



Electron-proton transfer theory and electrocatalysis

Part II

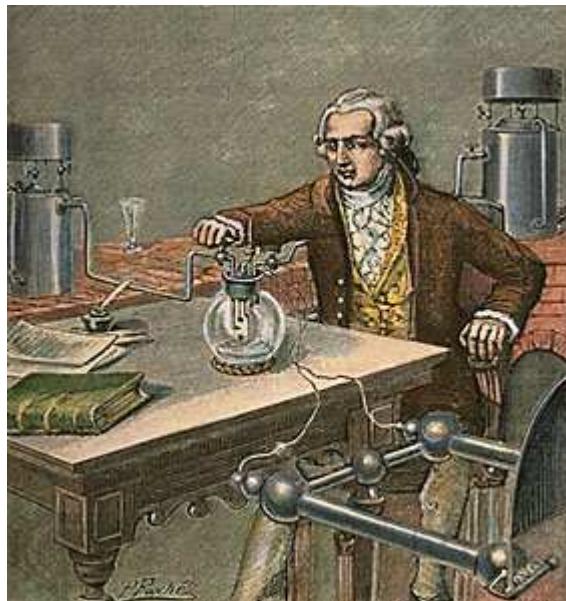


Universiteit Leiden

Marc Koper
ELCOREL Workshop

Haarlem 1789

First experiment on water electrolysis by
Paets van Troostwijk and Deiman:
Water plus electricity produces hydrogen and oxygen

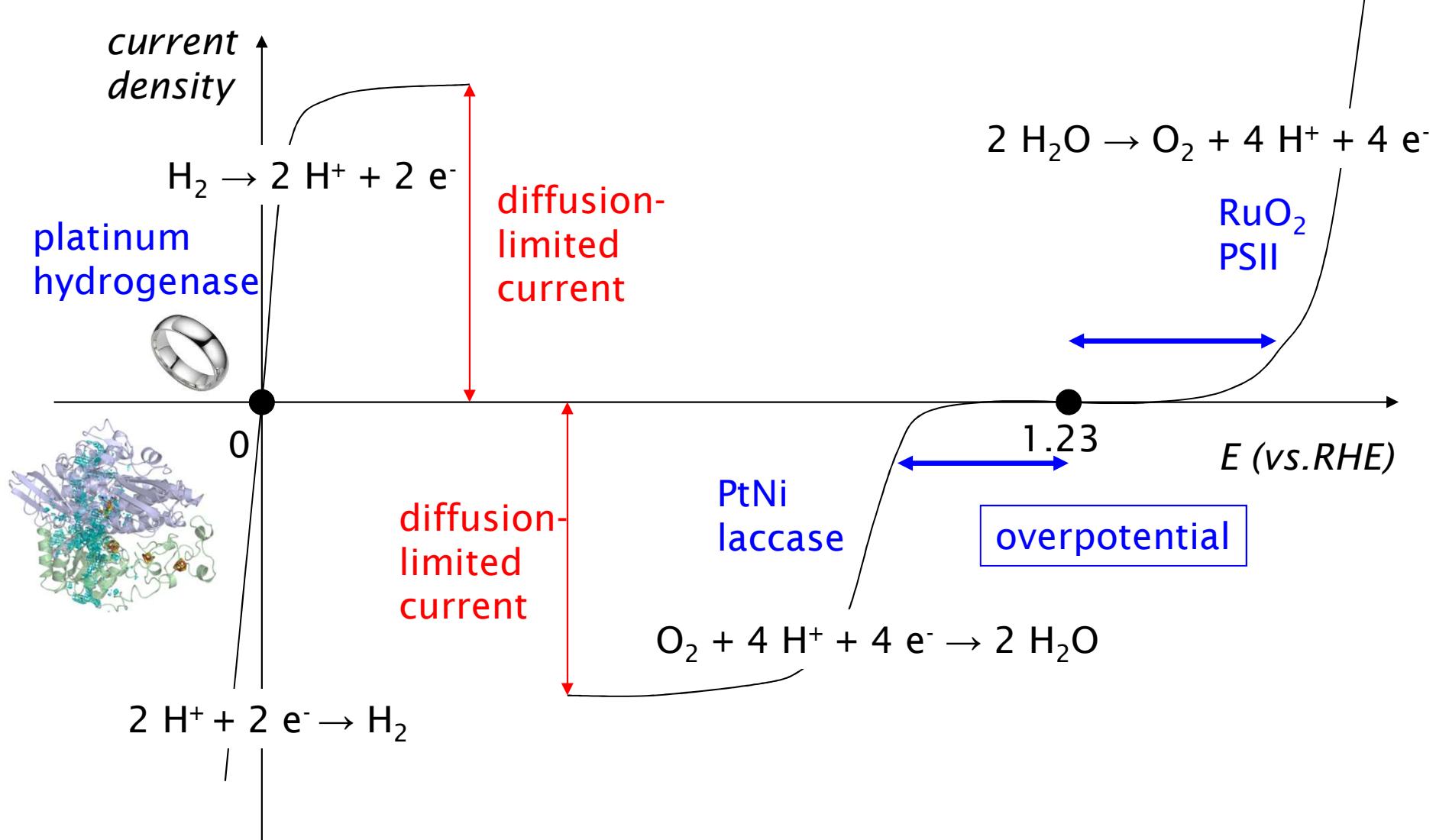


Museum Boerhaave, Leiden

“Sur une manière de décomposer l'Eau en Air inflammable et en Air vital”

A. Paets van Troostwijk, J.R. Deiman, *Obs. Phys.* 35 (1789) 369

Redox reactions of water



Catalysis of multi-step reactions

Practically every (interesting) chemical reaction happens in a series of steps; catalysis is about optimizing that sequence

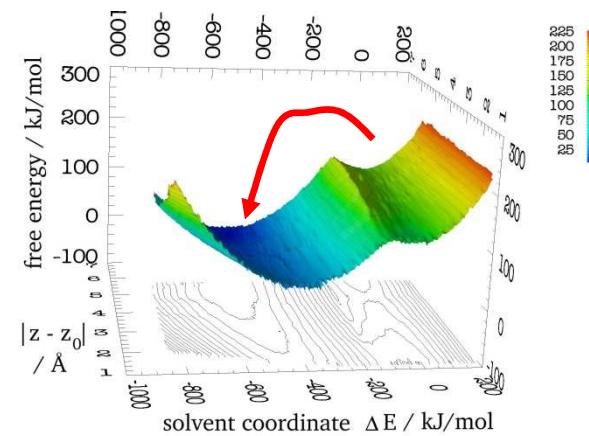
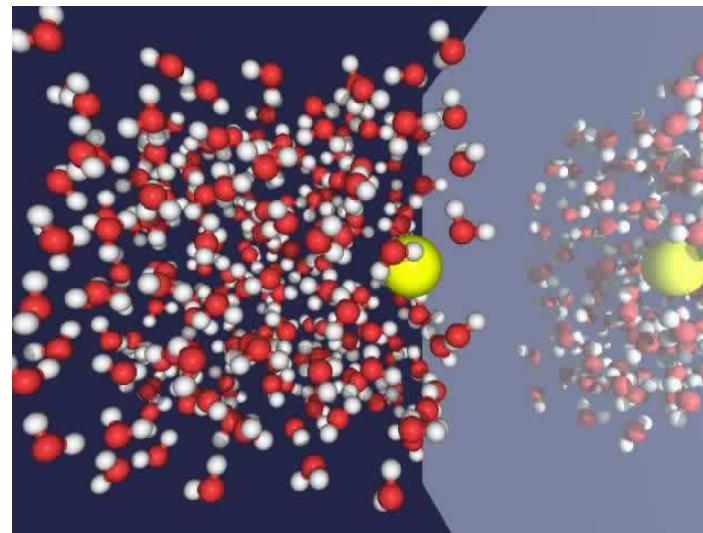
1 e⁻ / 1 step / 0 intermediate

2 e⁻ / 2 steps / 1 intermediate

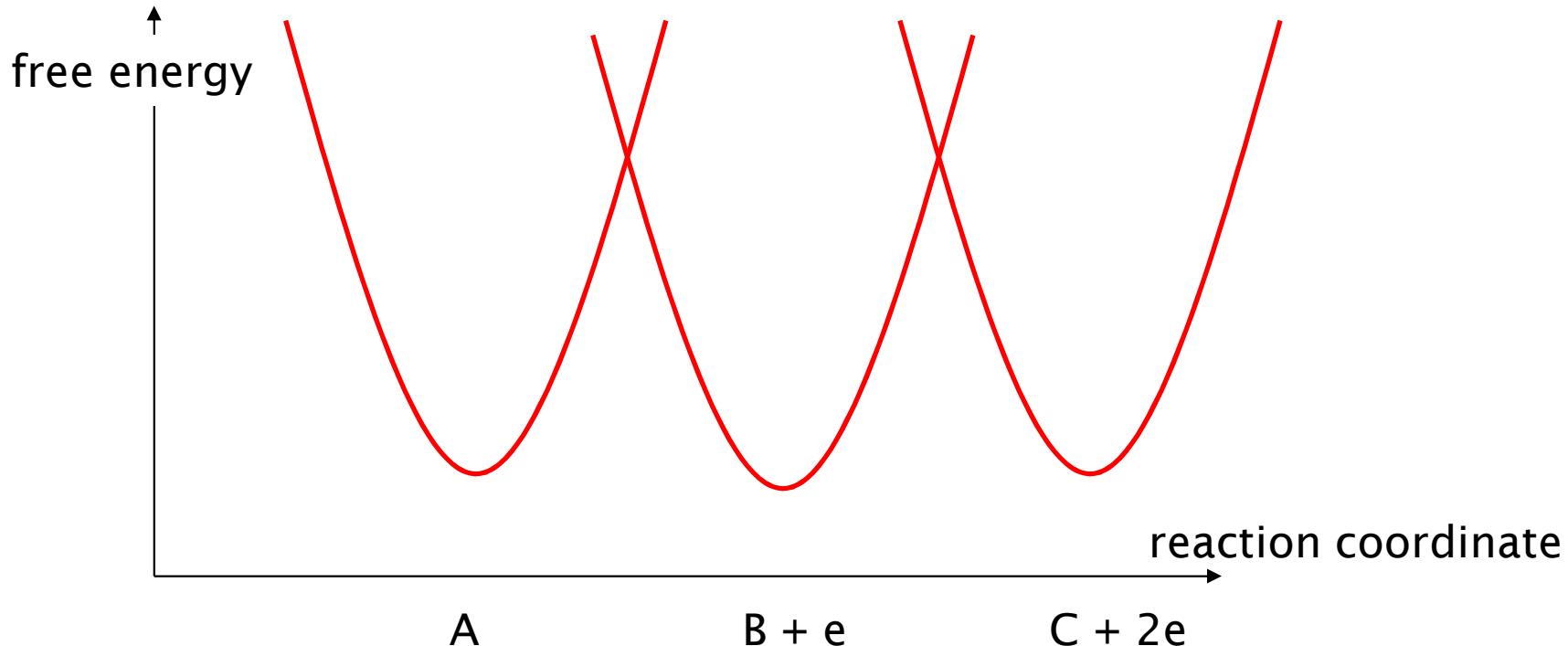
>2 e⁻ / >2 steps / >1 intermediate

Single electron transfer

- Marcus Theory
- Activation energy determined by solvent reorganization energy λ (a difficult quantity to calculate accurately)
- Marcus Theory does not account for bond breaking, proton transfer, or catalysis.

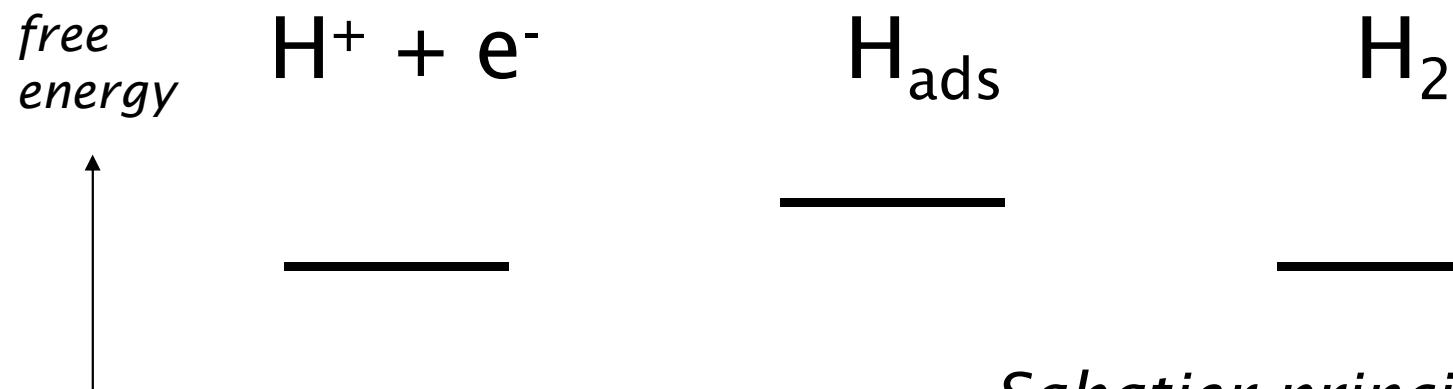
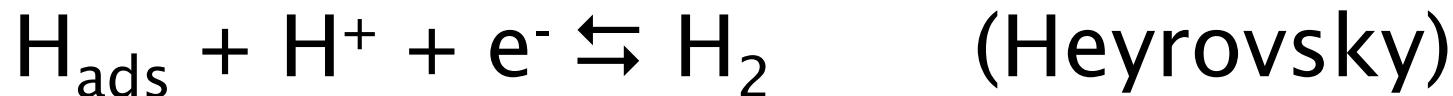


Multiple electron transfer



- Electrons transfer one-by-one, implying storage of charge and the existence of intermediates.
- Electrocatalysts optimize the energy of intermediates

Two electron transfer



Thermodynamics



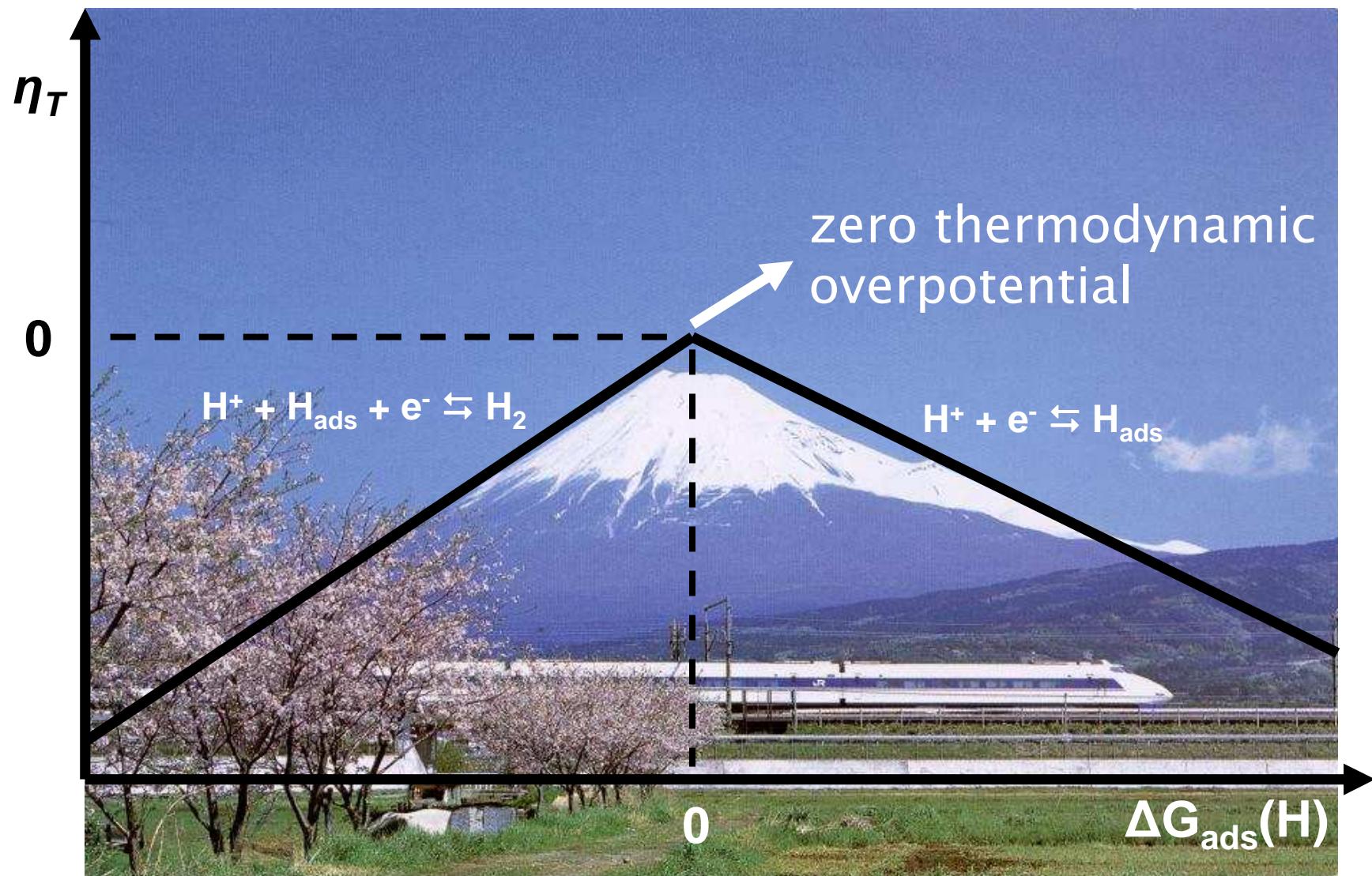
Thermodynamic restriction: $(E_1^0 + E_2^0)/2 = E^0$

Potential-determining step

*The potential-determining step
is the step with
the least favorable equilibrium potential*

The difference in the equilibrium potential of the potential-determining step and the overall equilibrium potential is the *thermodynamic overpotential η_T*

Thermodynamic volcano plot



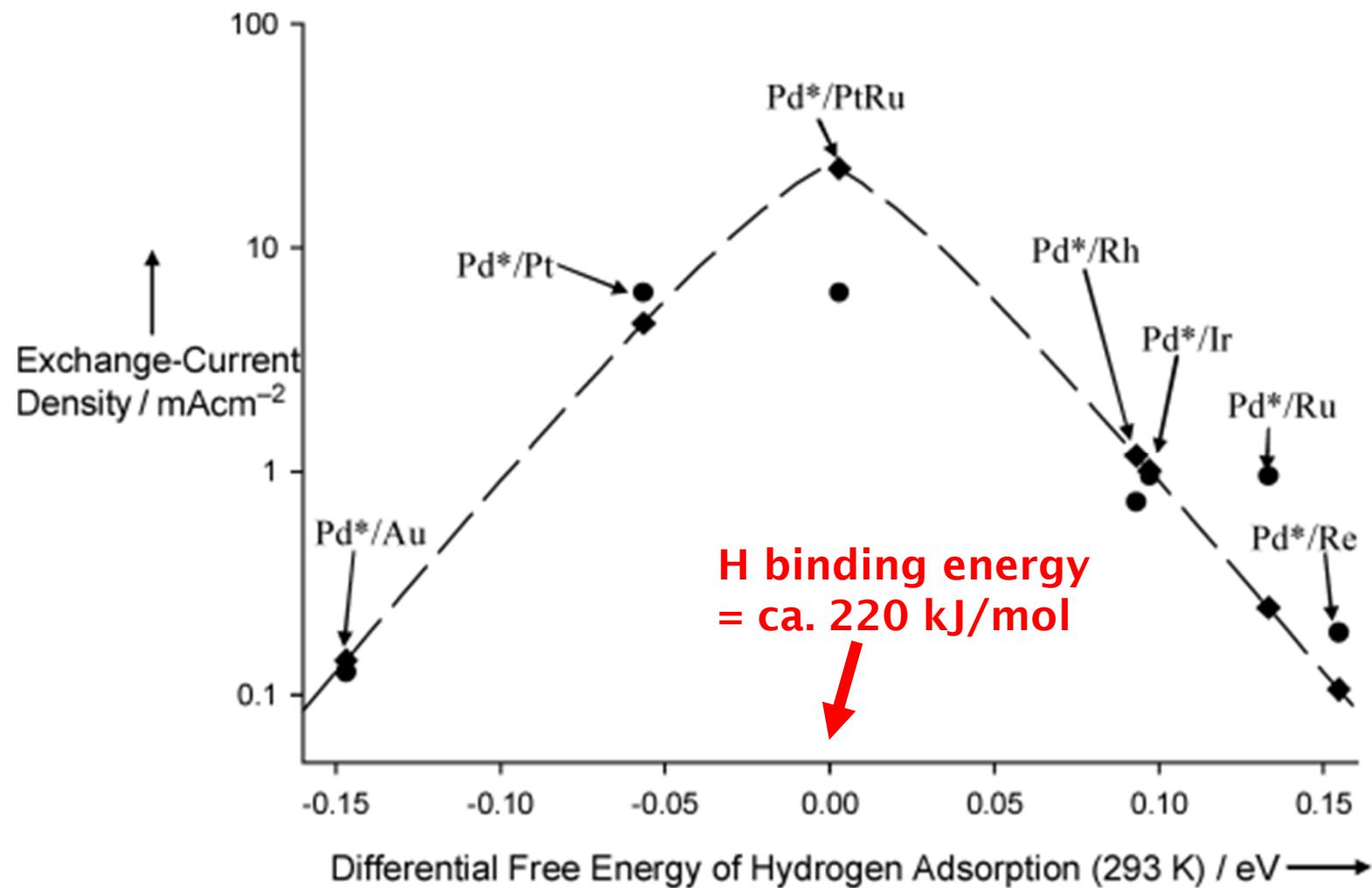
R.Parsons, Trans.Faraday Soc. (1958); H.Gerischer (1958)
J.K.Nørskov et al., J.Electrochem.Soc. (2004)

M.T.M.Koper, H.A.Heering, In Fuel Science Science
M.T.M.Koper, E.Bouwman, Angew.Chem.Int.Ed. (2010)

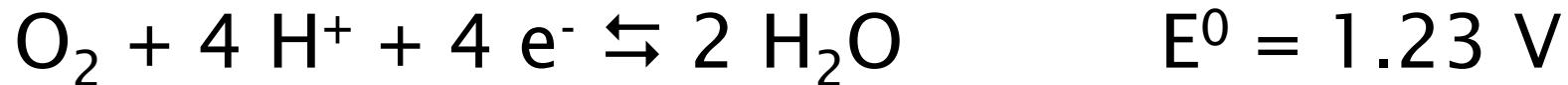
Side notes

- Can be generalized to other mechanisms
- The optimal electrocatalyst is achieved if each step is thermodynamically neutral: the H intermediate must bind to the catalyst with a bond strength equal to $\frac{1}{2} E(H-H)$
- Barriers are not included but if one believes in a relation between reaction energies and barriers (Bronsted-Evans-Polanyi) they are included implicitly
- Analysis works equally well for metal surfaces, molecular catalysts, and enzymes
- $\Delta G_{\text{ads}}(H)$ can be calculated from DFT

Experimental volcano for H₂ evolution



More than 2 electron transfers



The optimal catalyst

$$\Delta G(\text{OH}_{\text{ads}}) = C_O = 1.23 \text{ eV}$$

$$\Delta G(\text{O}_{\text{ads}}) = 2 \times C_O = 2.46 \text{ eV}$$

$$\Delta G(\text{OOH}_{\text{ads}}) = 3 \times C_O = 3.69 \text{ eV}$$

$$\Delta G(\text{O}_2) = 4 \times C_O = 4.92 \text{ eV}$$

Independent of the mechanism

However: scaling relationships

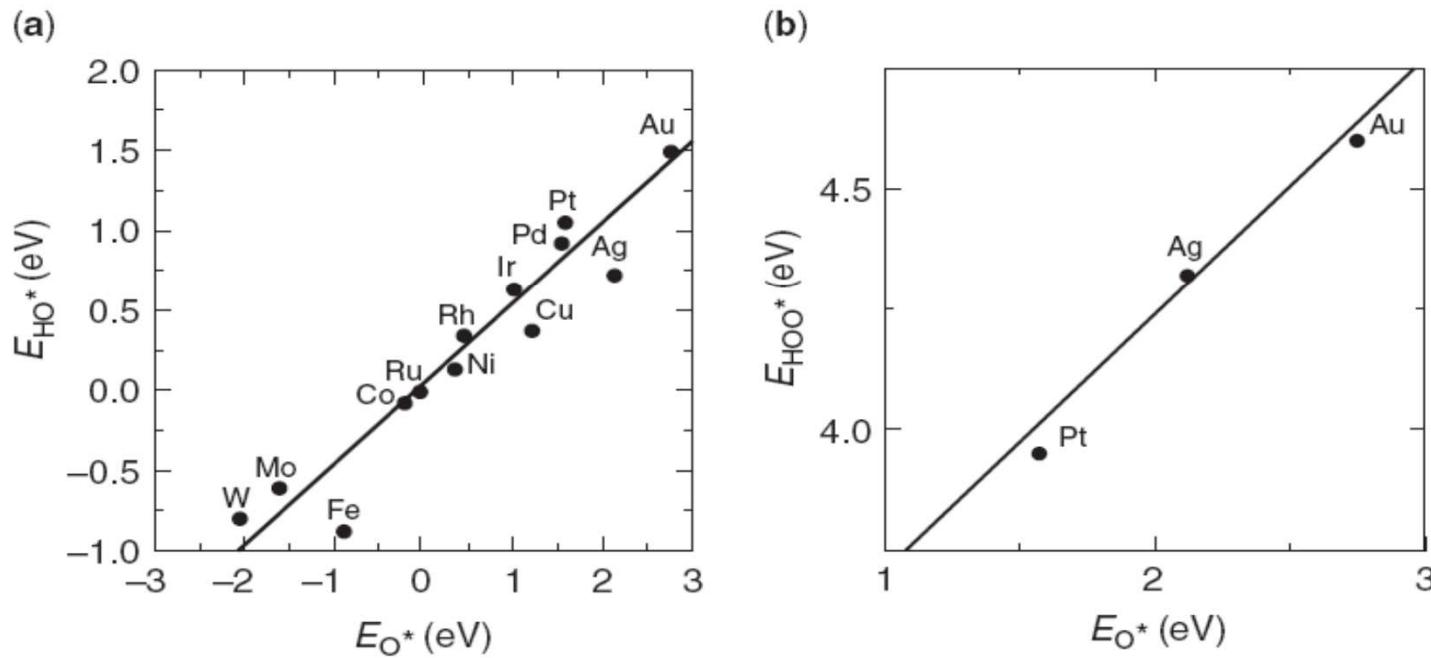


Figure 3.7 (a) Adsorption energy of HO* as function of the adsorption energy of O*, both on the terrace. The best linear fit is $E_{HO^*} = 0.50E_{O^*} + 0.05$ eV. (b) Adsorption energy of HOO* as function of the adsorption energy of O*, both on the terrace. The best linear fit is $E_{HOO^*} = 0.53E_{O^*} + 3.18$ eV.

For (111) metal surfaces

F. Abild-Petersen, J. Greeley, F. Studt, P.G. Moses, J. Rossmeisl, T. Munter, T. Bligaard, J.K. Nørskov,
Phys. Rev. Lett. 99 (2007) 016105

F. Calle-Vallejo, J.I. Martinez, J.M. Garcia-Lastra, J. Rossmeisl, M.T.M. Koper, Phys. Rev. Lett. 108 (2012) 116103

The optimal scaling relations

$$\Delta G(\text{OH}_{\text{ads}}) (\approx 0.50 \times \Delta G(\text{O}_{\text{ads}}) + 0.05 \text{ eV})$$

$$= 0.5 \times \Delta G(\text{O}_{\text{ads}}) + K_{\text{OH}}$$

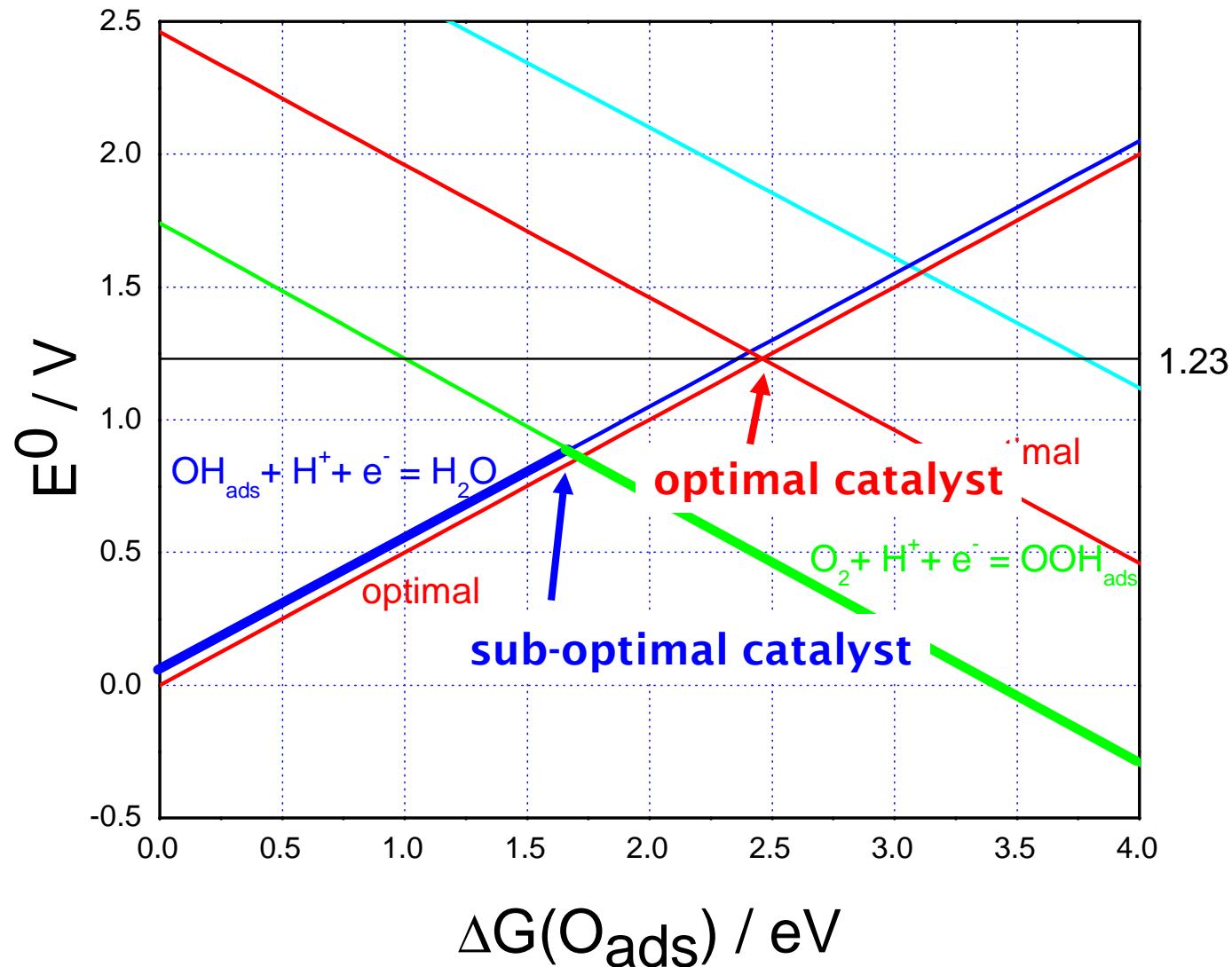
$$\Delta G(\text{OOH}_{\text{ads}}) (\approx 0.53 \times \Delta G(\text{O}_{\text{ads}}) + 3.18 \text{ eV})$$

$$= 0.5 \times \Delta G(\text{O}_{\text{ads}}) + K_{\text{OOH}}$$

$$K_{\text{OH}} = 0 \text{ eV}$$

$$K_{\text{OOH}} = 2.46 \text{ eV}$$

The optimal volcano



Does optimal scaling exist?

Metals:

$$\Delta G(\text{OH}_{\text{ads}}) \approx 0.50 \times \Delta G(\text{O}_{\text{ads}}) + 0.05 \text{ eV}$$

$$\Delta G(\text{OOH}_{\text{ads}}) \approx 0.53 \times \Delta G(\text{O}_{\text{ads}}) + 3.18 \text{ eV}$$

Oxides:

$$\Delta G(\text{OH}_{\text{ads}}) \approx 0.61 \times \Delta G(\text{O}_{\text{ads}}) - 0.90 \text{ eV}$$

$$\Delta G(\text{OOH}_{\text{ads}}) \approx 0.64 \times \Delta G(\text{O}_{\text{ads}}) + 2.03 \text{ eV}$$

$$K_{\text{OOH}} - K_{\text{OH}} = 3.13 \text{ eV}, 2.93 \text{ eV}; \text{Optimal} = 2.46 \text{ eV}$$

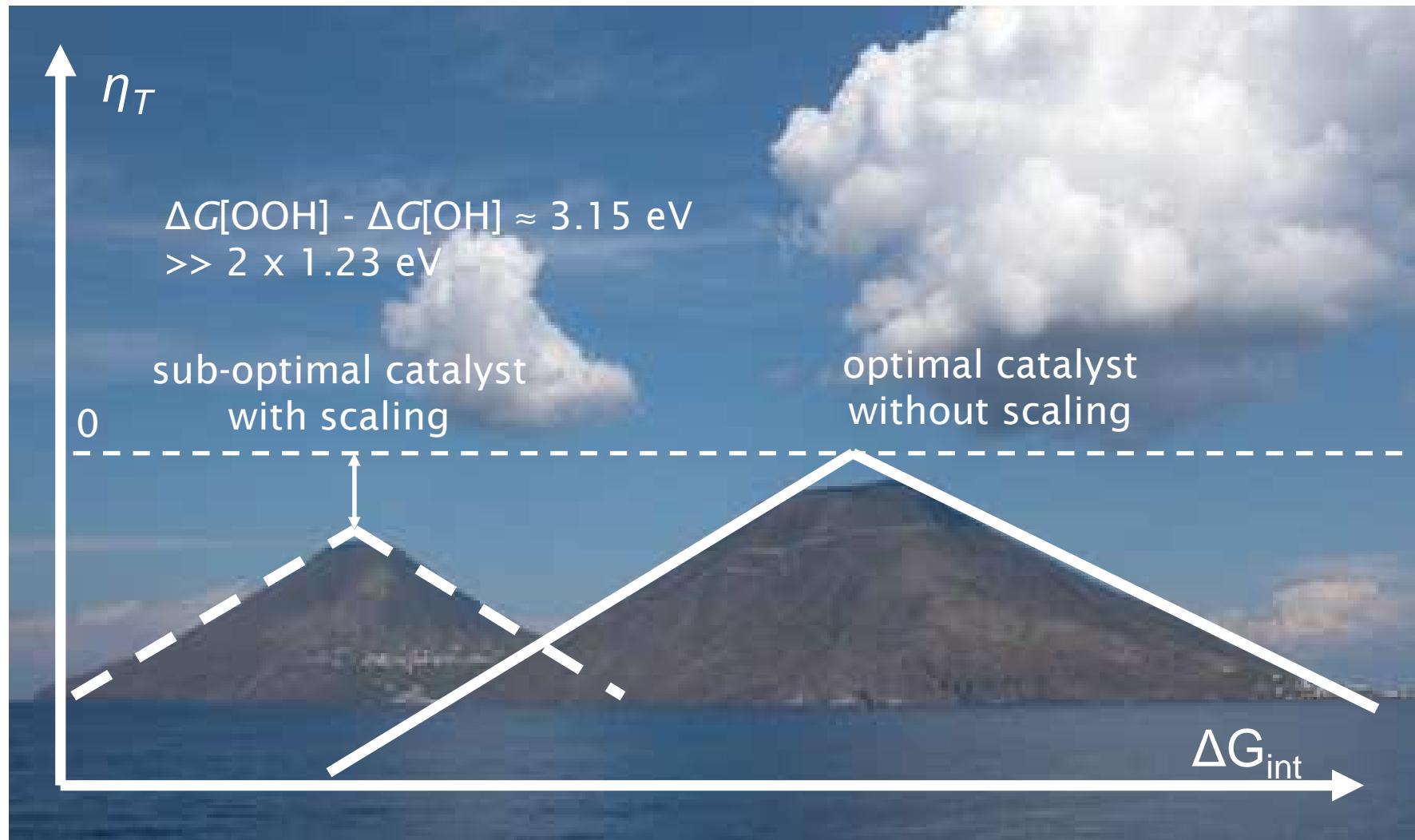
“Fundamental” overpotential?

$$\eta_T(\text{ORR,OER}) = \frac{\sim 3.15 \text{ eV}}{2 \text{ e}} = \frac{K_{\text{OOH}} - K_{\text{OH}} - 2.46 \text{ eV}}{2 \text{ e}} = \sim 0.35 \text{ V}$$

One does not even need to know the catalyst-oxygen interaction...

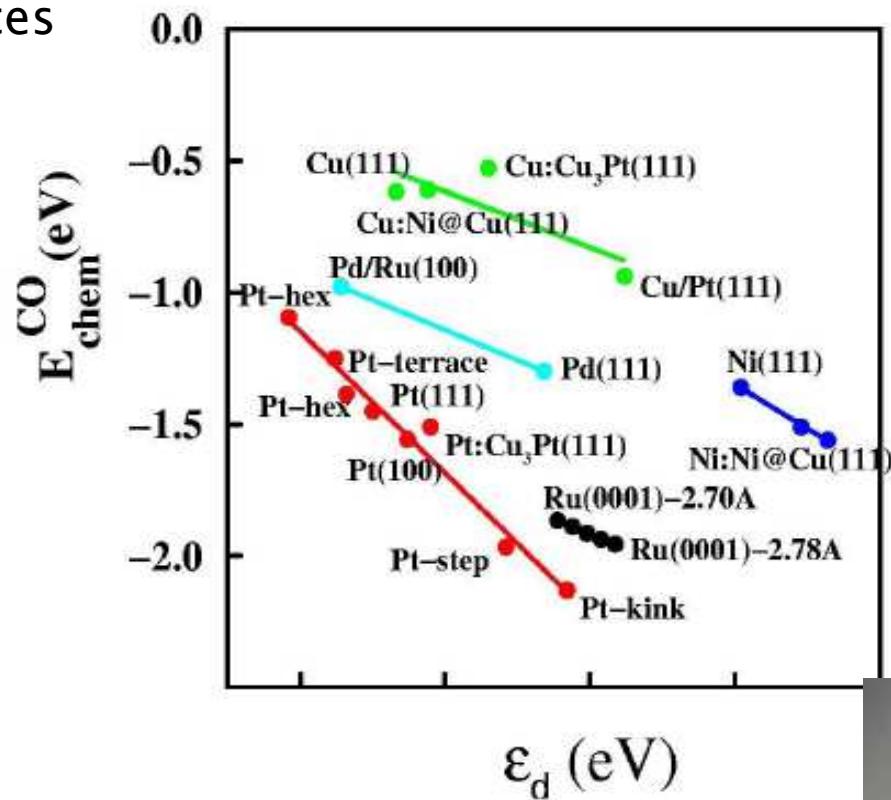
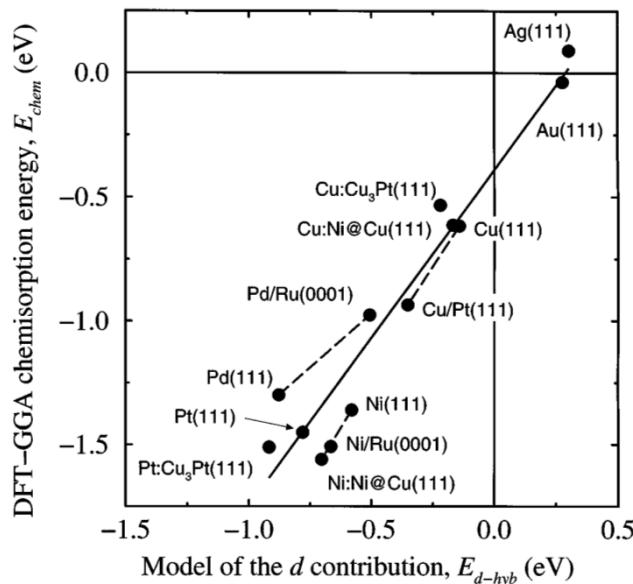
$$\Delta G[\text{HO}_2^-(\text{aq})] - \Delta G[\text{OH}^-(\text{aq})] = 3.4 \text{ eV}$$

Volcano plot for >2 ET reaction



Hammer-Nørskov *d-band* model

CO binding energy to surfaces



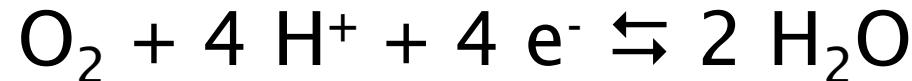
Binding energy of atoms and molecules to a metal surface is strongly influenced by the location of the energy of (the center of) the *d* band.
Higher *d* band: stronger binding



How to vary the *d* band?

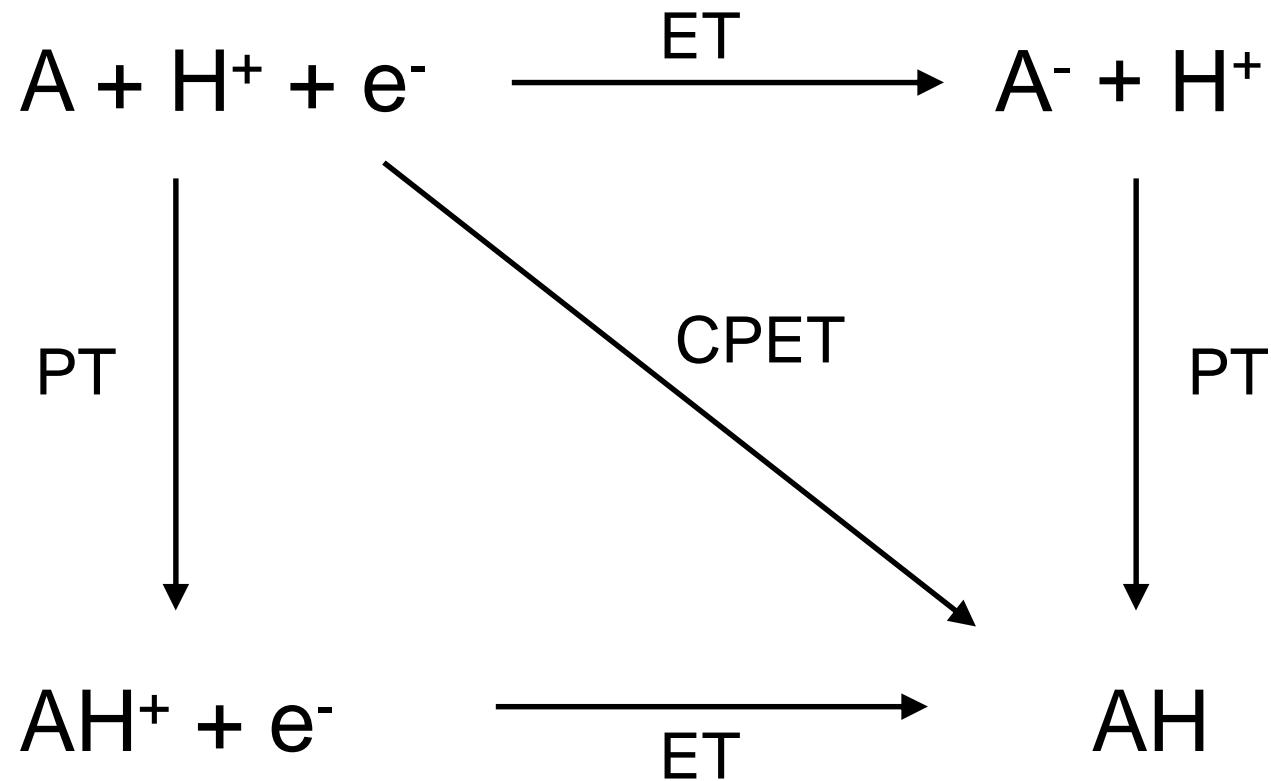
- By varying the chemical composition of the catalyst (transition metal elements to the upper left in the PT have a higher *d* band)
- By varying the structure of the catalyst (surface sites with a low coordination have a higher *d* band, they often are the active sites!)
- By varying the surface potential (electronic promoting, electrode potential)

Proton-coupled electron transfer



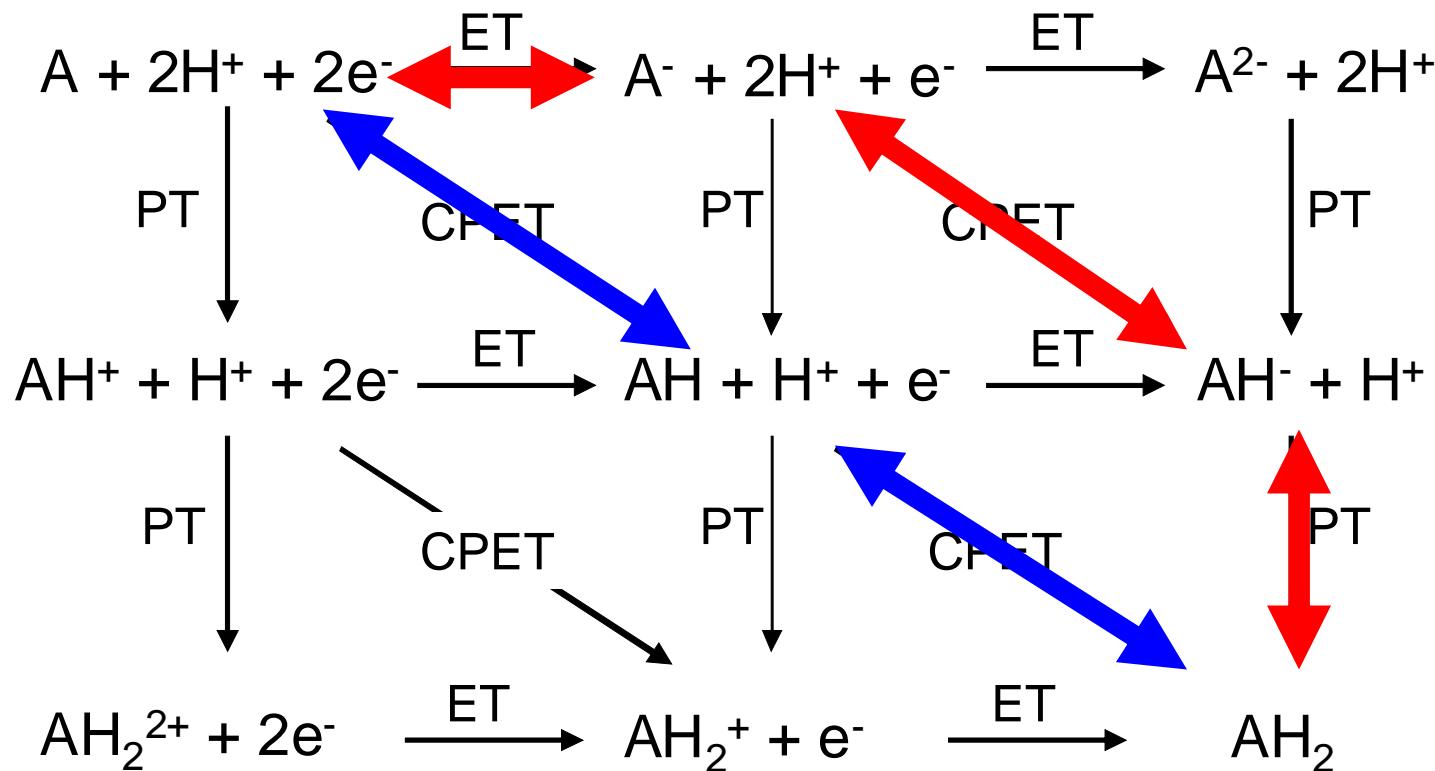
- Are proton and electron transfer always coupled?
- How does (de-)coupled proton-electron transfer manifest?

Proton-coupled electron transfer

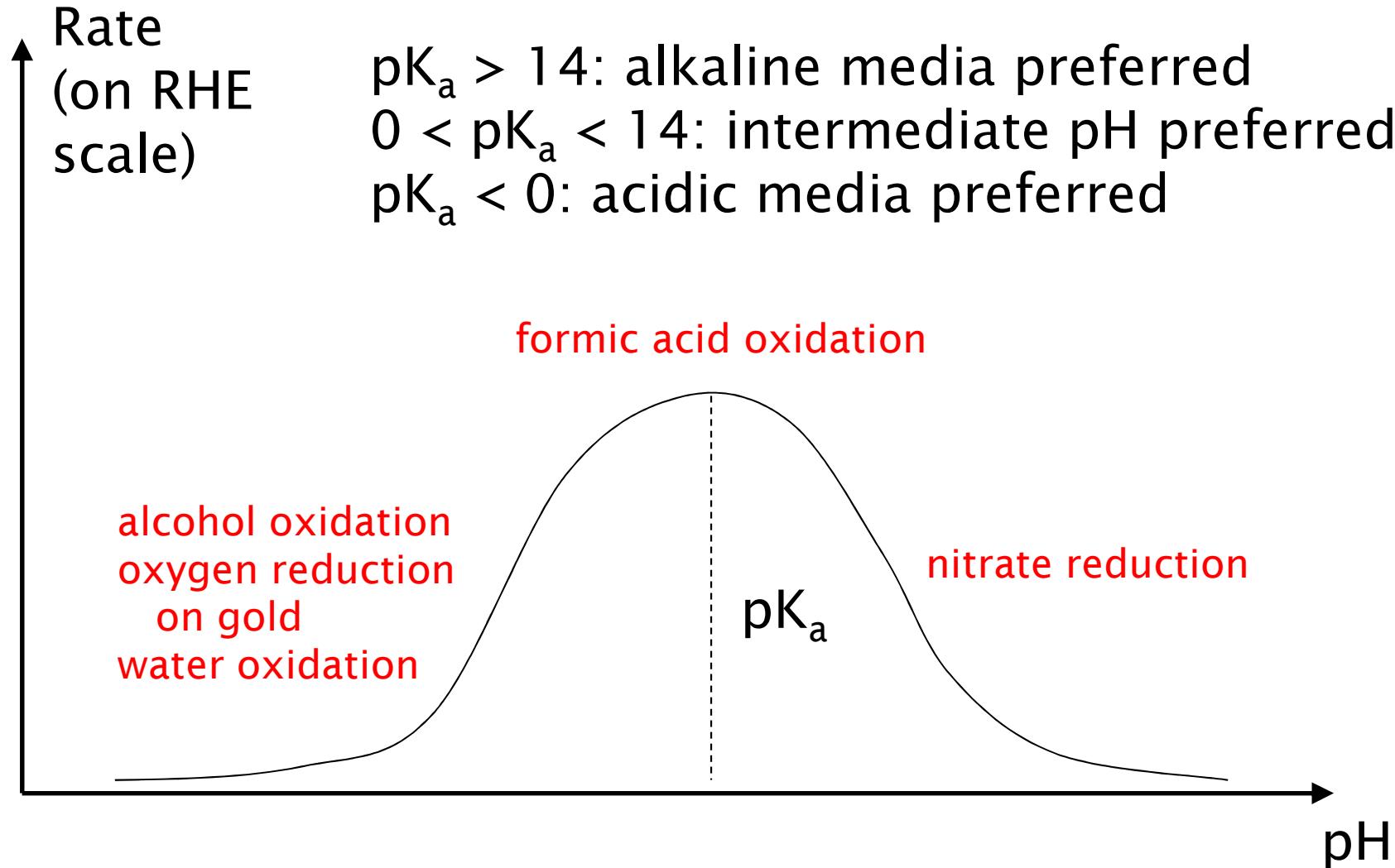


S. Hammes-Schiffer, A.A.Stuchebrukhov, *Chem.Rev.* 110 (2010) 6939
M.T.M.Koper, *Phys.Chem.Chem.Phys.* 15 (2013) 1399

Proton-coupled electron transfer



pH dependence of decoupled PCET

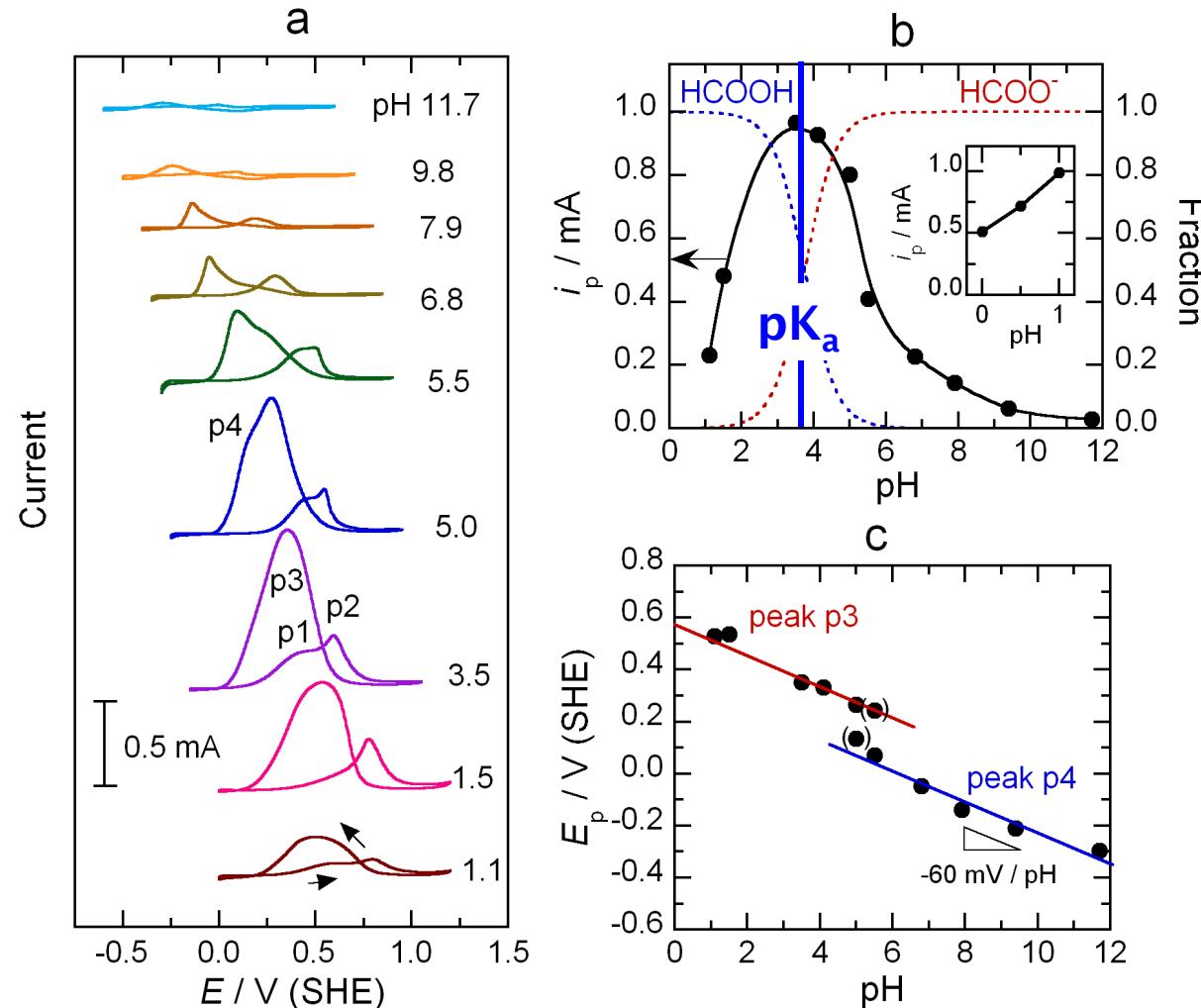


M.T.M.Koper, *Chem.Sci.* 4 (2013) 2710; *Top.Catal.* 58 (2015) 1153

J.Yang, P.Sebastian, M.Duca, T.Hoogenboom, M.T.M.Koper, *Chem.Comm.* 50 (2014) 2148

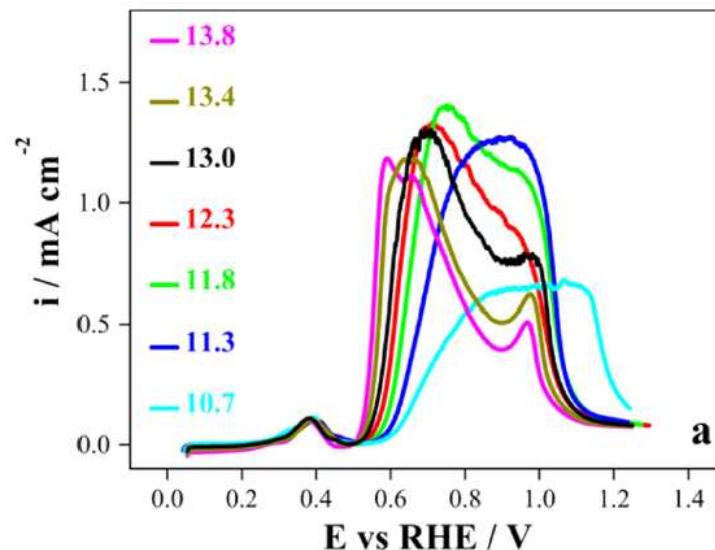
Y.Kwon, S.C.S.Lai, P.Rodriguez, M.T.M.Koper, *J.Am.Chem.Soc.* 133 (2011) 6914

Formic acid oxidation on Pt

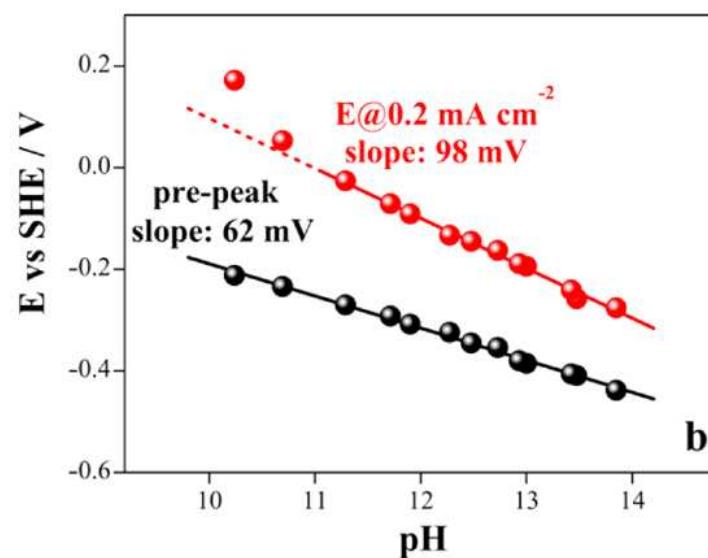


Formic acid oxidation prefers intermediate pH

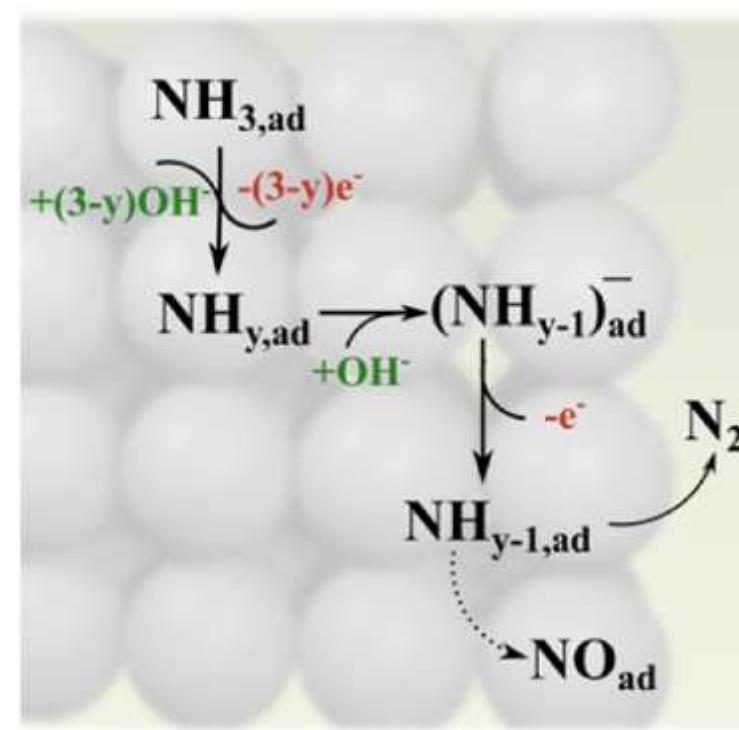
PCET of NH₃ oxidation on Pt(100)



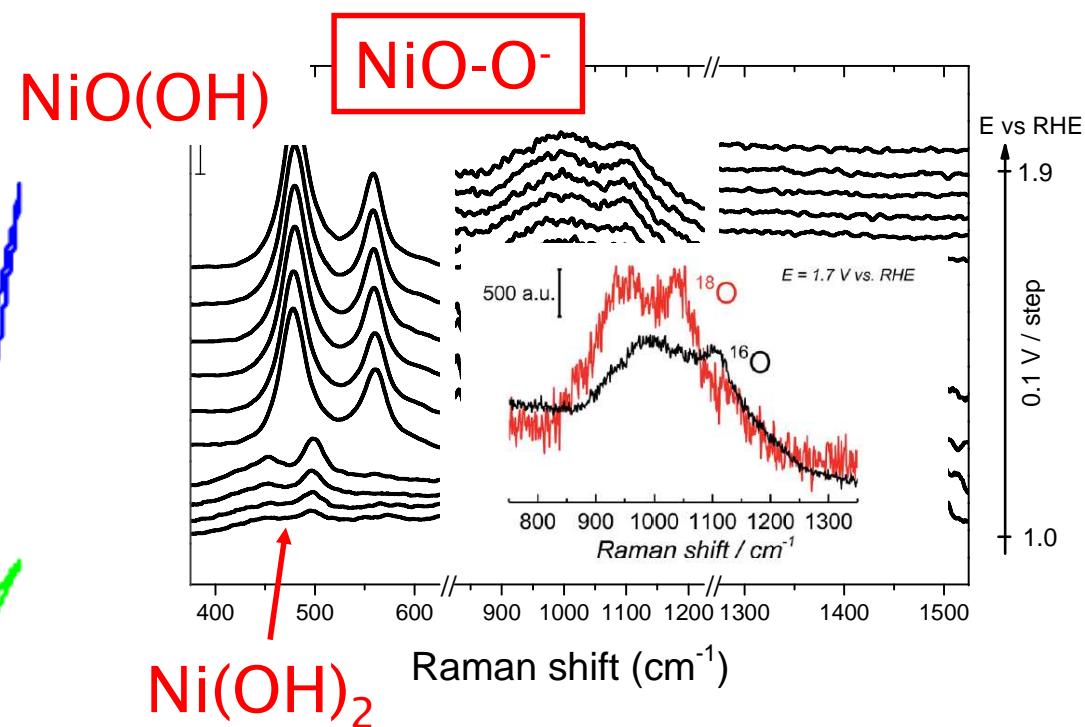
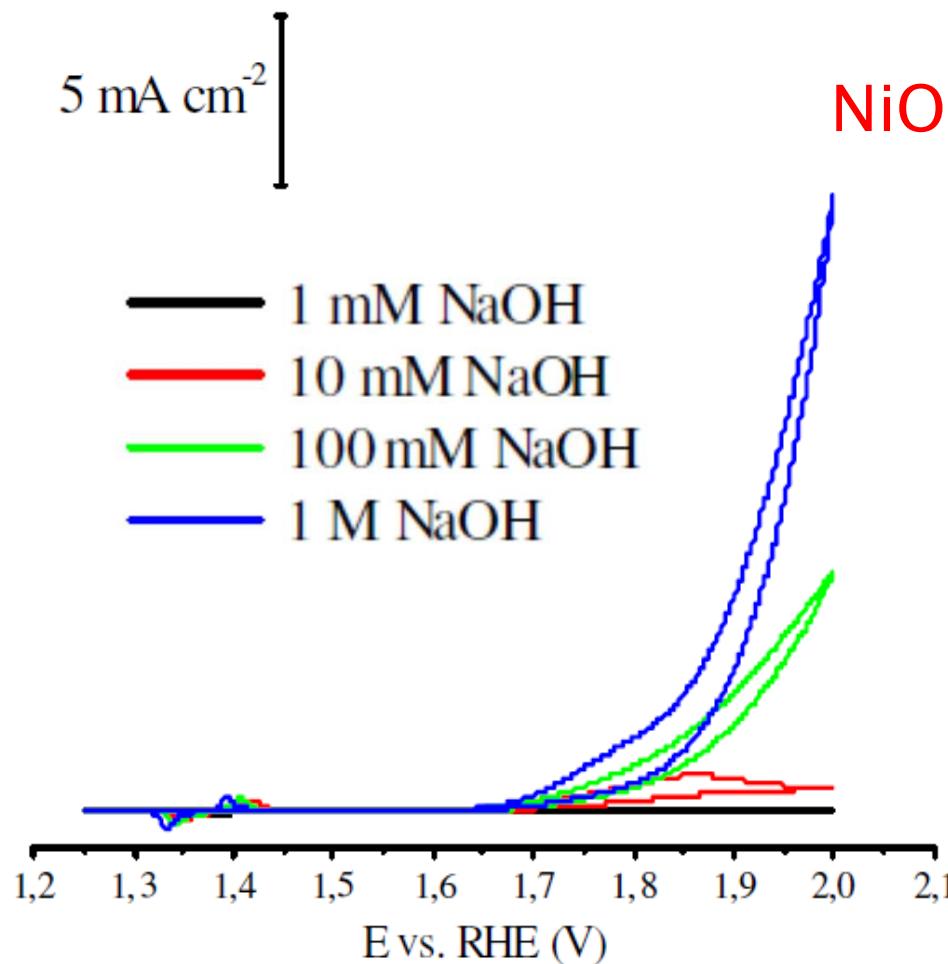
a



b



pH dependence of OER on NiOOH



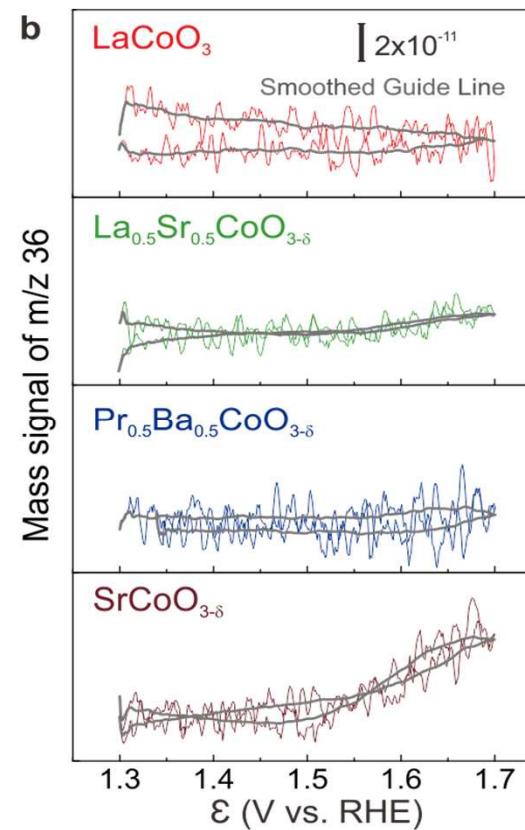
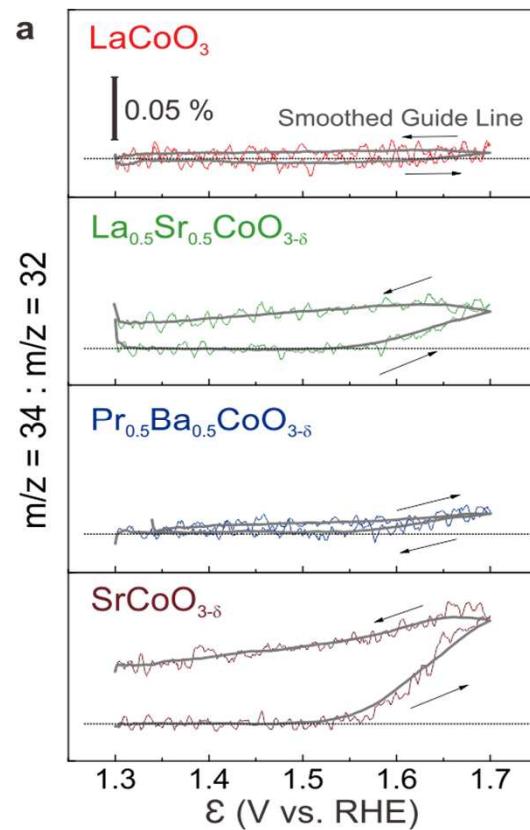
Formation of deprotonated surface (per)oxide

O.Diaz-Morales, D.Ferrus-Suspendra, M.T.M.Koper, Chem.Sci. 7 (2016) 2639

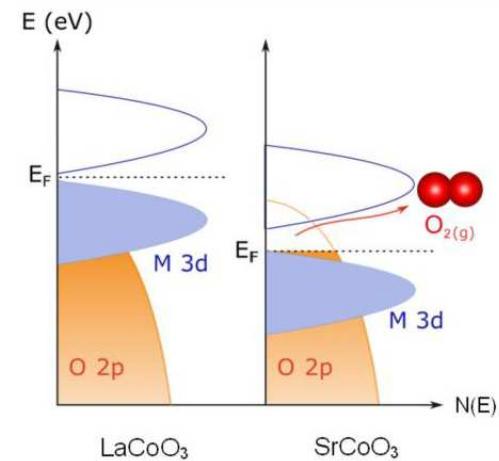
B.J. Trześniewski, O.Diaz-Morales, D.Vermaas, O.Longo, W.Bras, M.T.M.Koper, W.Smith, J.Am.Chem.Soc.137 (2015) 15112

Oxygen exchange in OER on Co-based perovskites

O_2 formation from ^{18}O -labeled oxides followed by online MS



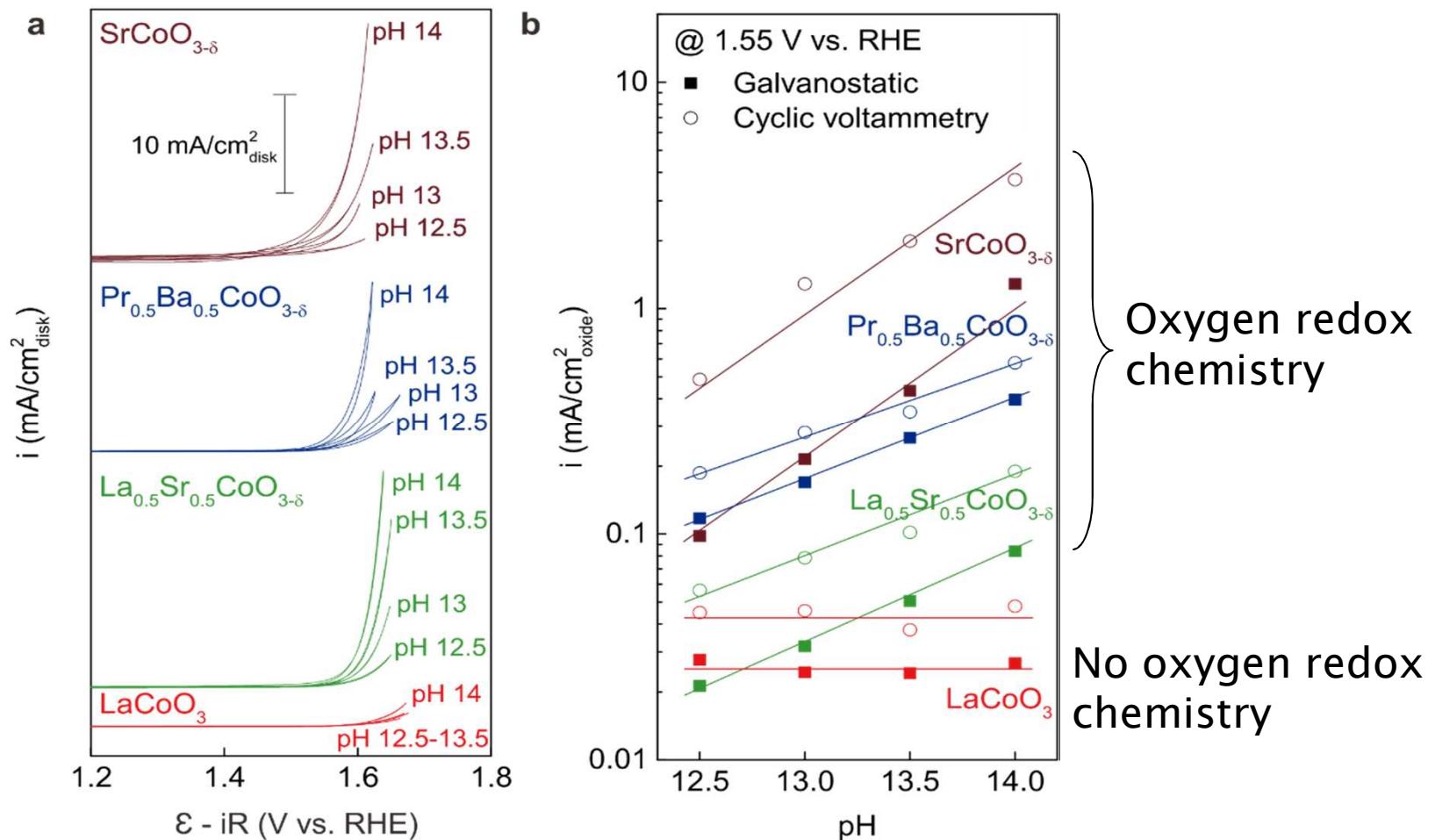
low O 2p band



high O 2p band,
close to Fermi level

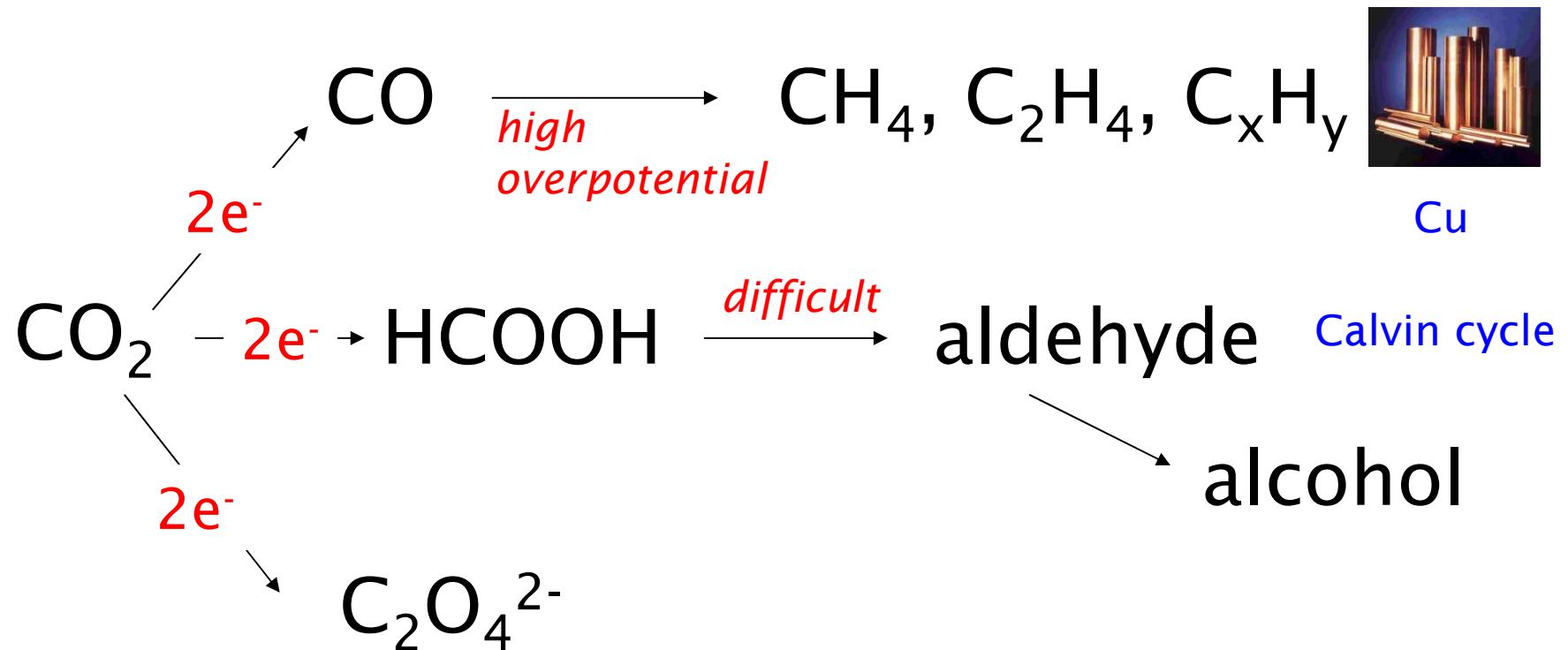
High O 2p band leads to oxygen redox chemistry and oxygen exchange during OER

pH dependent OER on Co-based perovskites



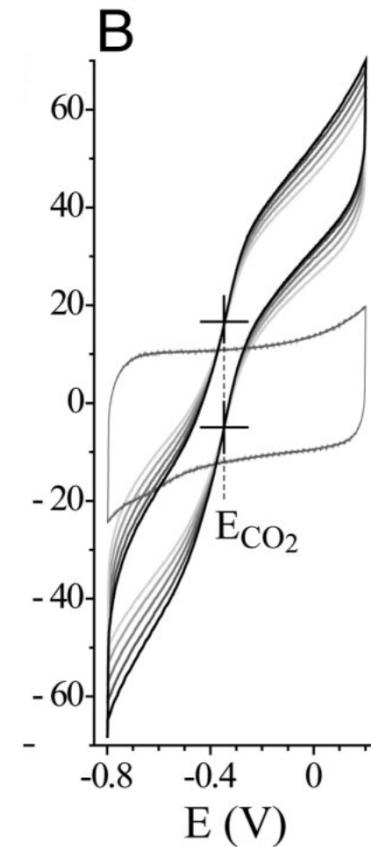
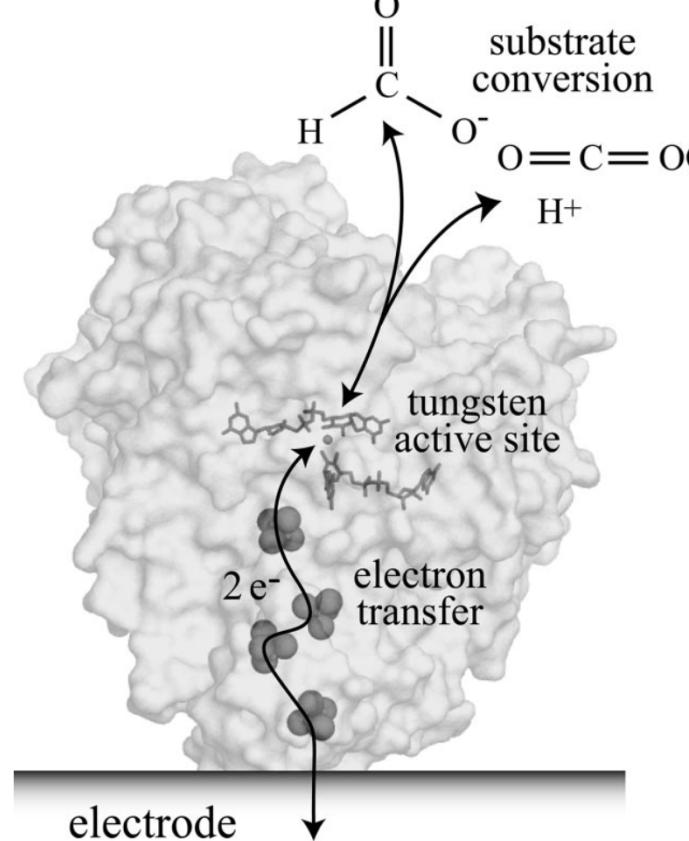
Oxygen redox chemistry leads to charged surface oxides

Electrocatalytic CO₂ reduction

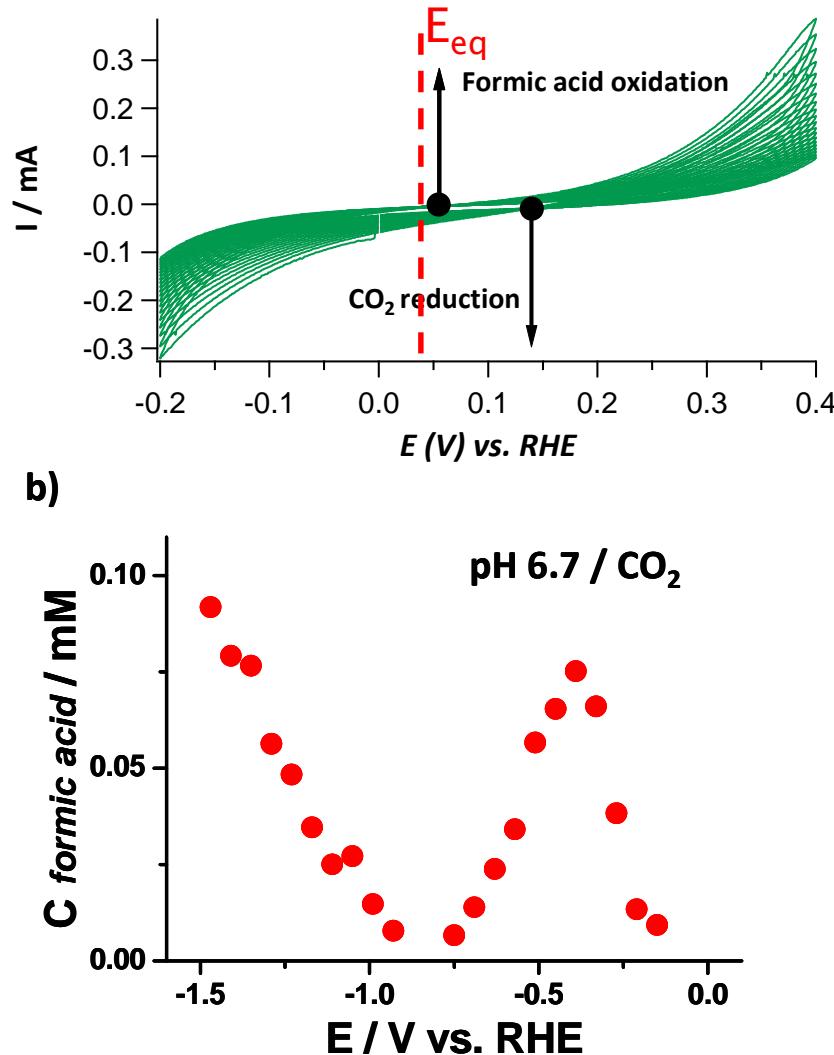


Reversibility is possible

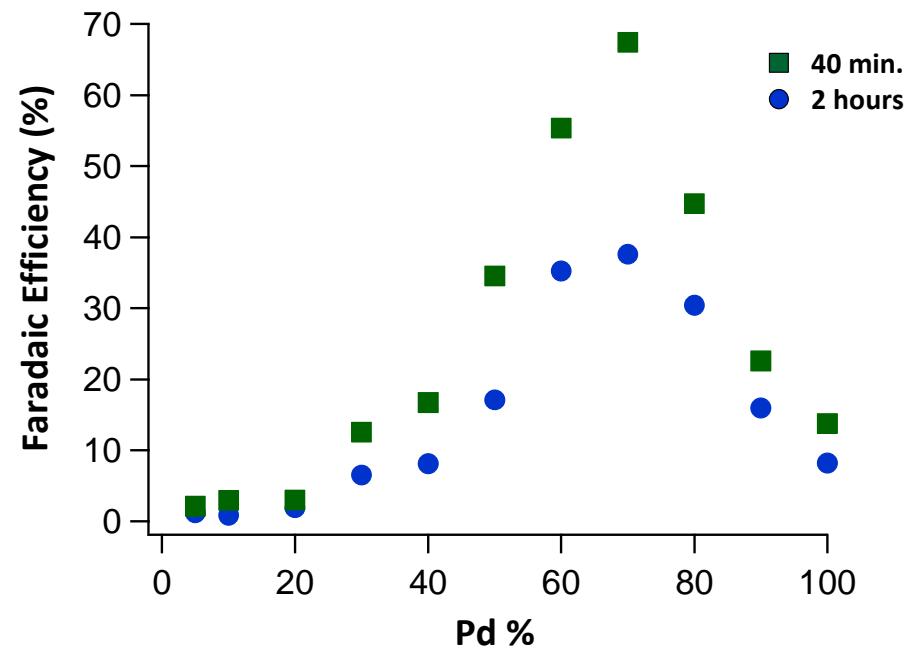
Reversible interconversion of carbon dioxide and formate by an electroactive enzyme.



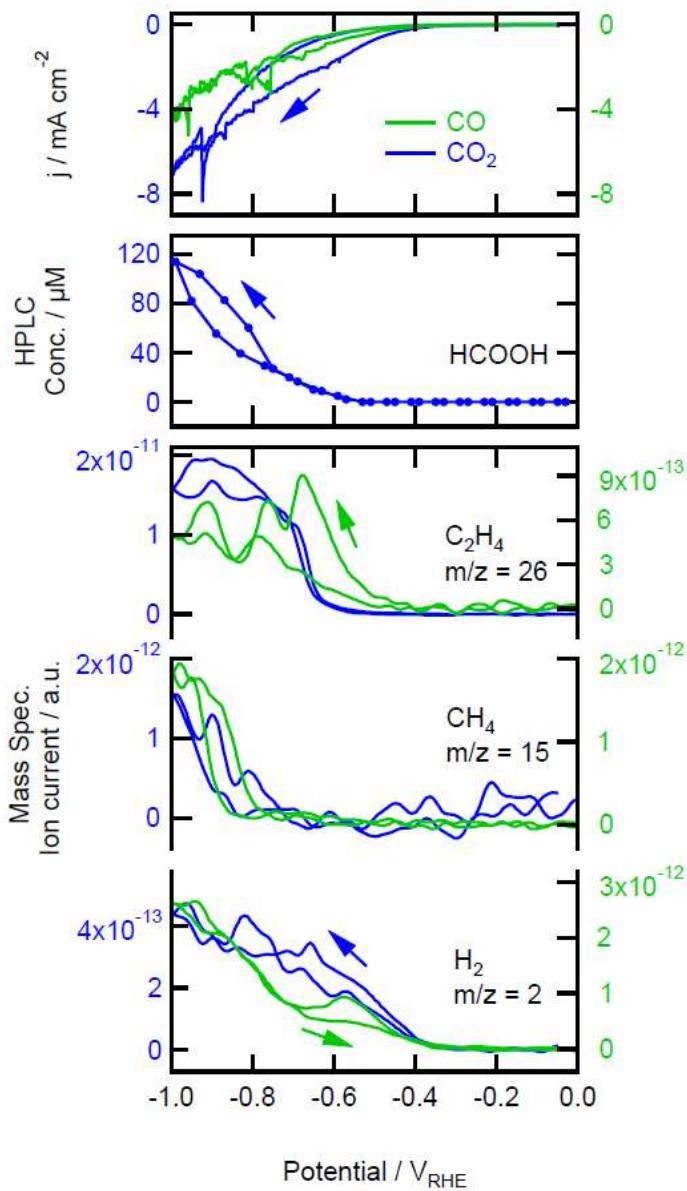
$\text{CO}_2/\text{HCO}_3^-$ reduction to formic acid



CO_2 and bicarbonate reduction
on a Pd-Pt formic acid
oxidation catalyst

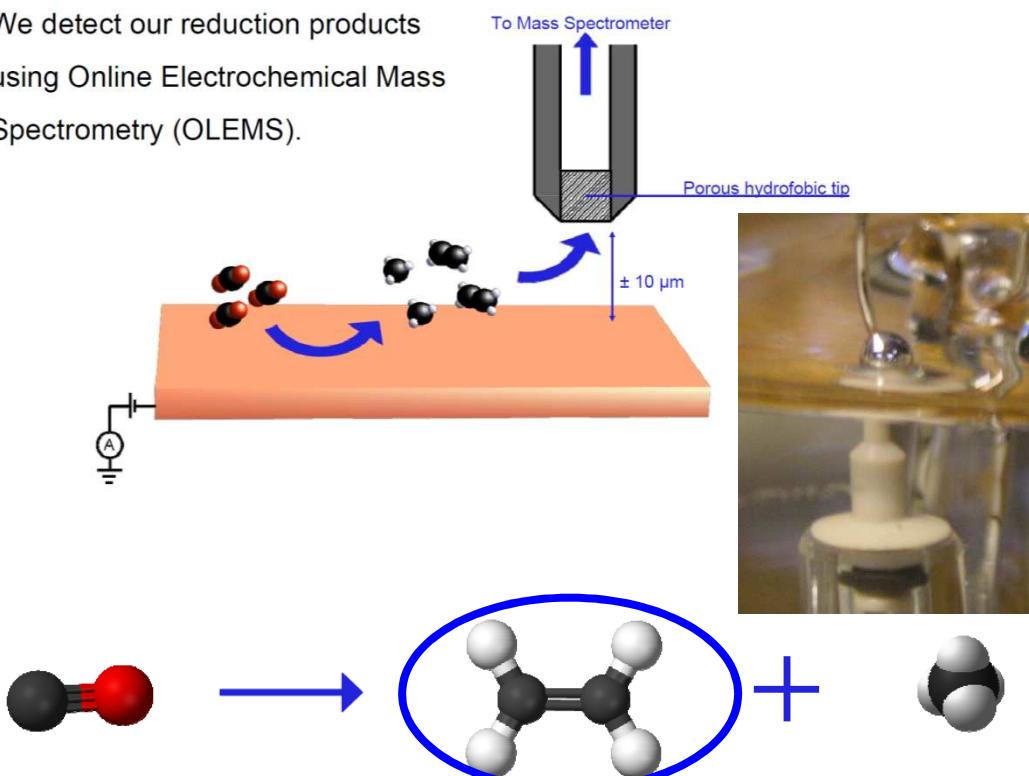


CO and CO₂ reduction on copper

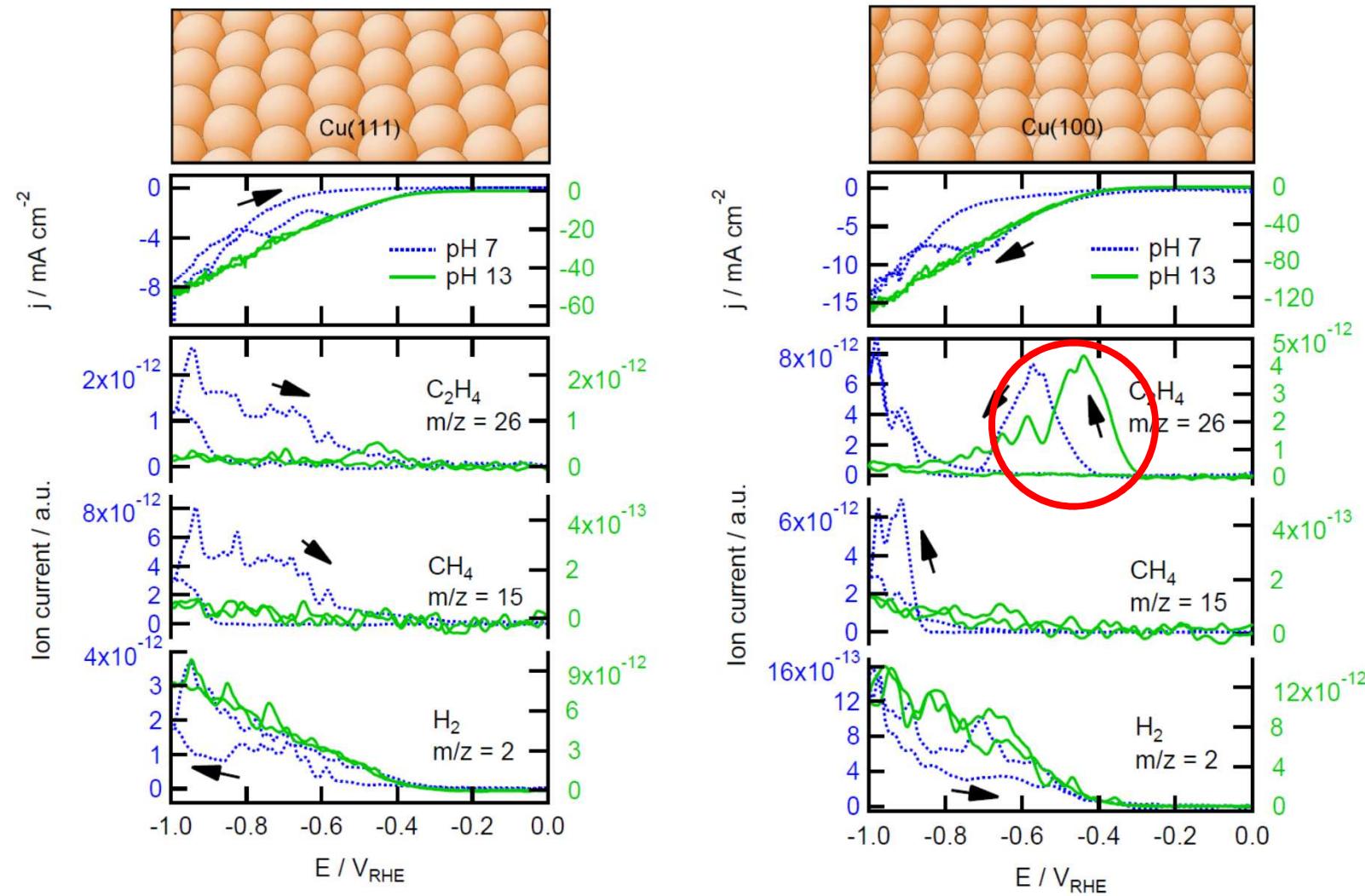


CO₂ and CO reduction on copper electrodes produces H₂, HCOOH, CH₄ and C₂H₄.

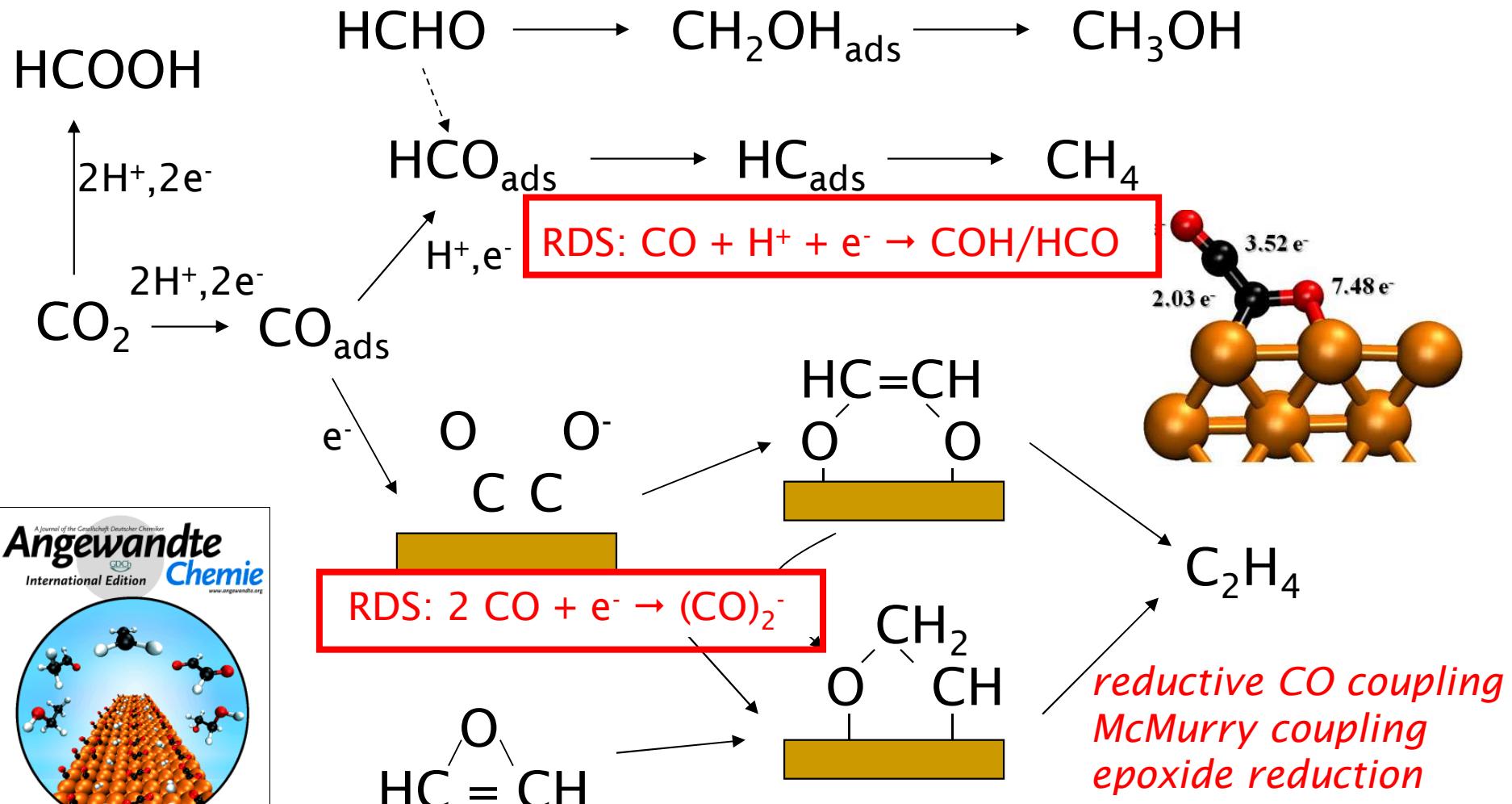
We detect our reduction products using Online Electrochemical Mass Spectrometry (OLEMS).



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



A consistent mechanism

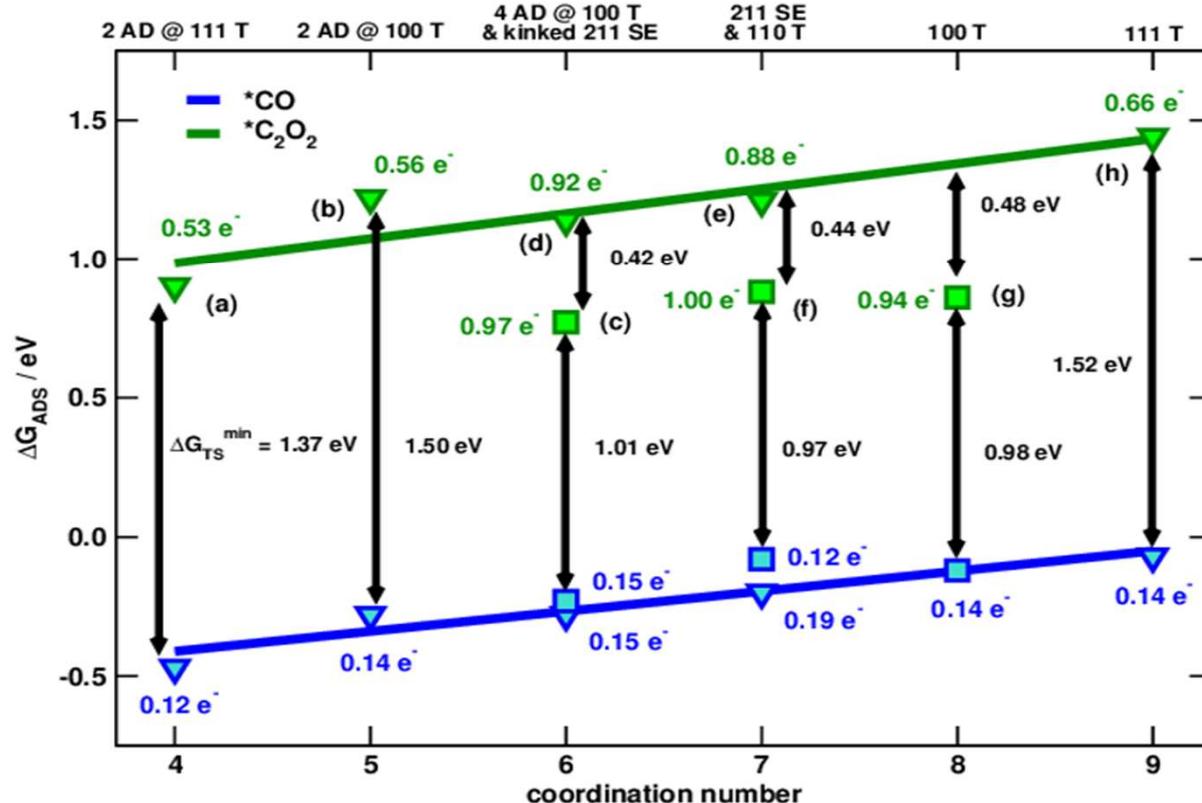
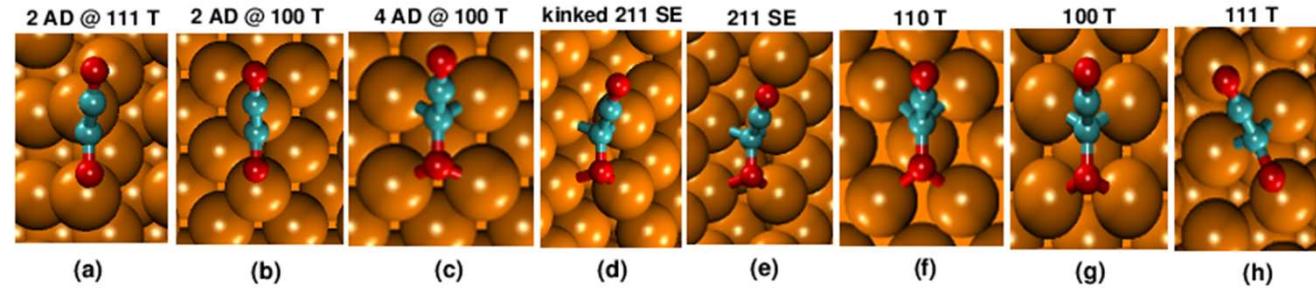


K.J.P.Schouten, Y.Kwon, C.J.M.van der Ham, Z.Qin, M.T.M.Koper, *Chem.Sci.* 2 (2011) 1902

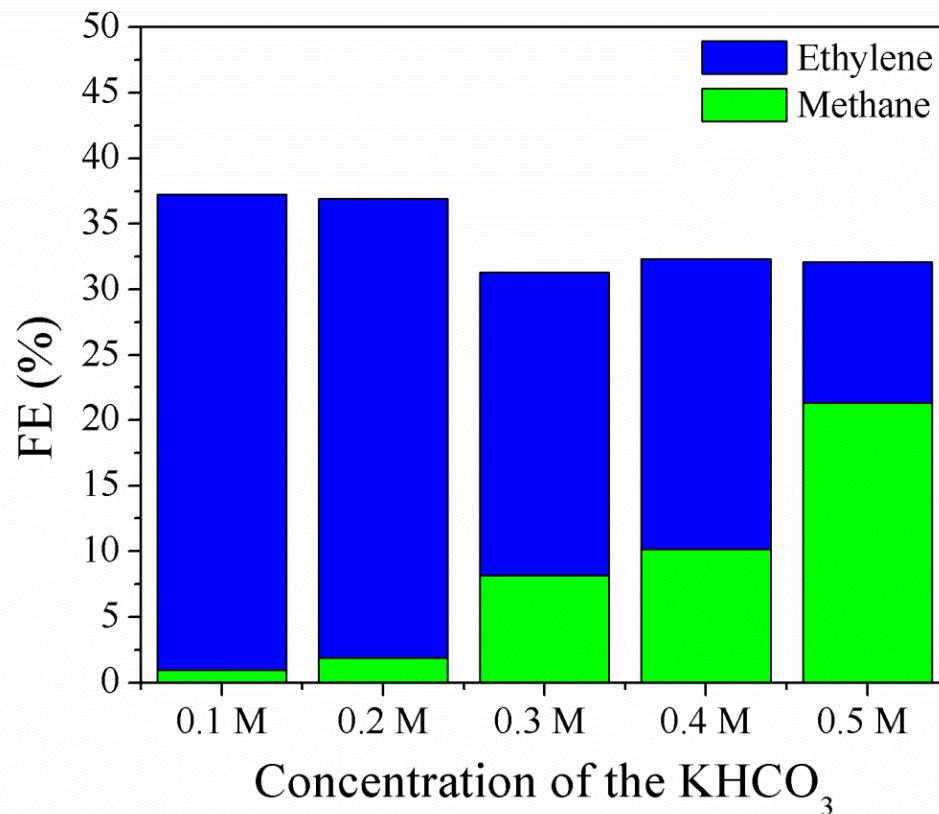
F.Calle Vallejo, M.T.M.Koper, *Angew.Chem.Int.Ed.* 52 (2013) 7282

R.Kortlever, J.Shen, K.J.P.Schouten, F.Calle-Vallejo, M.T.M.Koper, *J.Phys.Chem.Lett.* 6 (2015) 4073

(CO)₂ prefers Cu(100) sites



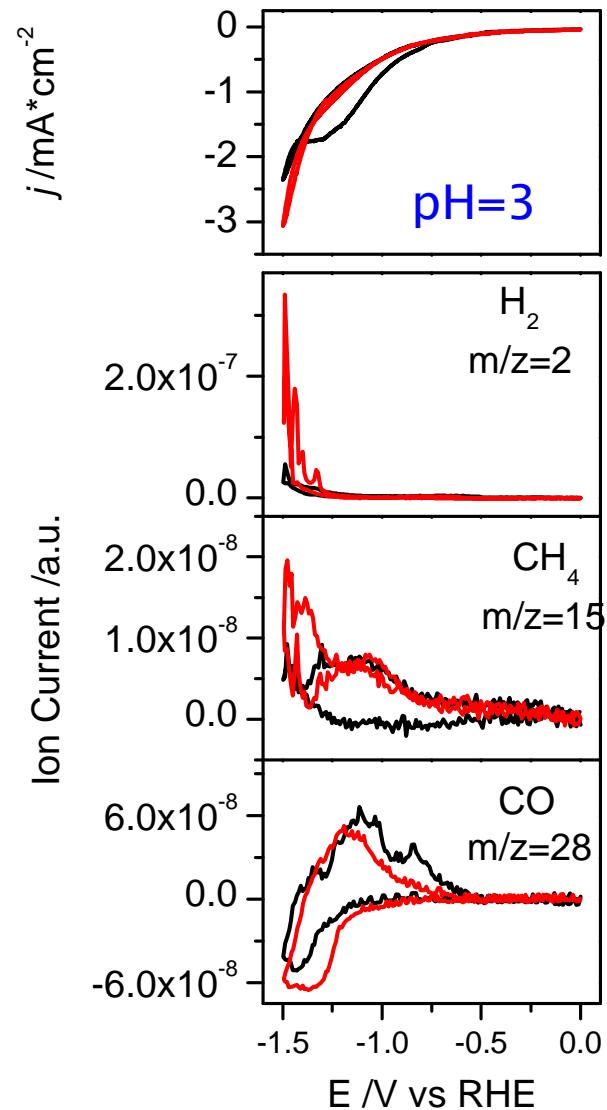
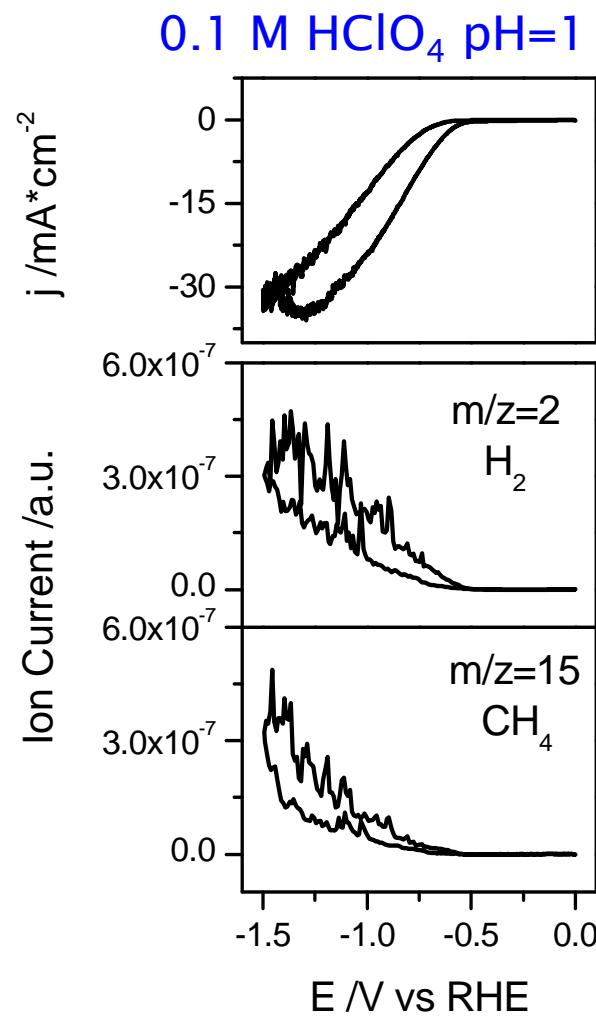
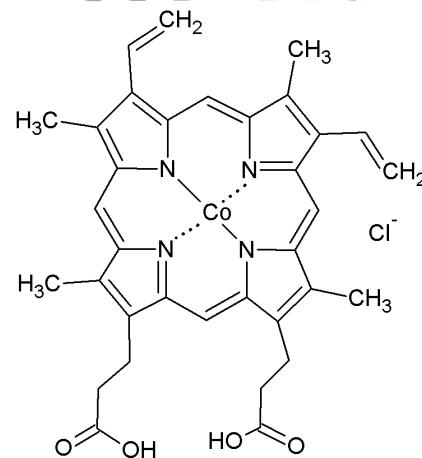
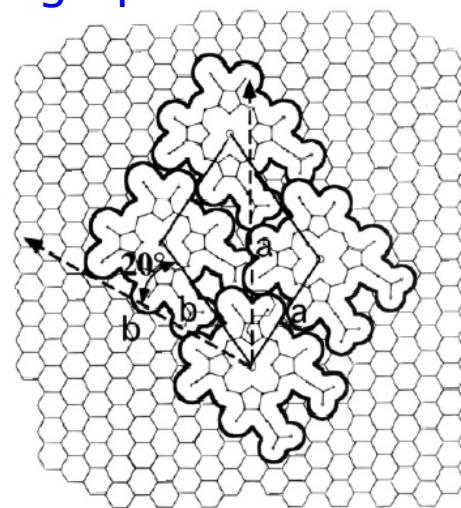
Steering selectivity to ethylene



Lowering buffering capacity leads to higher alkalinity near electrode surface

CO_2 reduction on Co-porphyrin

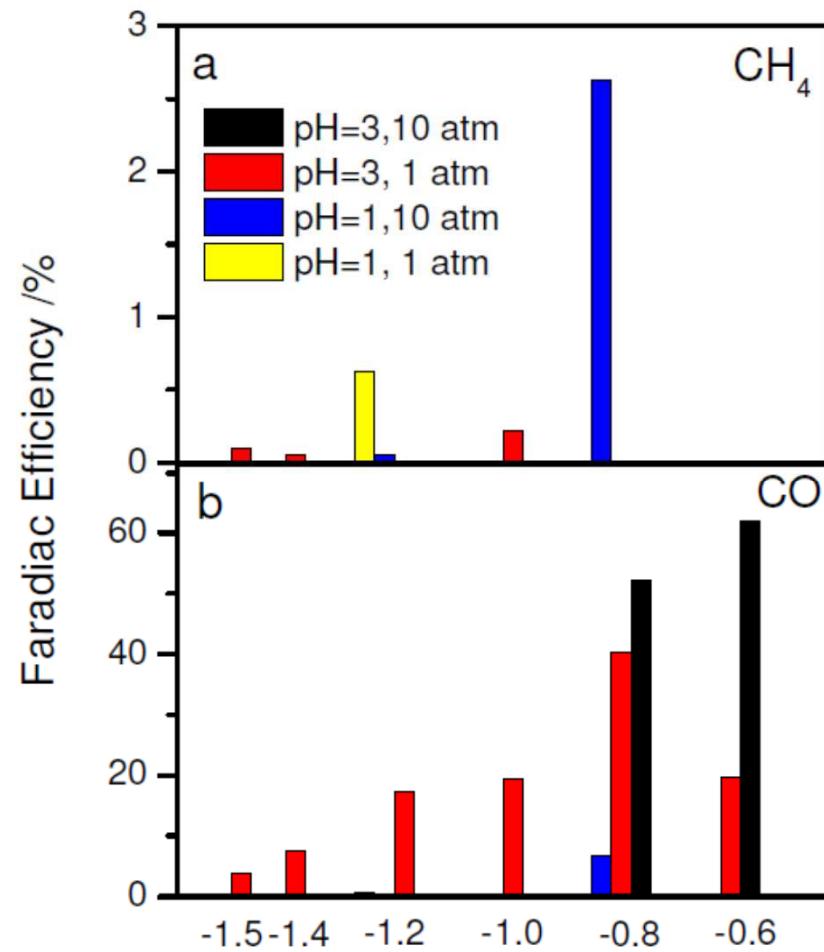
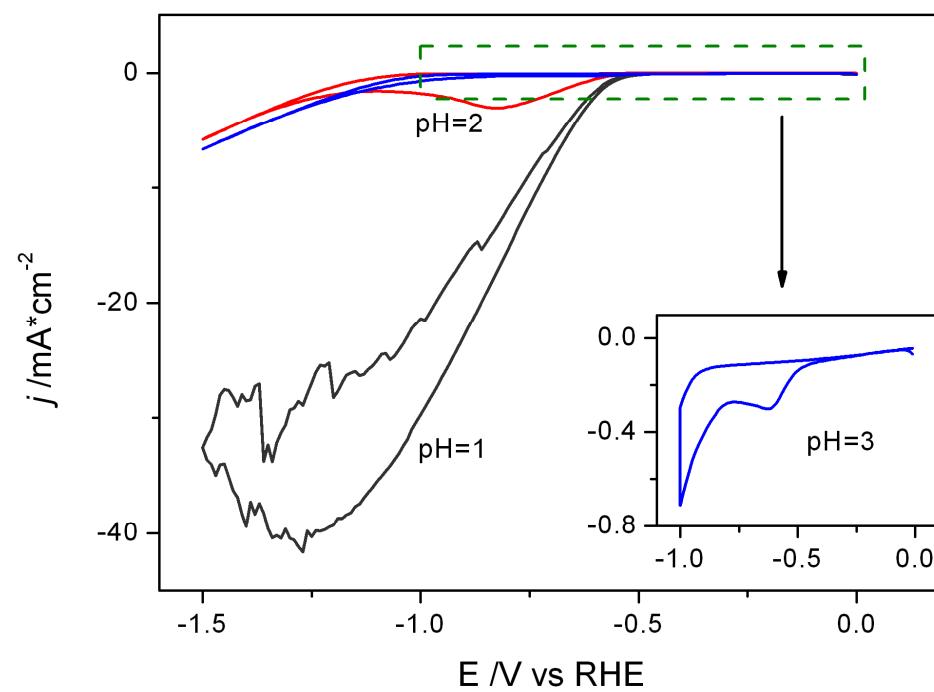
Co-protoporphyrine
on graphite electrode



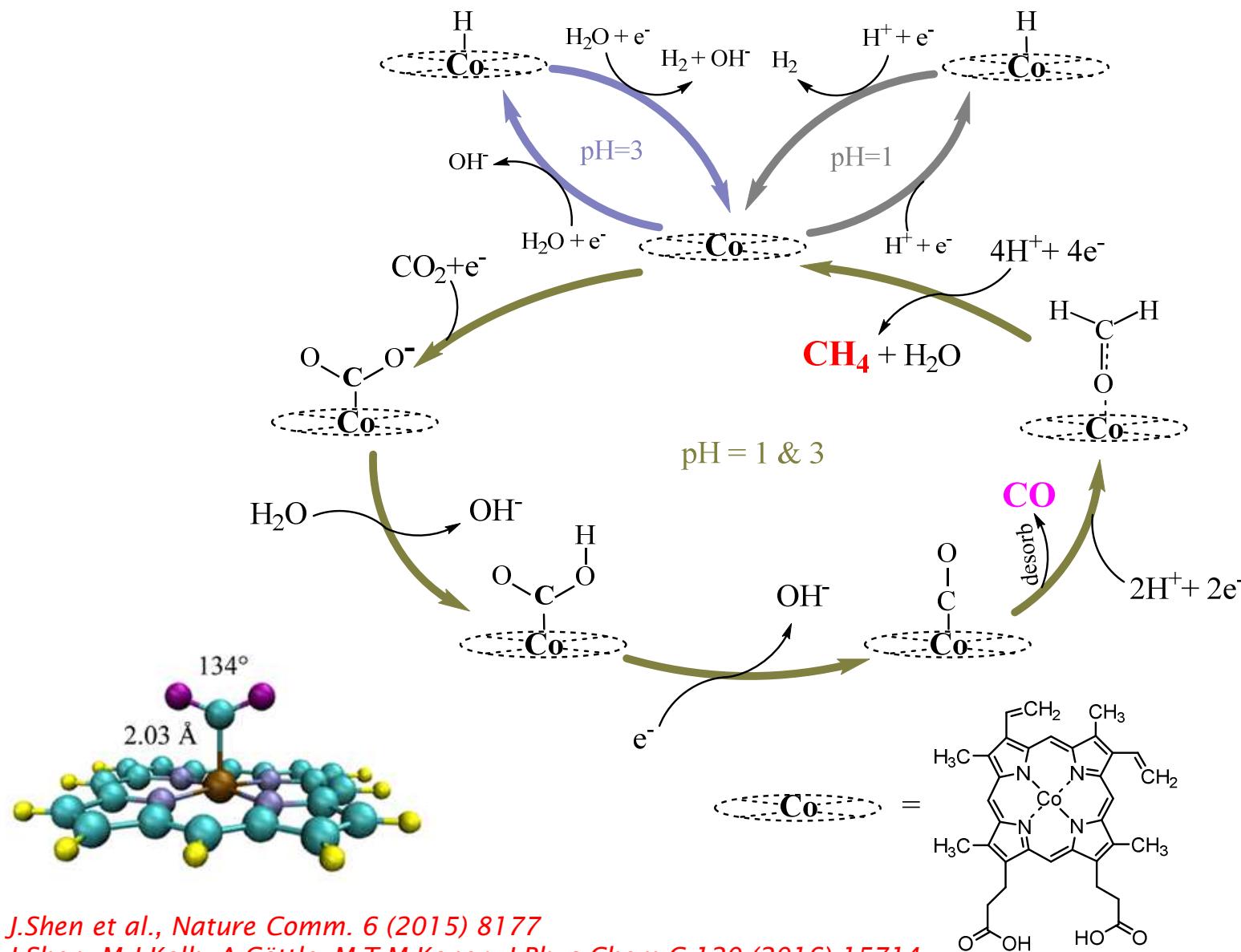
J.Shen, R.Kortlever, R.Kas, Y.Y.Birdja, O.Diaz-Morales, I.Ledezma-Yanez, Y.Kwon,
K.J.P.Schouten, G.Mul, M.T.M.Koper, Nature Comm. 6 (2015) 8177

pH dependent selectivity

pH dependent H₂ evolution



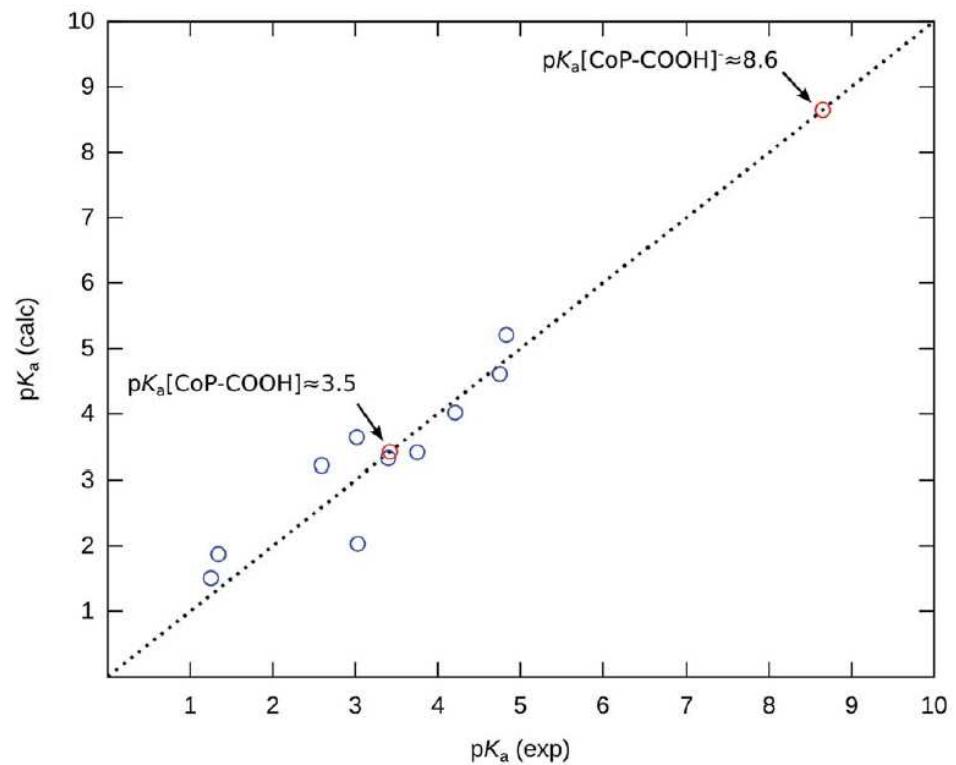
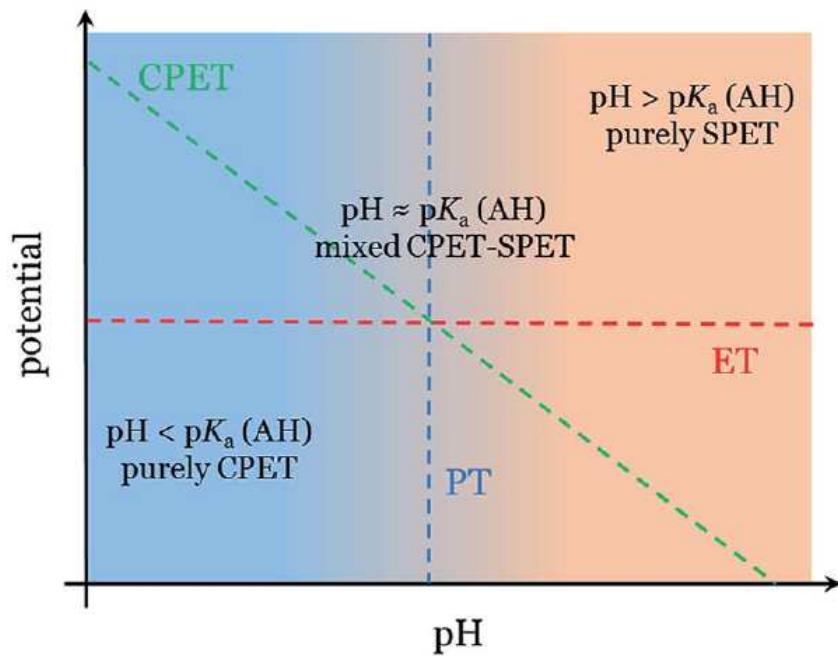
Mechanism



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

Predicting the pK_a of intermediates



Above $\text{pH} = pK_a$:

$$\text{CO}_2 + \text{e}^- + * \rightleftharpoons *\text{CO}_2^-$$

Calculation of pK_a of various R-COOH using DFT, with solvation

Conclusions

- Try to transfer 2 electrons at a time
- If you insist on transferring more than 2 electrons with 1 catalyst, be prepared to deal with scaling relationships...
- Unfavorable scaling between OOH and OH leads to irreversible kinetics of the oxygen electrode
- Proton-decoupled electron transfer leads to strong pH dependence of catalysis
- Each PCET reaction has an optimal pH, and an optimal catalyst at the optimal pH
- CO₂/CO electro-reduction is pH dependent