



## MILESTONE

3.1: Establish detailed understanding of mechanisms, intermediates, and reaction environments for effective CO<sub>2</sub>RR electrocatalysts.

## INTRODUCTION

Quantum mechanics provides essential physical insights to heterogeneous catalysis, especially when experimental measurements are challenging or insufficient. In particular, it predicts reaction mechanisms by evaluating feasible transition states and intermediates that are difficult to detect in experiments.

In electrochemical carbon dioxide reduction reactions (CO<sub>2</sub>RR),



the pathways to multi-carbon products (C<sub>x>1</sub>) are under debate, especially for three-carbon products (C<sub>3</sub>) molecules (propanol, propionaldehyde, allyl alcohol, acetone, hydroxyacetone, etc.)<sup>[1]</sup>

In the present study, we became the first group to propose and assess the C<sub>3</sub> pathways under the operating condition from the theoretical perspective. Our work was accomplished by evaluating Gibbs free energy profiles for elementary steps under the influence of solvent, electrolytes, and reduction potentials.<sup>[2]</sup>

## THEORY & COMPUTATION

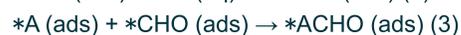
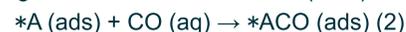
### Elementary Steps

An elementary step (\* representing the adsorption site on the copper surface)



takes one of the following forms:

1. Carbon chain propagation via a carbon-carbon (C-C) coupling mechanism:



2. Hydrogen incorporation via a Heyrovský mechanism:



The viability of this step is assessed through its thermodynamics (absolute free energy change)

$$\Delta G_{\text{reax}} = G(P) - G(R) \quad (6)$$

and kinetic (free energy barrier) information:

$$\Delta G^\ddagger = G([\text{TS}]^\ddagger) - G(R) \quad (7)$$

### Constant Electrode Potential

Based on the constant electrode potential (CEP) approach<sup>[3]</sup>,

$$G_{\text{tot}} = G_{\text{ele}} + G_{\text{int}} + G_{\text{mc}} \quad (8)$$

The electronic free energy (G<sub>ele</sub>) is evaluated using extended density functional theory (DFT)

$$G_{\text{ele}}[\rho_e; \rho_N, \phi] = T_s[\rho_e] + V_H[\rho_e] + V_{xc}[\rho_e] + V_{eN}[\rho_e; \rho_N] + V_{eS}[\rho_e; \rho_N, \phi] + V_{\text{cav}}[\rho_e; \rho_N] \quad (9)$$

where the electrostatic potential field  $[\phi = \phi(\mathbf{r})]$  in the presence of solvent and electrolyte is calculated using the linearized Poisson-Boltzmann equation<sup>[4]</sup>:

$$\nabla \cdot [\epsilon(\mathbf{r}) \nabla \phi(\mathbf{r})] - (k_B T / e) \kappa^2(\mathbf{r}) \sinh[e\phi(\mathbf{r}) / (k_B T)] + 4\pi[\rho_e(\mathbf{r}) + \rho_N(\mathbf{r})] = 0 \quad (10)$$

The total number of electrons (N<sub>e</sub>) is updated self-consistently until

$$-eU_{\text{RHE}} = E_F + \Phi_{\text{SHE}} - k_B T(\text{pH}) \ln 10 \quad (11)$$

The intramolecular free energy (G<sub>int</sub>) is calculated in the canonical ensemble (NVT)

## THEORY & COMPUTATION (CONTINUED)

$$G_{\text{int}} = F_{\text{int}} + PV = -k_B T \ln[Q_{\text{vib}}^{(3M)}] + PV \quad (12)$$

The mass conservation free energy (G<sub>mc</sub>) describes the flows of electrons and electrolytes to maintain a constant electrode potential (CEP):

$$G_{\text{mc}} = -\mu_e N_e - \sum \mu_{\text{ion}} N_{\text{ion}} \quad (13)$$

### Computational Details

Software packages: VASP<sup>[5]</sup>, VASPsol<sup>[6]</sup>, vTST.

Exchange-correlation functional: revised Perdew-Burke-Ernzerhof (RPBE)<sup>[7]</sup>.

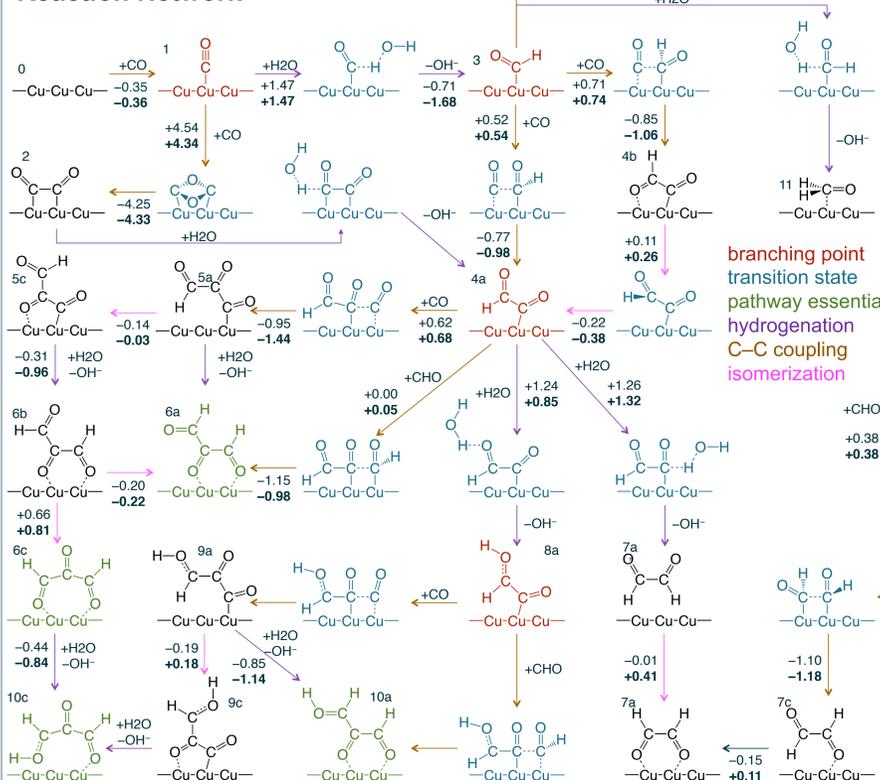
Crystal structure: Cu(100) facet, face-centered cubic (FCC), a = 3.6147 Å<sup>[8]</sup>.

Solvent and electrolyte: 0.1 M KHCO<sub>3</sub> in water, pH = 7, Φ<sub>SHE</sub> = +4.43 eV<sup>[9]</sup>.

Transition state searches: climbing image nudged elastic band (CI-NEB)<sup>[10]</sup> approach and improved dimer method (IDM)<sup>[11]</sup>.

## RESULTS & DISCUSSIONS

### Reaction Network<sup>[2,3,12]</sup>



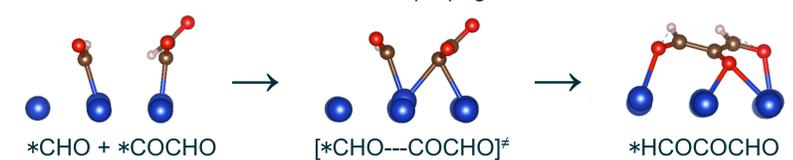
### Sample Reactions

Hydrogen incorporation:



## RESULTS & DISCUSSIONS (CONTINUED)

Carbon chain propagation



### Discussions

1. Early C<sub>3</sub> intermediates (COCOCHO, COCOCHOH, and HCOCOCHO) are essential to synthesize all downstream C<sub>3</sub> products.
2. Stability of an isomer depends on the competition between the dipolar repulsion between two -C=O groups and the electrostatic repulsion between the Cu surface and the negatively charged O atom.
3. Reaction pathways diverge at branching points between hydrogen incorporation (potential-sensitive) and carbon chain propagation (potential-insensitive). The free energy barrier for the former is comparable or even smaller than the later, and therefore the concentration of reactants also plays an important role.
4. Heyrovský mechanism for hydrogen incorporation is still mysterious.
  - a) In the stepwise hypothesis, a proton is relayed through a water wire:
 
$$*A + \text{H}_2\text{O} + \text{H}_2\text{O} + e^- \rightarrow [*A\text{---}H^+\text{---}OH^- + \text{H}_2\text{O}]^\ddagger (\text{TS}_0) \rightarrow *AH + \text{OH}^- + \text{H}_2\text{O}$$

$$\rightarrow [*AH + \text{HO}^-\text{---}H^+\text{---}OH^-]^\ddagger (\text{TS}_1) \rightarrow *AH + \text{H}_2\text{O} + \text{OH}^- \rightarrow \dots$$
 Due to different dipole moments, the early transition state (TS<sub>0</sub>) is potential-insensitive, and the late transition state (TS<sub>1</sub>) is potential sensitive.
  - b) In the concerted hypothesis, more protons are transferred simultaneously:
 
$$*A + \text{H}_2\text{O} + \text{H}_2\text{O} + e^- \rightarrow [*A\text{---}H^+\text{---}OH^-\text{---}H^+\text{---}OH^-]^\ddagger (\text{TS}_2) \rightarrow *AH + \text{H}_2\text{O} + \text{OH}^-$$
 The transition state has multiple delocalized protons.
4. \*CHO facilitates the C-C coupling reaction by reducing the dipolar repulsion. Its low surface coverage can be traded off by the low free energy barrier.
5. CO and \*CHO prefer to attack a pre-existing multi-carbon surfactant from one unsaturated end rather than insert into a C-C bond.

## CONCLUSIONS & OUTLOOK

In the present study, we managed to propose and assess the practical pathways of electrochemical CO<sub>2</sub>RR that lead to the formation of C<sub>3</sub> intermediates on the Cu(100) surface. We applied a combination of quantum mechanics, statistical mechanics, and electrostatics, and evaluated the Gibbs free energies for all products, intermediates, and transition states.

In the near future, we will complete the downstream reaction pathways that end in the final C<sub>3</sub> products<sup>[1]</sup> assuming negligible free energy barriers, and model the kinetics for the full reaction network.

## REFERENCE

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