Thermodynamic theory of multiple proton-electron transfer reactions

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Outline

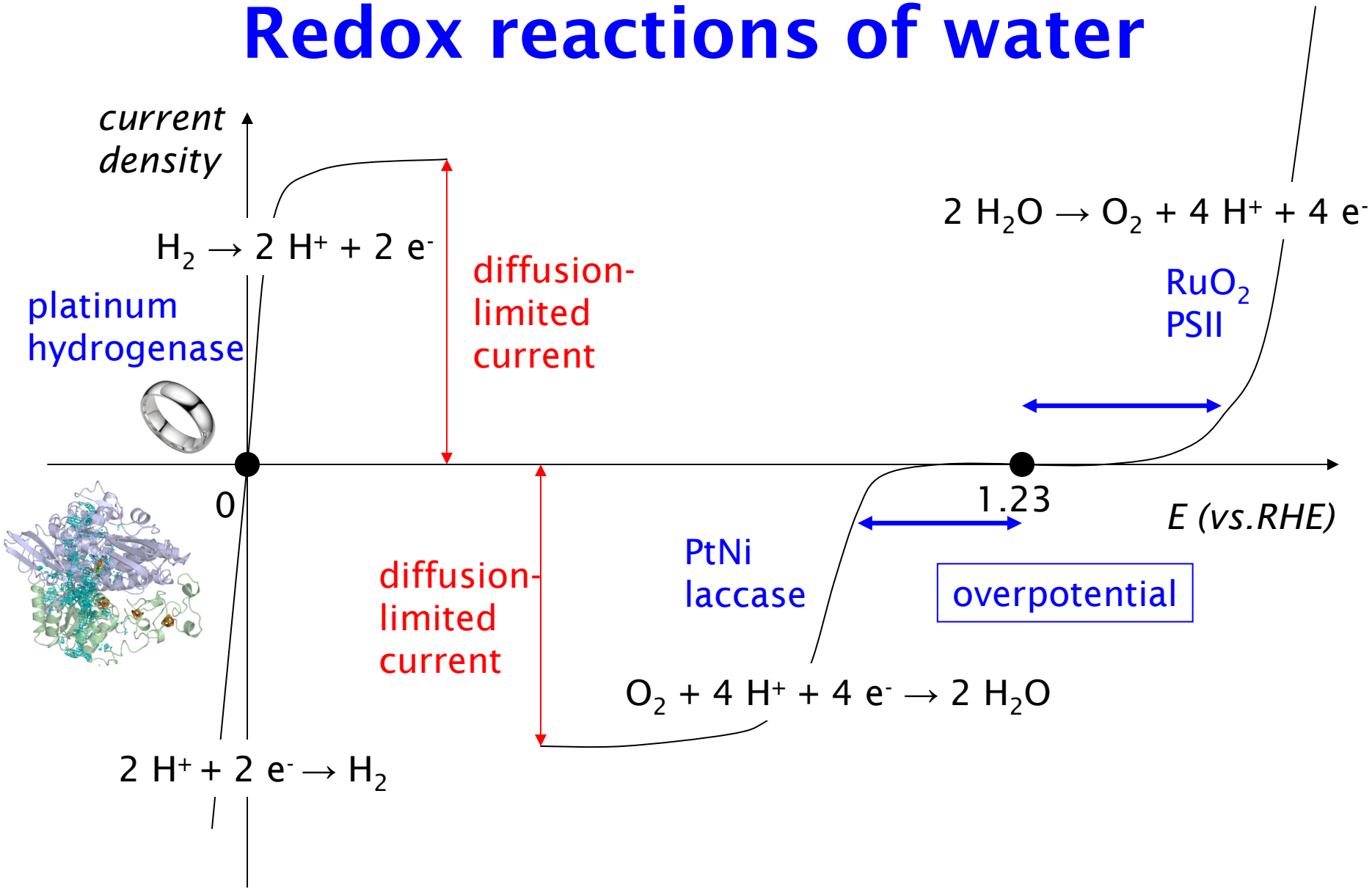
Thermodynamics of multi-electron transfer

- 1 e^- transfer
- 2 e^- transfer
- > 2 e^- transfer

Theory of proton-(de)coupled electron transfer

- 1 H^+/e^- transfer
- 2 H^+/e^- transfer
- Comparison to experiment

Redox reactions of water



M.T.M.Koper, H.A.Heering, in "Fuel Cell Science", Eds. A.Wieckowski, J.K.Nørskov, Wiley (2010), p.71-110

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

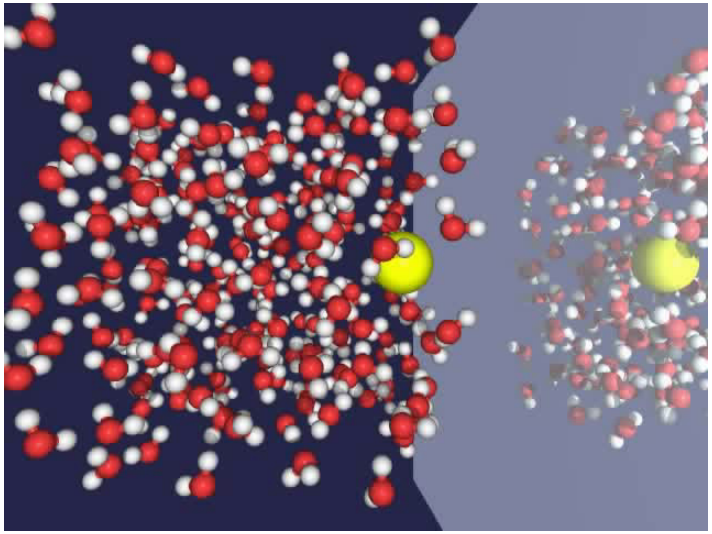
2 e^- / 2 steps / 1 intermediate

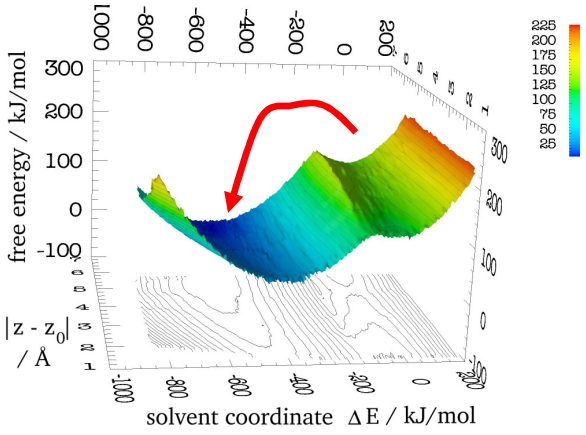
>2 e^- / >2 steps / >1 intermediate

M.T.M.Koper, J.Electroanal.Chem. 660 (2011) 254

Single electron transfer

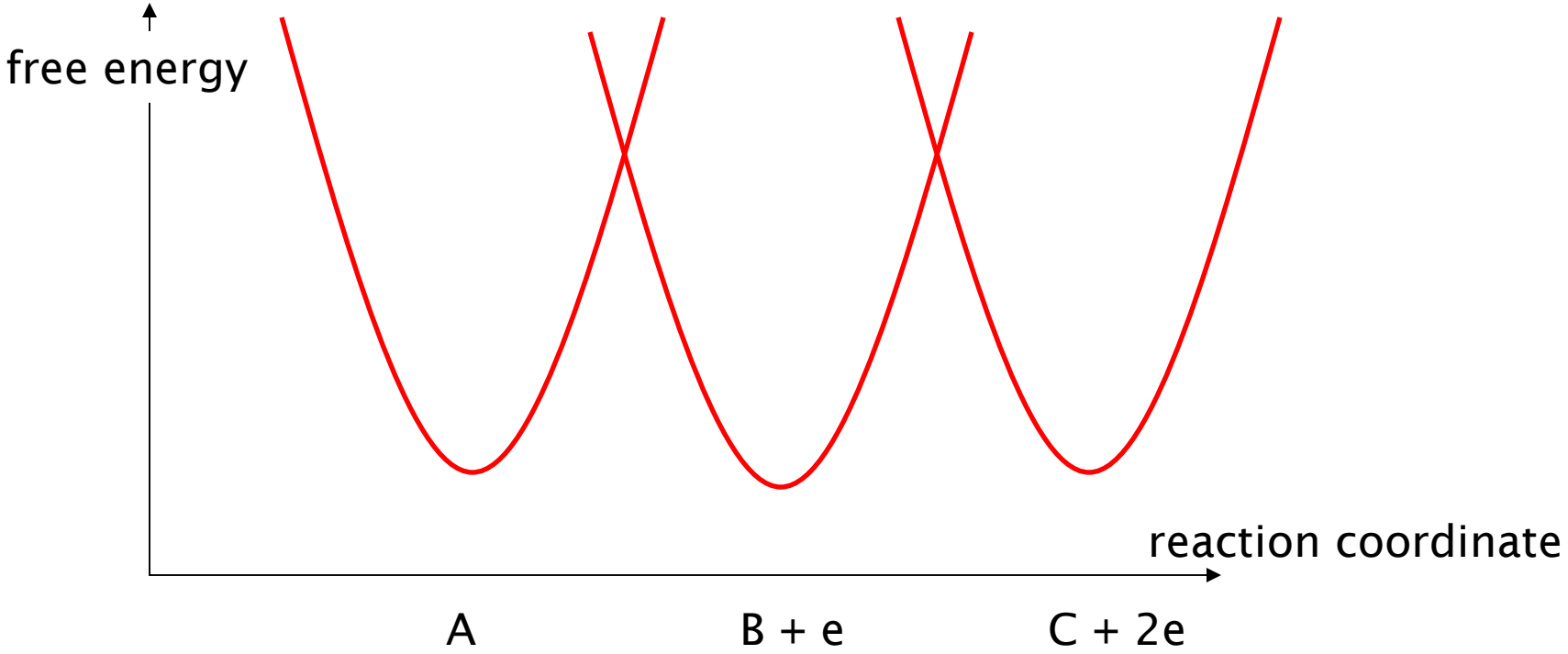
- Marcus Theory
- Activation energy determined by solvent reorganization energy λ (a difficult quantity to calculate accurately)
- Marcus Theory does not account for bond breaking, proton transfer, or catalysis.





C.Hartnig, M.T.M.Koper, J.Am.Chem.Soc. 125 (2003) 9840

Multiple electron transfer



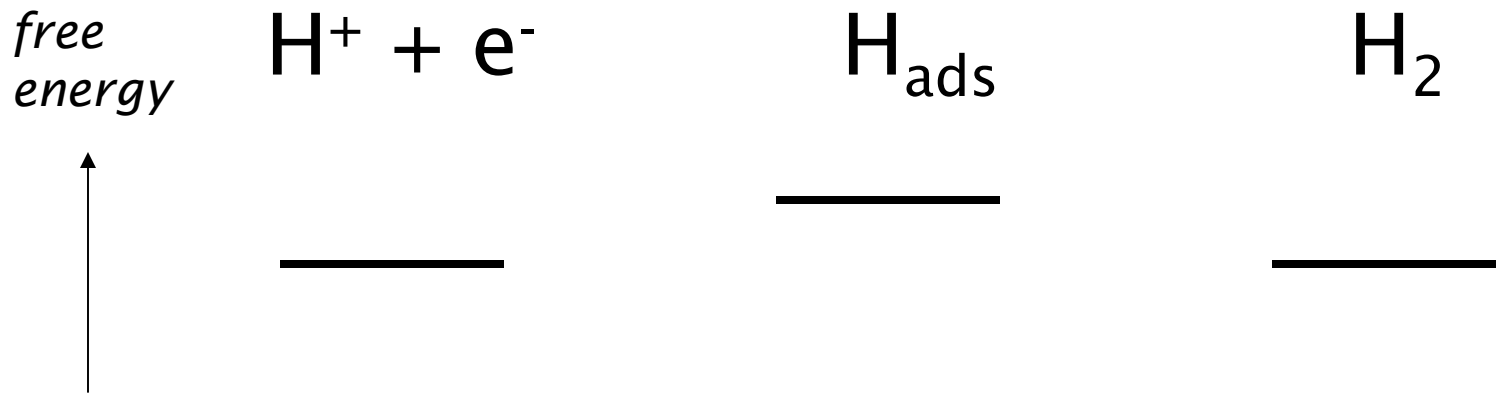
- Electrons transfer one-by-one, implying storage of charge and the existence of intermediates.
- Electrocatalysts optimize the energy of intermediates

Two electron transfer

$$2\ H^+ + 2\ e^- \leftrightarrows H_2$$

$$H^+ + e^- \leftrightarrows H_{ads} \qquad \text{(Volmer)}$$

$$H_{ads} + H^+ + e^- \leftrightarrows H_2 \qquad \text{(Heyrovsky)}$$



Thermodynamics

$2\ H^+ + 2\ e^- \leftrightarrows H_2$ $\qquad E^0 = 0\ V$

$H^+ + e^- \leftrightarrows H_{ads}$ $\qquad E_1^0 = -\ \Delta G_{ads}(H)/e_0$

$H_{ads} + H^+ + e^- \leftrightarrows H_2$ $\qquad E_2^0 = \Delta G_{ads}(H)/e_0$

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

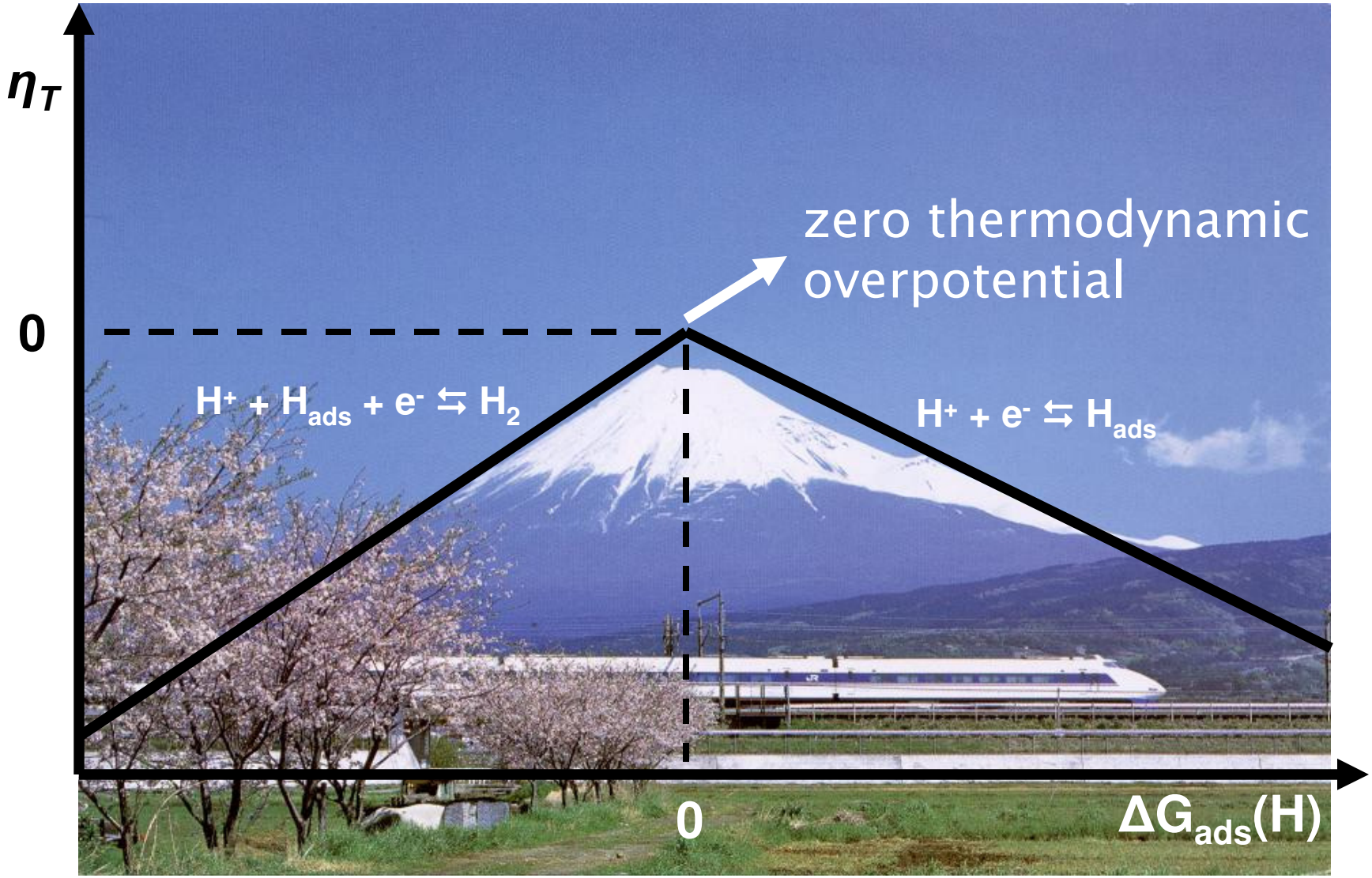
Potential-determining step

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

M.T.M.Koper, J.Solid State Electrochem. 17 (2013) 339

Thermodynamic volcano plot



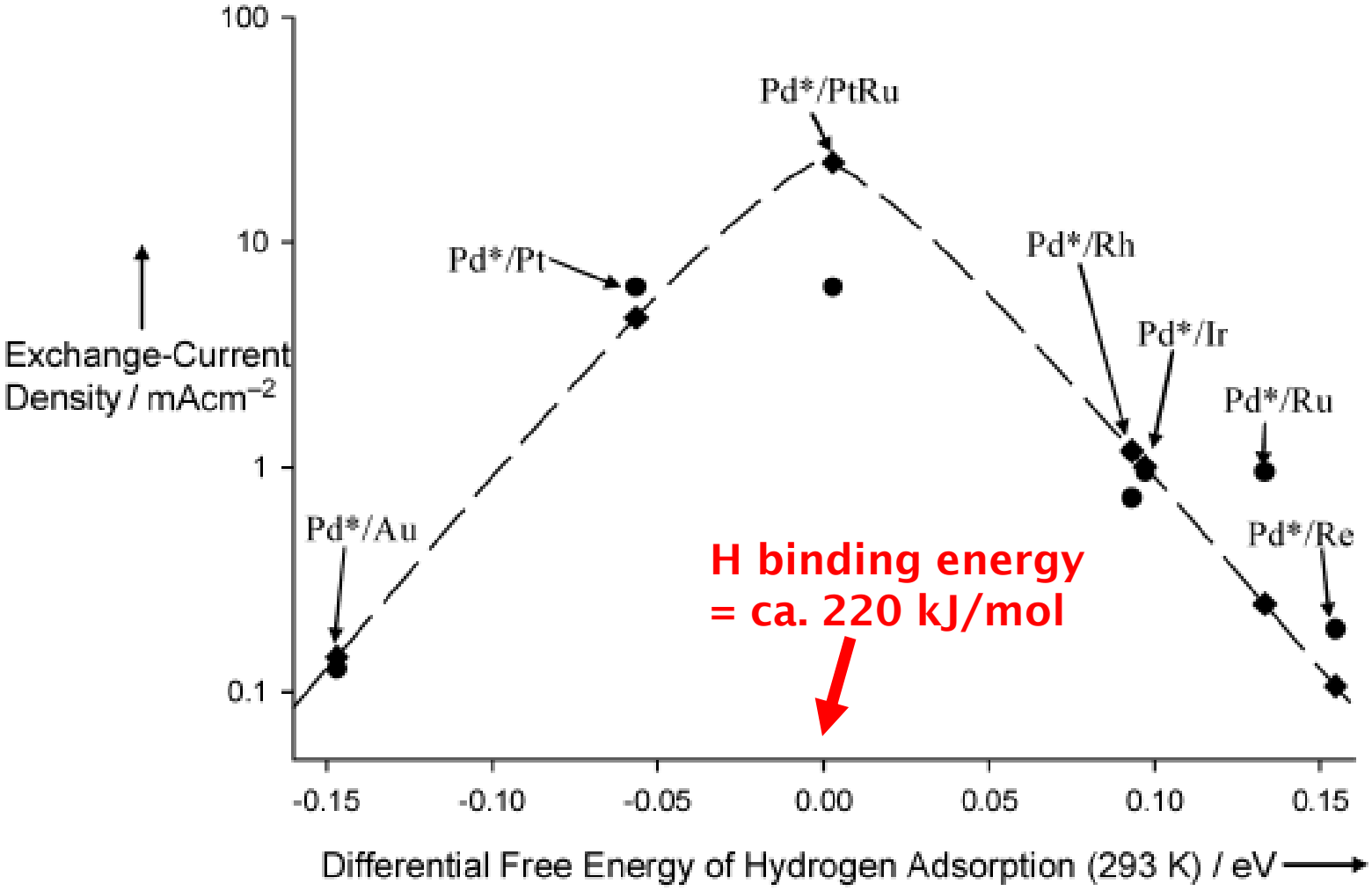
R.Parsons,Trans.Faraday Soc. (1958); H.Gerischer (1958)
J.K.Nørskov et al., J.Electrochem.Soc. (2004)

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 ½ 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 implicity
- Analysis works equally well for metal surfaces, molecular catalysts, and enzymes
- $\Delta G_{ads}(H)$ can be calculated from DFT

Experimental volcano for H_2 evolution



J.Greeley, J.K.Nørskov, L.A.Kibler, A.M.El-Aziz, D.M.Kolb, ChemPhysChem 7 (2006) 1032

More than 2 electron transfers

$O_2 + 4\ H^+ + 4\ e^- \leftrightarrows 2\ H_2O$ $\qquad E^0 = 1.23\ V$

$O_2 + H^+ + e^- \leftrightarrows OOH_{ads}$ $\qquad E_1^0$

$OOH_{ads} \leftrightarrows O_{ads} + OH_{ads}$ $\qquad \Delta G$

$O_{ads} + H^+ + e^- \leftrightarrows OH_{ads}$ $\qquad E_2^0$

$OH_{ads} + H^+ + e^- \leftrightarrows H_2O$ $\qquad E_3^0$

The optimal catalyst

$$\Delta G(OH_{ads}) = C_O = 1.23 \text{ eV}$$
$$\Delta G(O_{ads}) = 2 \times C_O = 2.46 \text{ eV}$$
$$\Delta G(OOH_{ads}) = 3 \times C_O = 3.69 \text{ eV}$$
$$\Delta G(O_2) = 4 \times C_O = 4.92 \text{ eV}$$

Independent of the mechanism

The optimal scaling relations

$$\Delta G(OH_{ads}) \approx 0.50 \times \Delta G(O_{ads}) + 0.05 \text{ eV})$$
$$= 0.5 \times \Delta G(O_{ads}) + K_{OH}$$
$$\Delta G(OOH_{ads}) \approx 0.53 \times \Delta G(O_{ads}) + 3.18 \text{ eV})$$
$$= 0.5 \times \Delta G(O_{ads}) + K_{OOH}$$

$$K_{OH} = 0 \text{ eV}$$
$$K_{OOH} = 2.46 \text{ eV}$$

Scaling relationships

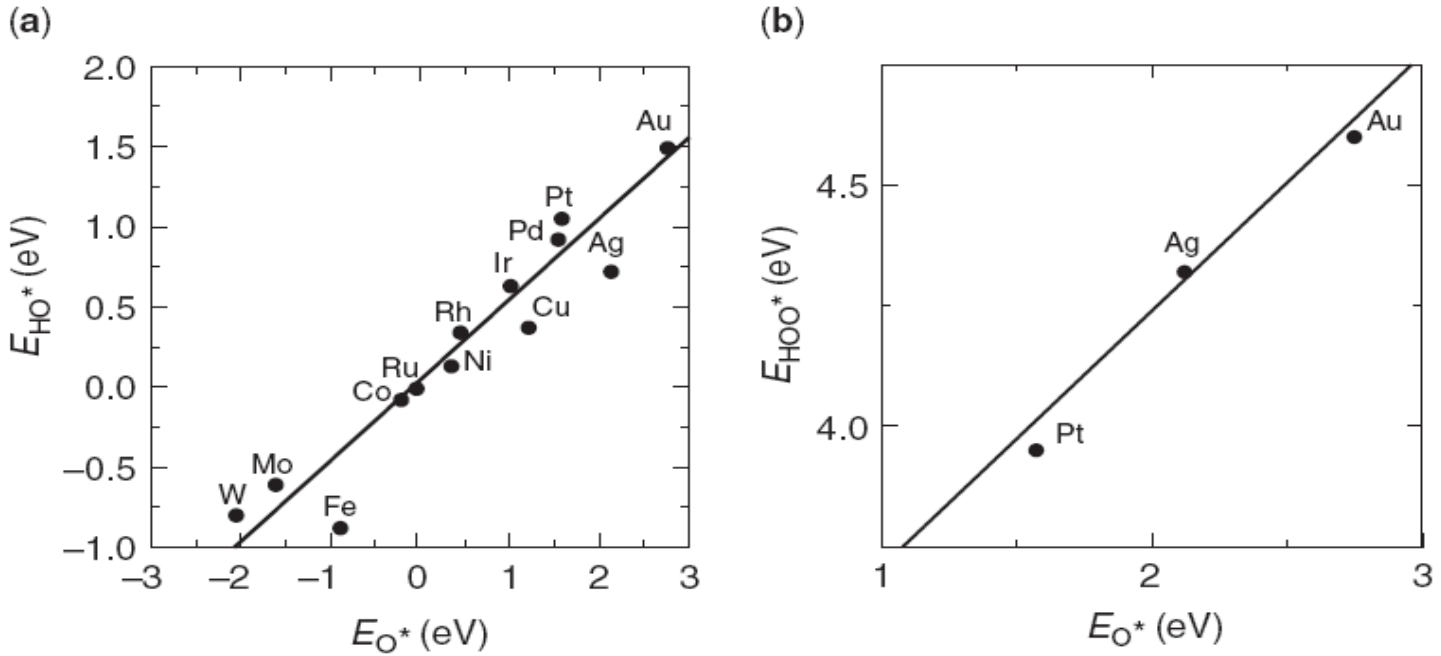
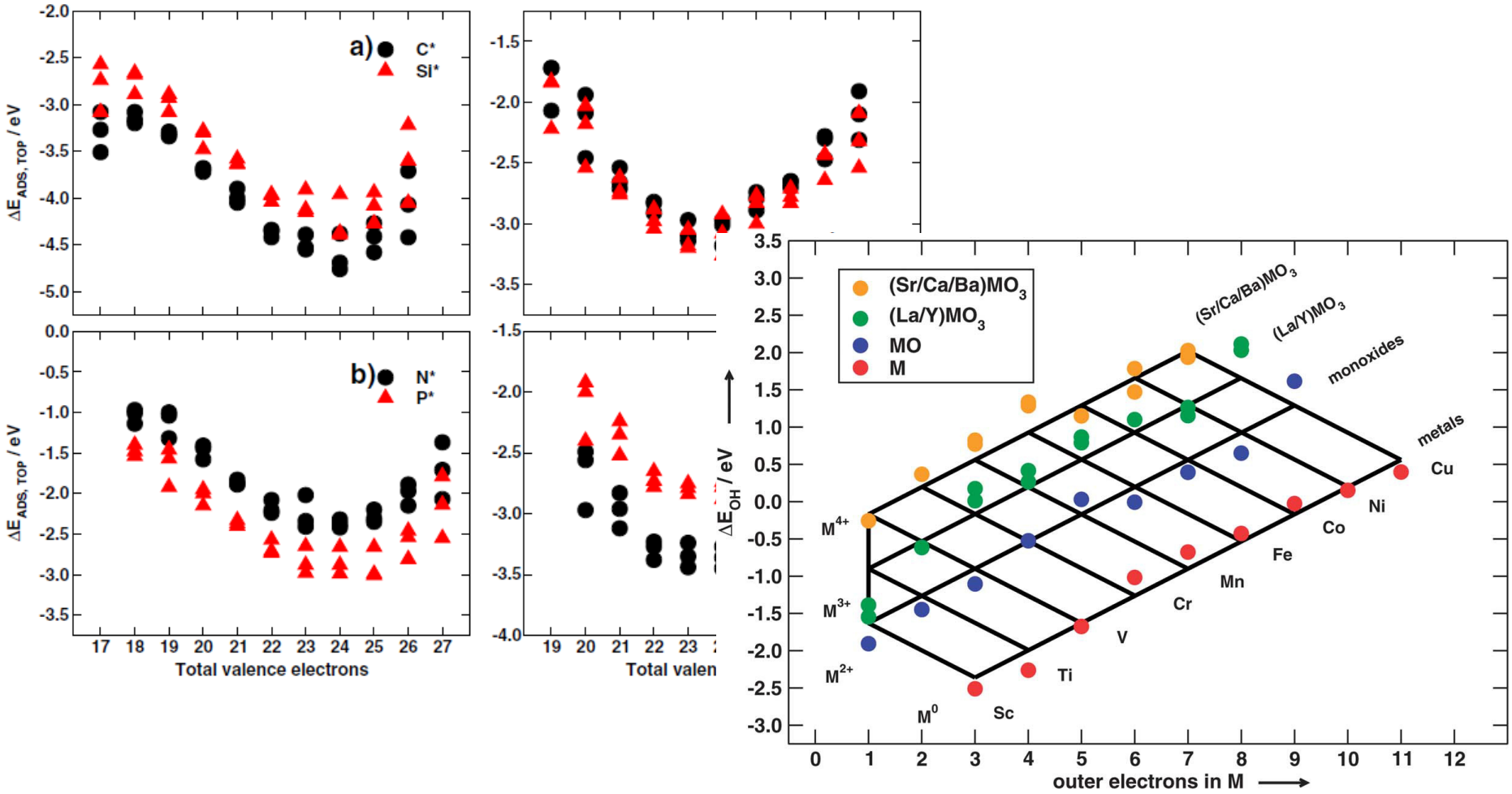


Figure 3.7 (a) Adsorption energy of HO^* as function of the adsorption energy of O^*, both on the terrace. The best linear fit is $E_{HO^*} = 0.50E_{O^*} + 0.05$ eV. (b) Adsorption energy of HOO^* as function of the adsorption energy of O^*, both on the terrace. The best linear fit is $E_{HOO^*} = 0.53E_{O^*}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

For (111) metal surfaces

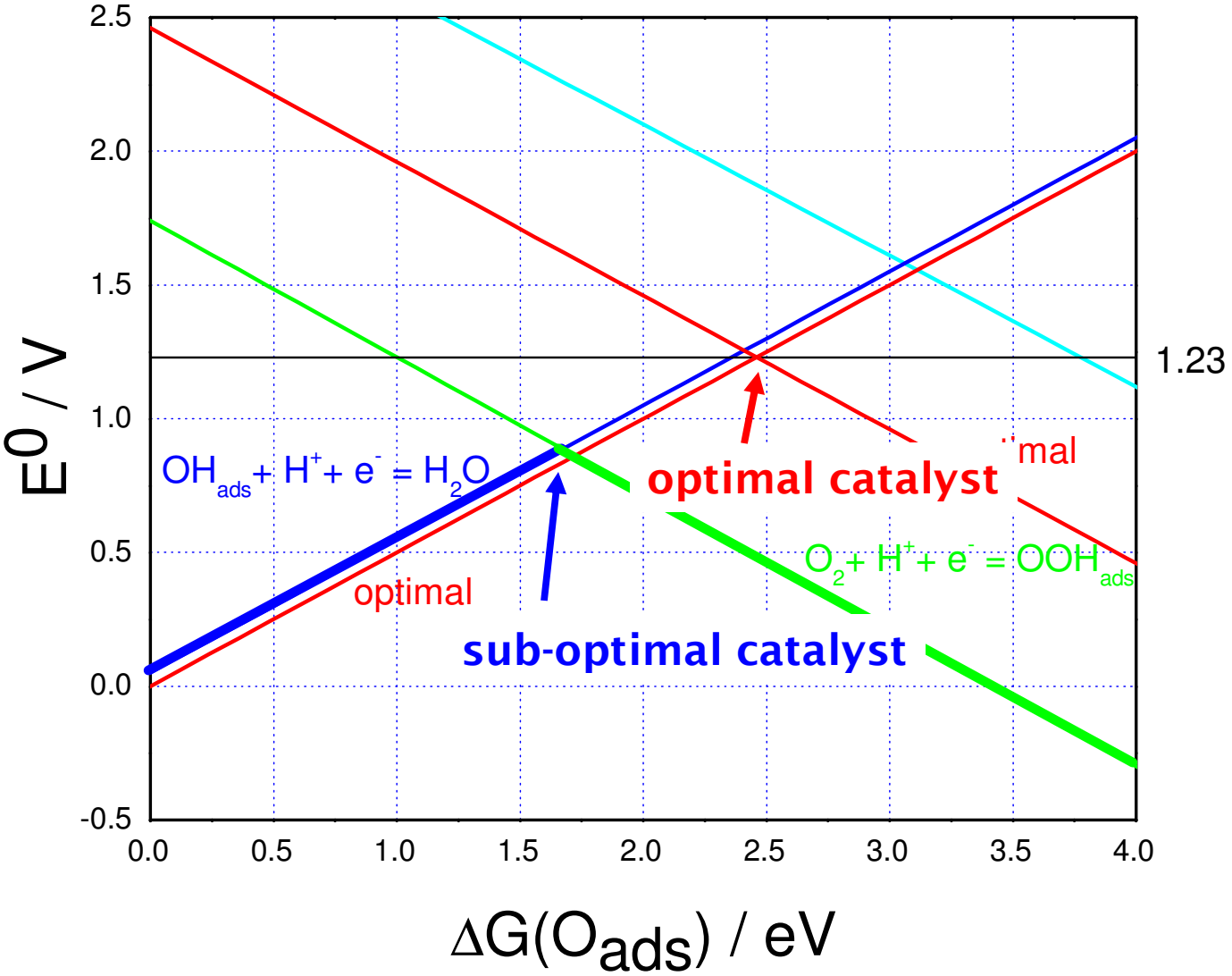
F.Abild-Petersen, J.Greeley, F.Studt, P.G.Moses, J.Rossmeisl, T.Munter, T.Bligaard, J.K. Nørskov, Phys.Rev.Lett. 99 (2007) 016105

Scaling relations = valence bond?



F.Calle-Vallejo, J.I.Martinez, J.M.Garcia-Lastra, J.Rossmeisl, M.T.M.Koper, Phys.Rev.Lett. 108 (2012) 116103
F.Calle-Vallejo, N.G.Inoglu, H.Su, J.I.Martinez, I.C.Man, M.T.M.Koper, J.R.Kitchin, J.Rossmeisl, Chem.Sci. 4 (2013) 1245

The optimal volcano



Does optimal scaling exist?

Metals:

$\Delta G(OH_{ads}) \approx 0.50 \times \Delta G(O_{ads}) + 0.05$ eV

$\Delta G(OOH_{ads}) \approx 0.53 \times \Delta G(O_{ads}) + 3.18$ eV

Oxides:

$\Delta G(OH_{ads}) \approx 0.61 \times \Delta G(O_{ads}) - 0.90$ eV

$\Delta G(OOH_{ads}) \approx 0.64 \times \Delta G(O_{ads}) + 2.03$ eV

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

M.T.M.Koper, J.Electroanal.Chem. 660 (2011) 254

“Fundamental” overpotential?

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

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

$$\Delta G[HO_2^-(aq)] - \Delta G[OH^-(aq)] = 3.4\ \mathrm{eV}$$

I.Man et al. ChemCatChem 3 (2011) 1159
M.T.M.Koper, J.Electroanal.Chem. 660 (2011) 254
M.T.M.Koper, Chem.Sci. 4 (2013) 2710

Proton-coupled electron transfer

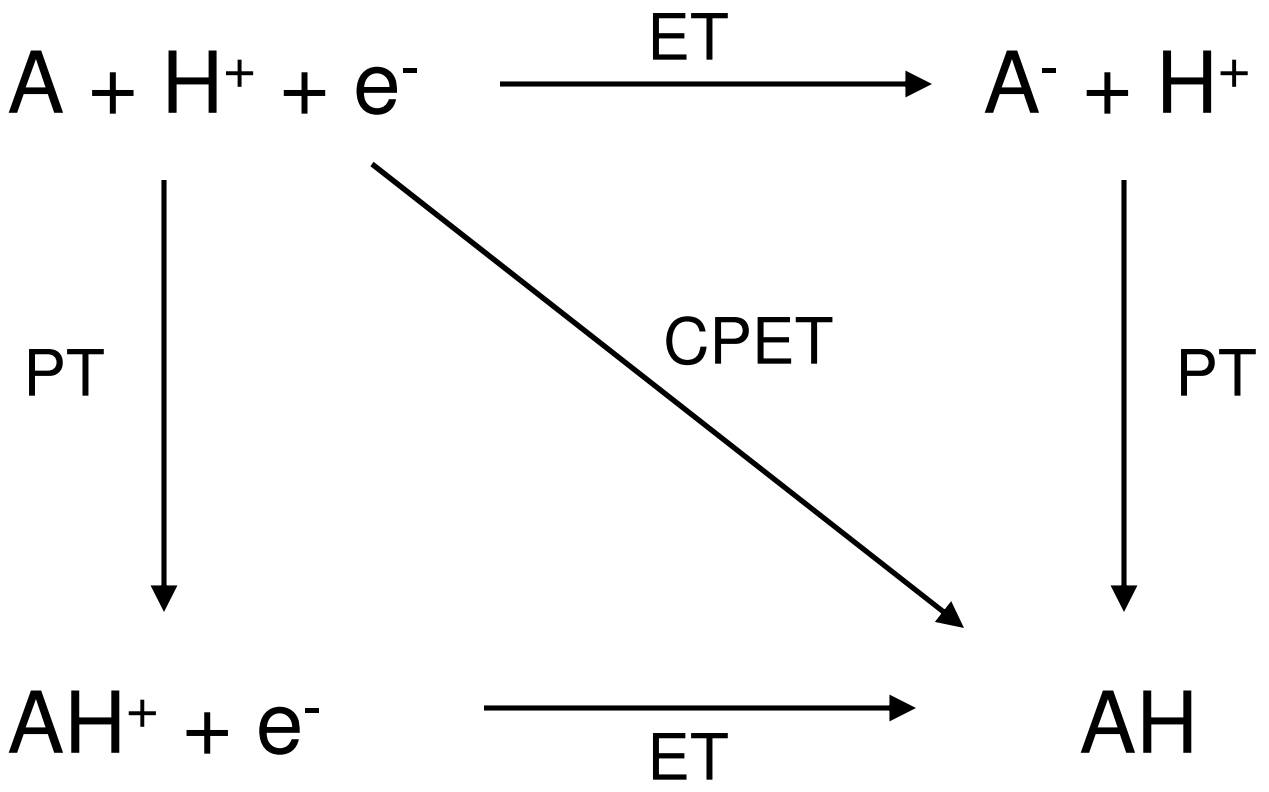
$$2\ H^+ + 2\ e^- \leftrightarrows H_2$$

$$O_2 + 4\ H^+ + 4\ e^- \leftrightarrows 2\ H_2O$$

$$CO_2 + 6\ H^+ + 6\ e^- \leftrightarrows\ CH_3OH + H_2O$$

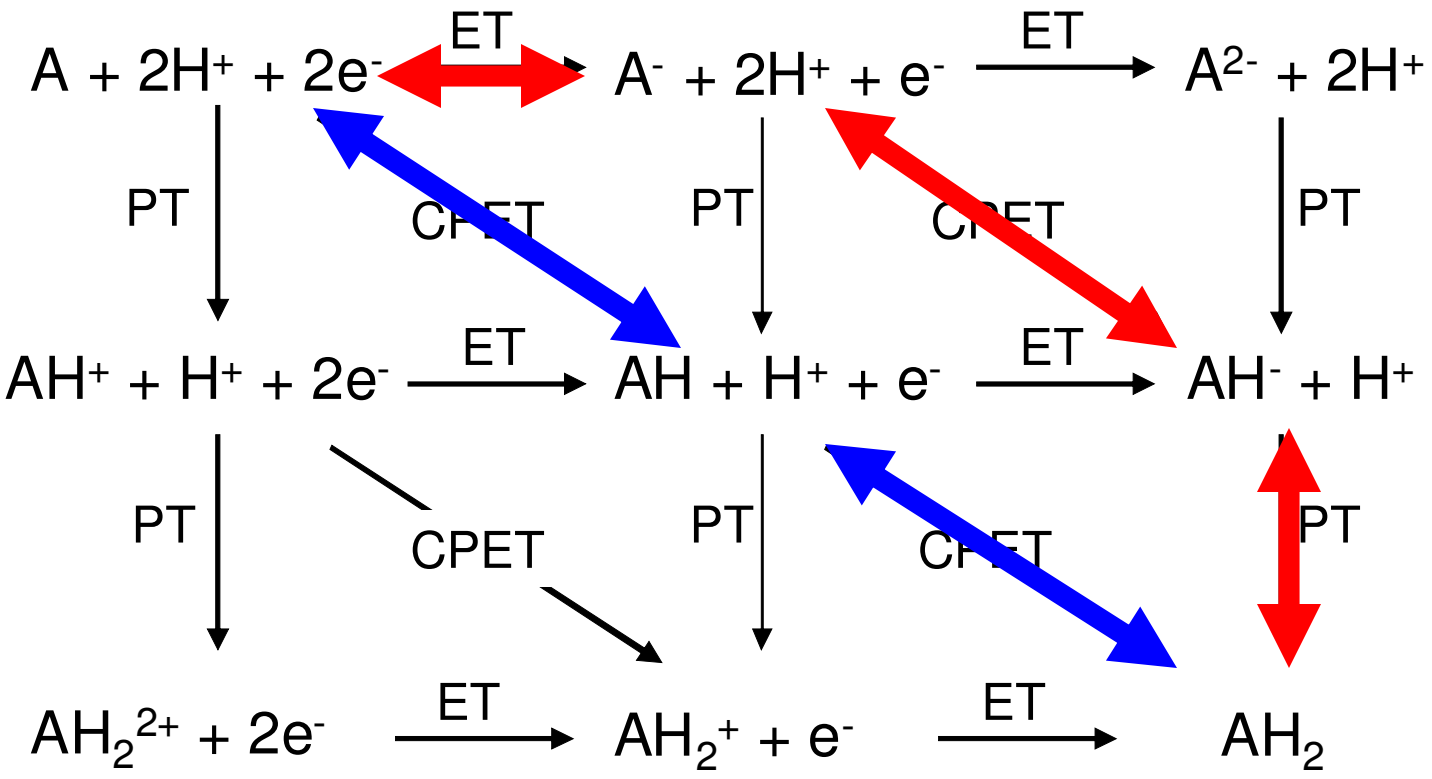
- Are proton and electron transfer always coupled?
- How does (de-)coupled proton-electron transfer manifest?

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



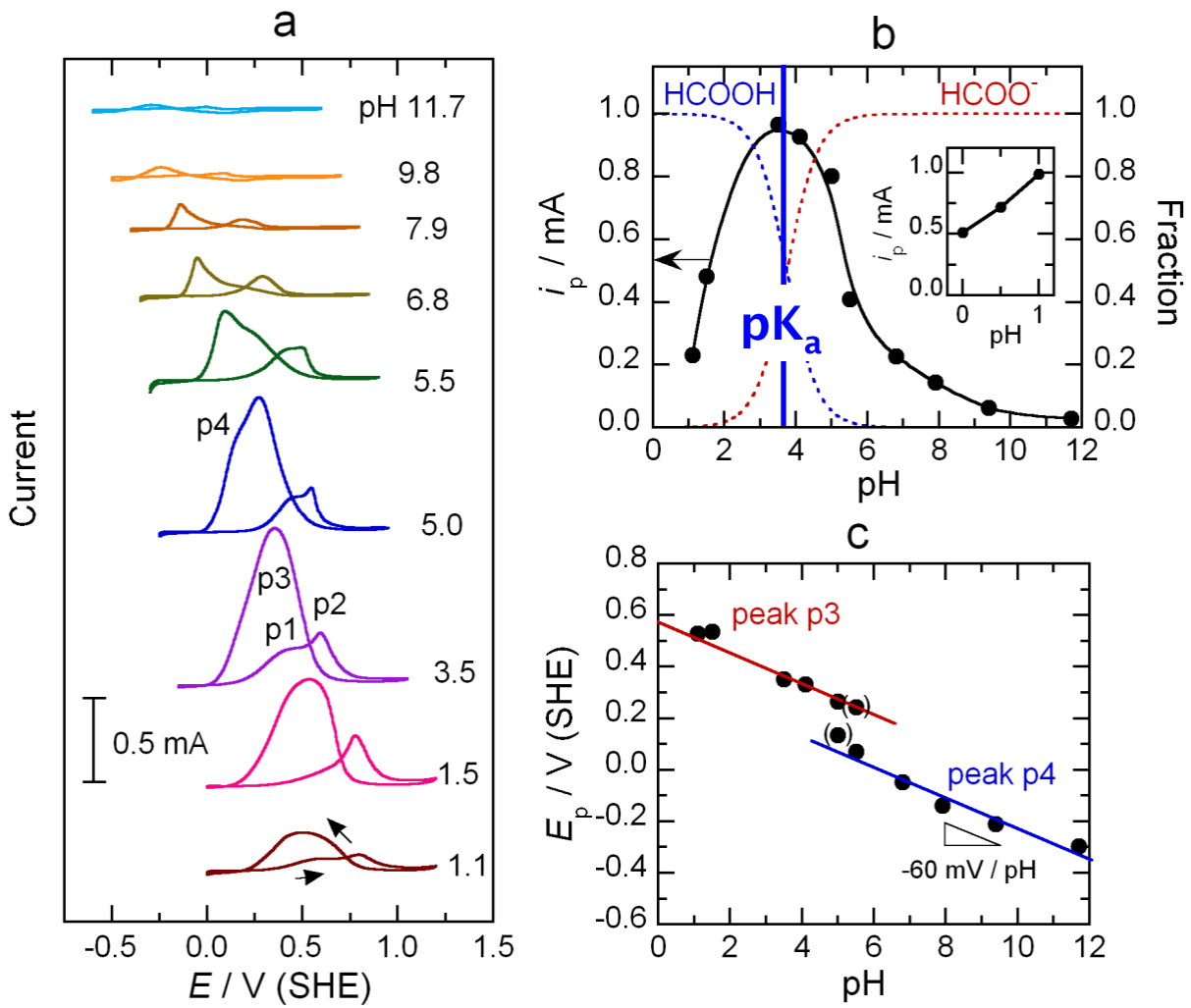
M.T.M.Koper, Phys.Chem.Chem.Phys. 15 (2013) 1399
M.T.M.Koper, Chem.Sci. 4 (2013) 2710

When PT and ET decouple

- PT and ET are concerted if off-diagonal states are energetically unfavorable. Reaction rate is independent of pH on the RHE potential scale.
- For a reduction reaction, ET happens first if the intermediate has a high electron affinity.
- For an oxidation reaction, PT happens first if the intermediate has a low proton affinity.
- If PT and ET decouple, the reaction rate becomes pH dependent on the RHE potential scale. Optimal activity is at $pH=pK_a$

M.T.M.Koper, Phys.Chem.Chem.Phys. 15 (2013) 1399
M.T.M.Koper, Chem.Sci. 4 (2013) 2710

Formic acid oxidation on Pt

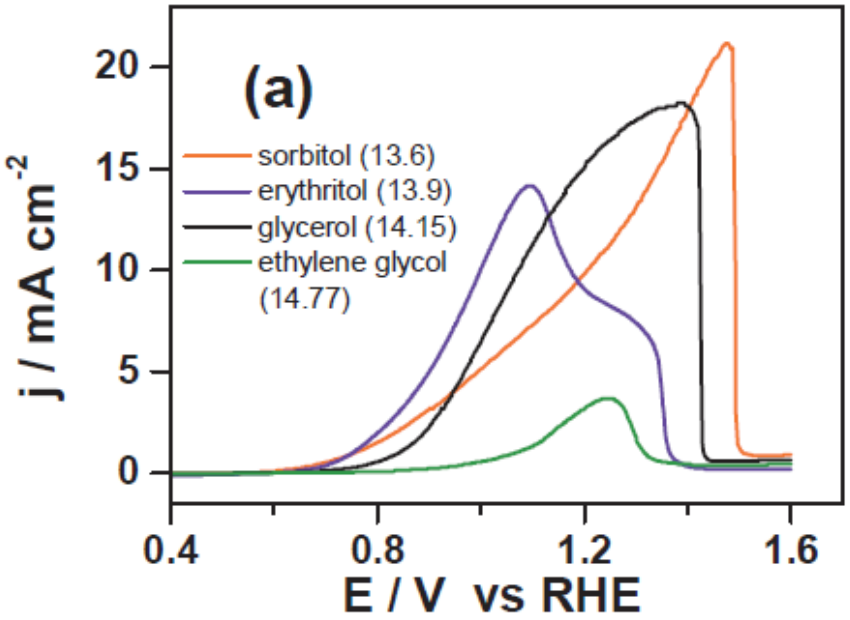


Formic acid oxidation prefers intermediate pH

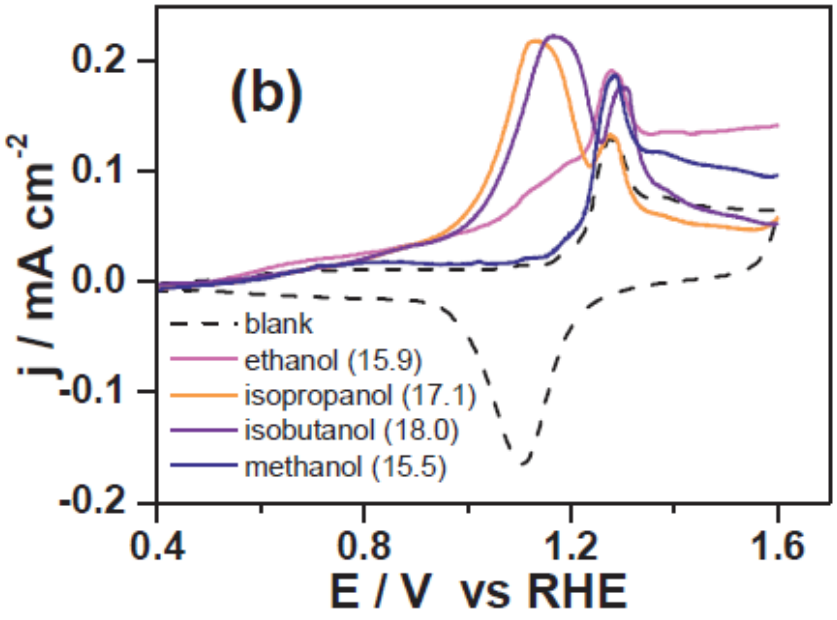
J.Joo, T.Uchida, A.Cuesta, M.T.M.Koper, M.Osawa, J.Am.Chem.Soc. 135 (2013) 9991

Oxidation of poly-ols

$$H_\beta R\text{-}OH_\alpha \leftrightarrows H_\beta R\text{-}O^- + H_\alpha^+$$



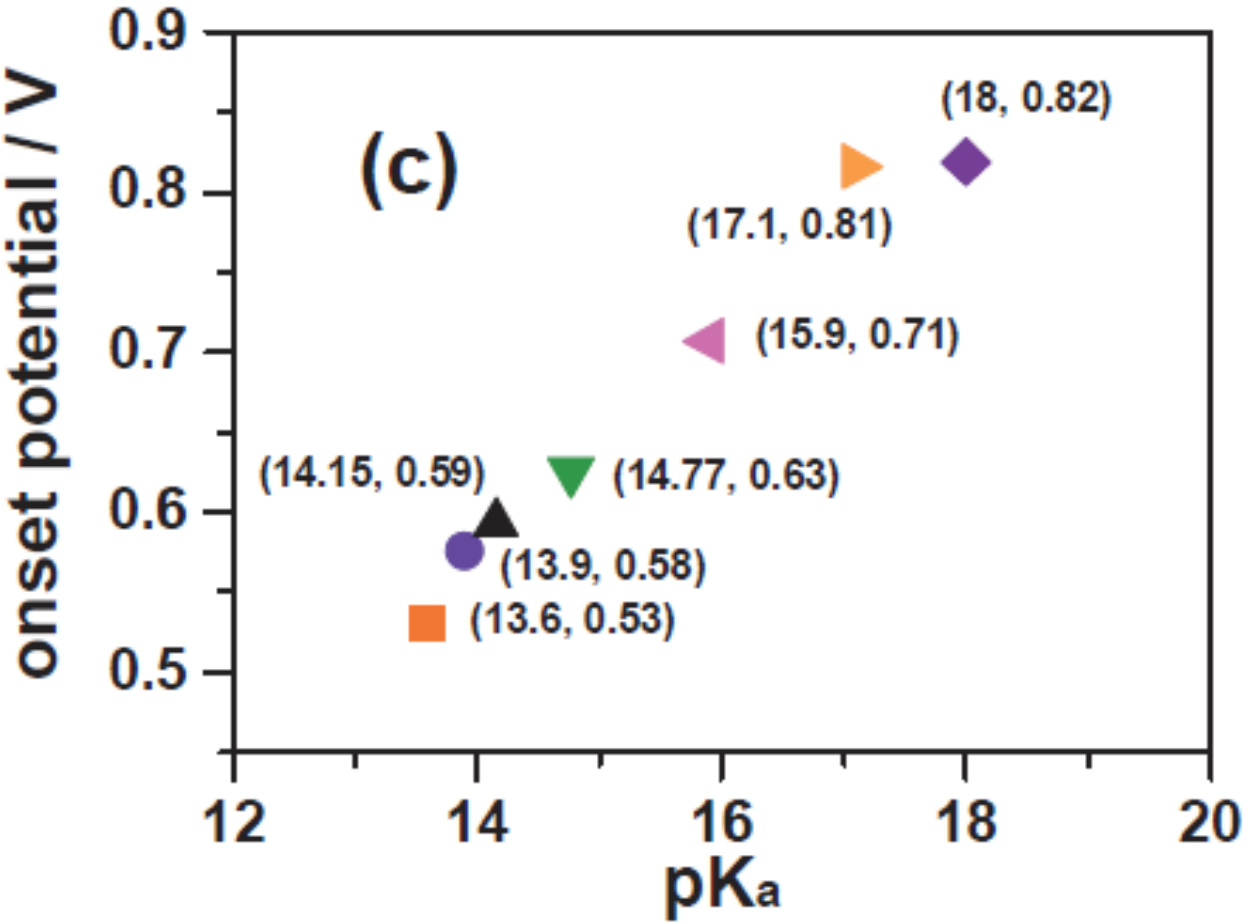
"sugar alcohols", poly-ols



mono-ols

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

Hammond relationship



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

More detailed mechanism

Overall: $R\text{-}CHH_{\beta}\text{-}OH_{\alpha} \rightarrow R\text{-}CH{=}O + H_{\alpha}^{+} + H_{\beta}^{+} + 2\ e^{-}$

1. First proton: $R\text{-}CHH_{\beta}\text{-}OH_{\alpha} + OH^{-} \rightarrow R\text{-}CHH_{\beta}\text{-}O^{-} + H_2O$

"base catalyzed"

2. OH adsorption on gold:

$OH^{-} + * \rightleftharpoons OH^{\delta-}_{ads} + (1\text{-}\delta)\ e^{-}$

CO_{ads} favors OH_{ads} formation

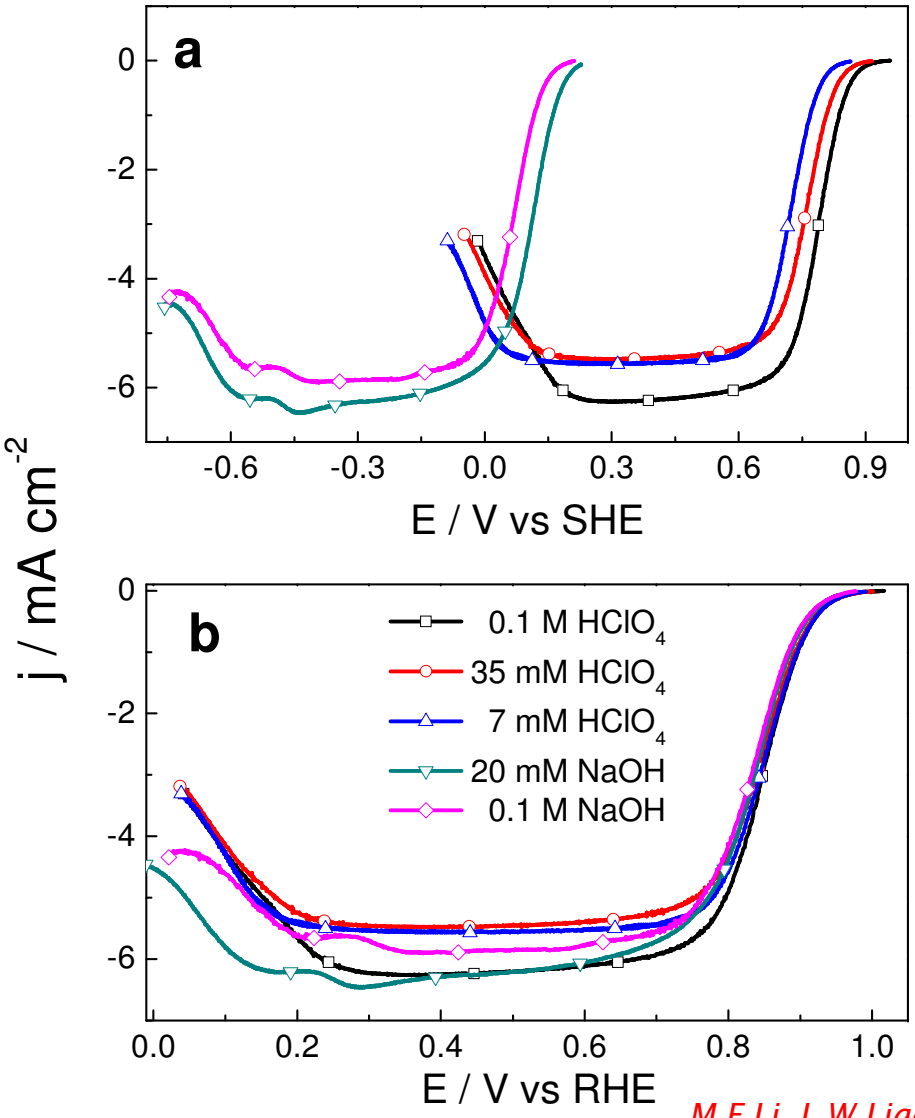
3. Second proton:

$R\text{-}CHH_{\beta}\text{-}O^{-} + OH_{ads} \rightarrow R\text{-}CH{=}O + H_{\alpha}OH_{\beta} + e^{-}$

gold catalyzed

P.Rodriguez, Y.Kwon, M.T.M.Koper, Nature Chem. 4 (2012) 177

CPET in oxygen reduction on Pt

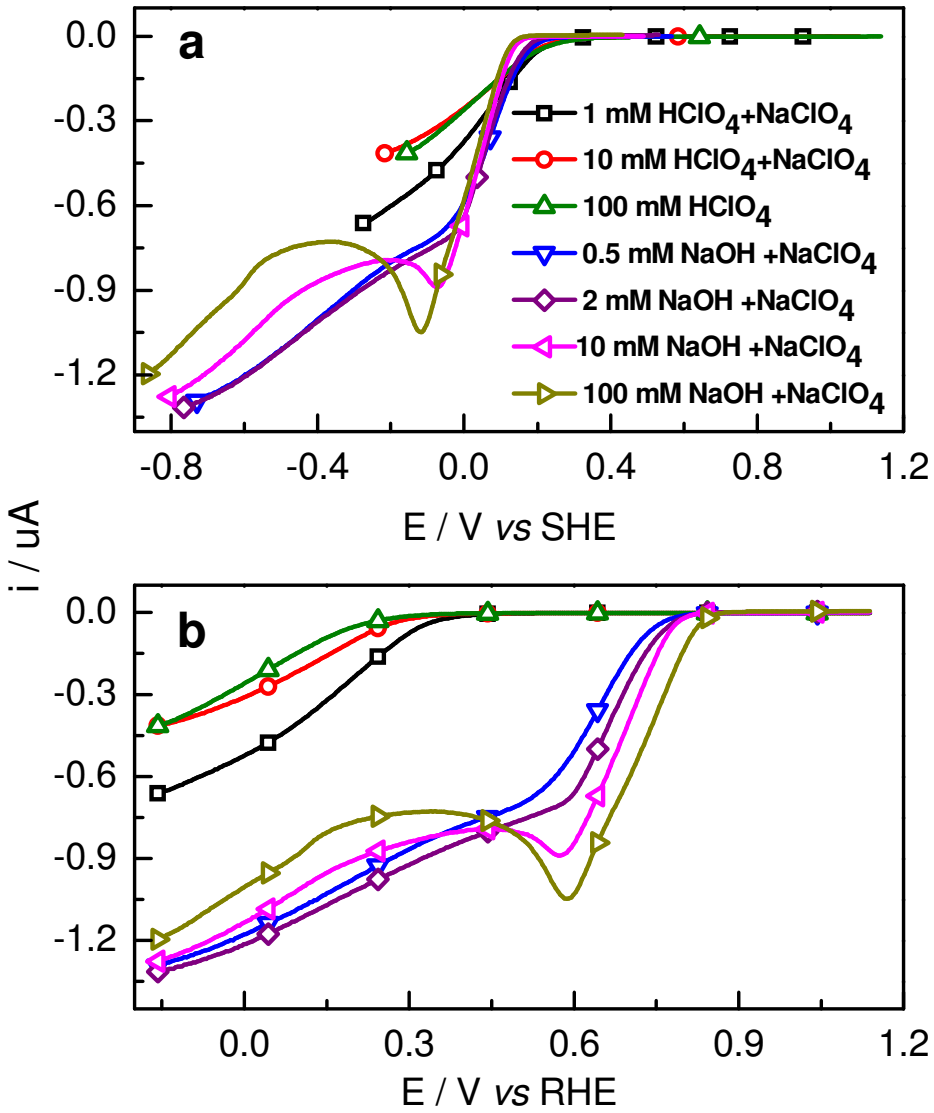


The ORR rate on Pt is independent of pH on the RHE scale.

Concerted proton-electron transfer.

M.F.Li, L.W.Liao, D.F.Yuan, D.Mei, Y.-X.Chen, Electrochim.Acta (2013), in press

Decoupled PCET in ORR on Au

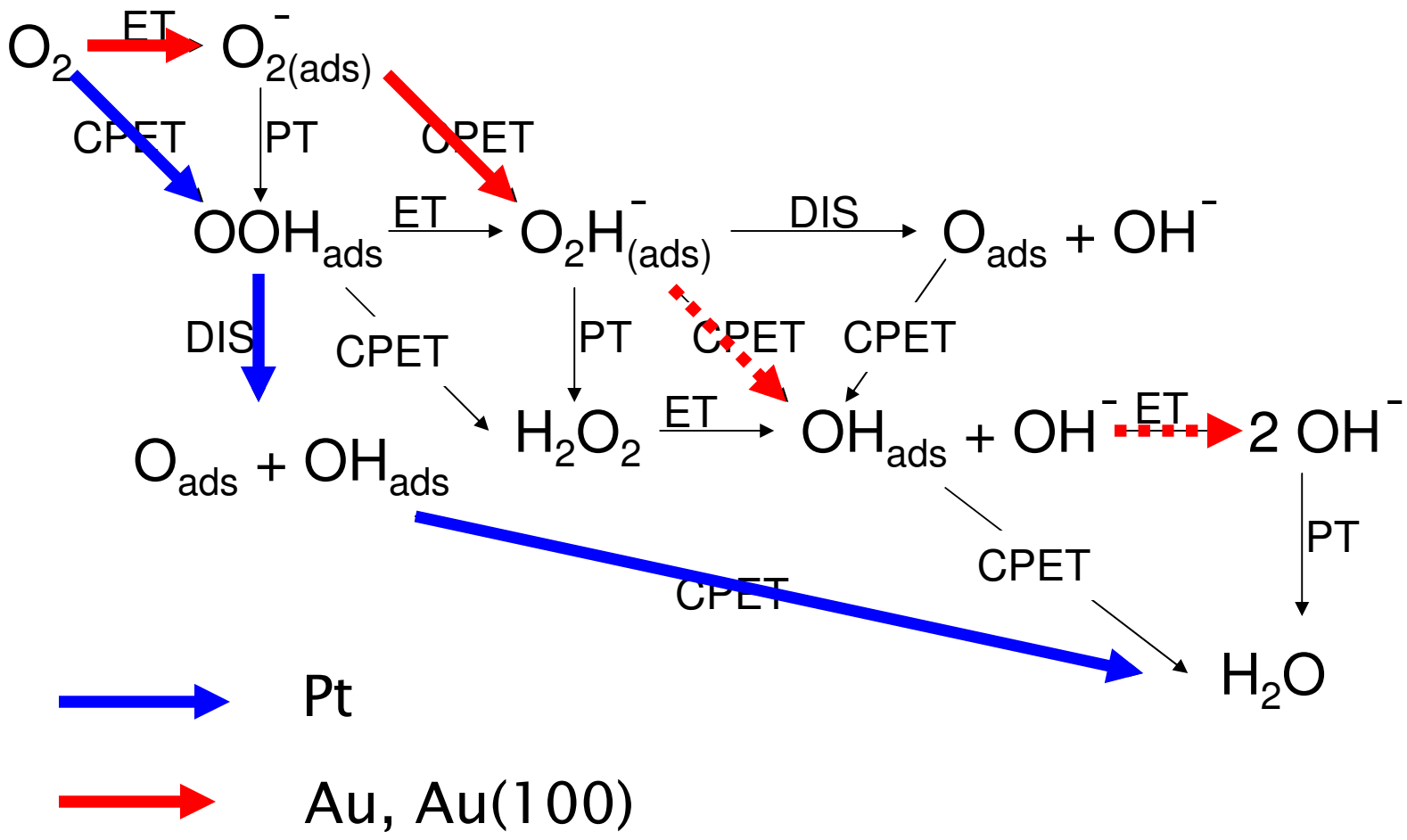


The ORR rate on Au is dependent of pH on the RHE scale.

Decoupled proton-electron transfer.

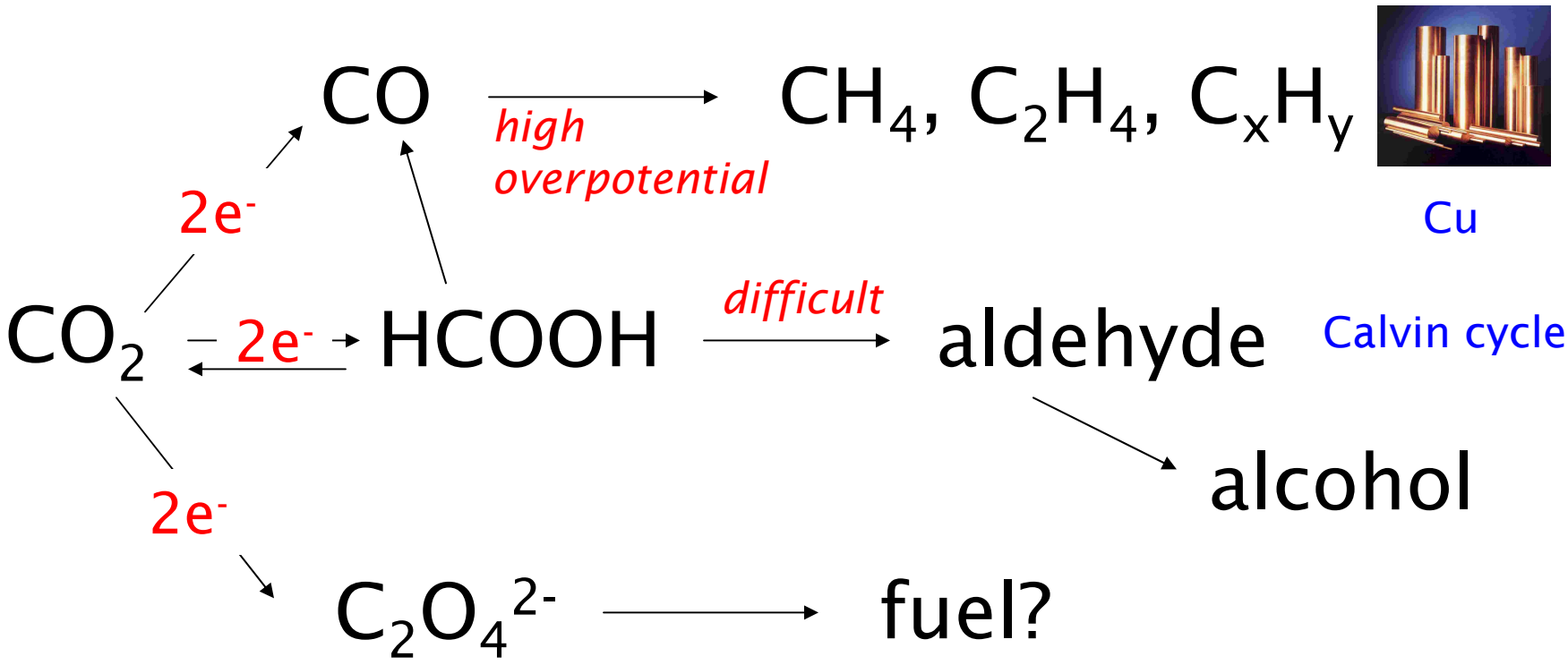
Q.J.Chen, Y.L.Zheng, L.W.Liao, J.Kang, Y.-X.Chen, Scientia Sinica Chimica 41 (2011) 1777

Mechanism of ORR

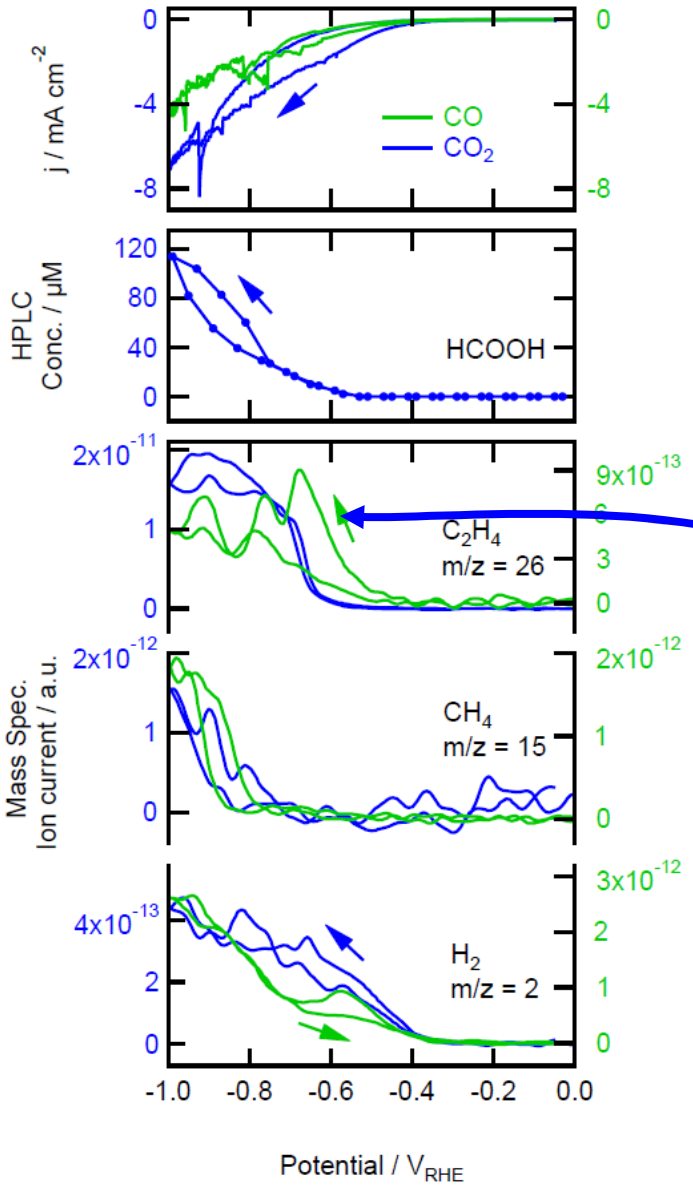


M.T.M.Koper, Chem.Sci. 4 (2013) 2710

Electrocatalytic CO_2 reduction

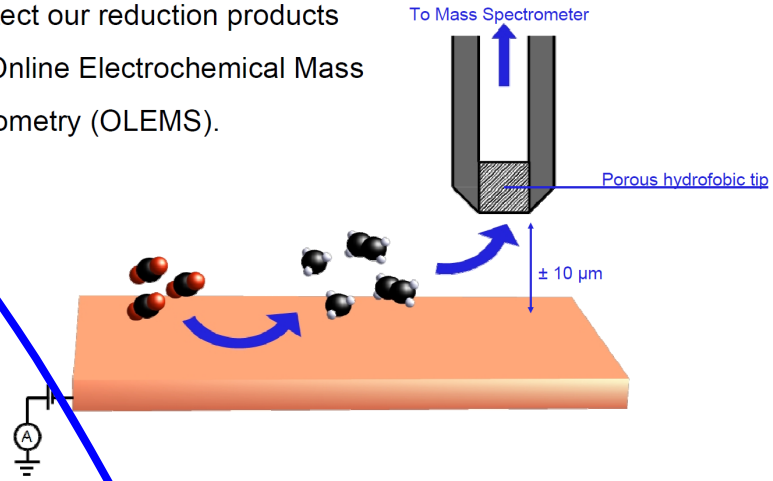


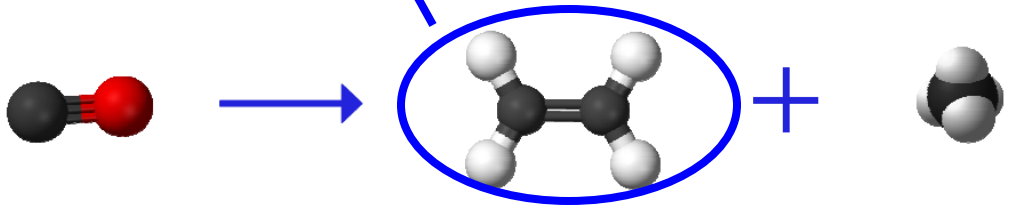
CO and CO_2 reduction on copper



CO_2 and CO reduction on copper electrodes produces H_2, HCOOH, CH_4 and C_2H_4.

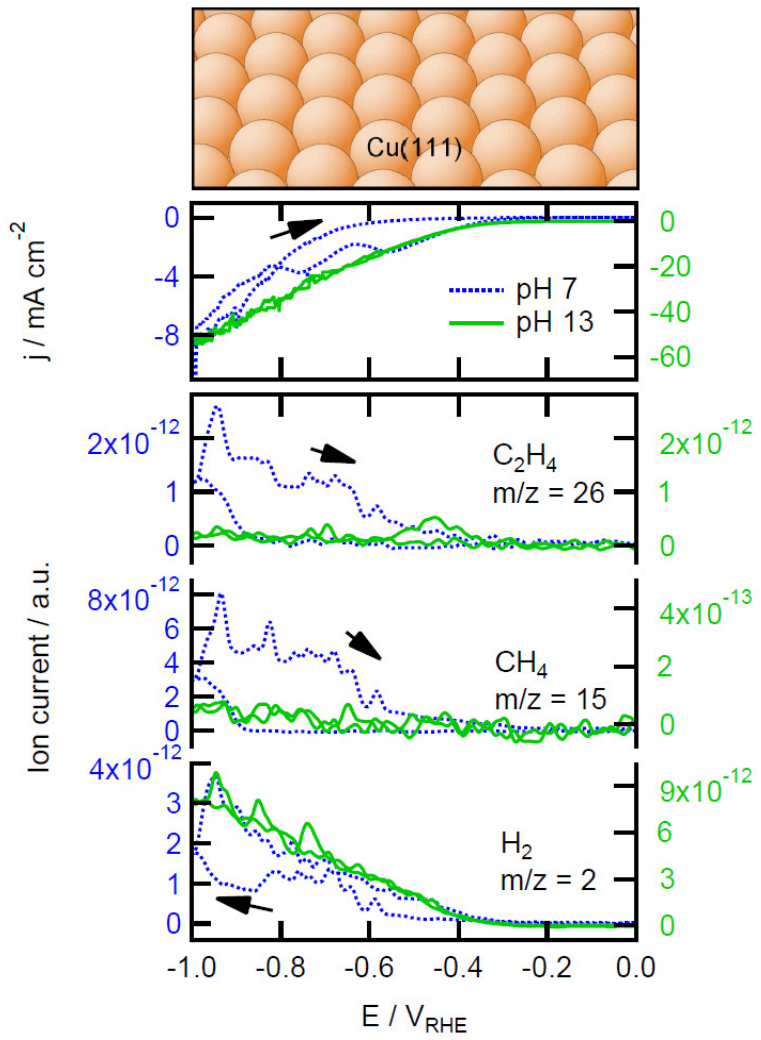
We detect our reduction products using Online Electrochemical Mass Spectrometry (OLEMS).

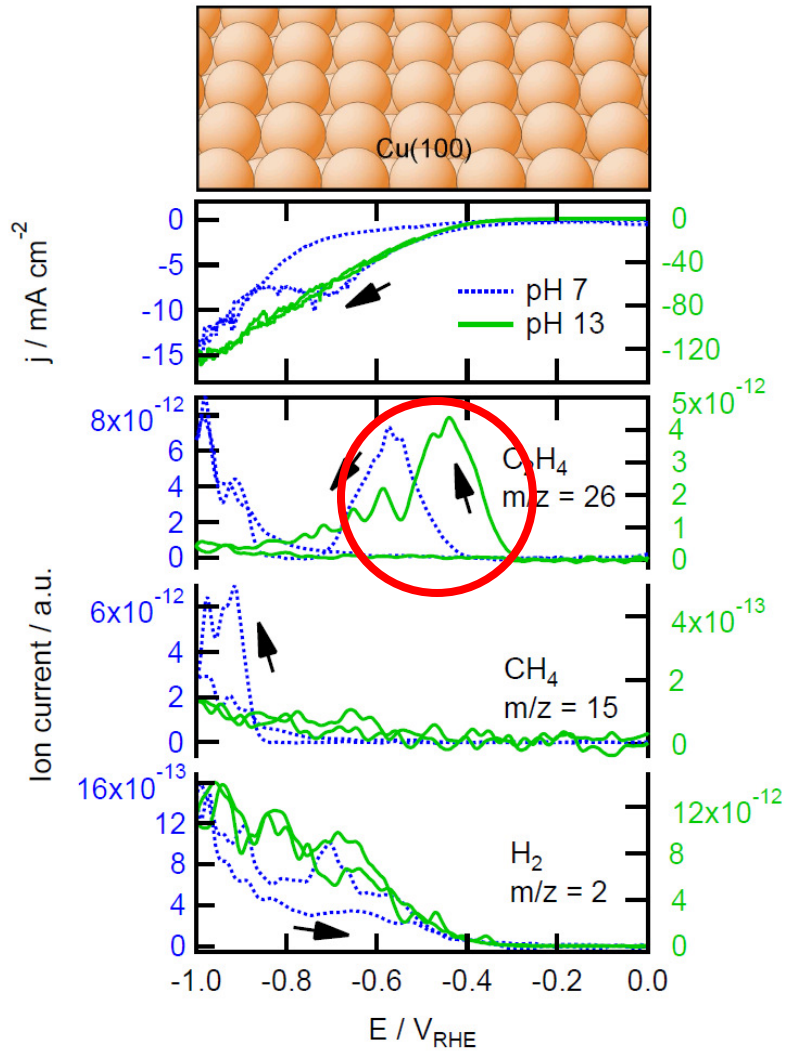




Y.Hori, Mod.Asp.Electrochem (2008) *K.J.P.Schouten, Y.Kwon, C.J.M.van der Ham, Z.Qin, M.T.M.Koper, Chem.Sci. (2011)*

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



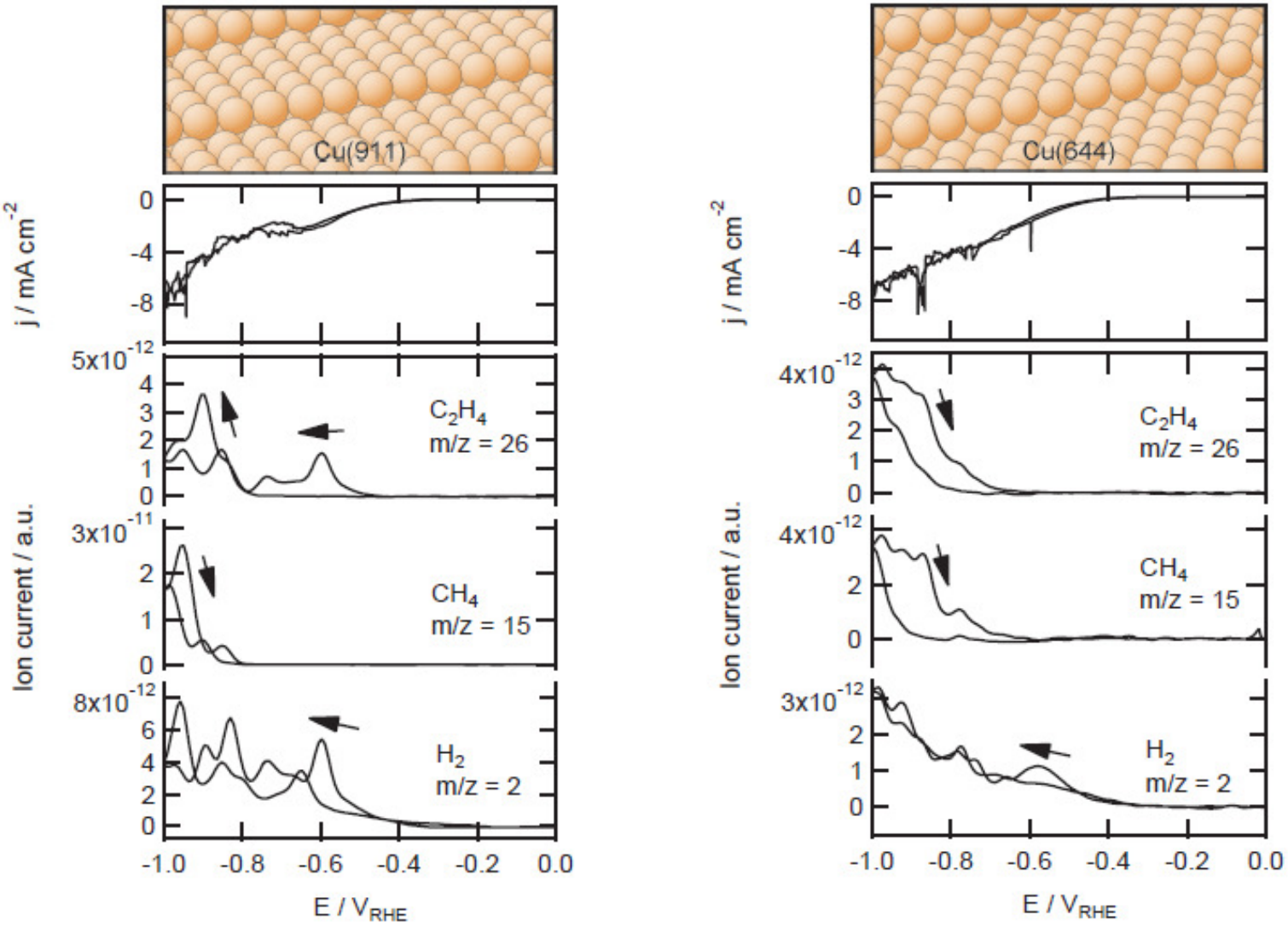


$CO + 6\ H^+ + 6\ e^- \rightarrow CH_4 + H_2O$

$2\ CO + 8\ H^+ + 8\ e^- \rightarrow C_2H_4 + 2\ H_2O$

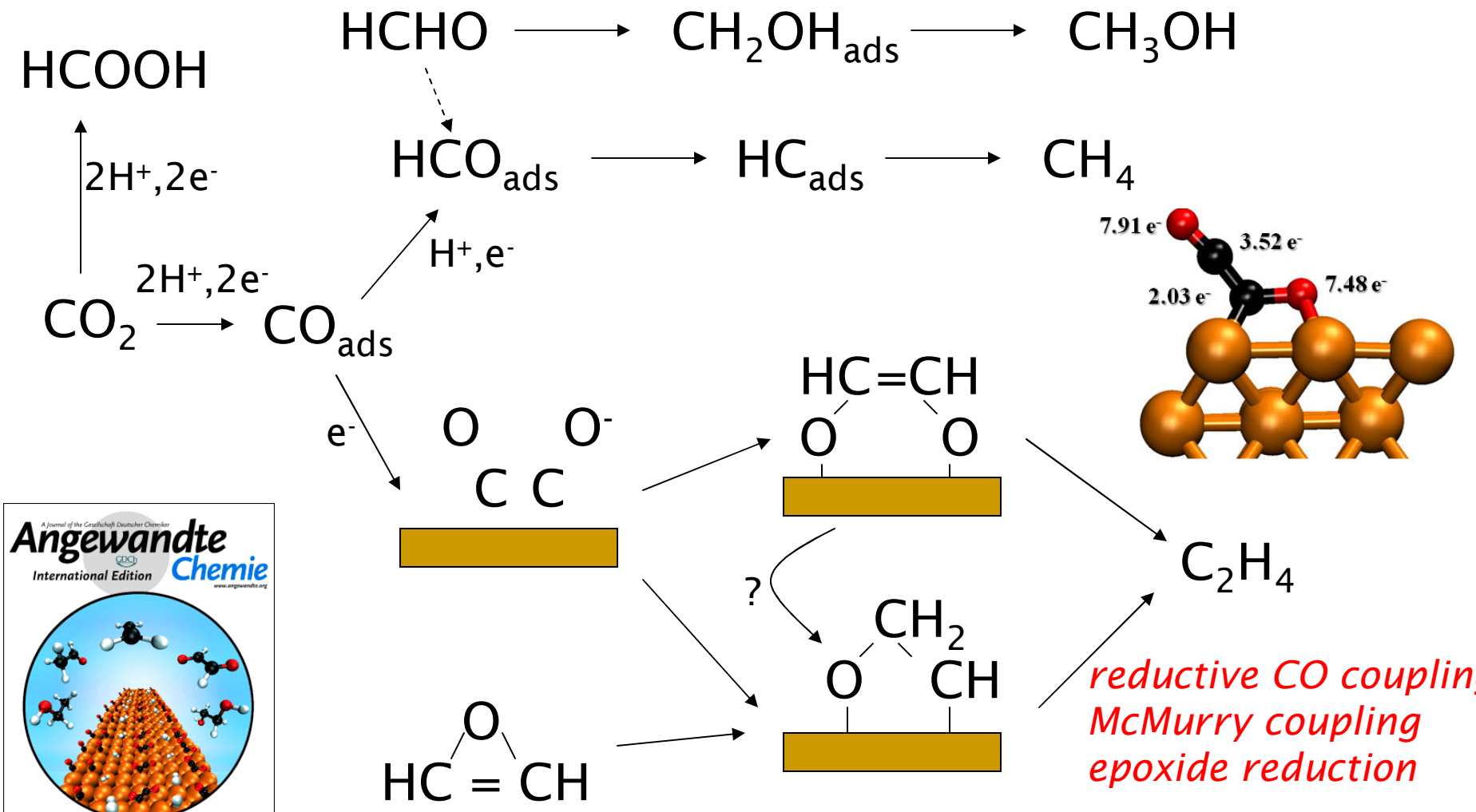
K.J.P.Schouten, Z.Qin, E..Perez Gallent, M.T.M.Koper, J.Am.Chem.Soc. 134 (2012) 9864

(100) terraces - not (100) steps



K.J.P.Schouten, E.Perez Gallent, M.T.M.Koper, ACS Catal. 3 (2013) 1292

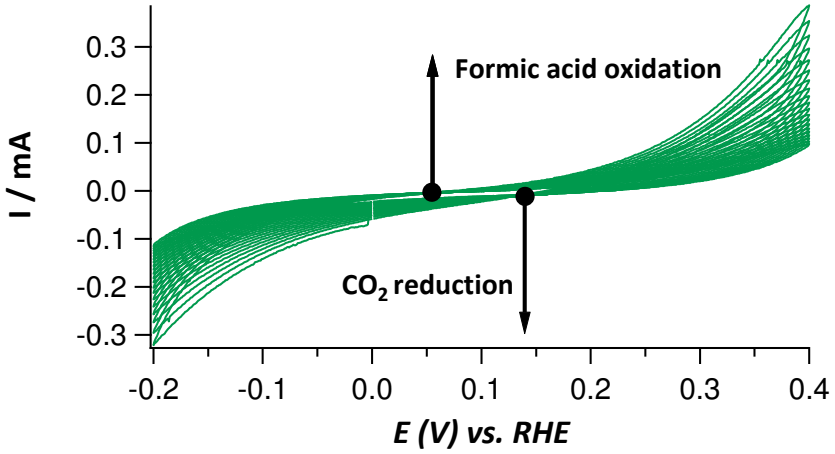
A consistent mechanism



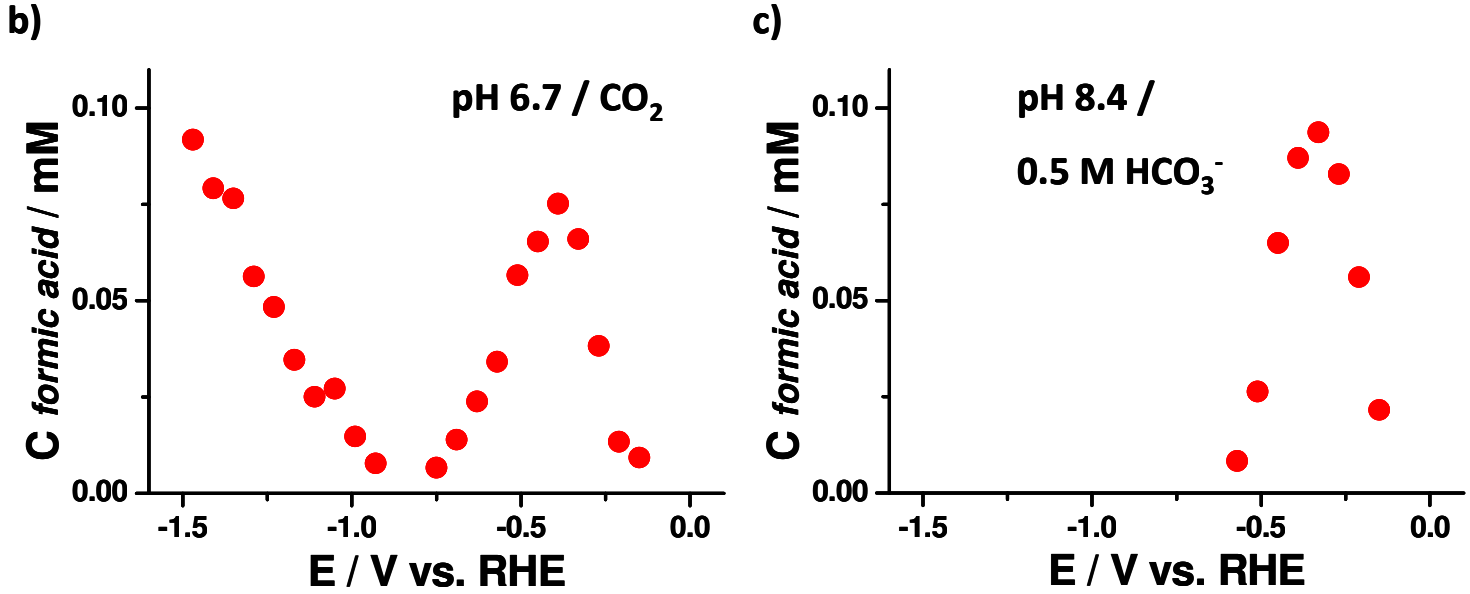
reductive CO coupling
McMurry coupling
epoxide reduction

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

CO_2 reduction to formic acid



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



R.Kortlever, C.Balemans, Y.Kwon, M.T.M.Koper, to be submitted

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
- CO_2/CO electro-reduction is pH dependent