

Mechanistic Analysis of CO₂ Electroreduction through Microkinetic Modelling

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Aims

To develop microkinetic models of proposed CO₂ reduction pathways and compare their predicted electrochemical behaviour with experimental data to identify the most plausible reaction mechanism

Background & Motivation

- **CO₂ Electroreduction (CO₂RR)** converts CO₂ into useful chemicals and fuels
- **Multiple reaction pathways** have been proposed, complicating mechanistic identification. Understanding these pathways is essential for improving catalytic activity and product selectivity
- **Microkinetic modelling** links proposed mechanisms to measurable electrochemical behaviour, allowing them to be evaluated against experimental observations.

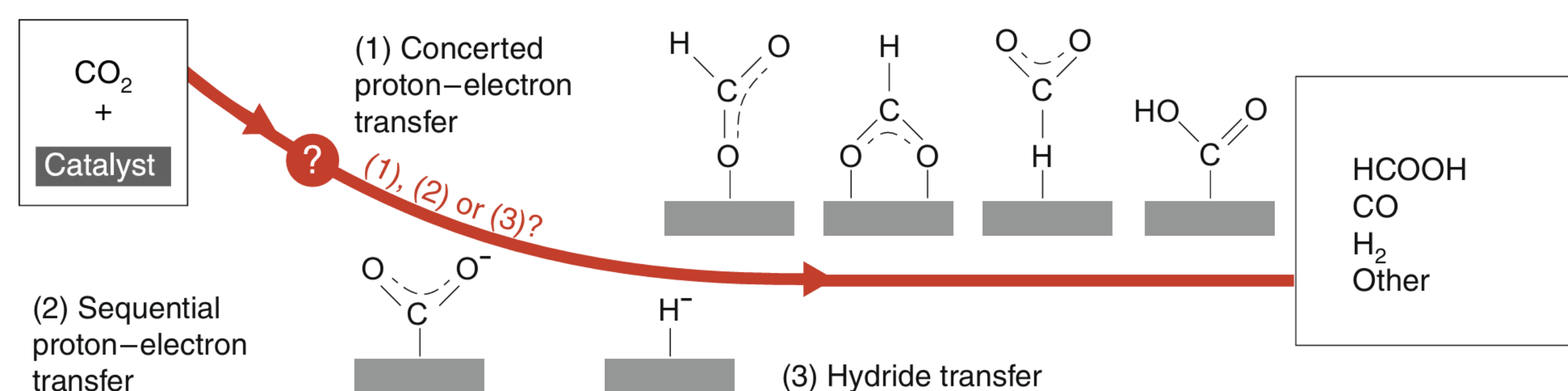
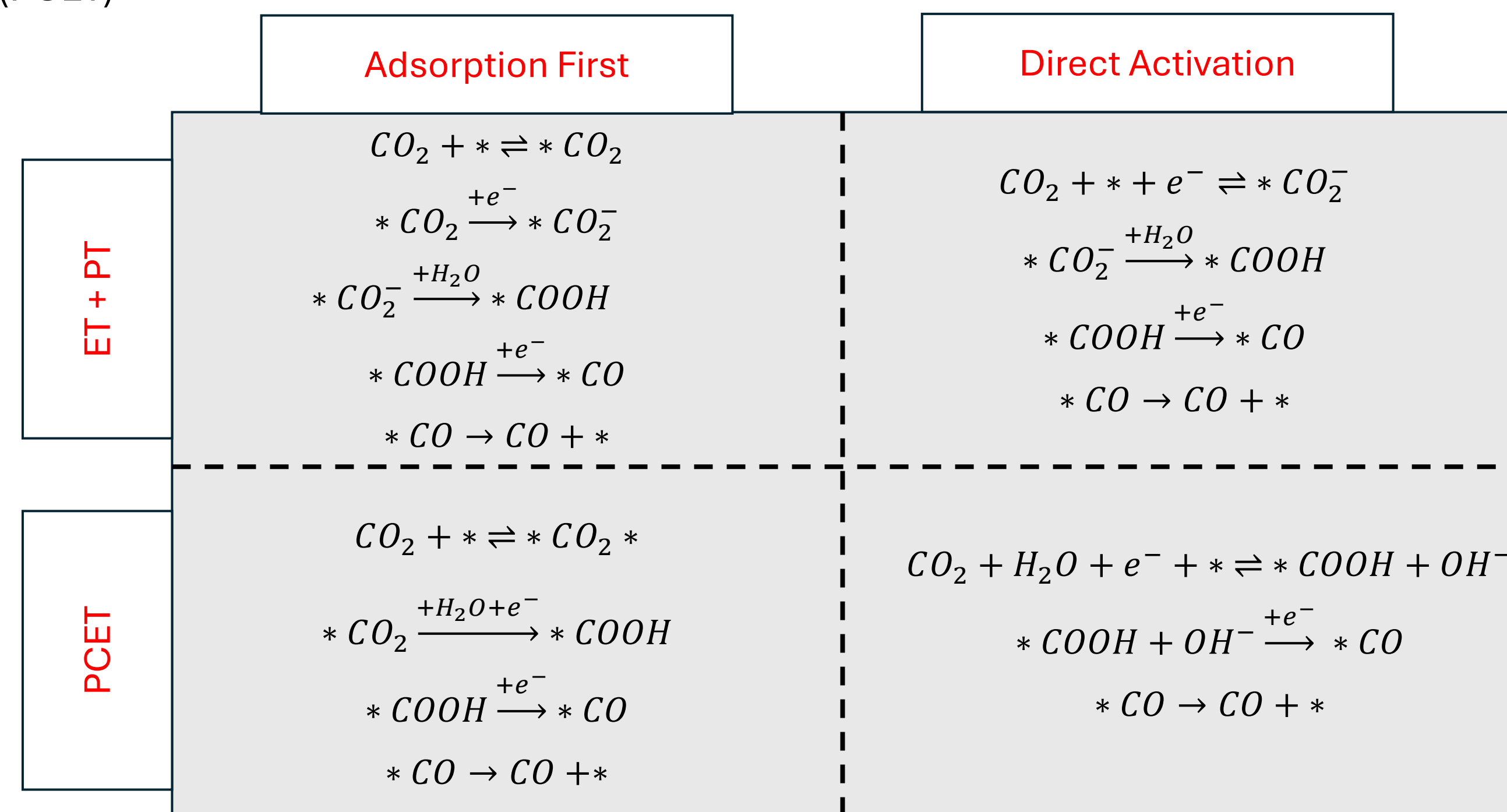


Fig 1. Proposed Pathways for Initial CO₂RR³:
CO₂ can undergo initial activation through different mechanisms, such as concerted proton-electron transfer, sequential proton-electron transfer or hydride transfer, forming distinct surface intermediates that influence subsequent reaction pathways and product selectivity

Proposed Reaction Mechanisms

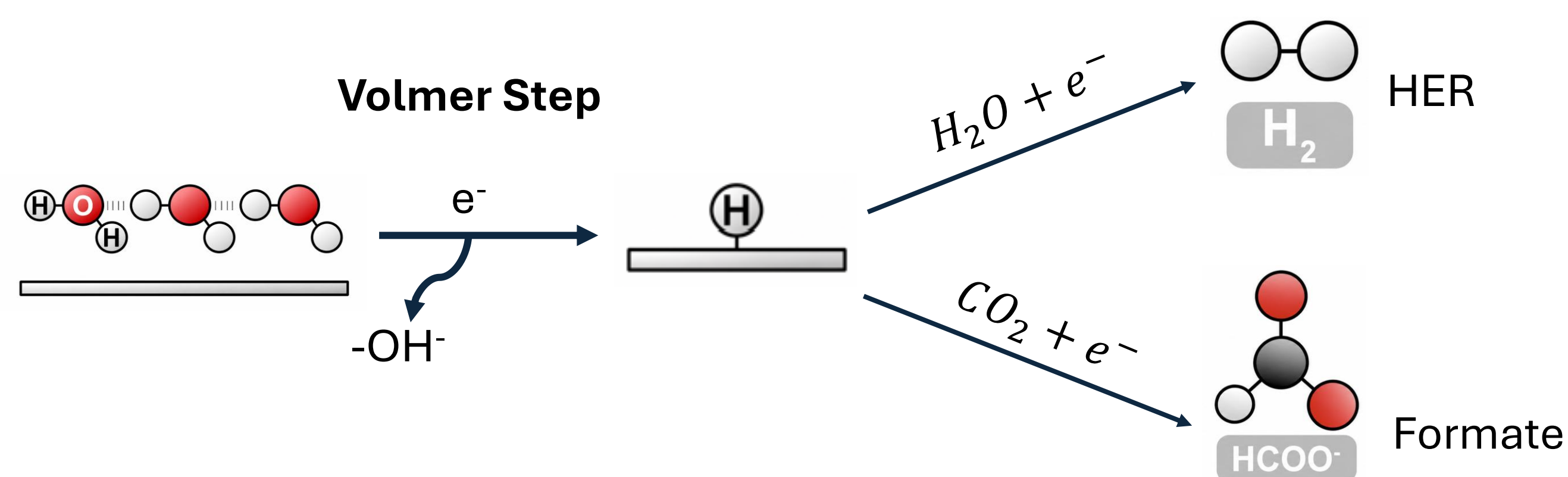
CO Formation

- Four CO formation pathways were investigated, differing in whether CO₂ adsorption precedes activation and whether electron and proton transfer occur sequentially (ET - PT) or concertedly (PCET)



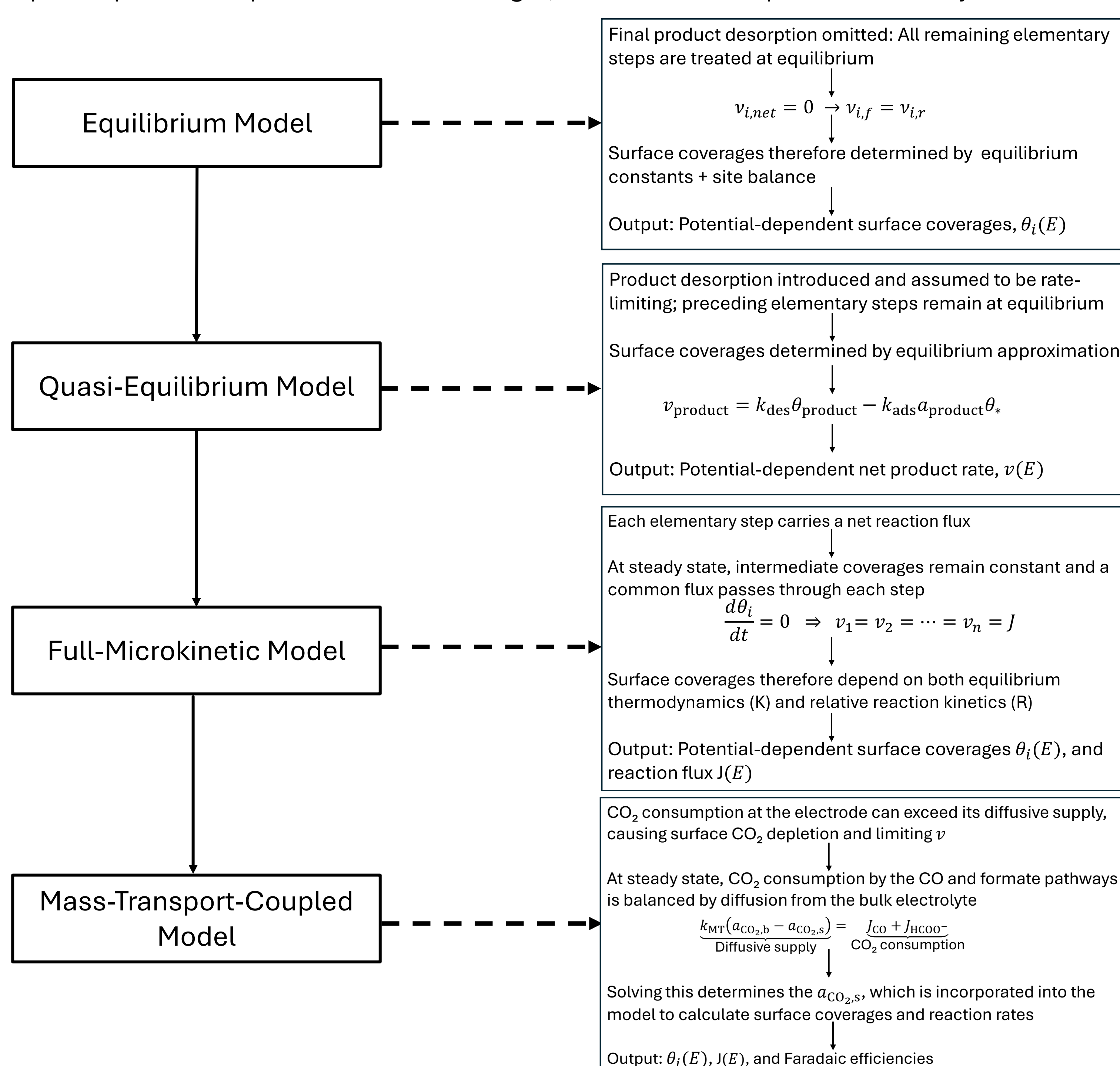
Competing *H Pathways: Formate and H₂ Production

- Alongside CO formation, reduction of water generates the *H intermediate, which can subsequently form either H₂ or formate.



Modelling Methodology

- Each proposed reaction mechanism was translated into a microkinetic model, with assumptions progressively relaxed to capture increasingly realistic reaction kinetics and mass transport, and predict potential-dependent surface coverages, reaction rates and product selectivity.



Results

A. Full Microkinetic Modelling of CO Formation

- A full microkinetic model was developed to calculate steady-state surface coverages and net CO formation rates from the kinetics of individual elementary reaction steps.

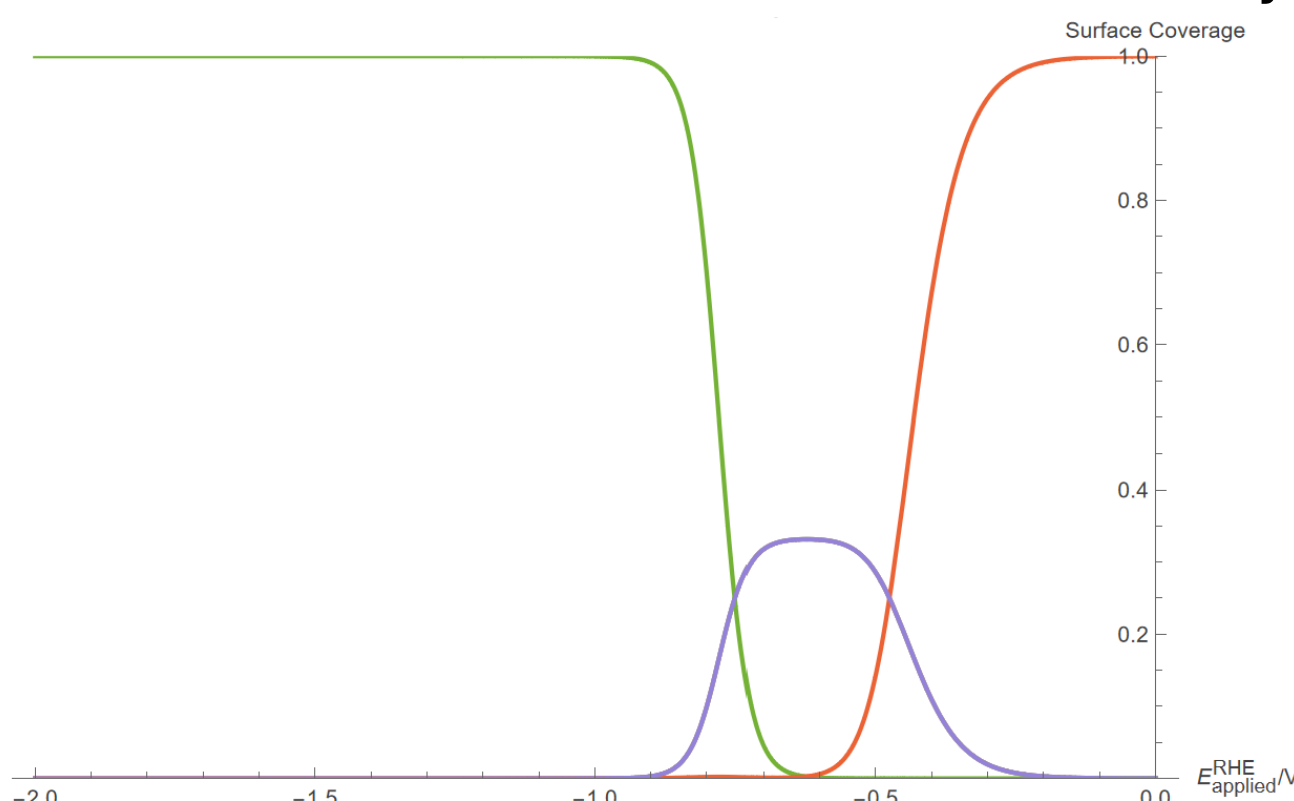


Fig 2. Surface Coverage vs Potential:
Predicted distribution of surface intermediates as a function of electrode potential and kinetic parameters.

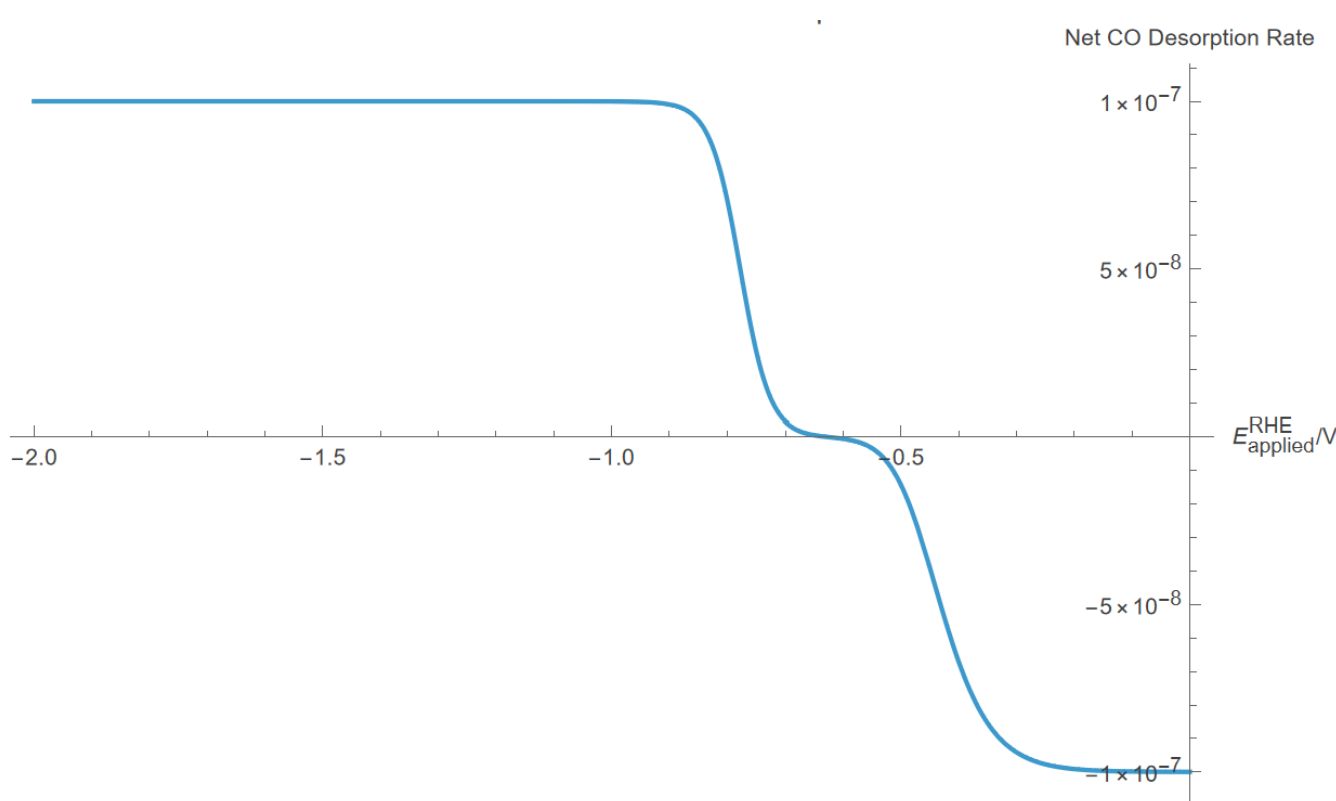


Fig 3. Net CO Desorption vs Potential:
Predicted net CO desorption flux from steady-state coverages and elementary-step kinetics.

B. Competitive Modelling of CO₂ Reduction and Hydrogen Evolution

- A combined quasi-equilibrium model was developed to investigate competition between CO formation, formate production and HER, predicting their potential-dependent Faradaic efficiencies.

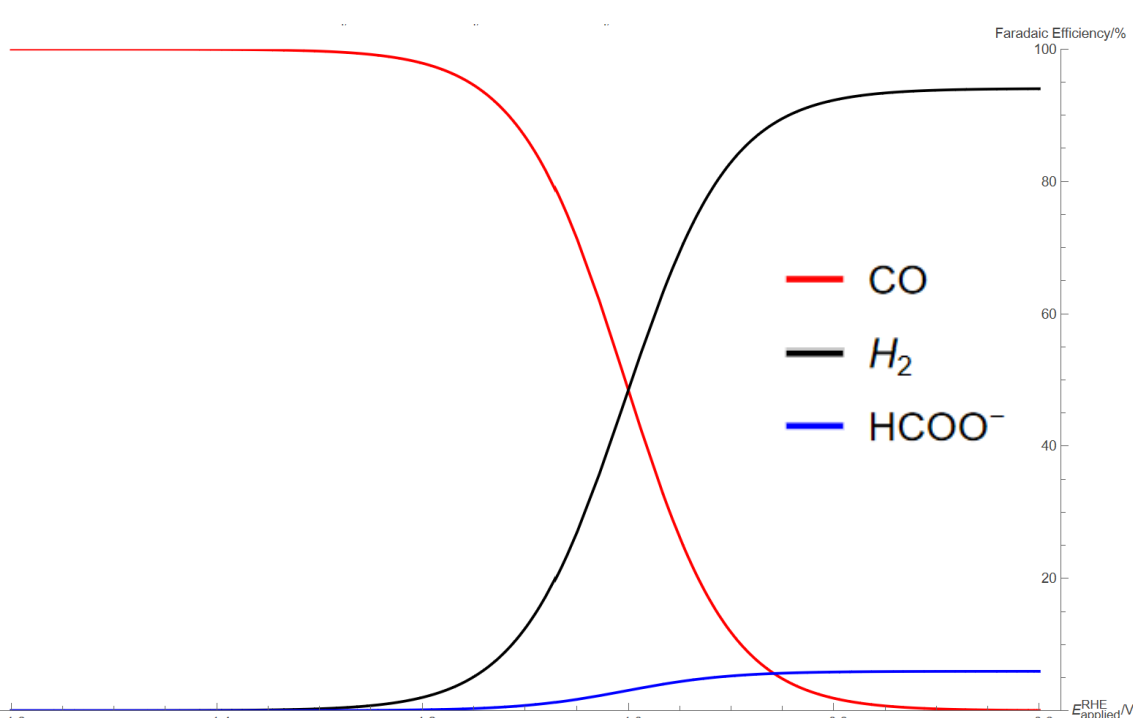


Fig 4. Predicted FE vs Potential:
Predicted selectivity towards CO, formate and H₂ from the combined quasi-equilibrium model.

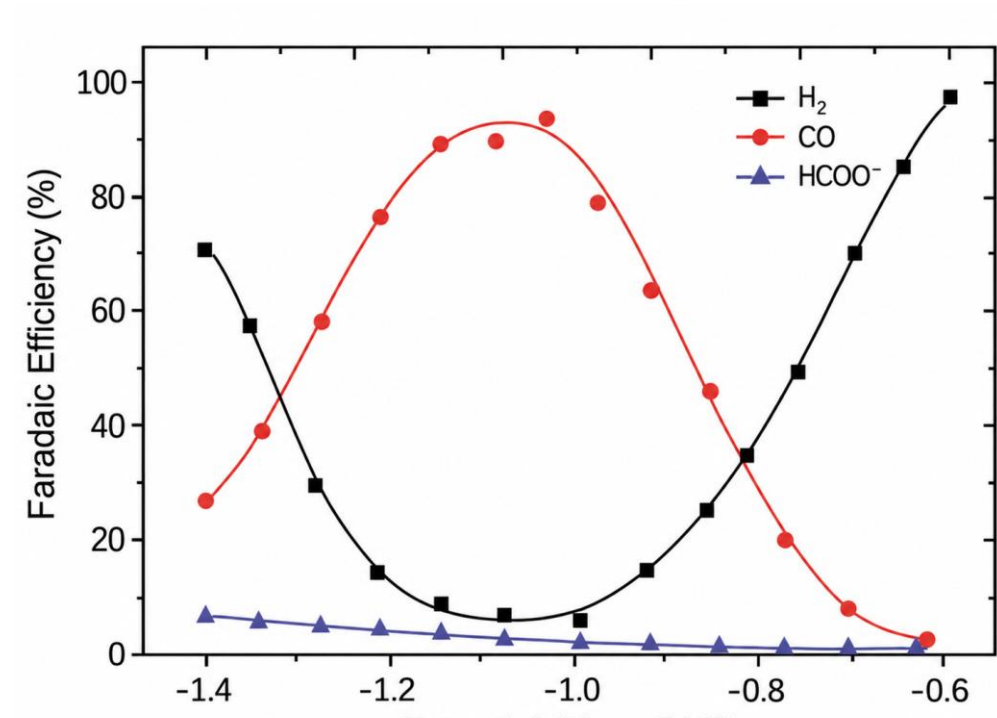


Fig 5. Experimental FE vs Potential⁵:
Experimentally measured product selectivity as a function of potential

Comparison

- **Observation:** The model captures some experimental selectivity trends but fails to reproduce the rise in H₂ and decline in CO at strongly negative potentials.
- **Potential limitation:** Assuming constant surface CO₂ activity neglects transport-induced depletion, which may overestimate CO₂RR selectivity
- **Next step:** Incorporate CO₂ mass transport to investigate its influence on product selectivity.

Next Steps & Outlook

A. Completing the Competitive Microkinetic Models

- 01 Complete the Mechanistic Investigation**
 - Extend the full microkinetic framework to incorporate competing CO, formate and H₂ formation pathways, coupled with CO₂ mass transport, for each proposed mechanism.
- 02 Obtain Experimental Data**
 - Compile published electrochemical measurements or generate new experimental data under controlled conditions.
- 03 Evaluate Competing Mechanisms**
 - Compare predicted Faradaic efficiencies and reaction rates with experimental measurements to identify the most plausible mechanism

B. Future Research Directions

- Expand the Reaction Network**
 - Extend the framework to additional CO₂ reduction pathways and products, including multi-carbon compounds.
- Investigate Catalyst Dependence**
 - Examine how catalyst-specific adsorption energies and reaction kinetics influence mechanistic pathways and product selectivity.
- Guide Catalyst Design**
 - Identify key intermediates and rate-controlling steps to inform the development of more selective and efficient CO₂RR catalysts