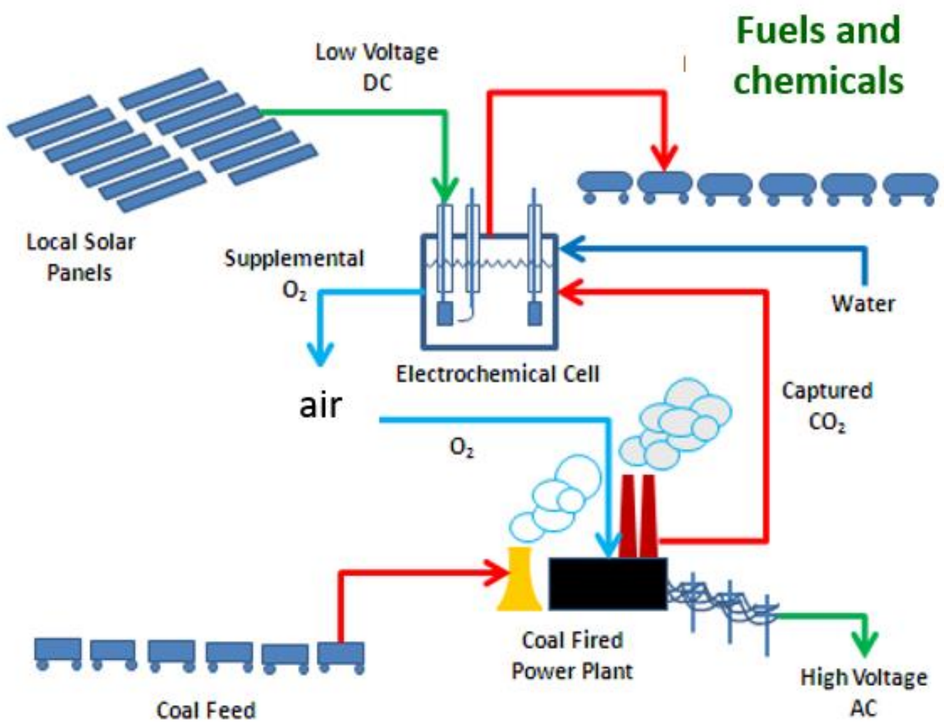
- Fossil fuels and anthropologic CO_2 emission
  - Not sustainable
  - Environmental consequences

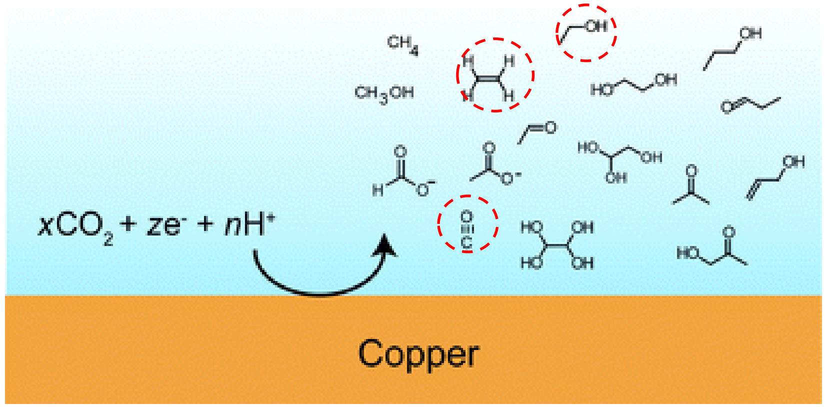
- Many renewable energies are intermittent
  - e.g. Solar/wind electricity
  - Energy Source

- Store intermittent energy in chemical bonds
  - $xCO_2 + ne^- + yH \rightarrow C_xH_yO_z + mOH^-$
  - Protons from H_2O equals OH^- at cathode
  - Competition from $2H+ \rightarrow H_2$ reaction
    - Can also come from H_2O

- Diffusivity of CO_2 in solution is another barrier
  - 1.9E-9 $m^2\ s^{-1}$ in liquid phase
  - 1.7E-5 $m^2\ s^{-1}$ in gas phase
  - Also, CO_2 reacts with OH^-, acid-base reaction



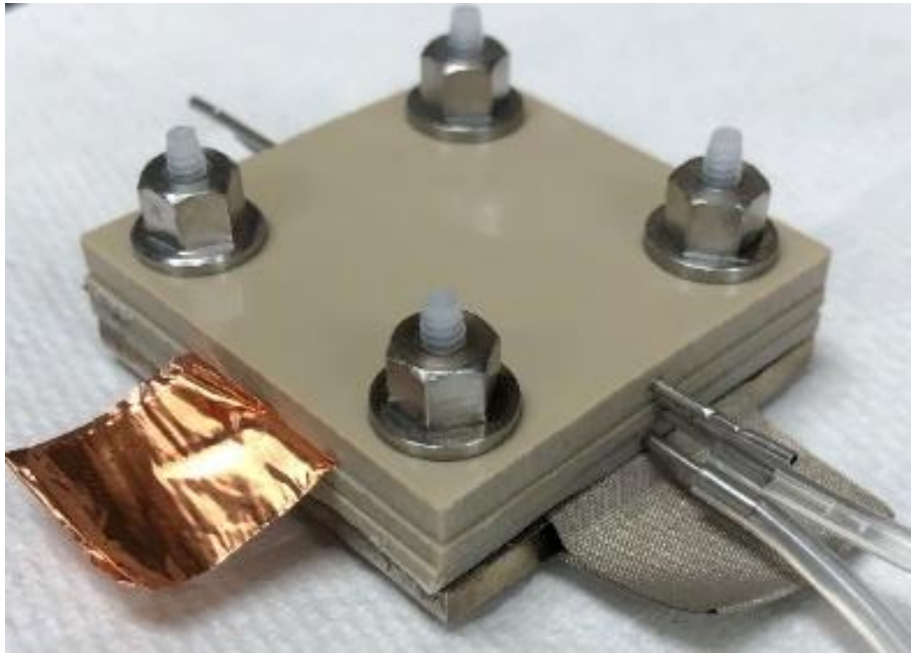


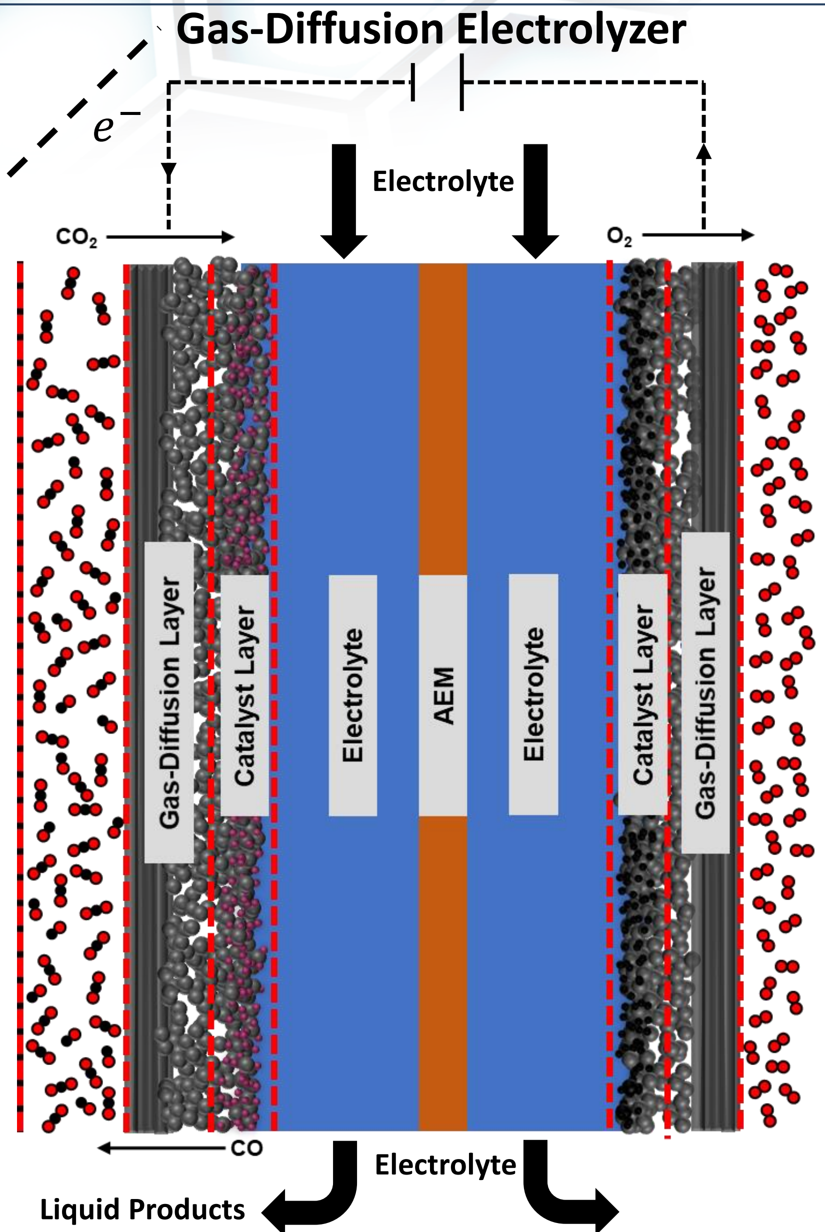


Stites & Associates, LLC. (SALLC)
Olah et al., J. Am. Chem. Soc. 2011, 133, 12881.
4th International Conference on Advances in Energy Research 2013

Increasing Mass Transfer of CO_2….Studying CO_2 Electrolysis in a Gas-Diffusion Electrolyzer

- Moves the bulk of CO_2 transport to the gas phase
  - Gas phase diffusion coefficient of CO_2 is ≈10000x greater than the liquid phase.
  - Enables high CO_2 mass transport
- The boundary layer of this system is minimized by the active flow of electrolyte over the catalyst.
- Several fold enhancement in current density observed experimentally.

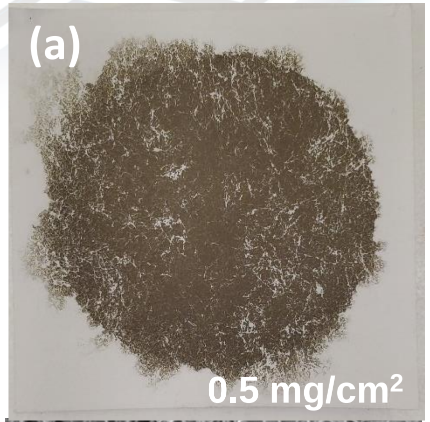


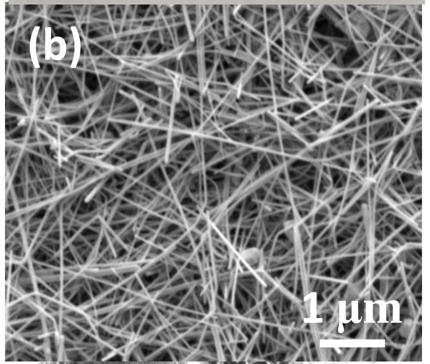


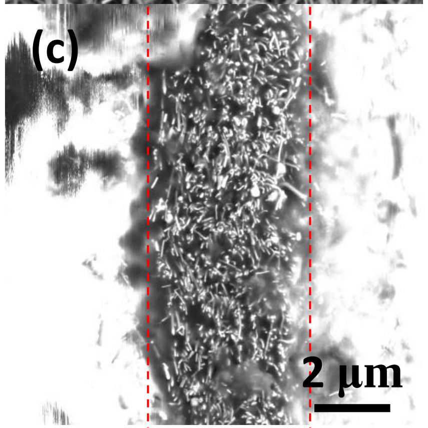
Kim et al. *J. Power Sources* **2016,** *312,* 192-198.
Ma et al. J. Electrohem Soc. **2014,** *161*, F1124-31.

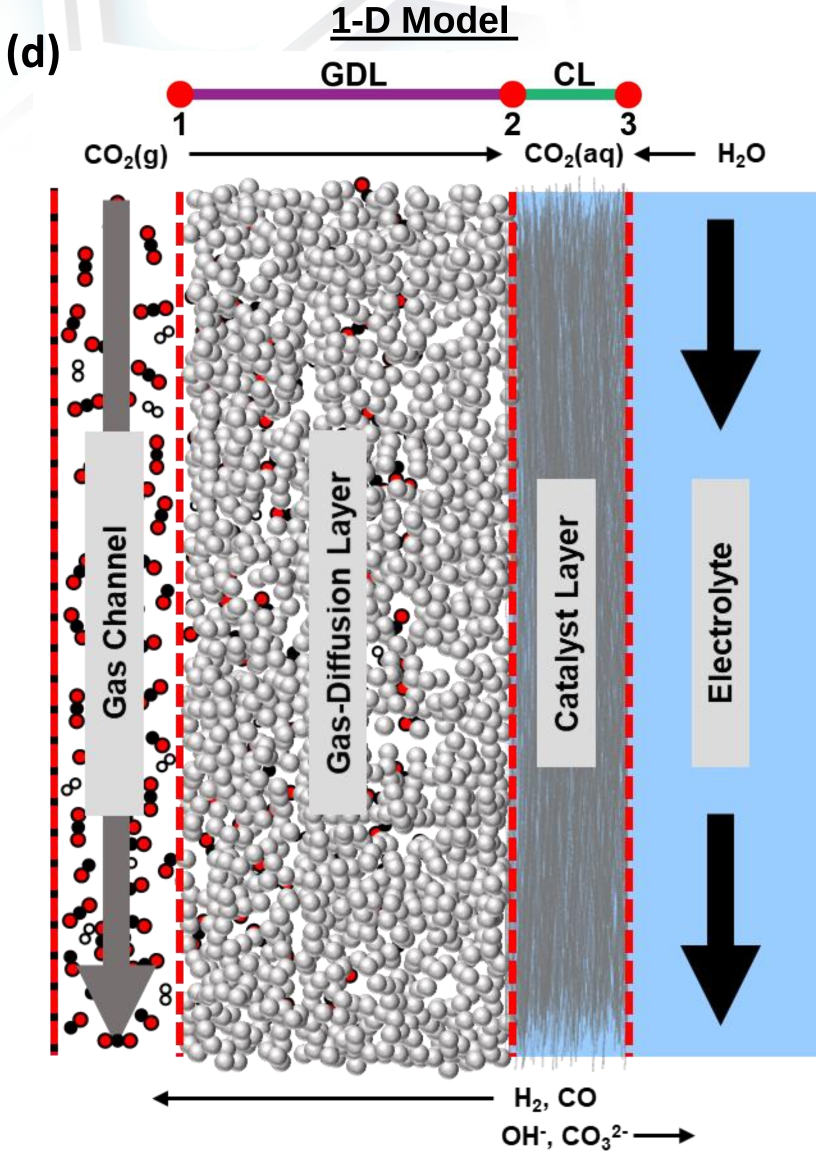
Model Construction: Simulating Ag Nanowire Array on PTFE based GDL

- Experimental system: 1-D Ag nanowires on a PTFE GDL (a)
  - Non-conductive GDL = current produced only from Ag
  - (b) Interwoven network of Ag = self-conducting
  - (c) Layer thickness measured by cross-section image
- System can be broken into 2 domains, 3 bounds (e)
  - Assuming random isotropic nature of system we assume 1-D will capture the average behavior.
  - Bound 1: Gas Channel to GDL
    - Gas concentration based on gas channel
  - Domain 1: PTFE Gas-diffusion layer
    - Only gas and solid phases….no flooding
  - Bound 2: GDL with Ag catalyst-layer
    - Gaseous species exchange
  - Domain 2: Ag nanowire catalyst layer
    - Assume complete flooding due to hydrophilicity of Ag nanowires
      - Only liquid and solid phases
    - Conductivity measurements determined potential drops across Ag nanowires
  - Bound 3: Catalyst Layer with Bulk Electrolyte
    - Mass Transfer across bound follows Sherwood-Reynolds-Schmidt Correlation







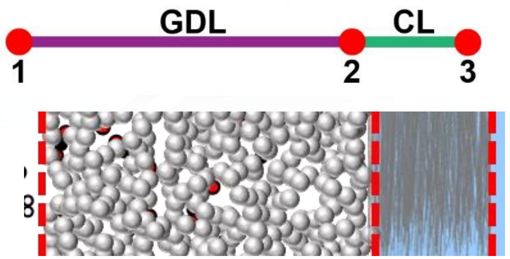


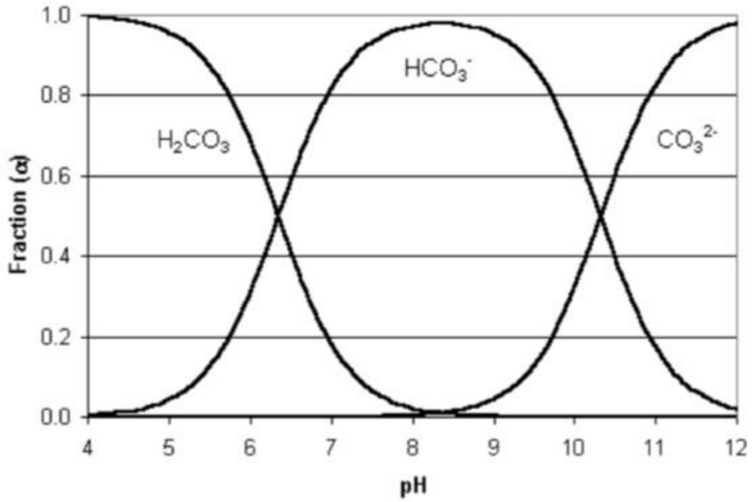
Weng et al. *PCCP* **2018,** *20,* 16973-84.
Raciti et al. *Nanotechology* **2018,** *29,* 044001.

Model Overview: Physical Phenomenon/Equations

- **PTFE Gas-Diffusion Layer**
    - **Gaseous species transport**
        - **Mixture-averaged model**
        - **Porous media transport**
    - **Darcy's Law**

- **Ag Nanowire Catalyst Layer**
    - **Liquid Species Transport**
    - **Homogenous Acid-Base Reactions**
        - **Electrolyte: 0.5 M $KHCO_3$**
    - **Tertiary Current Distribution**
        - **Nernst-Planck**
        - **Porous Electrode Coupling**
            - **Electrochemical Reactions**
                - **Concentration Dependent Tafel Kinetics**





Electrochemical Reactions

$$CO_2(aq) + 2H_2O + 2e^- \rightarrow CO + 2OH^- \quad (1)$$

$$2H^+ + 2e^- \rightarrow H_2(g) \quad (2)$$

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \quad (3)$$

Weng et al. *PCCP* **2018,** *20,* 16973-84.
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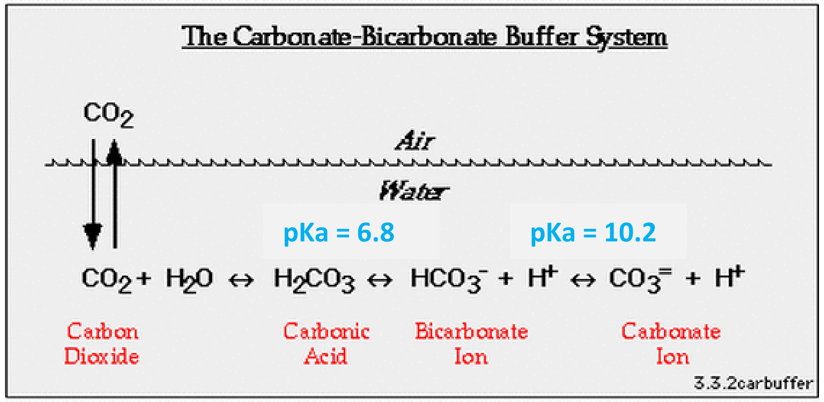
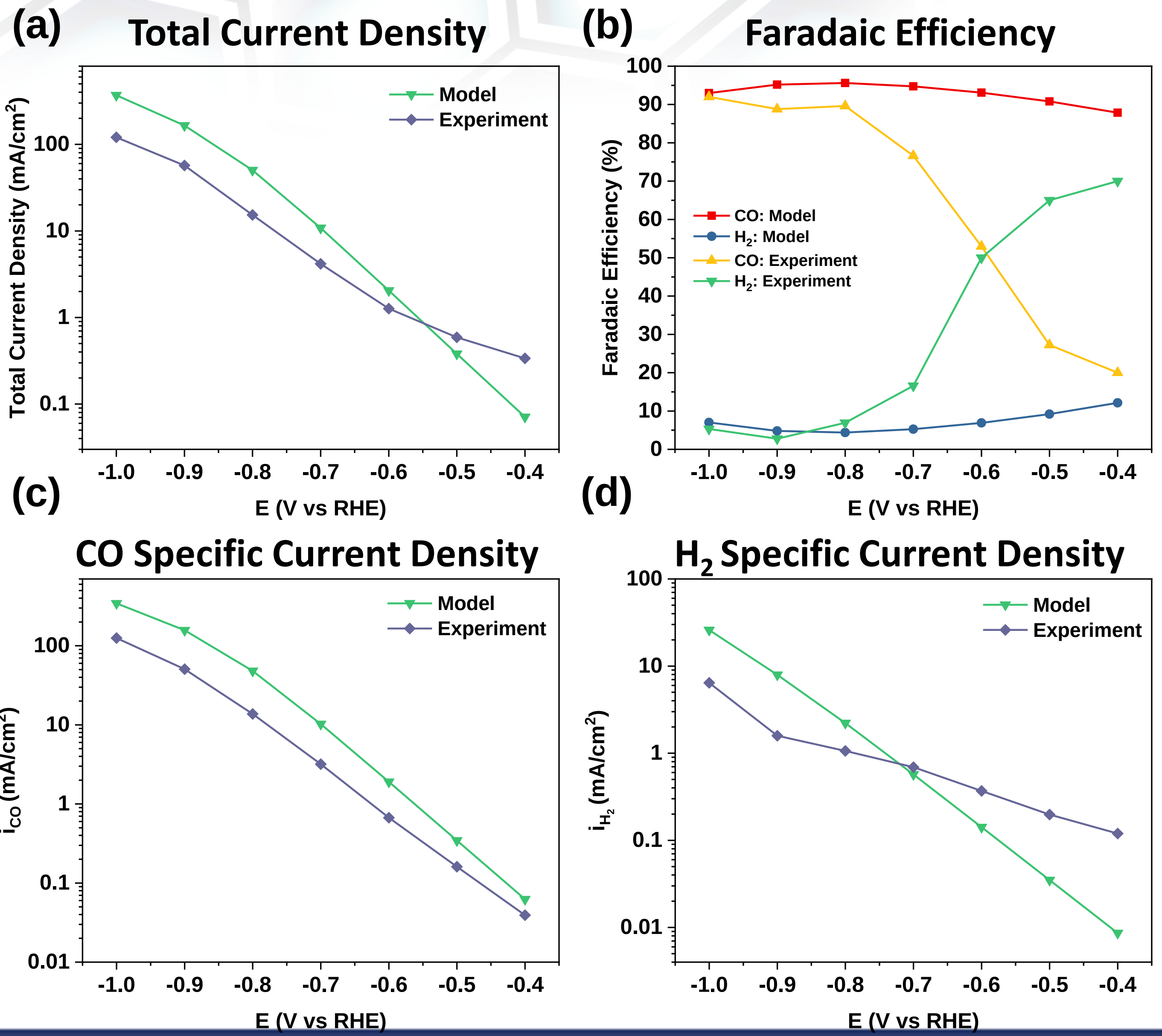
Comparing Model Results to Experimental Results

- (a) Model underpredicts total current density at potential >-0.6 V and overpredicts it at <-0.5 V.
- (b) Current efficiency between model and experiment are off >-0.8 V.
- (c) CO specific current density overpredicted at all potentials, but more so at the more negative potentials.
- (d) Hydrogen specific current density is underpredicted >-0.7 V and overpredicted <-0.7 V.
- The prediction for HER is worse than CO_2RR.

- Perhaps an alternative accessible reaction possible for H_2 production.
  - Electrolyte: 0.5 M $KHCO_3$, pH = 8.9
  - Known buffer with 2 pKas: Could be source of protons at neutral to slightly basic pHs.





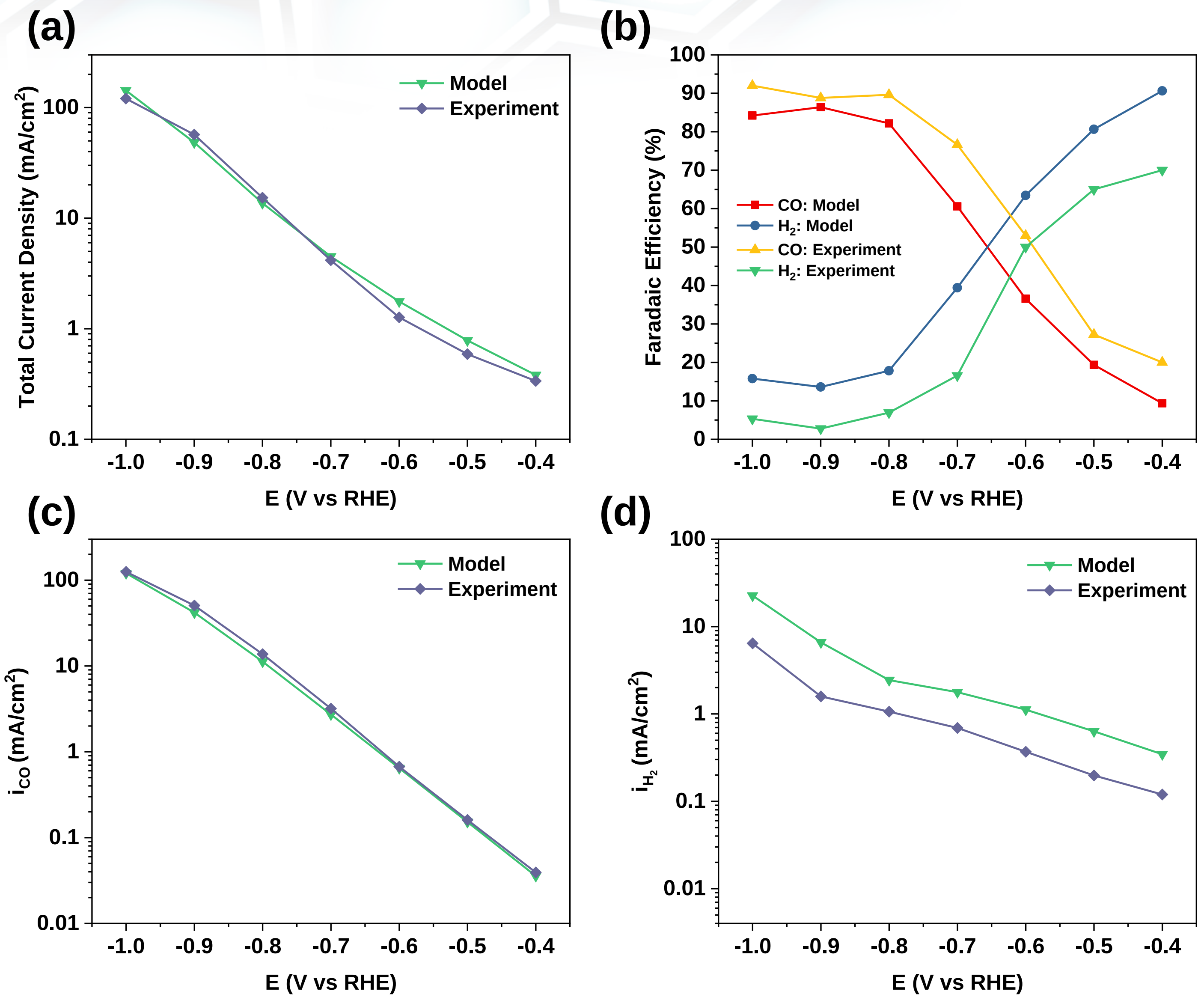
Goyal et al. *JACS* **2020**, *142*, *4154*-61.
Raciti et al. *in preparation*

Model 2: Other Possible Sources of H^+ for H_2 production?

$$HCO_3^- + 2e^- \rightarrow H_2 + 2CO_3^{2-}$$

- New model with additional electrochemical reaction based on concentration dependent Tafel kinetics.
  - Concentration component was modeled as:
    - $[HCO_3]/[HCO_3+CO_3]$
      - Assumes $[H_2CO_3]$ is negligible
  - The activity coefficient was extracted from experimental data.
- We also used a tafel slope from experimental data to tune the CO_2 reaction.

- (a) Results predict total current at all potentials.
- (b) Faradaic efficiencies between model and experiment very similar.
  - Offset due to overpredicted H_2 evolution
- (c) CO specific current matches
- (d) HER overpredicted at all potentials now.
  - Competitive adsorption, slightly different kinetics for H_2 from HCO_3^-, polarization effects at high overpotentials.



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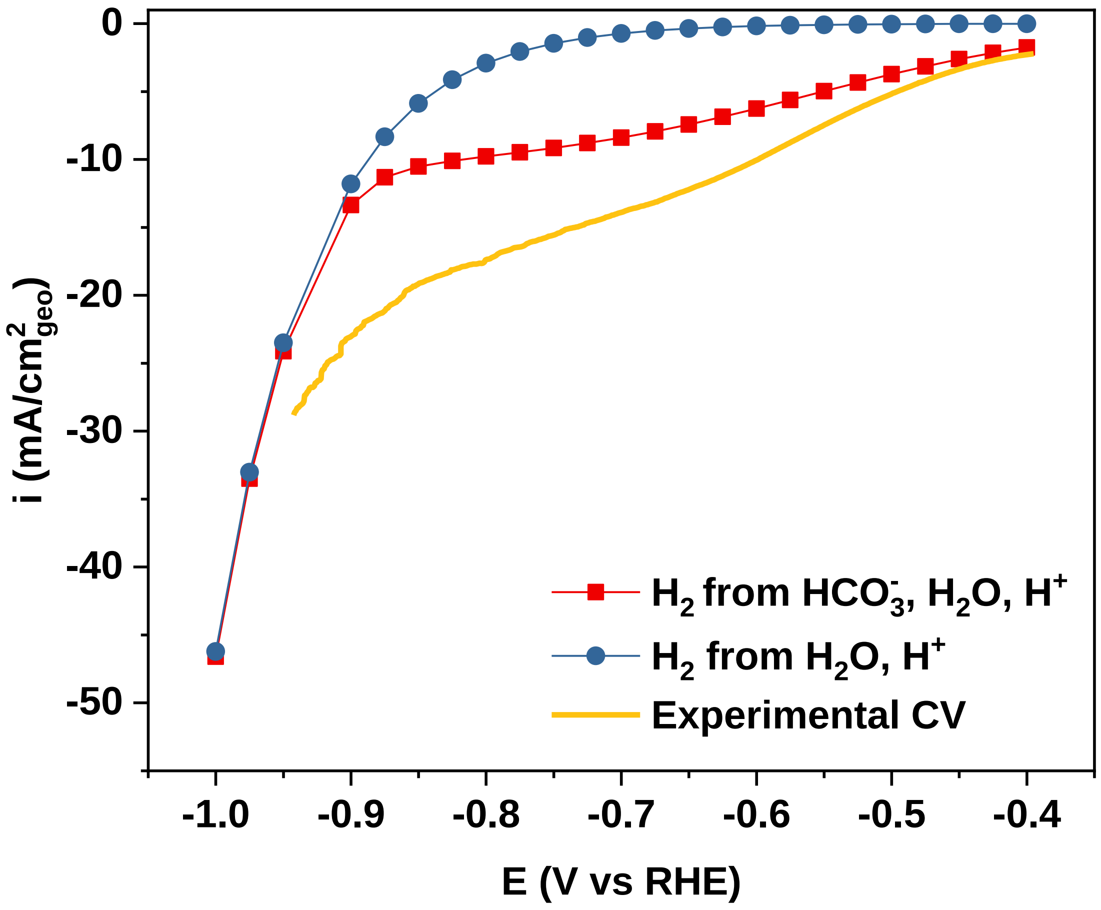
Experimental Validation of New Electrochemical Reaction

- Initial test case using cyclic voltammetry
  - e.g. quick acquisition time, but not steady-state. Likely to overpredict current density at potentials where mass transfer and other effects take hold.
- Isolate the HER reaction to nullify competitive adsorption
  - No CO_2 present
- Looking for characteristic HCO_3^- depletion event
  - @ -0.7 V
- Event observed and current densities between theory and experiment much more similar when bicarbonate is included.

Preliminary Results



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Summary and Future Work: Continue to Improve the Model

- **Model enabled observation that additional reaction pathway to produce H2 was accessible with the electrolyte chosen for the experiment.**
- **Inclusion of targeted pathways was validated via experiment.**
- **Future work includes:**
    - **Better representation of water splitting to H_2.**
    - **Build in other components of total cell to accurately capture additional limitations like solution/membrane resistance.**

- **Acknowledgements go to:**
    - **The National Research Council for funding my postdoctoral work.**
    - **The National Institute of Standards and Technology for hosting me.**
    - **Collaborators at Duke University for the Ag nanowires: Heng Xu, Dr. Mutya Cruz and Prof. Wiley**
    - **Co-workers and Mentors at NIST: Dr. Trevor Braun and Dr. Tom Moffat**

Thanks for your attention!

Questions/Comments: dmr5@nist.gov

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