



Electrocatalysis for sustainable energy conversion: transferring protons and electrons at solid-liquid interfaces

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Washington 18 November 2019*

Outline

Proton-coupled electron transfer at electrodes

Electrocatalysis of CO₂ reduction

Importance of understanding the role of pH, pH gradients, cations, and mass transport

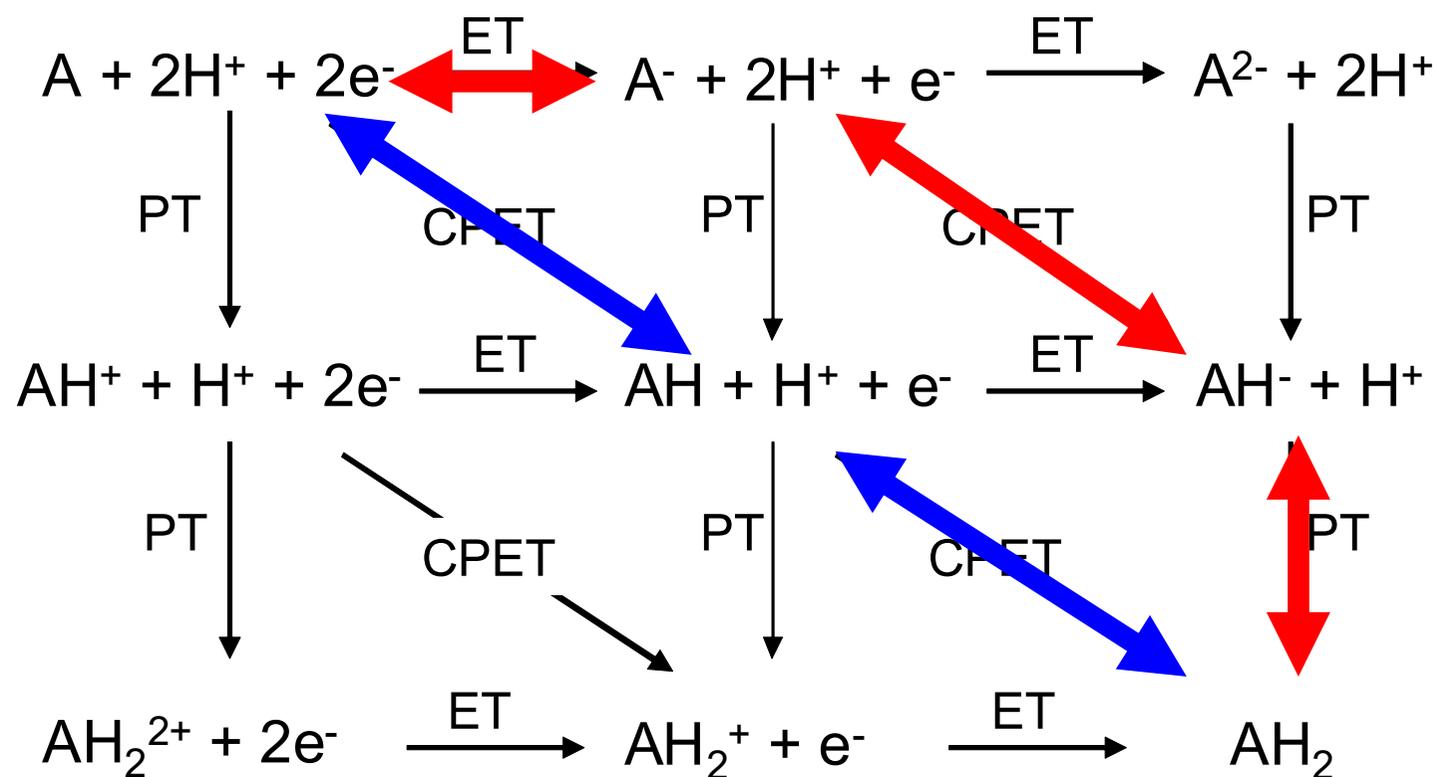
Theory of multi ET reactions

- Transfer of 1 electron:
 - Marcus Theory, solvent reorganization
- Transfer of 2 electrons: 1 intermediate
 - Optimization of only a single intermediate
“Zero” overpotential
- Transfer of >2 electrons (4,6...): >1 intermediate
 - Energetic scaling relation between intermediates
Non-zero overpotential

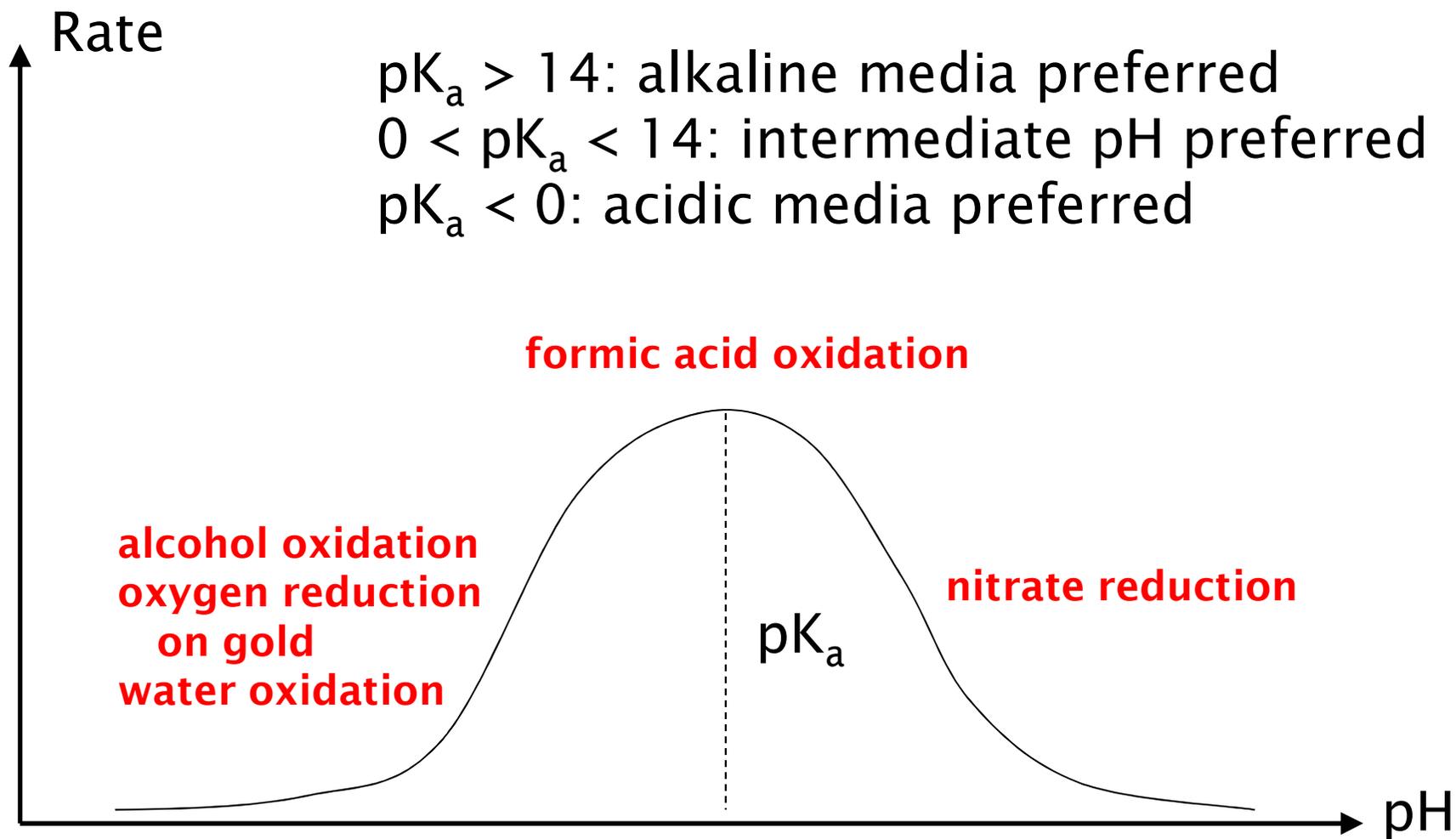
I.Man, J.Rossmisl et al., ChemCatChem 3 (2011) 1159

M.T.M.Koper, J.Electroanal.Chem. 660 (2011) 254; Chem.Sci. 4 (2013) 2710

Proton-coupled electron transfer

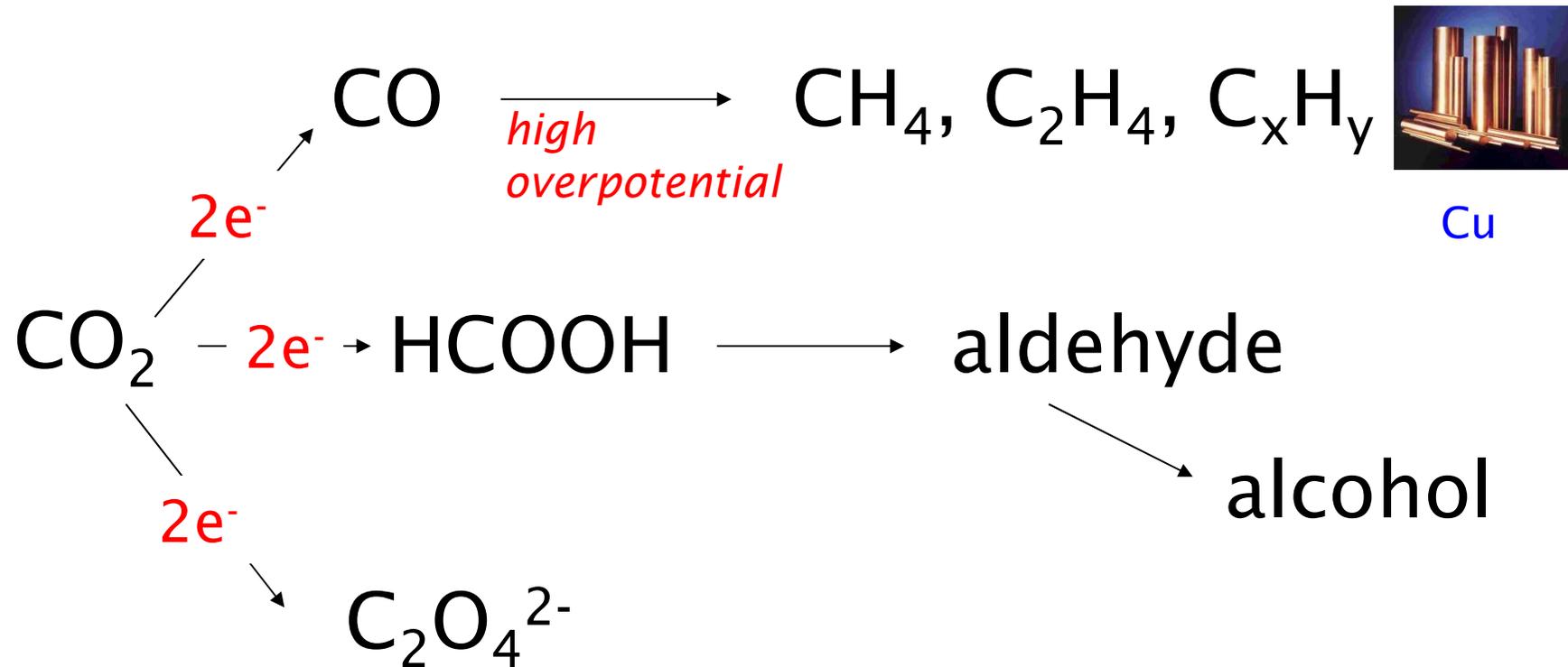


pH dependence of decoupled PCET



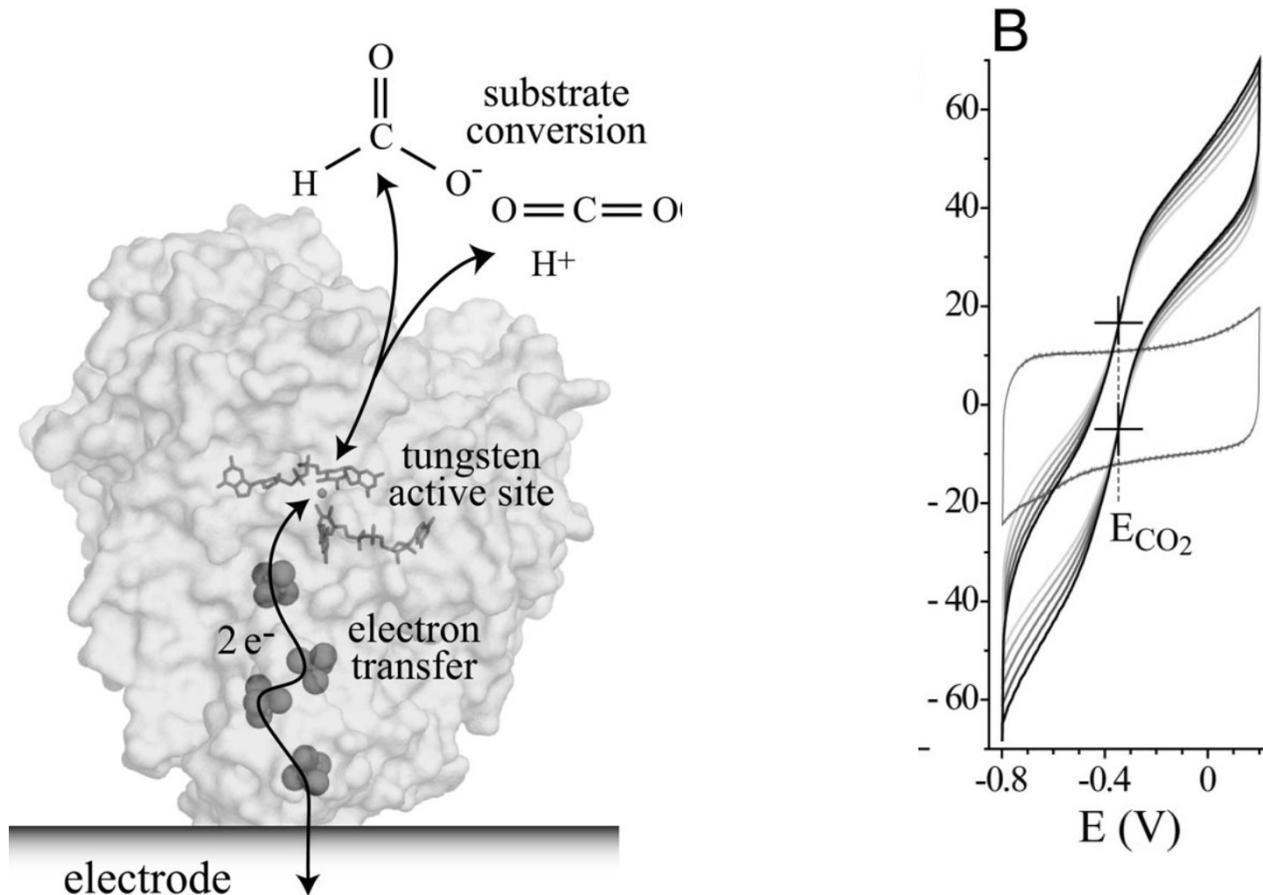
M.T.M.Koper, Chem.Sci. 4 (2013) 2710; Top.Catal. 58 (2015) 1153
J.Yang, P.Sebastian, M.Duca, T.Hoogenboom, M.T.M.Koper, Chem.Comm. 50 (2014) 2148
J.Joo, T.Uchida, A.Cuesta, M.T.M.Koper, M.Osawa, J.Am.Chem.Soc. 135 (2013) 9991

Electrocatalytic CO₂ reduction

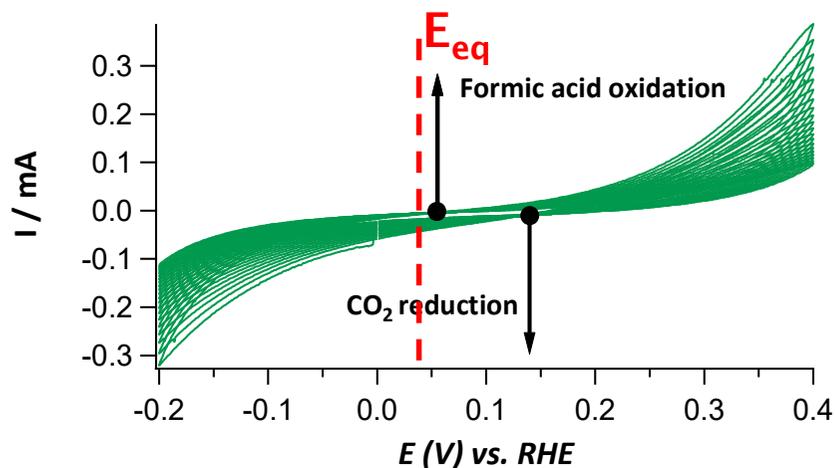


Reversibility is possible

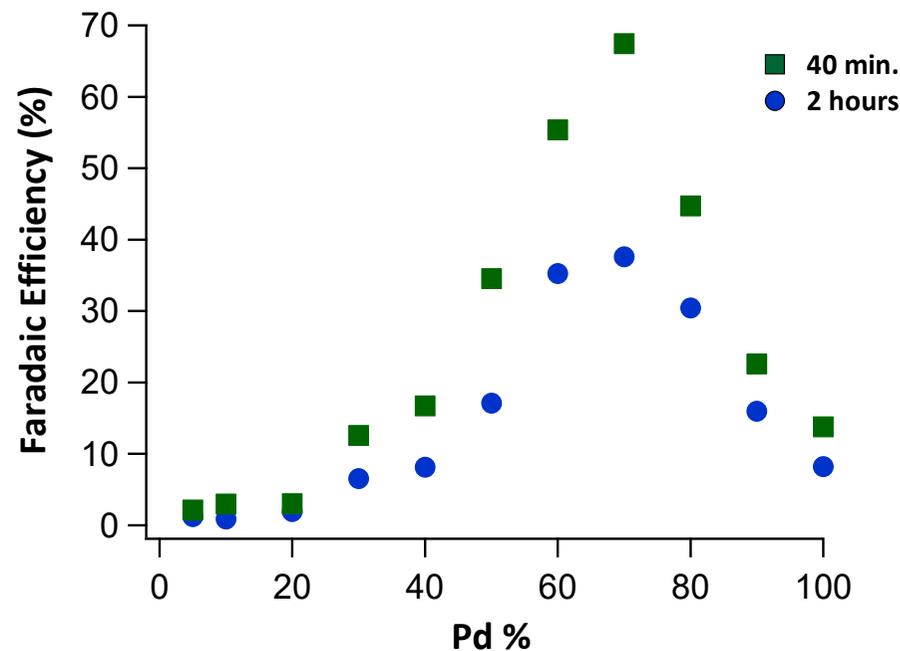
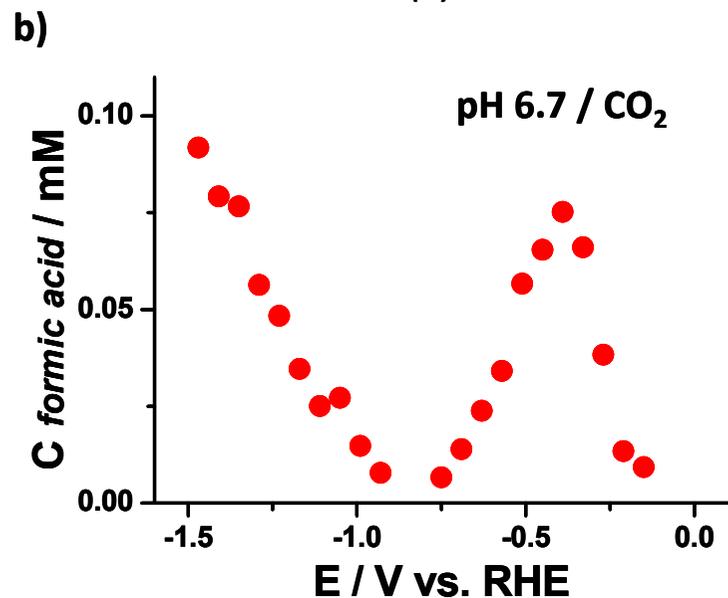
Reversible interconversion of carbon dioxide and formate by an electroactive enzyme.



CO₂/HCO₃⁻ reduction to formic acid

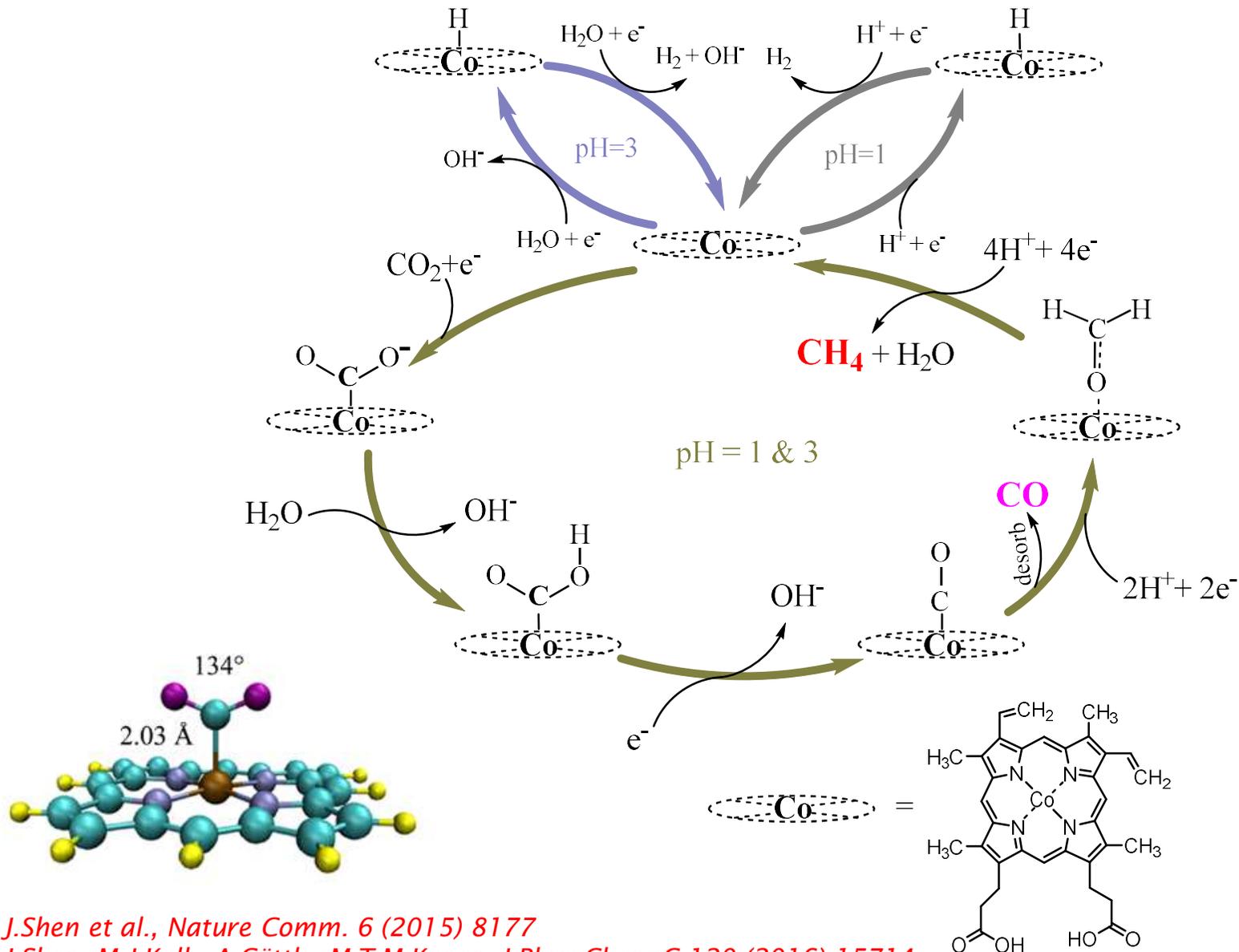


CO₂ and bicarbonate reduction on a Pd-Pt formic acid oxidation catalyst



R.Kortlever, C.Balemans, Y.Kwon, M.T.M.Koper, Catal.Today 244 (2015) 58
R.Kortlever, I.Peters, S.Koper, M.T.M.Koper, ACS Catal. 5 (2015) 3916

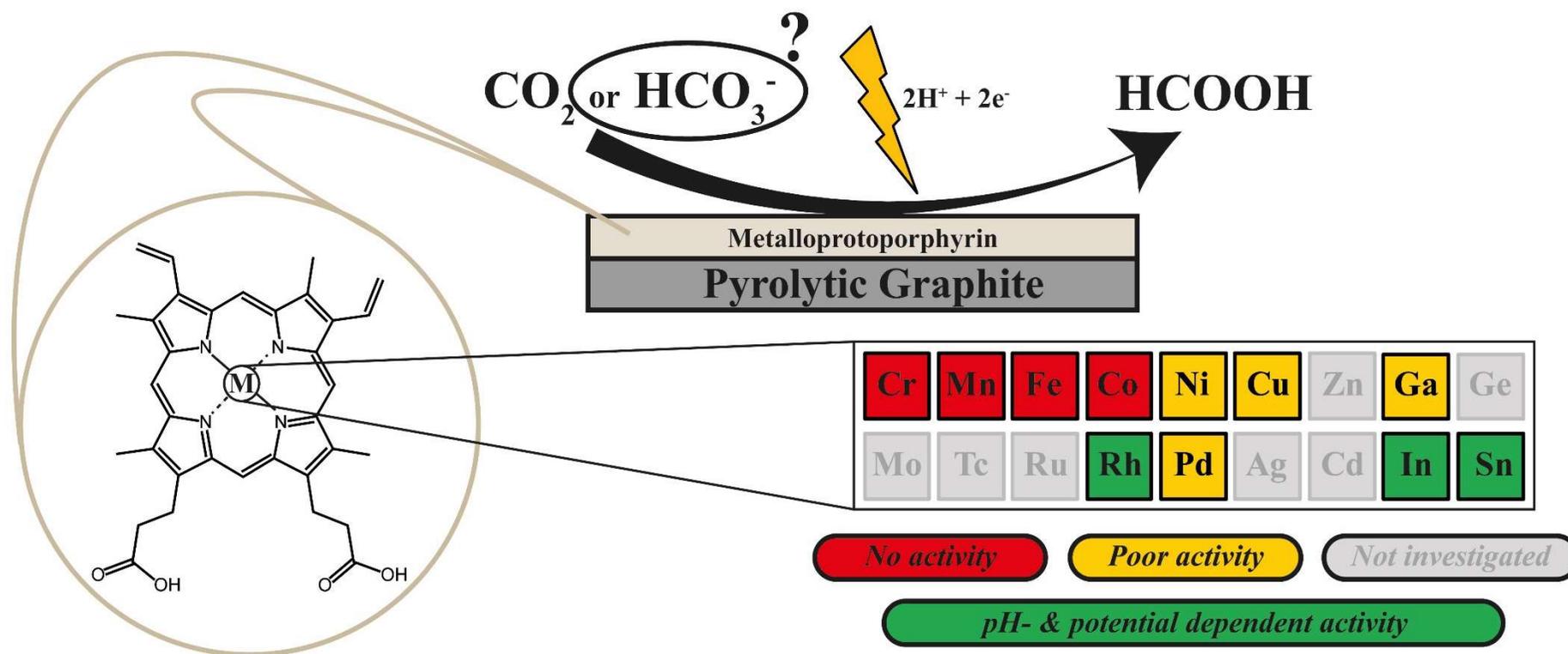
CO₂ reduction on Co-porphyrin



J.Shen et al., Nature Comm. 6 (2015) 8177

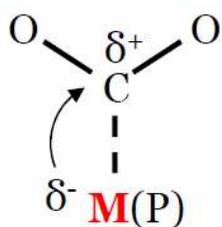
J.Shen, M.J.Kolb, A.Göttle, M.T.M.Koper, J.Phys.Chem.C 120 (2016) 15714

Selectivity to formic acid



Selectivity on metalloporphyrins

metal-activated pathway



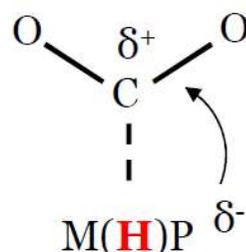
reduced-metal



CO, formaldehyde,
methanol, methane

Fe, Co

hydride-activated pathways

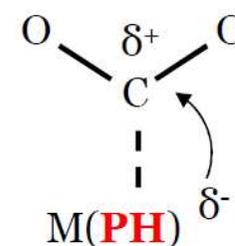


metal-hydride



HCOOH / HCOO⁻

Rh?



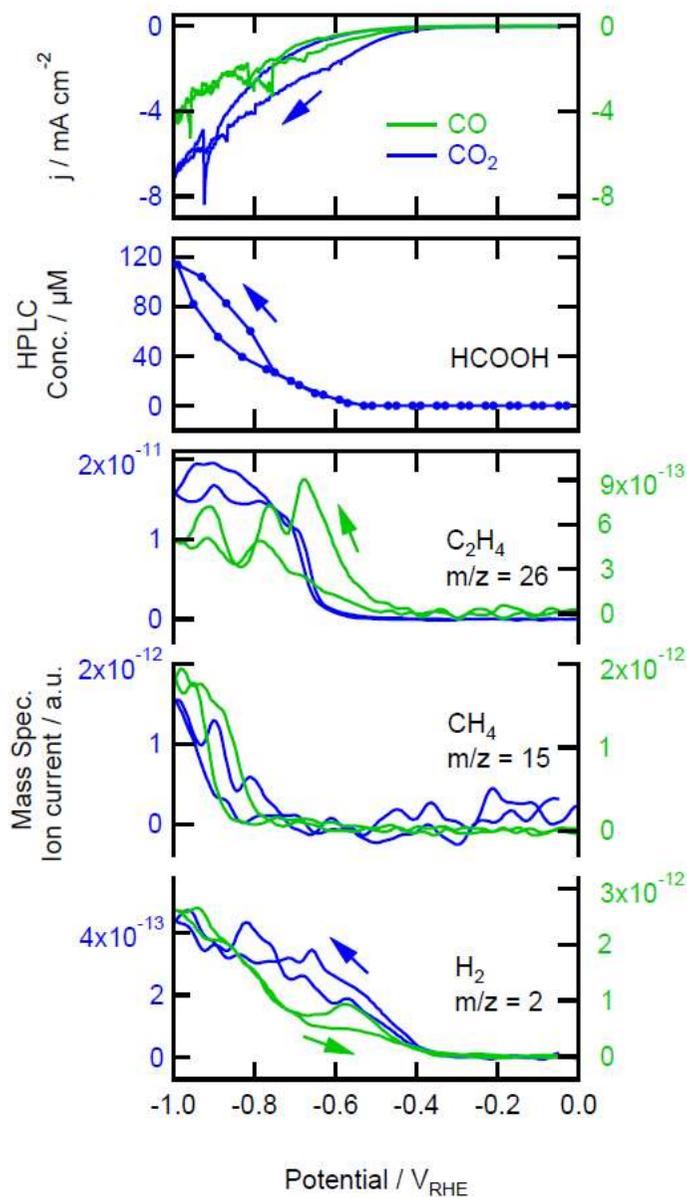
phlorin ligand



HCOOH / HCOO⁻

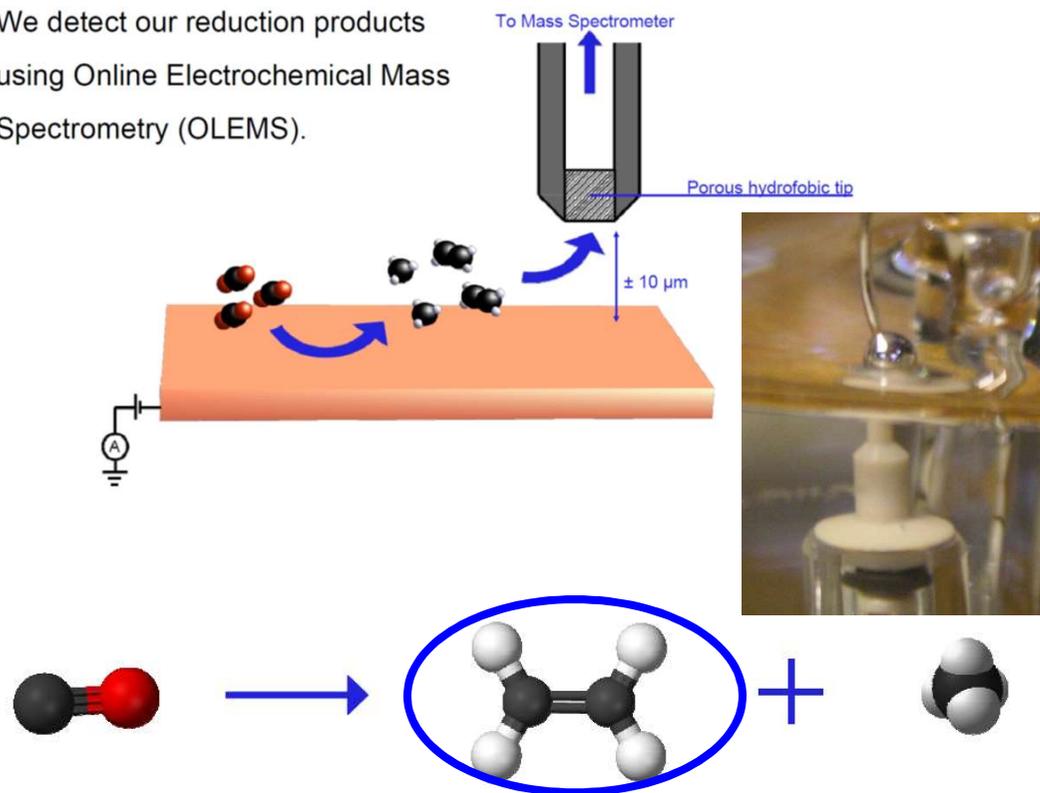
In, Sn, Rh?

CO and CO₂ reduction on copper

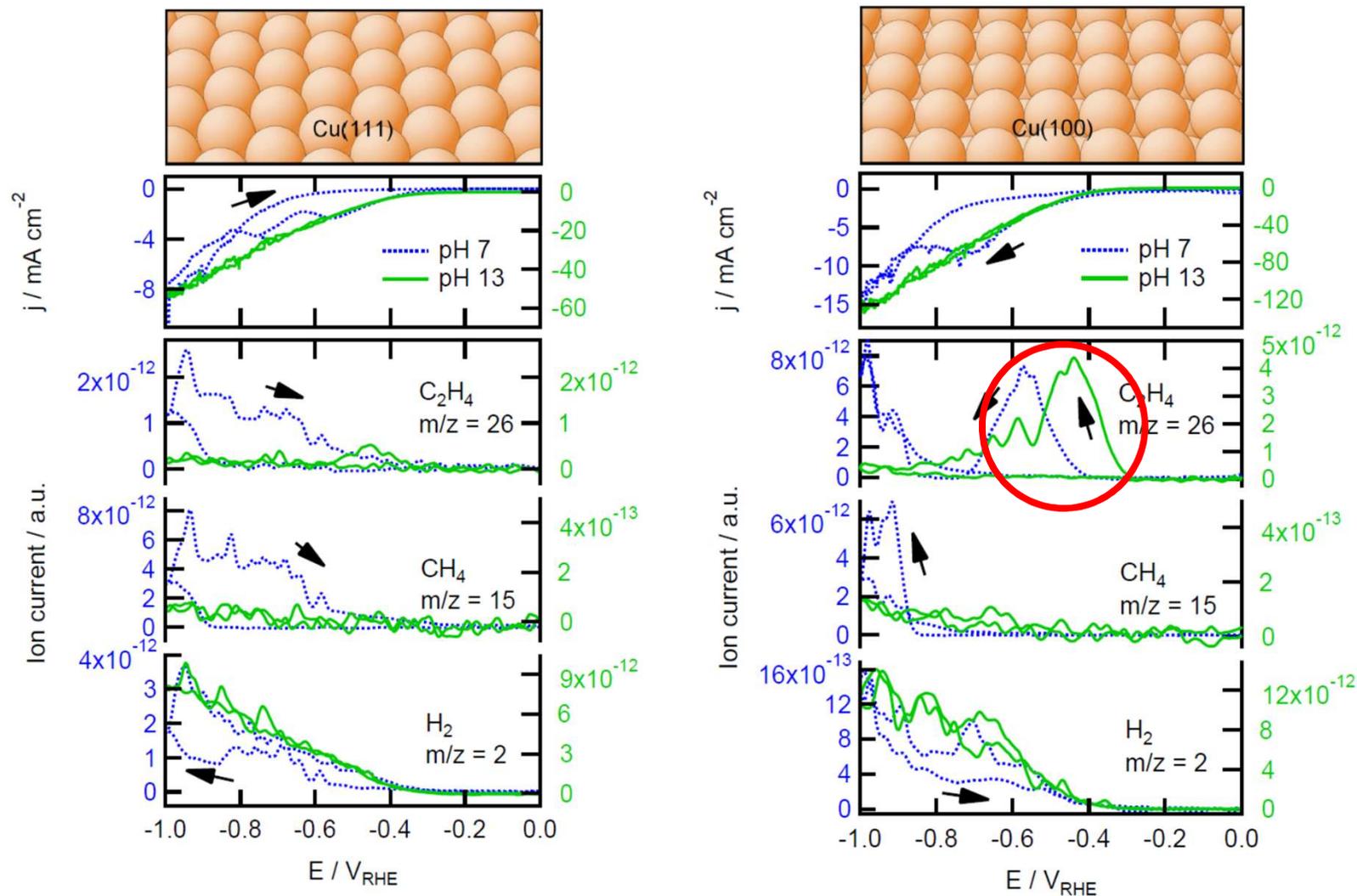


CO₂ and CO reduction on copper electrodes produces H₂, HCOOH, CH₄ and C₂H₄.

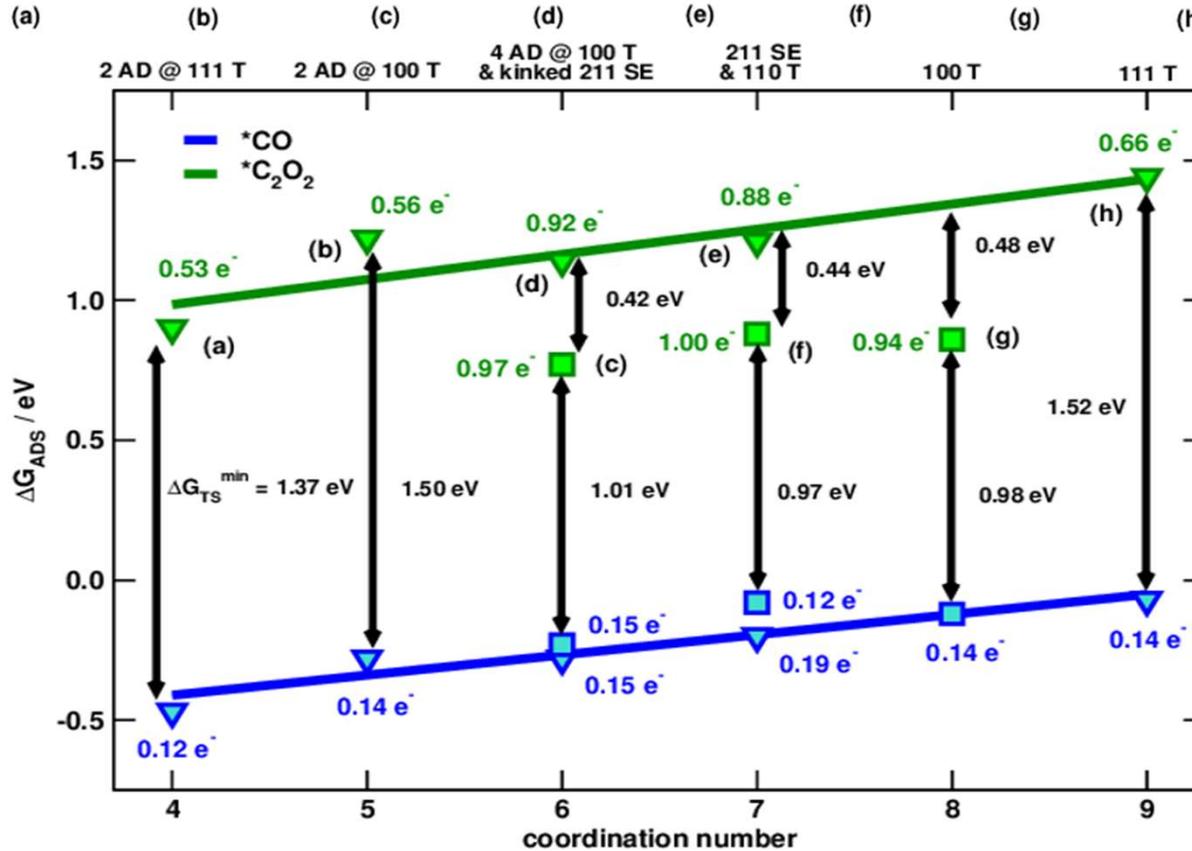
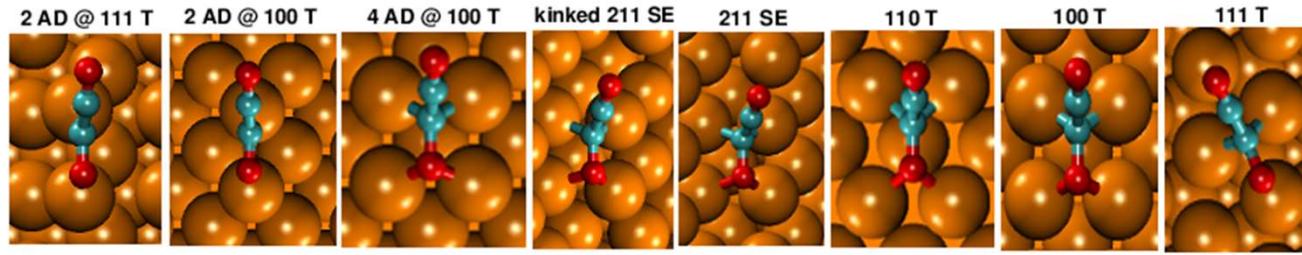
We detect our reduction products using Online Electrochemical Mass Spectrometry (OLEMS).



CO reduction on Cu(111) and Cu(100)



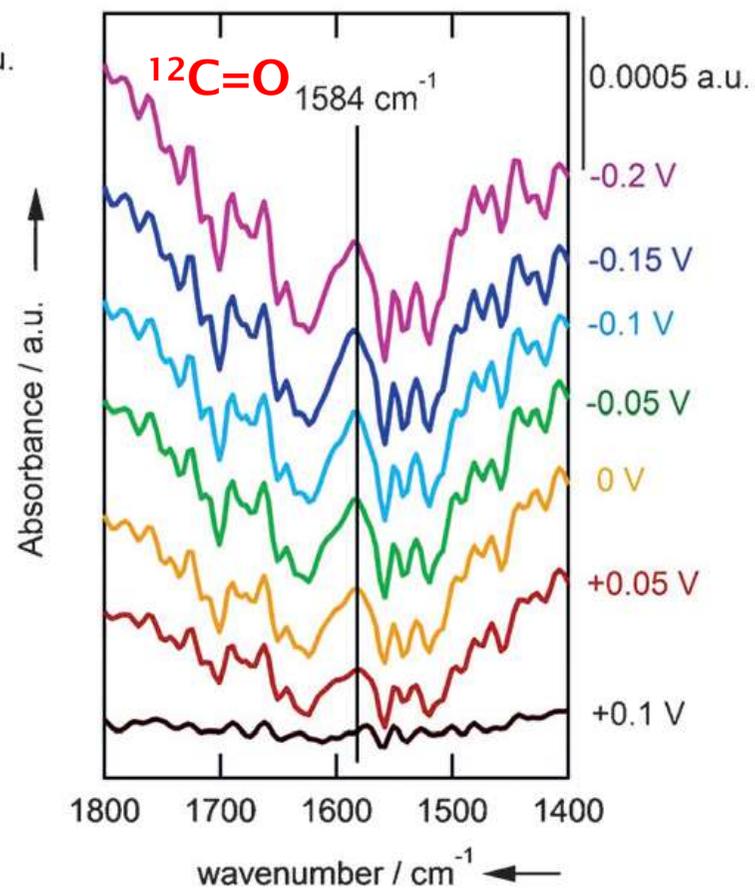
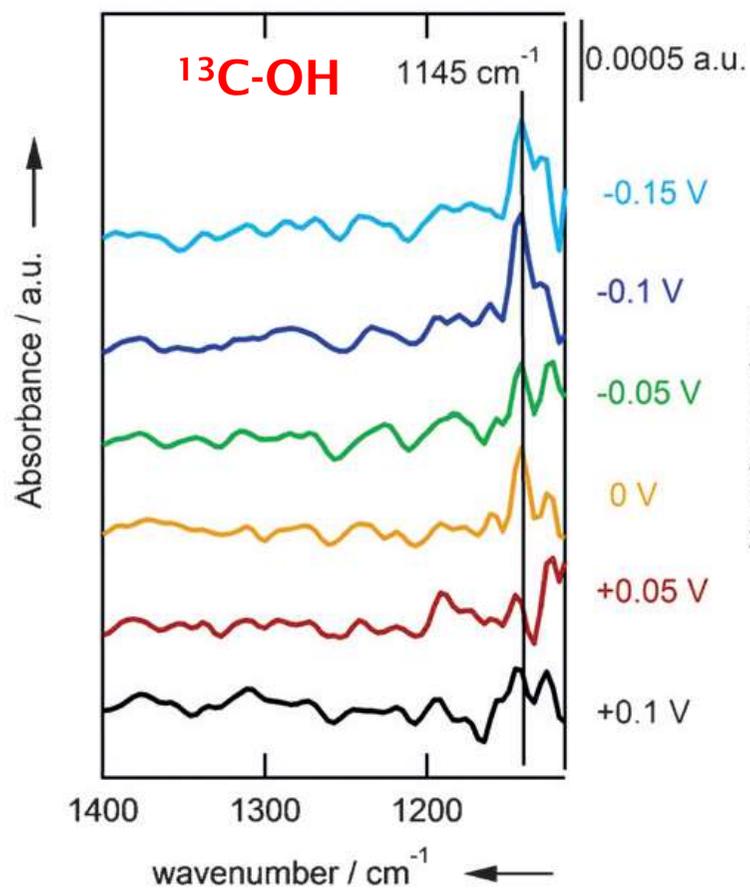
(CO)₂ prefers Cu(100) sites



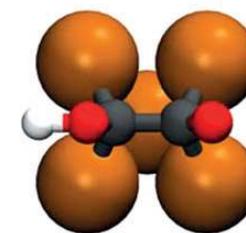
Spectroscopic FTIR evidence

a) Cu (100), 0.1 M LiOH, ^{13}CO atmosphere

b) Cu (100), 0.1 M LiOH in D_2O , ^{12}CO atm.

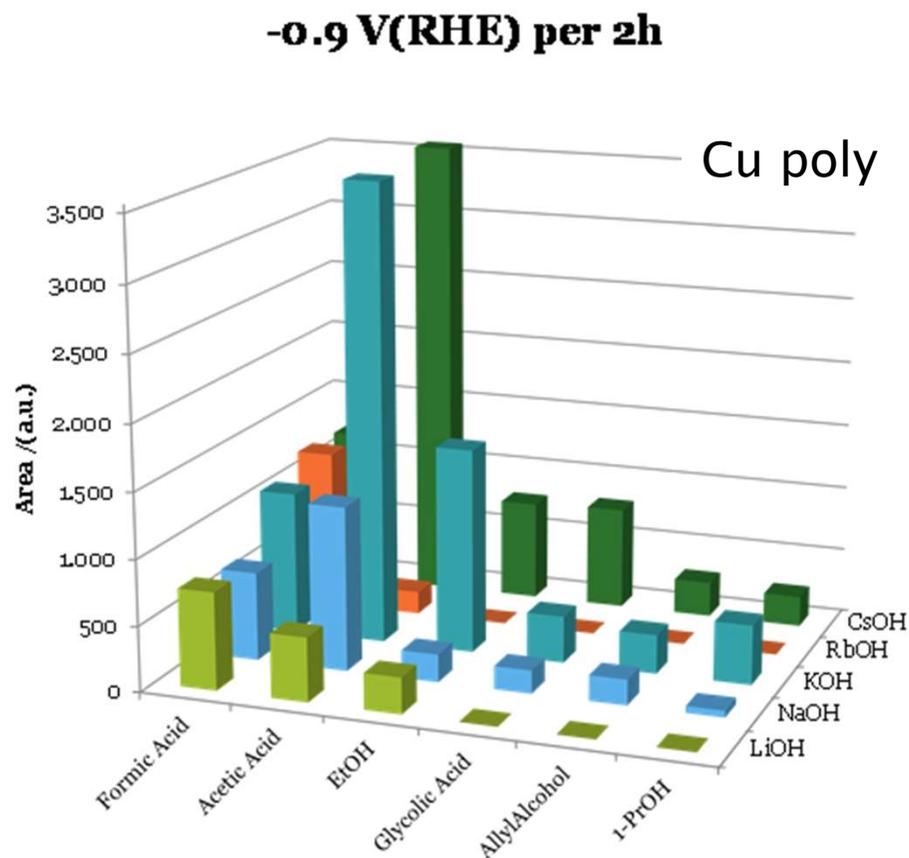
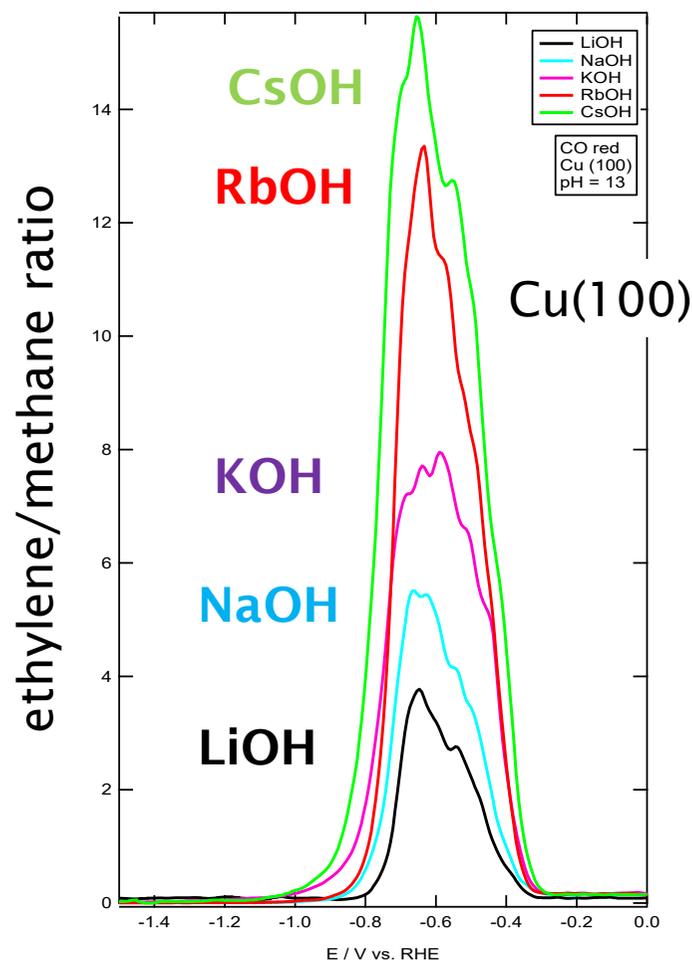


f) OCCOH



1576, 1235 cm^{-1}

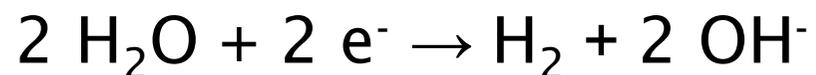
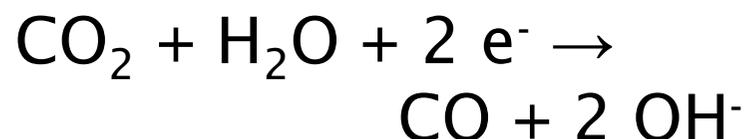
Cation effect on C₂ and C₃ formation



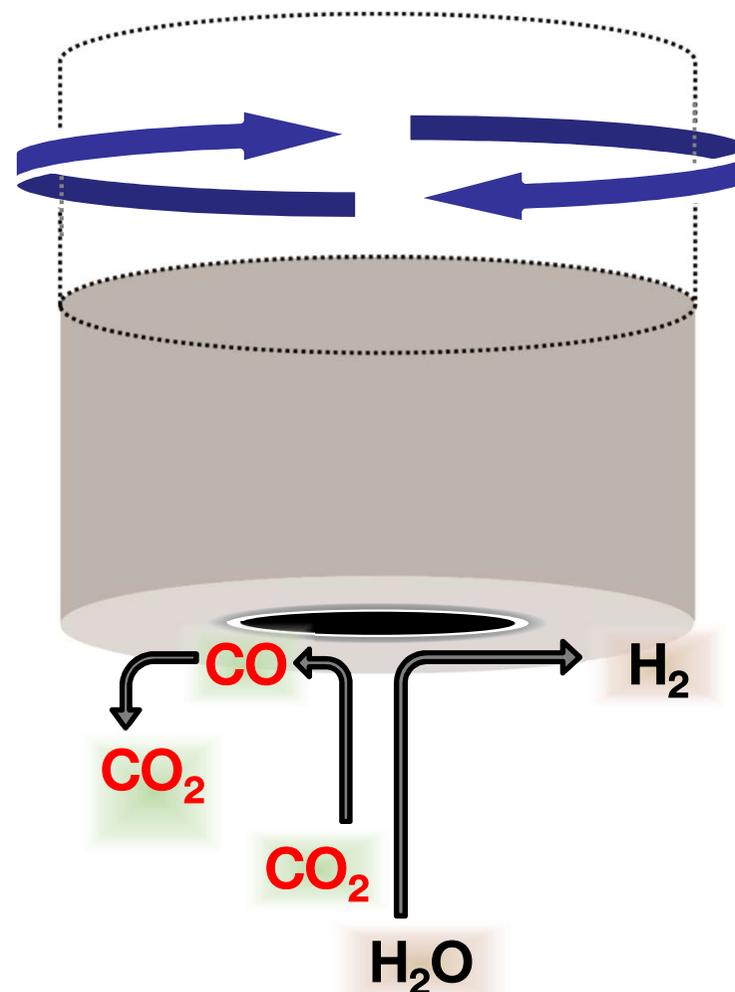
Larger cations enhance C-C bond formation →
they enhance the (CO)₂⁻ pathway

CO₂ reduction on gold electrode

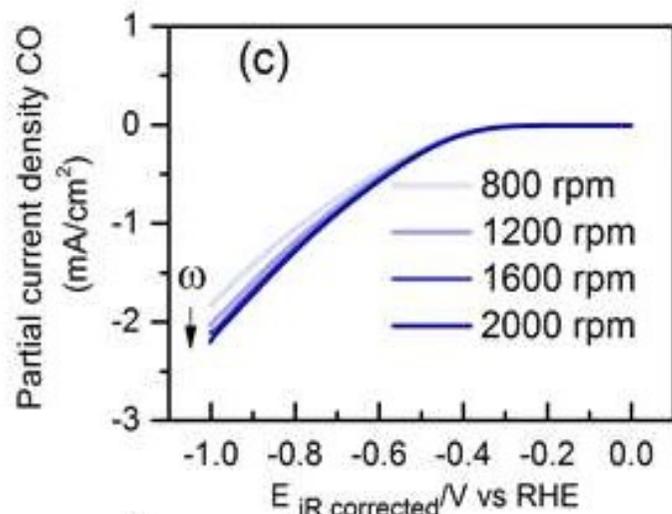
Two competing reactions,
CO₂RR and HER:



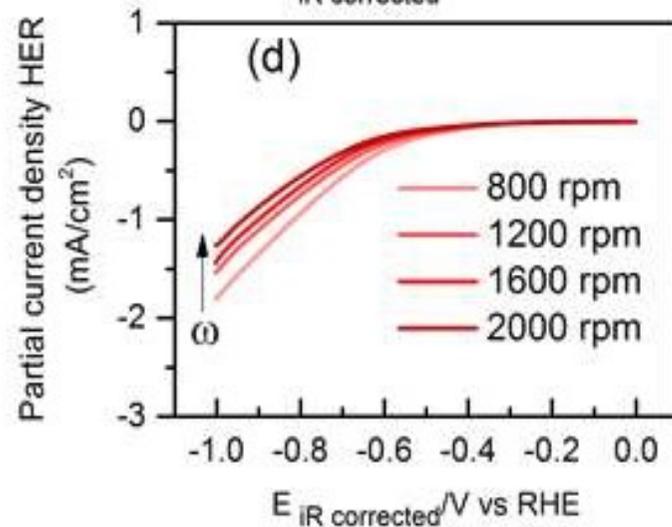
Gold disk; gold ring



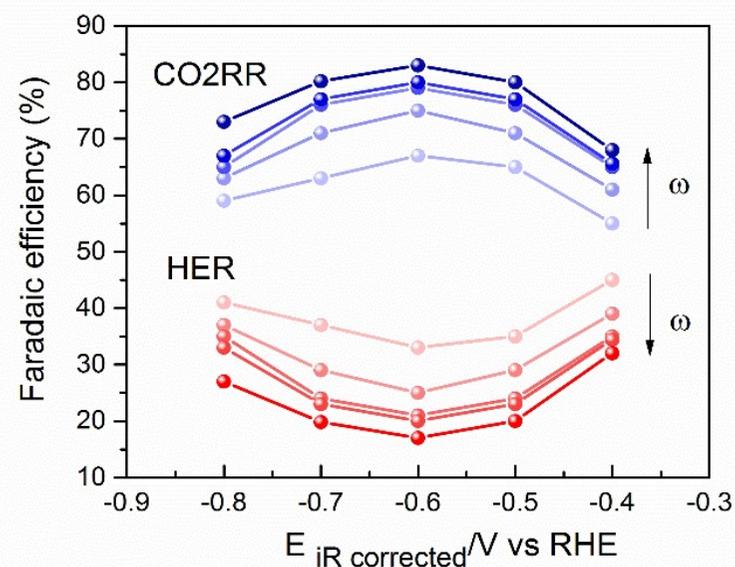
Partial current densities



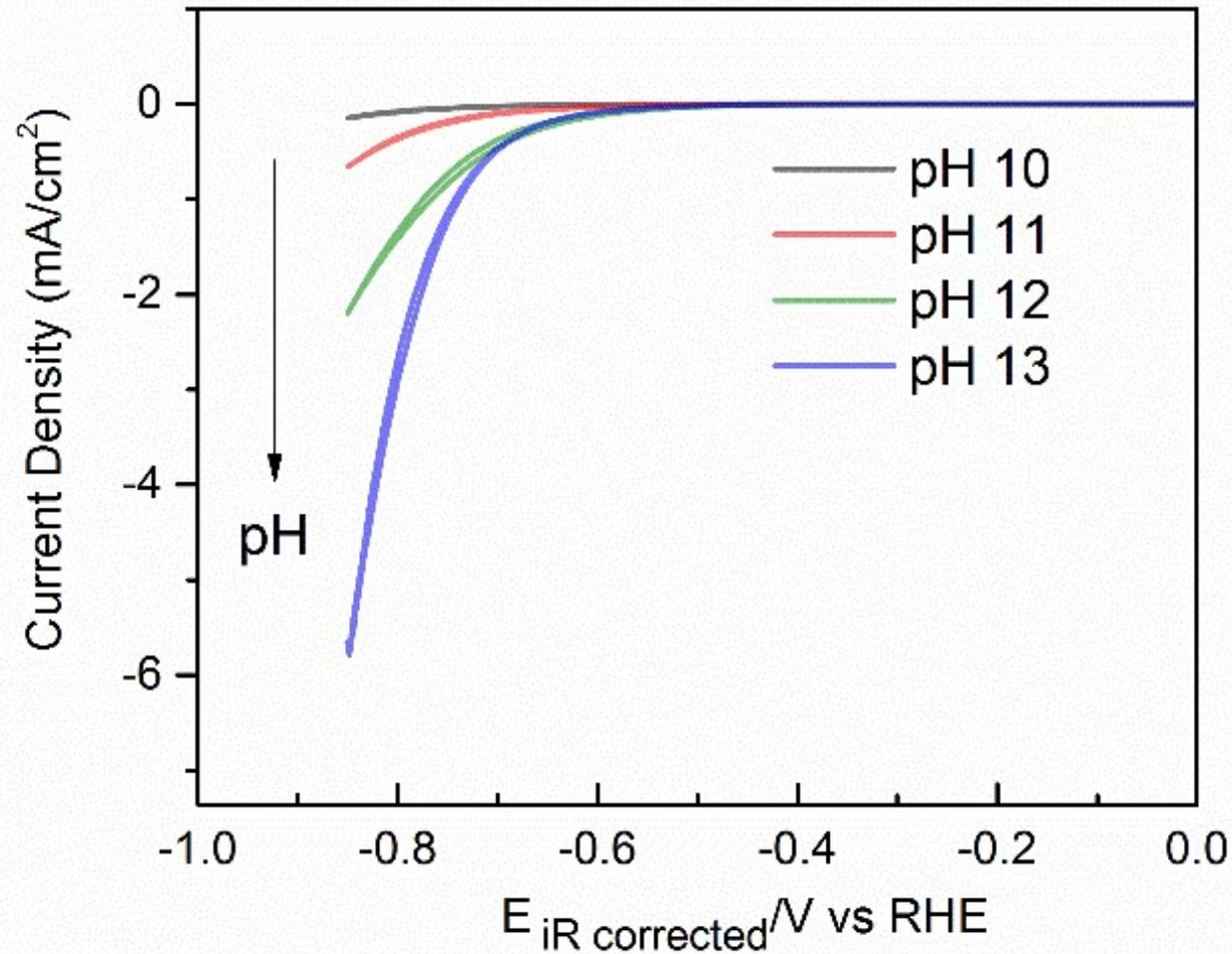
CO production increases (a little) with enhanced mass transport



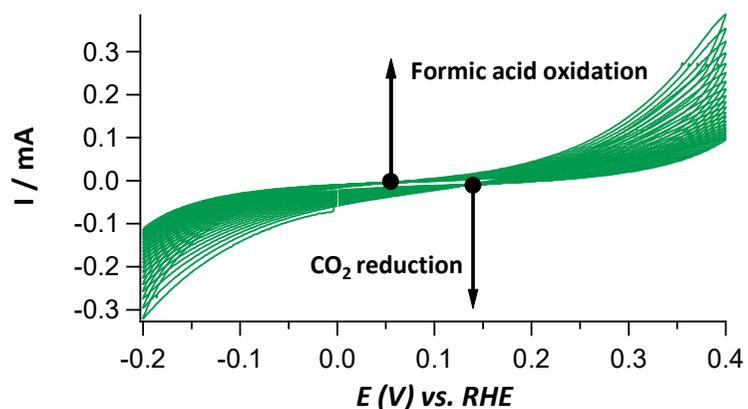
H₂ production decreases with enhanced mass transport (!)



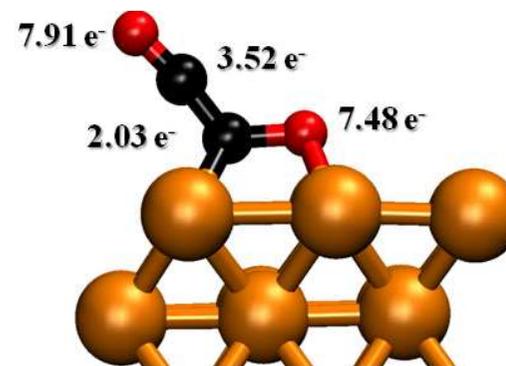
HER depends on (local) pH



Conclusions

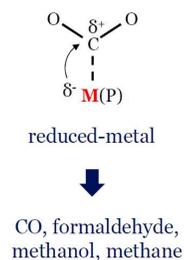


Reversible CO₂ reduction

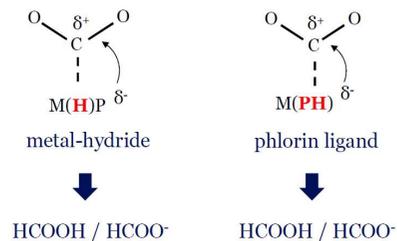


Charged intermediates (CO₂⁻, H⁻, (CO)₂⁻) are important

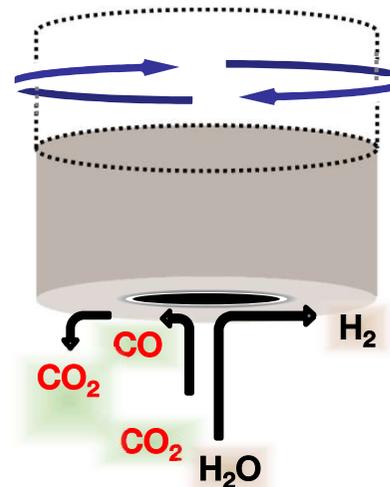
metal-activated pathway



hydride-activated pathways



Activation to CO and HCOOH follow different pathways



Electrolyte and mass transport effects are important

Some thoughts

“Understanding of complex electrode reactions”

Role of the electrolyte is still far from completely understood, even for the hydrogen evolution reaction

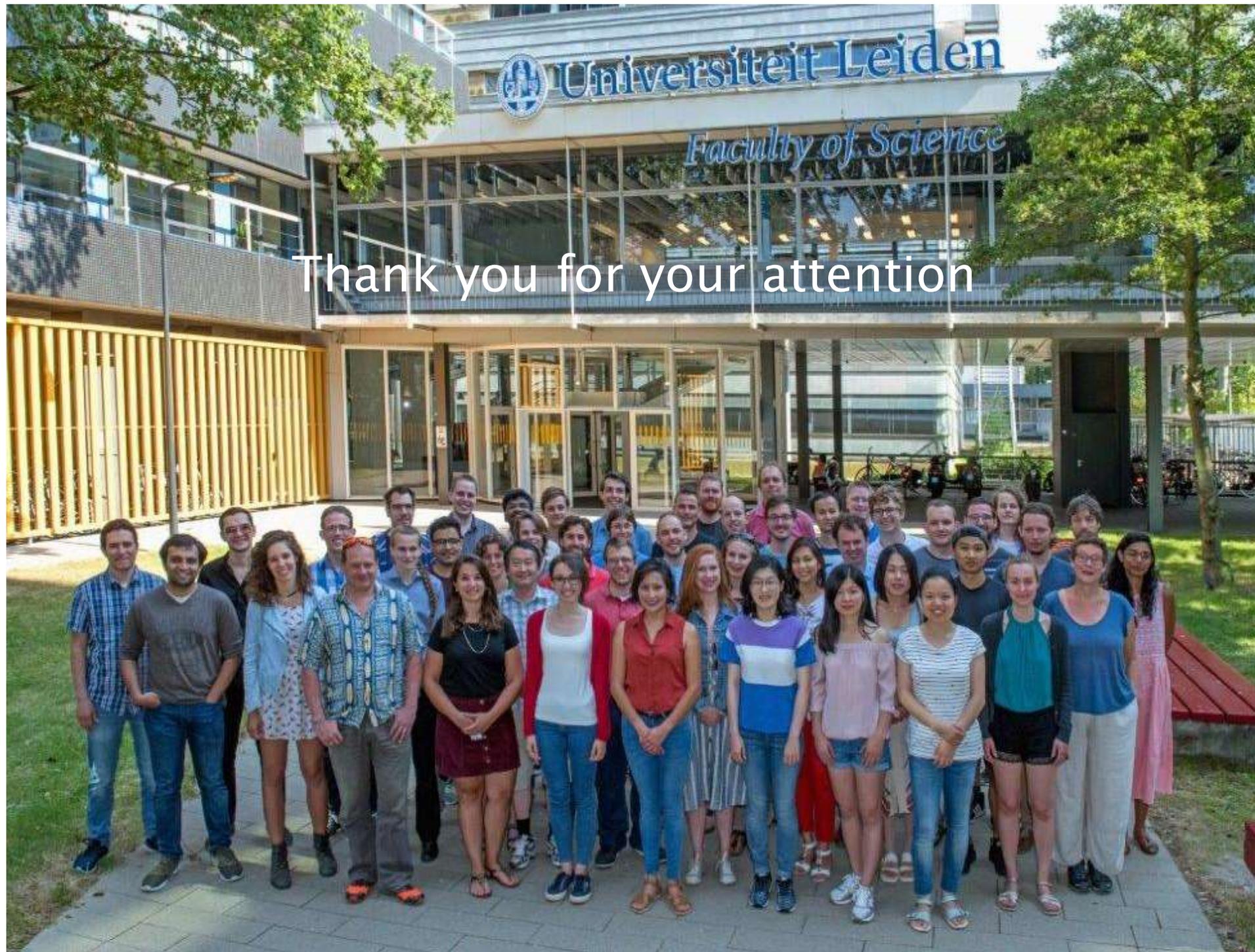
What is the exact role of the double layer structure?
Is the Gouy-Chapman-Stern model applicable (quantitatively)?

Need for new interfacial spectroscopies and theory/computer simulations

Fundamentals of the long-term (in)stability of electrodes

Acknowledgements

- Ruud Kortlever, Jing Shen, Adrien Göttle, Klaas Jan Schouten, Elena Perez-Gallent, Giulia Marcandalli, Federico Calle-Vallejo, Marta Figueiredo, Yuvraj Birdja, Akansha Goyal, Giulia Marcandalli, Vlad Mints
- Recep Kas, Guido Mul (Twente)
- Netherlands Organization for Scientific Research (NWO)
- NanoNextNL
- CO2 neutral fuels program (NWO/FOM/Shell)
- Solar-to-Products program (NWO/Shell/TNO)
- ARC-CBBC (NWO/Shell)
- Chinese Scholarship Council
- Japan Society for the Promotion of Science (JSPS)
- Covestro (Bayer MaterialScience)



Thank you for your attention