Descriptors for C_1 product selectivity in Electrochemical CO_2R

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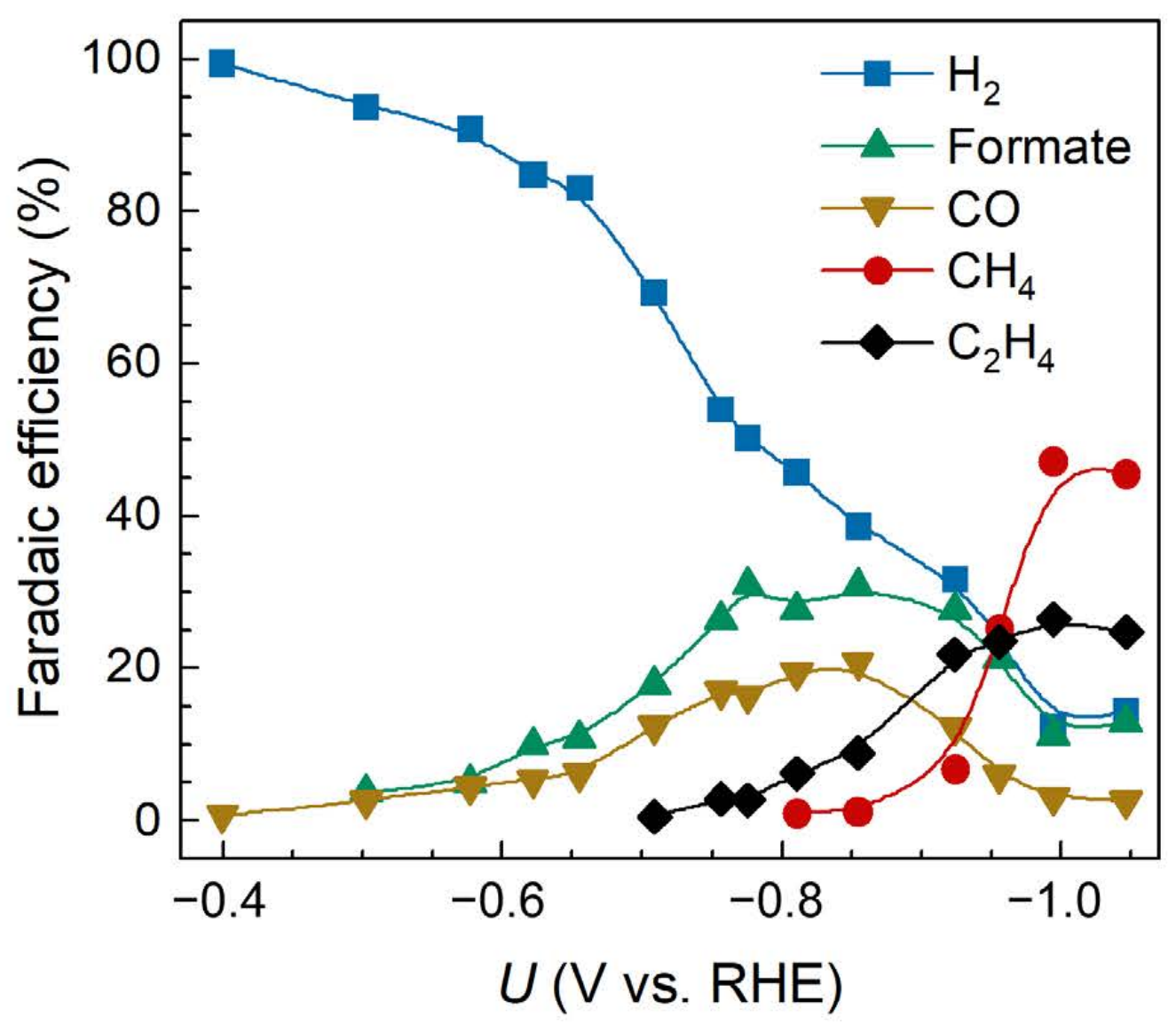
Abstract:

The conversion of CO2 back into chemical fuels via electricity involves very complex reaction mechanisms. In this study, we combine evidence from the experimental literature with a theoretical analysis of energetics to rationalize that not all reaction steps in the reduction of CO2 are concerted proton-electron transfer steps. This insight enables us to create a selectivity map for two-electron products (carbon monoxide (CO) and formate) on pure metal surfaces using only the CO and OH binding energies as descriptors. We find Cu to be uniquely capable of reducing CO2 to products beyond 2-electrons via the proposed COH pathway and we identify atomic carbon as the key component leading to the production of methane.

Introduction

- Hydrogen evolution reaction (HER) competes with CO2R under reducing potentials (< 0V vs. RHE).
- CO (and further products) compete with formate on Cu surfaces across varying applied potentials
- Hydrocarbon formed at potentials where CO onset has occurred.
- There is very little to no methanol produced at early potentials
- Previous studies rely on the assumption that all intermediate steps in CO2R are proton-electron transfer steps, directly from water.



Outlook

- Validate the formation of surface carbon or the formation of formyl (CHO) intermediate
- Examine the kinetics of the methanol pathway on Cu(100)

Broad Impact

- We have developed a theoretical model to understand how different materials selectively convert CO2 into valued products used in industry.

Acknowledgments

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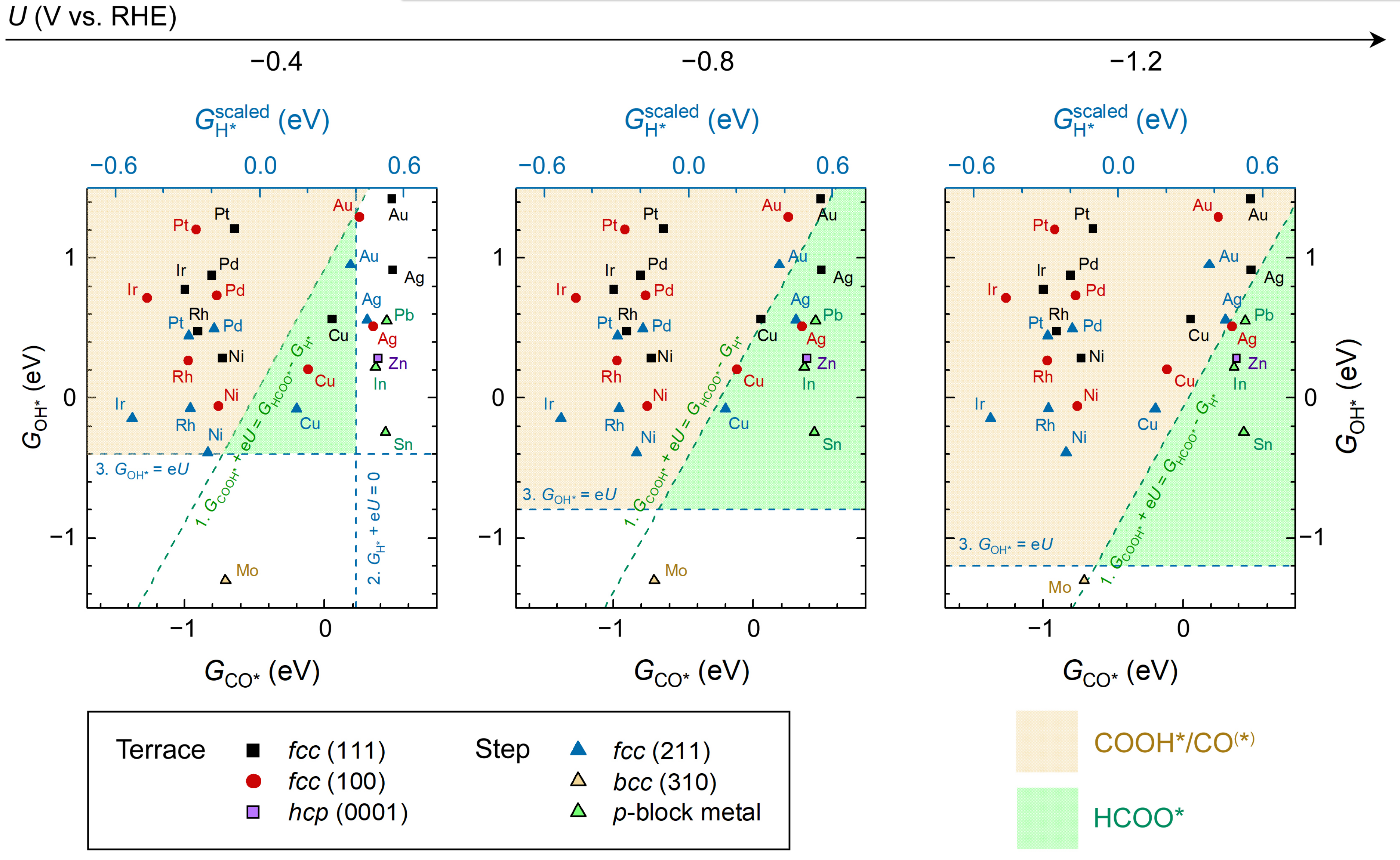
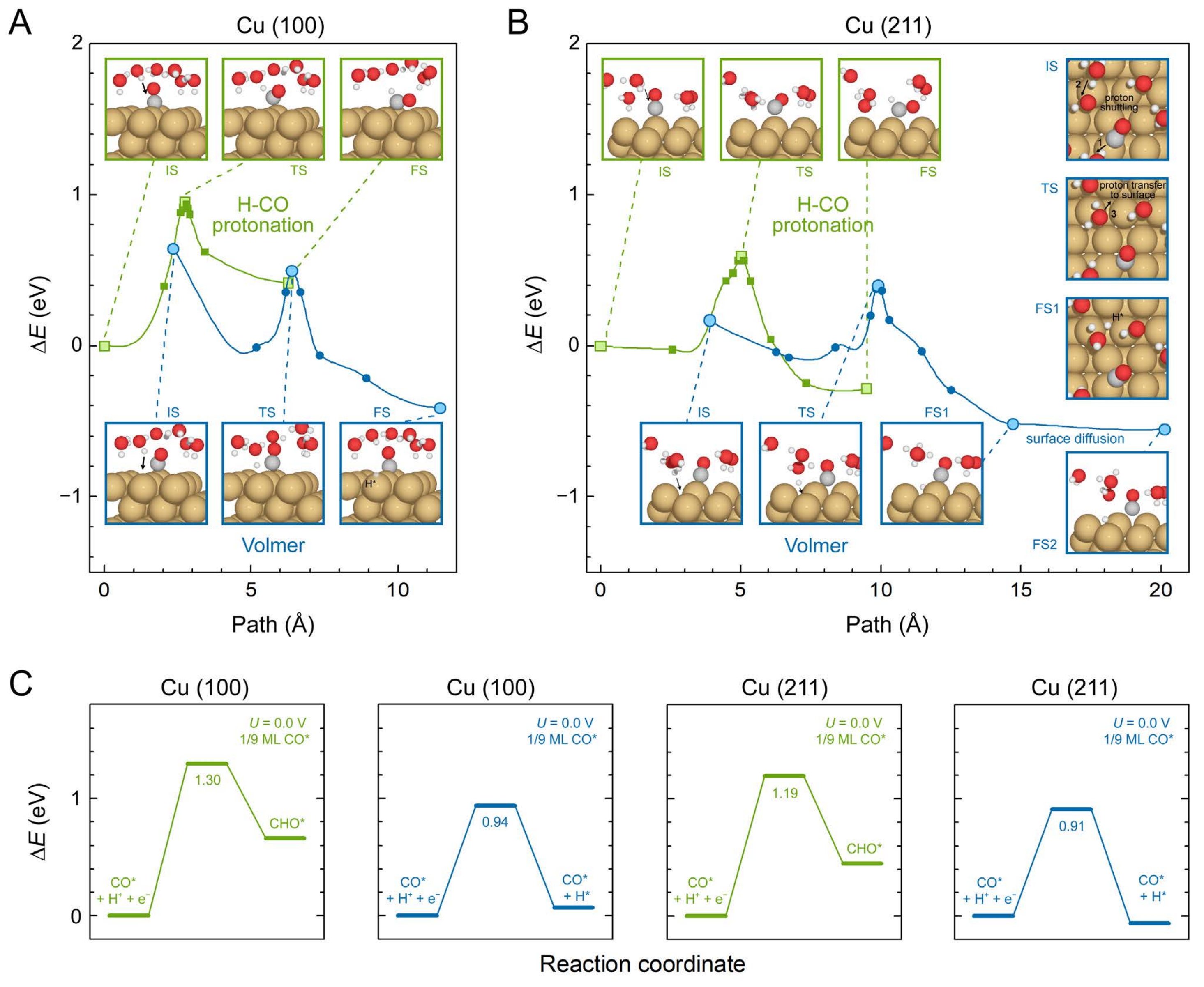
Results, Highlights, and Accomplishments

Potential-Dependent COOH vs. OCHO Selectivity Map



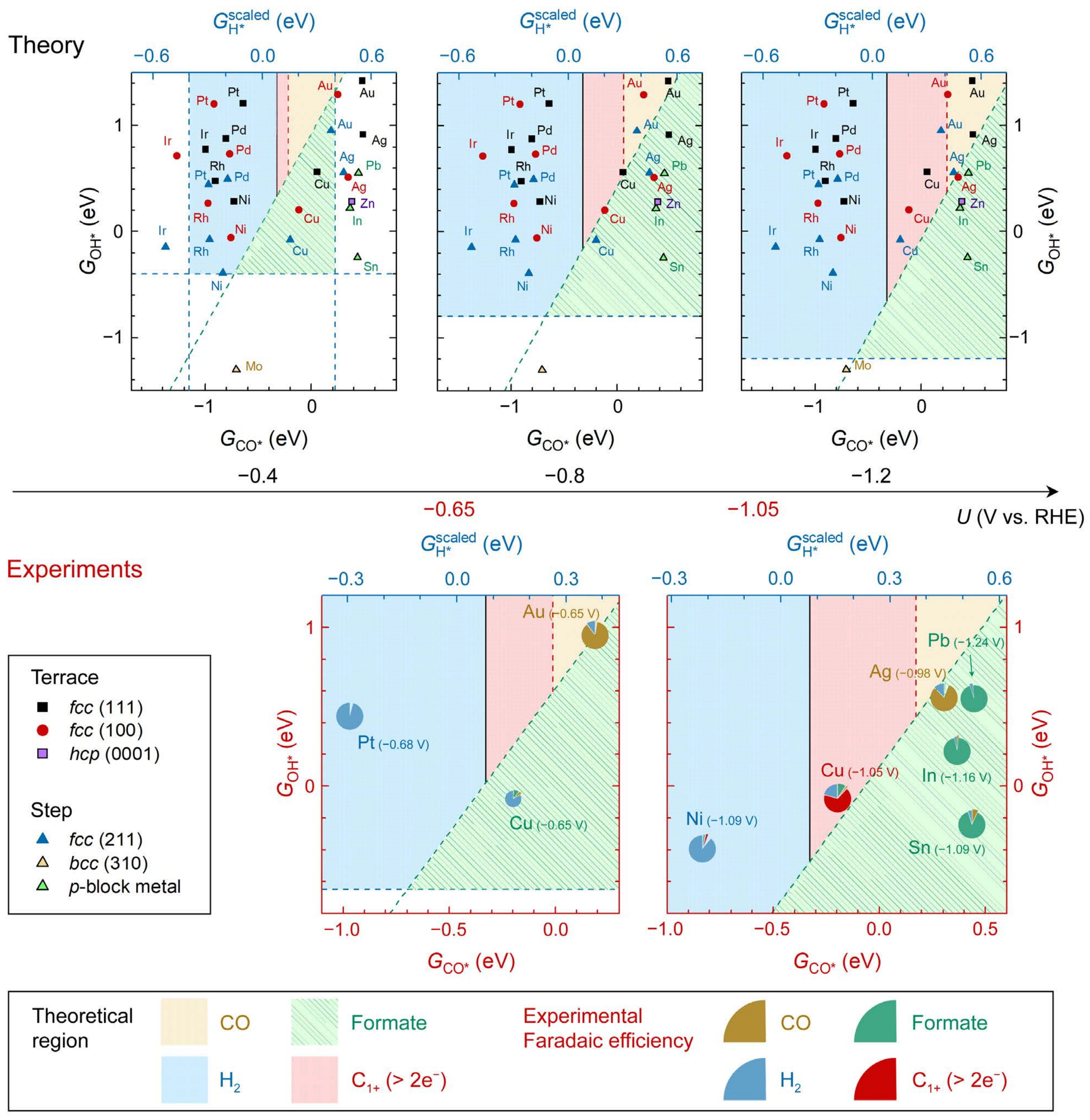
- Assuming similar field effects and solvation effects on OCHO* and COOH*, there should be a strong preference to form formate across all potentials.
- Because OCHO* binds much stronger vs. COOH* on Cu(100), we postulate that it is unlikely OCHO* forms electrochemically
- CO* vs. OH* as descriptors to relate ΔG_{CO} vs ΔG_{HCOO} selectivity
- $G_{COOH*} - G_{CO_2} + eU = G_{HCOO*} - G_{H*} - G_{CO_2}$
- Overpotential drives the HER *Volmer step* where formate is produced via CO2 attacking H*; in contrast, overpotential drives the COOH* formation step directly.
- At high overpotentials, selectivity moves from formate production to CO production: $\Delta G_{COOH} < \Delta G_{HCOO}$ (relative to H*)

CHO vs. HER Volmer Kinetics



- CHO* as energetically more favorable energetically than COH* on Cu(100).
- We argue that the formation of CHO* via CO protonation needs to consider the competing Volmer step from HER.
- If HER competing steps are considered, the Volmer step is found to be both energetic.and kinetically favorable over CO protonation to CHO
- CHO* formation can therefore be treated as a surface-driven reaction, while COH* is formed electrochemically
- COH* leads to the formation of methane via: COH → C → CH → CH2 → CH3 → CH4

Towards >2-electrons C1 products



- In terms of material screening so far, our model rationalizes copper as a unique element that enables further reduction of CO in to methane; on Pt-like metals, the late CH to CH2 reaction step has to compete with Heyrovsky step from HER.

Reference

1. M. Tang, H. Peng, P. S. Lamoureux, M. Bajdich, F.Abild-Pedersen. *App. Cat B* under review (2020)