Hydrogen Reduction as a Novel Approach to Formic Acid Synthesis

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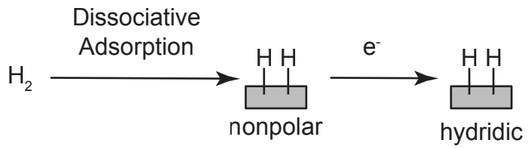
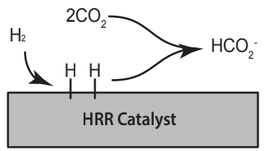
Introduction: Hydrogen Reduction Reaction



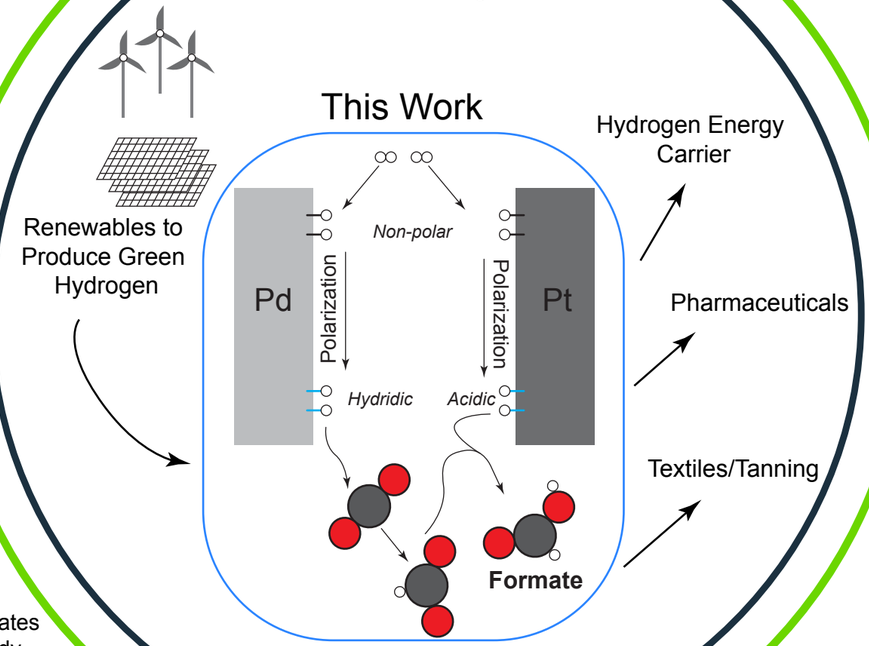
Electrochemical polarization allows for the formation of surface hydrides that can then be transferred to a hydride acceptor. This process makes up the hydrogen reduction reaction (HRR).[1]

CO2 can be used as a hydride acceptor, generating formate as the product while consuming CO2.



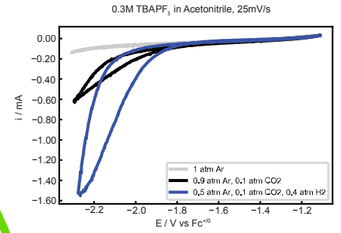
Coupling HRR with the hydrogen oxidation reaction (HOR) produces a single electrochemical cell that produces formic acid.

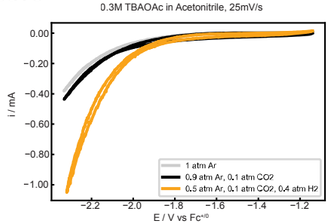
Electrochemical Formic Acid Synthesis



Results

Cyclic voltammetry shows **significant current enhancement upon the addition of H_2 to the system**. The increase in reductive current only upon the indroduction of H_2 (and notably not upon additon of CO_2) is **indicative of HRR**.





$\frac{1}{2}\ H_2 + e^- \xrightarrow{\Delta G_{H2/H^-}} H^-$ $\Delta G^\circ_{H2/H^-} = 51.8$

$CO_2 + H^- \xrightarrow{-\Delta G_{H^-}} HCOO^-$ $\Delta G^\circ_{H^-} = 31.0$ kcal/mol*

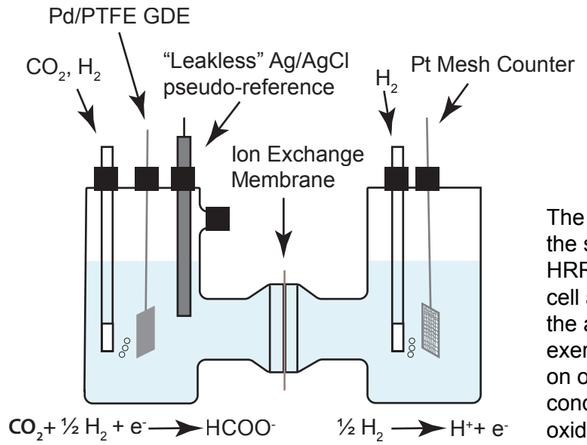
$CO_2 + \frac{1}{2}\ H_2 + e^- \longrightarrow HCOO^-$ $\Delta G^\circ = 20.8$ kcal/mol

$E^\circ = -2.03$ V

Calculation of the thermodynamic voltage of the cathode reaction gives an extimate for onset of HRR

*some uncertainty in this value

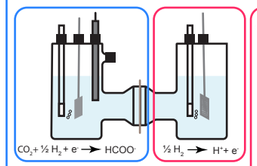
Materials and Methods



The cell shown illustrates the setup used to study HRR at the cathode. The cell above shows HOR at the anode, but preliminary exeriments focused explicitly on optimizing HRR can be conducted with solvinet oxidation as the counter reaction.

Future Directions

- Optimize electrolyte conditions by screening additional salts
- Better understand selectivity of reaction to maximize HRR current
- Conduct rate order studies to optimize gas flow conditions



- Study counter reaction in optimized HRR conditions to control the pH of the cell during electrolysis

References and Sponsors

1. Wang, H-X., et al *Nat. Catal.* **2023,** *6*, 351–362.
2. Eppinger, J. et al. *ACS Energy Lett.* **2017**, *2*(1), 188–195.

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