Electrocatalysis:
catalysis of redox reactions
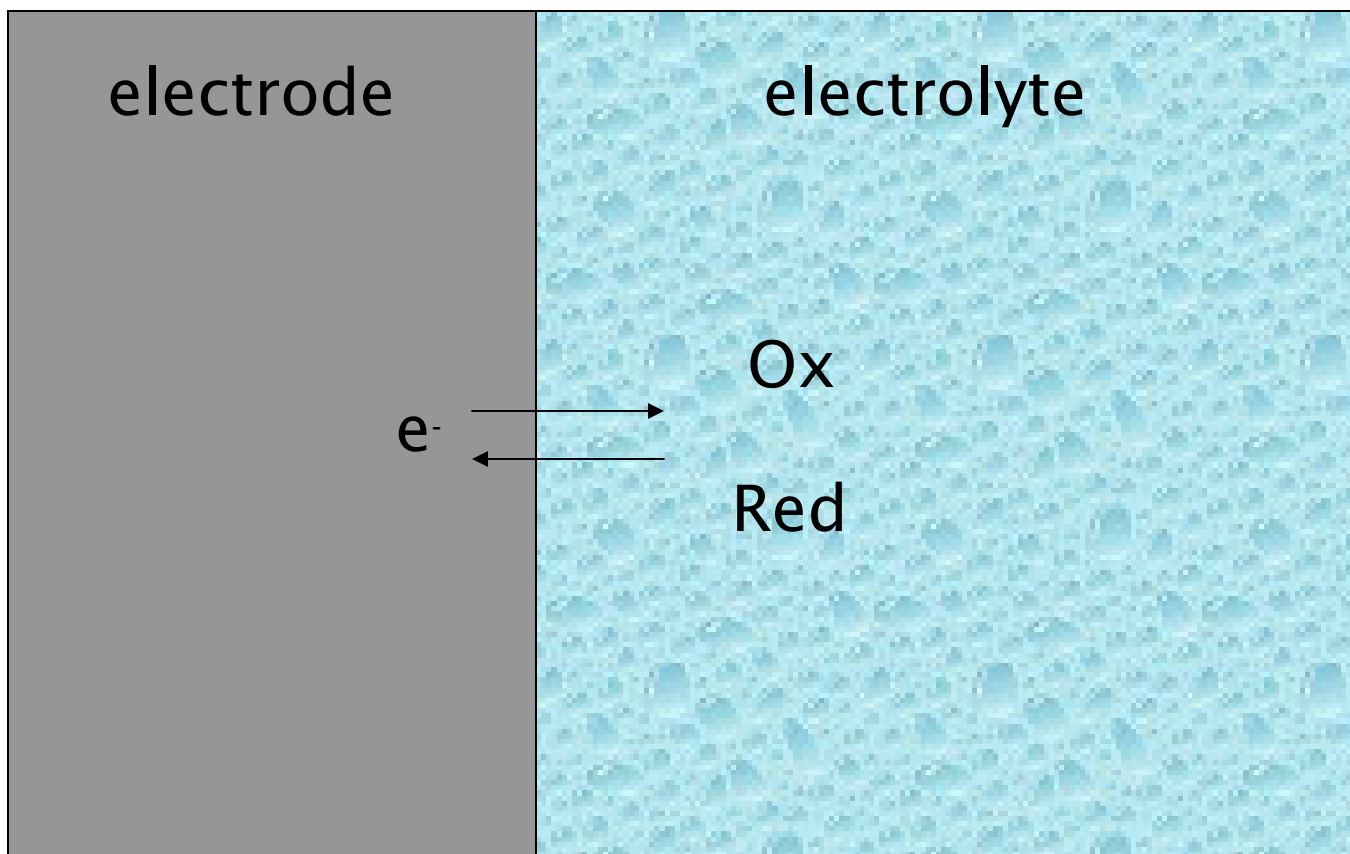
Marc Koper

Leiden University (NL)
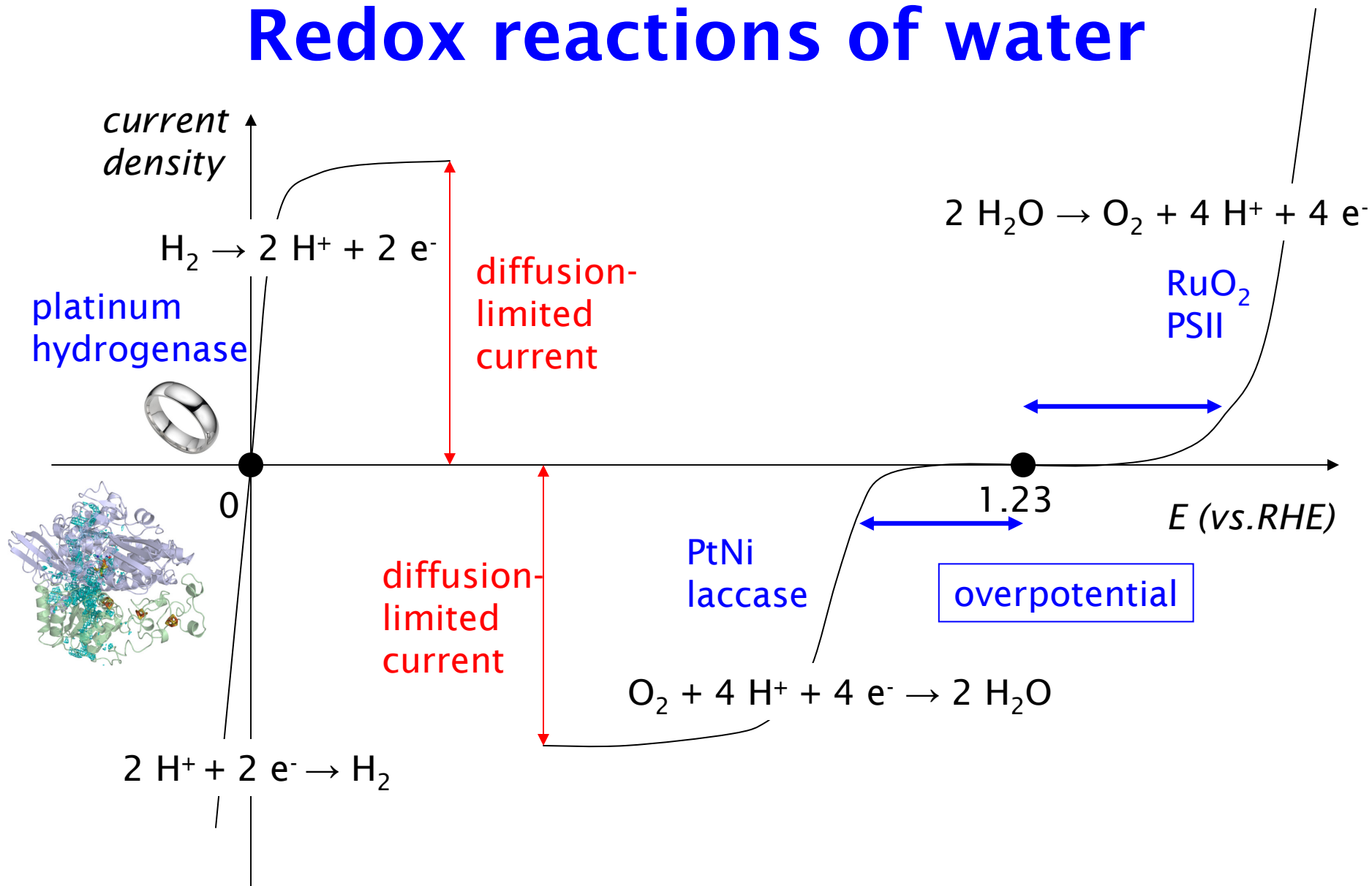
Summerschool Norderney
21-26 July 2013

Universiteit Leiden

Redox reactions

$$Ox + e^- \leftrightharpoons Red$$

electrode	electrolyte
	Ox
e^-	
	Red

Redox reactions of water

current density

$H_2 \rightarrow 2\,H^+ + 2\,e^-$

platinum
hydrogenase

diffusion-limited current

0

diffusion-limited current

$2\,H^+ + 2\,e^- \rightarrow H_2$

$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-$

RuO_2
PSII

1.23

E (vs.RHE)

PtNi
laccase

overpotential

$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$

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
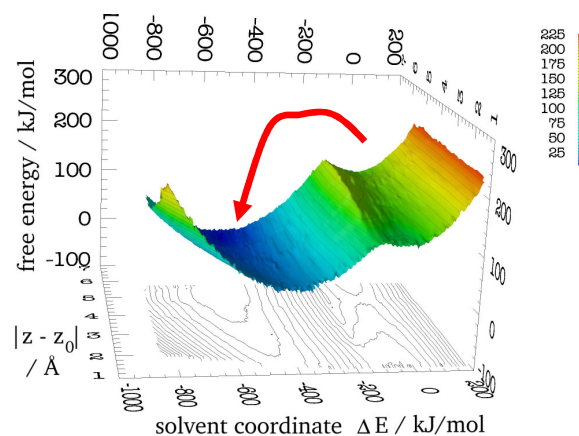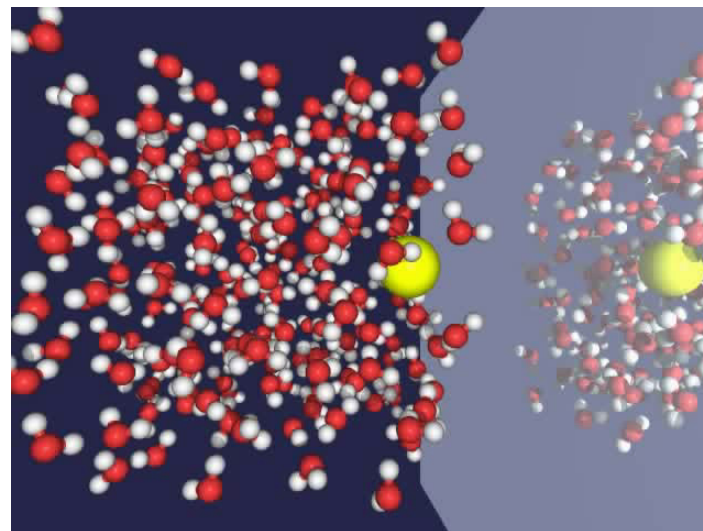
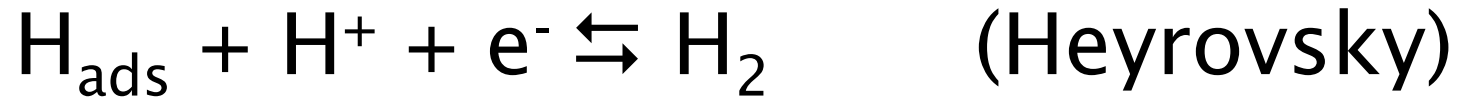1 e^- / 1 step / 0 intermediate
2 e^- / 2 steps / 1 intermediate
>2 e^- / >2 steps / >1 intermediate
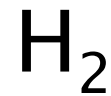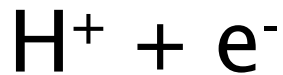
Single electron transfer

- Marcus Theory

- Activation energy
  determined by solvent
  reorganization energy λ
  (a difficult quantity to
  calculate accurately)

- Marcus Theory does not
  account for bond
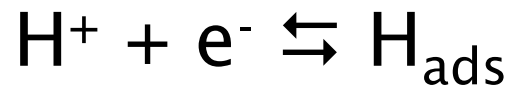 breaking, proton
  transfer, or catalysis.

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

Two electron transfer

$$2\,H^+ + 2\,e^- \rightleftarrows H_2$$

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

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

free energy

$H^+ + e^-$ H_{ads} H_2

Thermodynamics

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

$$H^+ + e^- \leftrightarrows H_{ads} \qquad\qquad E_1^{\,0} = -\,\Delta G_{ads}(H)/e_0$$
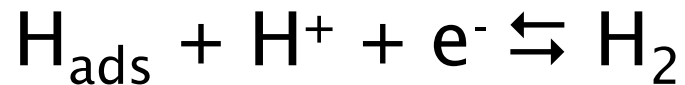
$$H_{ads} + H^+ + e^- \leftrightarrows H_2 \qquad\qquad E_2^{\,0} = \Delta G_{ads}(H)/e_0$$

Thermodynamic restriction: $(E_1^{\,0} + E_2^{\,0})/2 = E^0$

Thermodynamic volcano plot

Potential of thermodynamically least favorable reaction

zero thermodynamic overpotential

0

$H^+ + H_{ads} + e^- \leftrightarrows H_2$

$H^+ + e^- \leftrightarrows H_{ads}$

0

$\Delta G_{ads}(H)$
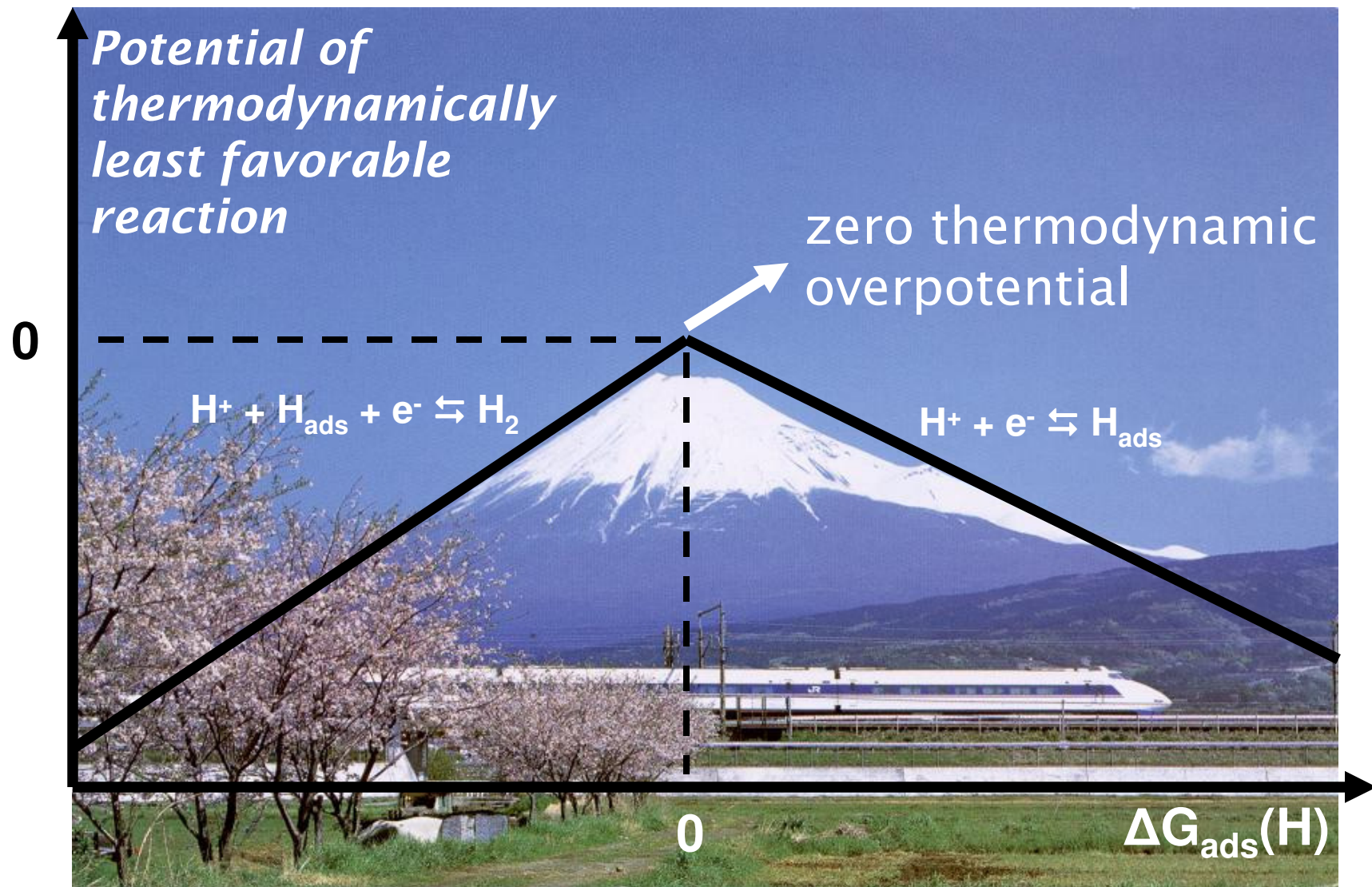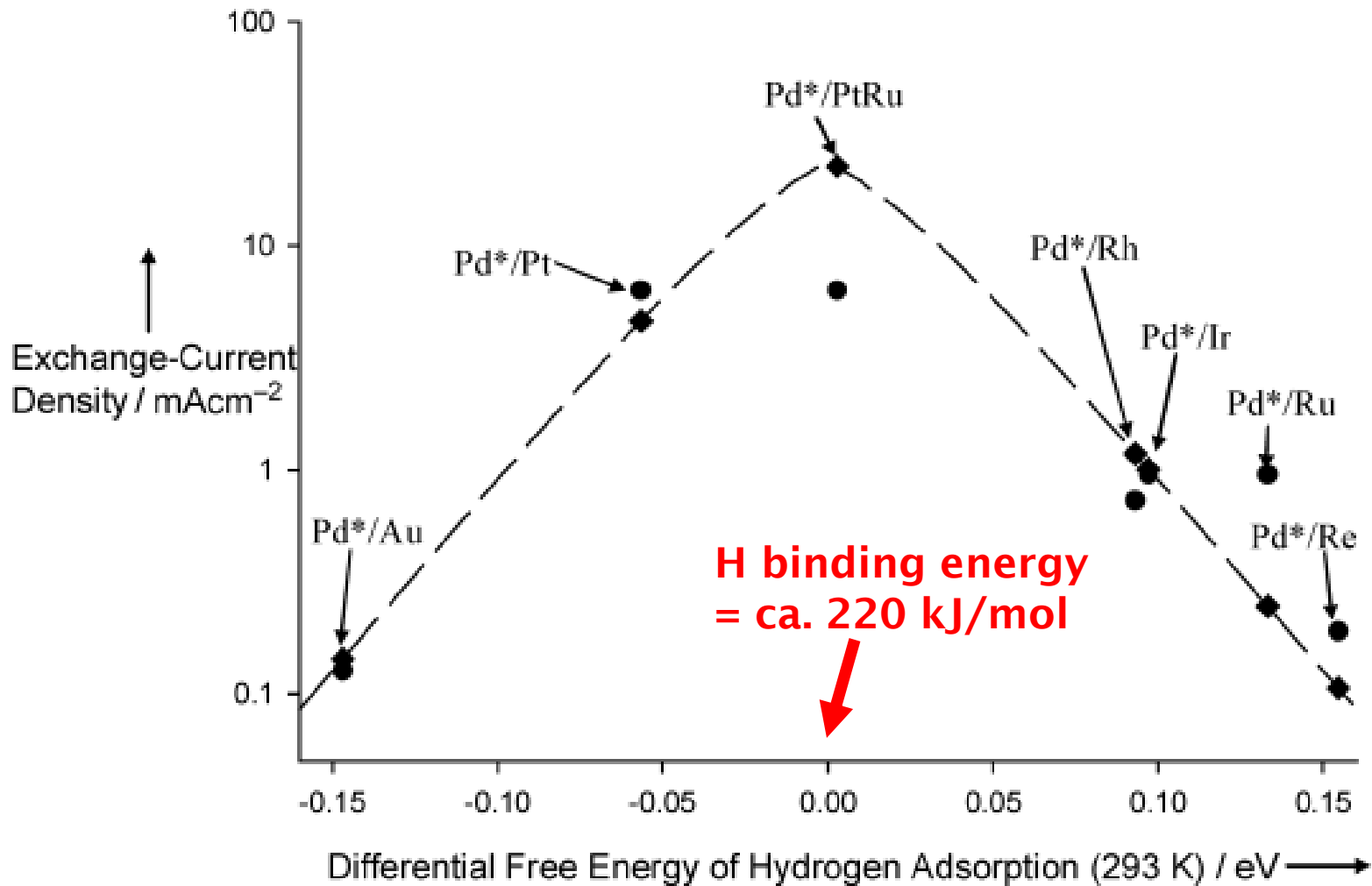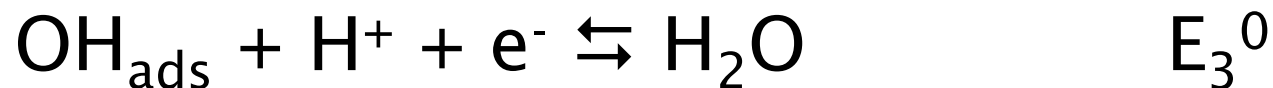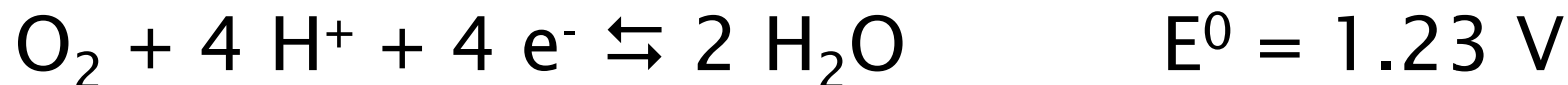
R.Parsons,Trans.Faraday Soc. (1958); H.Gerischer (1958)
J.K.Nørskov et al., J.Electrochem.Soc. (2004)

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

Experimental volcano for H₂ 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

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

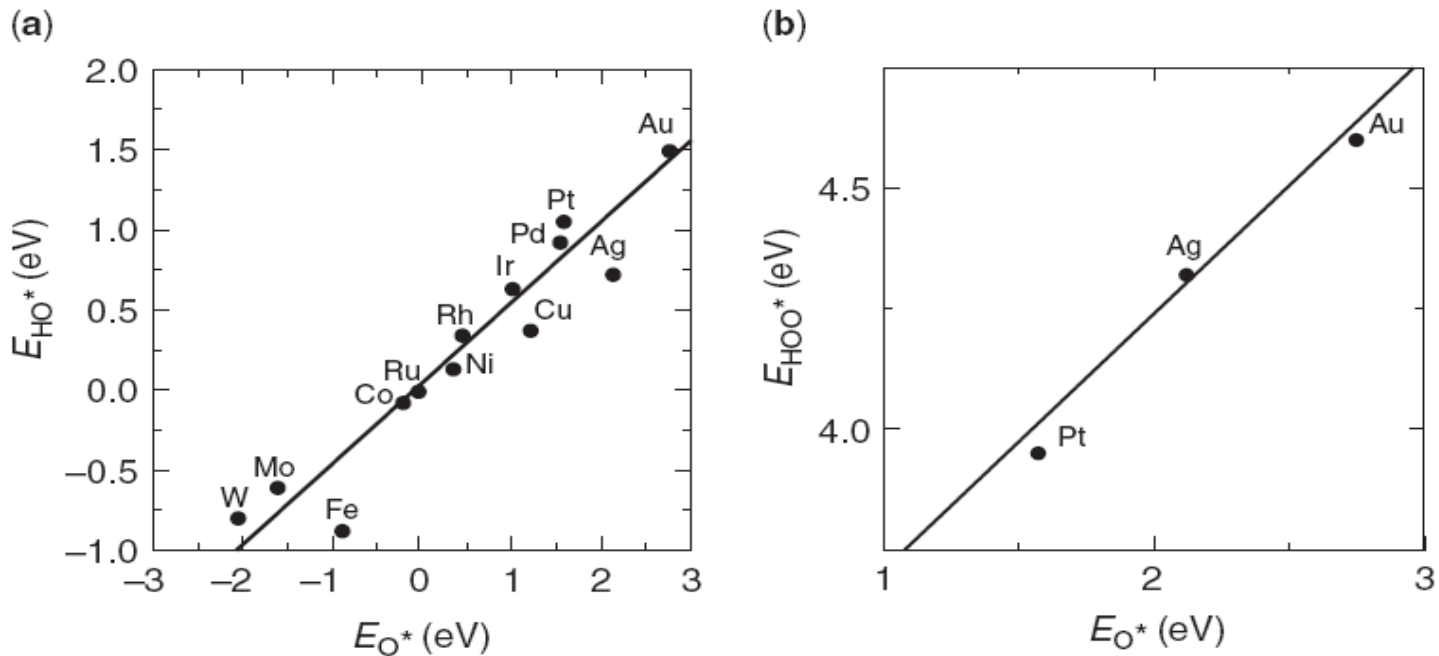**Independent of the mechanism**

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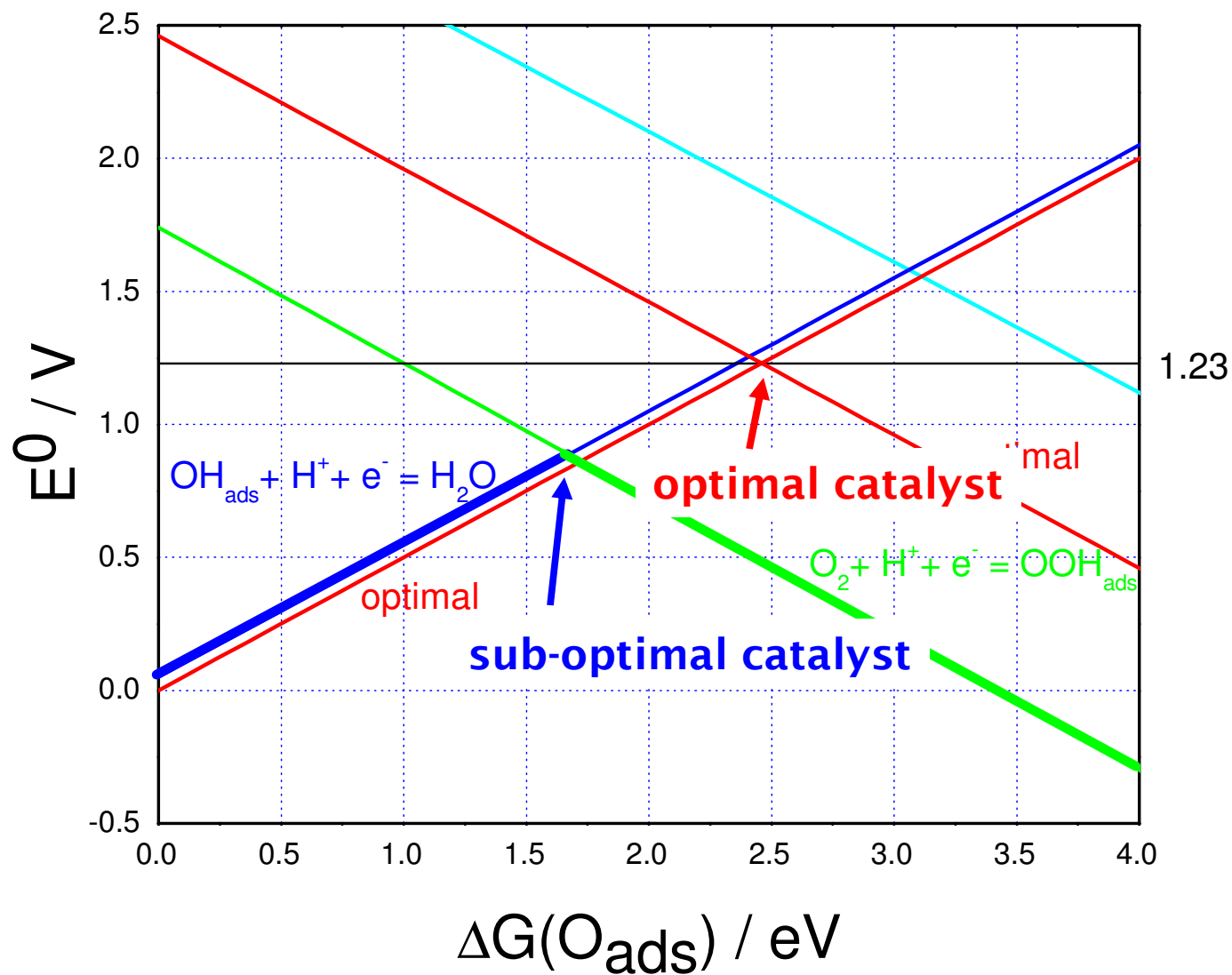
The optimal scaling relations

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

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

The optimal volcano

$OH_{ads} + H^+ + e^- = H_2O$

optimal catalyst

''mal

optimal

$O_2 + H^+ + e^- = OOH_{ads}$

sub-optimal catalyst

1.23

E^0 / V

$\Delta G(O_{ads})$ / eV

Does optimal scaling exist?

Metals:

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

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

Oxides:

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

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

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

"Fundamental" overpotential?

$$\eta_T(\text{ORR,OER}) = \frac{\overbrace{K_{OOH} - K_{OH}}^{\sim\,3.15\ \text{eV}} - 2.46\ \text{eV}}{2\,e} = \sim 0.35\ \text{V}$$
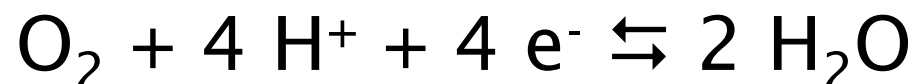
One does not even need to know the catalyst-oxygen interaction...

$$\Delta G[\text{HO}_2^-(\text{aq})] - \Delta G[\text{OH}^-(\text{aq})] = 3.4\ \text{eV}$$
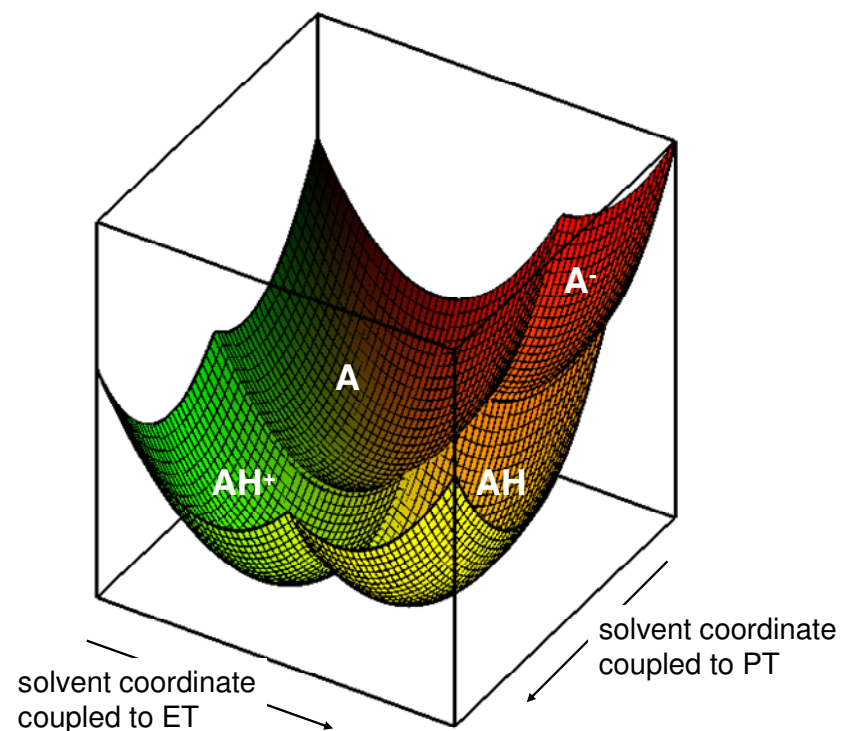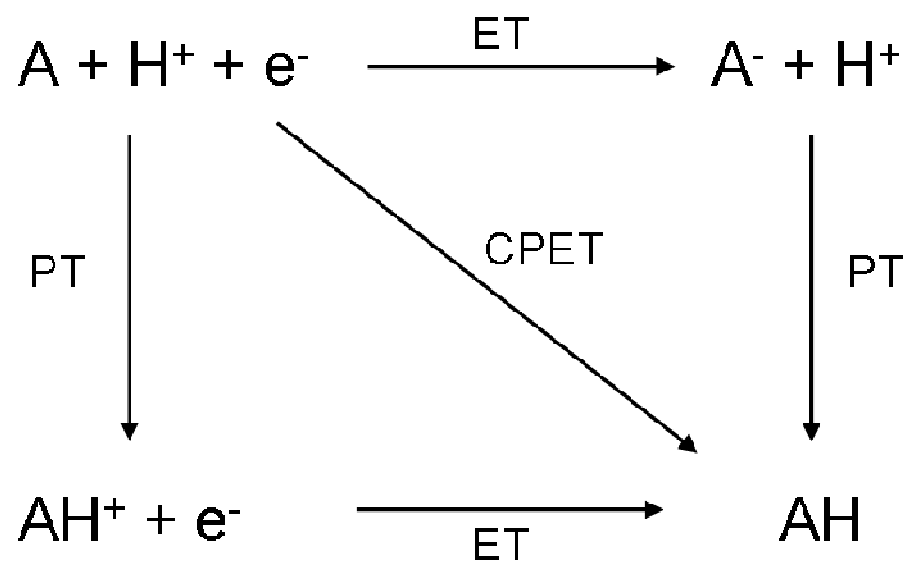
I.Man, J.Rossmeisl et al., ChemCatChem 3 (2011) 1159
M.T.M.Koper, J.Electroanal.Chem. 660 (2011) 254; Chem.Sci. 4 (2013) 2710
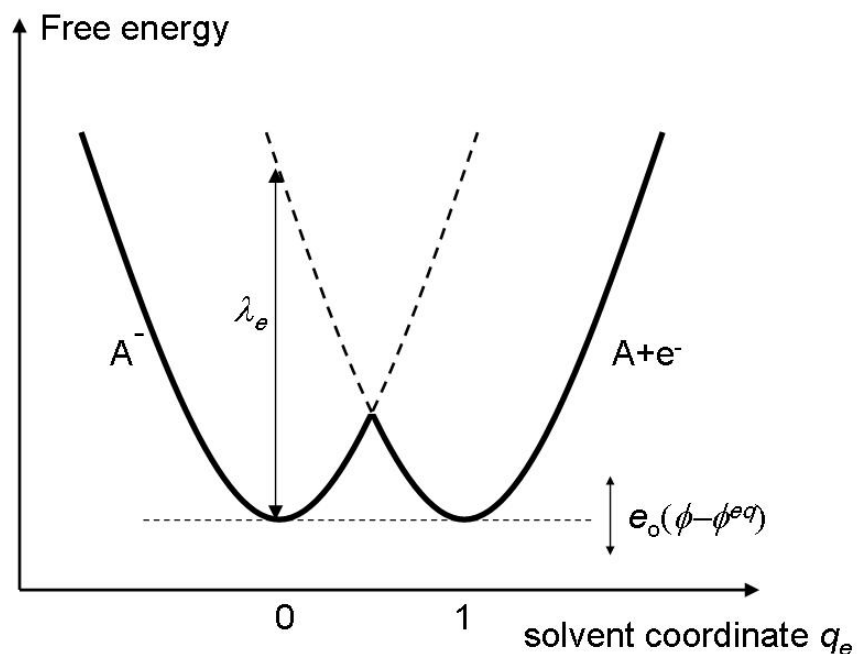
Proton-coupled electron transfer

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

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

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

- Are proton and electron transfer always coupled?

- How does (de-)coupled proton-electron transfer manifest?
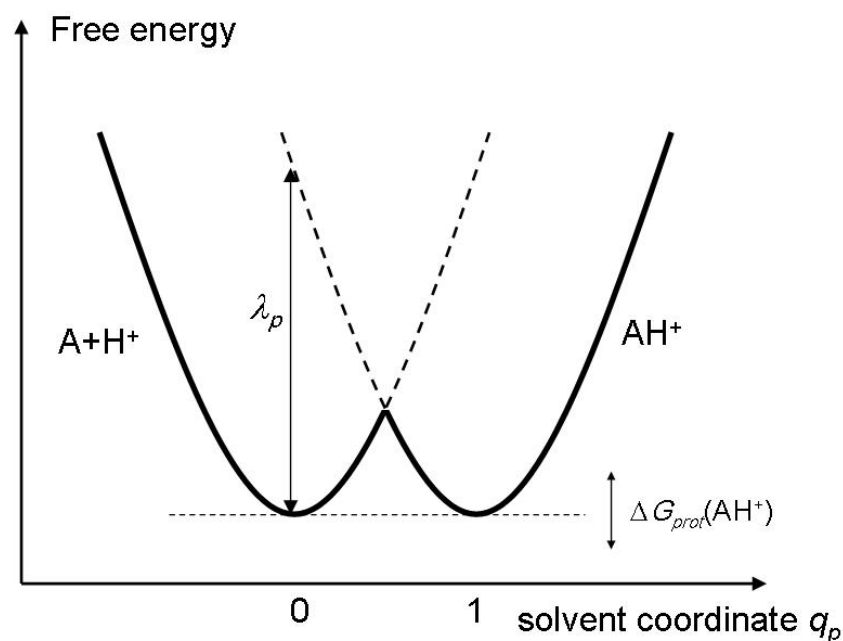
Proton-coupled electron transfer

$$A + H^+ + e^- \xrightarrow{\text{ET}} A^- + H^+$$

PT — CPET — PT

$$AH^+ + e^- \xrightarrow{\text{ET}} AH$$

solvent coordinate coupled to ET

solvent coordinate coupled to PT

A⁻   A   AH⁺   AH

S. Hammes-Schiffer, A.A.Stuchebrukhov, Chem.Rev.110 (2010) 6939

Hamiltonian of PCET

$$H(q_e, q_p) = \varepsilon_A n_A + \sum_k \varepsilon_k n_k + \sum_k \left(V_k c_k^+ c_A + V_k^* c_A^+ c_k \right) + \varepsilon_{p,1} n_1 + \varepsilon_{p,2} n_2 + V_{pt} c_1^+ c_2 + V_{pt}^* c_2^+ c_1$$

$$+ \lambda_e q_e^2 + \lambda_p q_p^2 - 2\overline{\lambda} q_e q_p - 2\lambda_e q_e - 2\lambda_p q_p + \beta n_A n_2$$
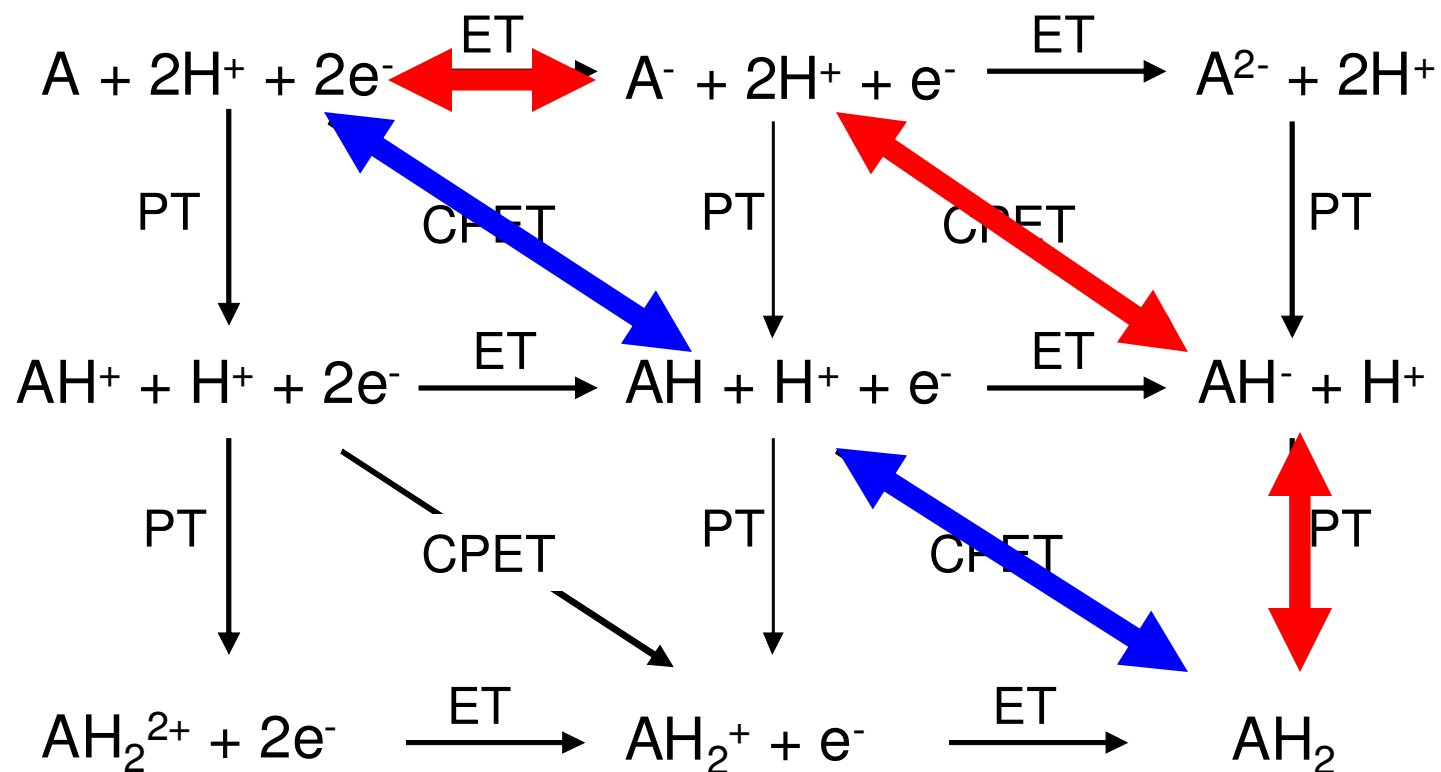

Electron affinity + solvation energy

Proton affinity = pK$_a$(AH$^+$)

j.Grimminger, S.Bartenschlager, W.Schmickler, Chem.Phys.Lett. 416 (2005) 316
M.T.M.Koper, Phys.Chem.Chem.Phys. 15 (2013) 1399

Proton-coupled electron transfer

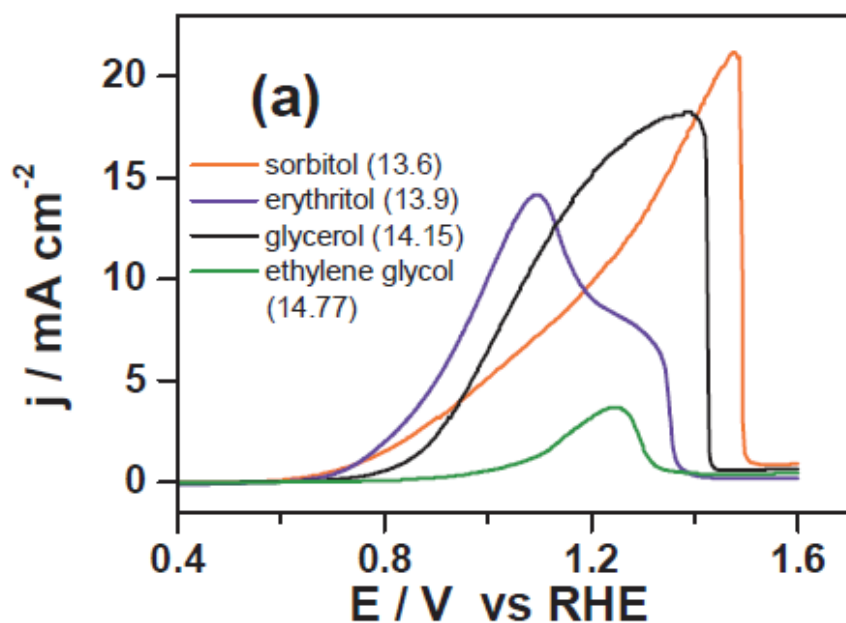# When PT and ET decouple

- PT and ET are concerted if off-diagonal states are energetically unfavorable. Reaction rate is independent of pH on the <u>RHE</u> 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 <u>RHE</u> 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
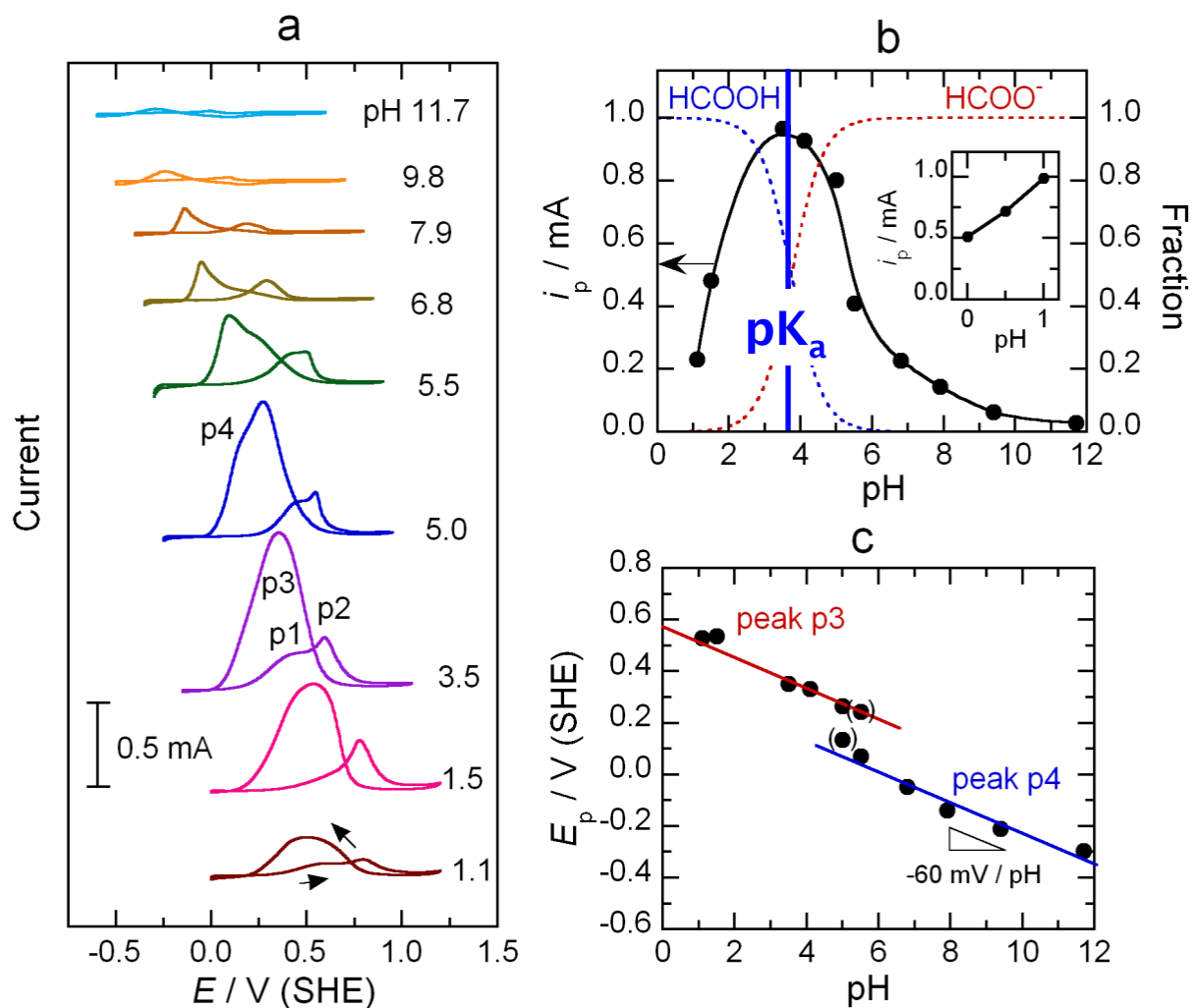
Formic acid oxidation prefers intermediate pH

Oxidation of poly-ols

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

"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
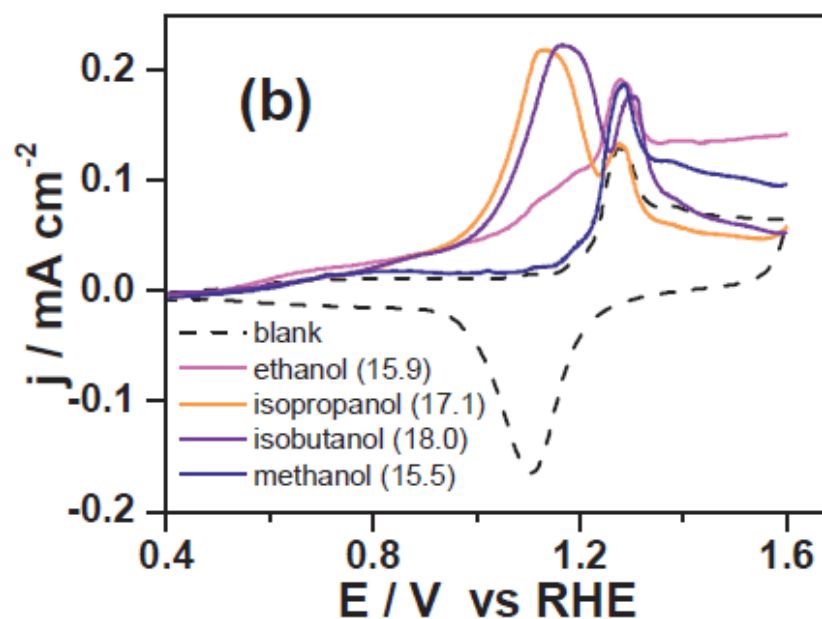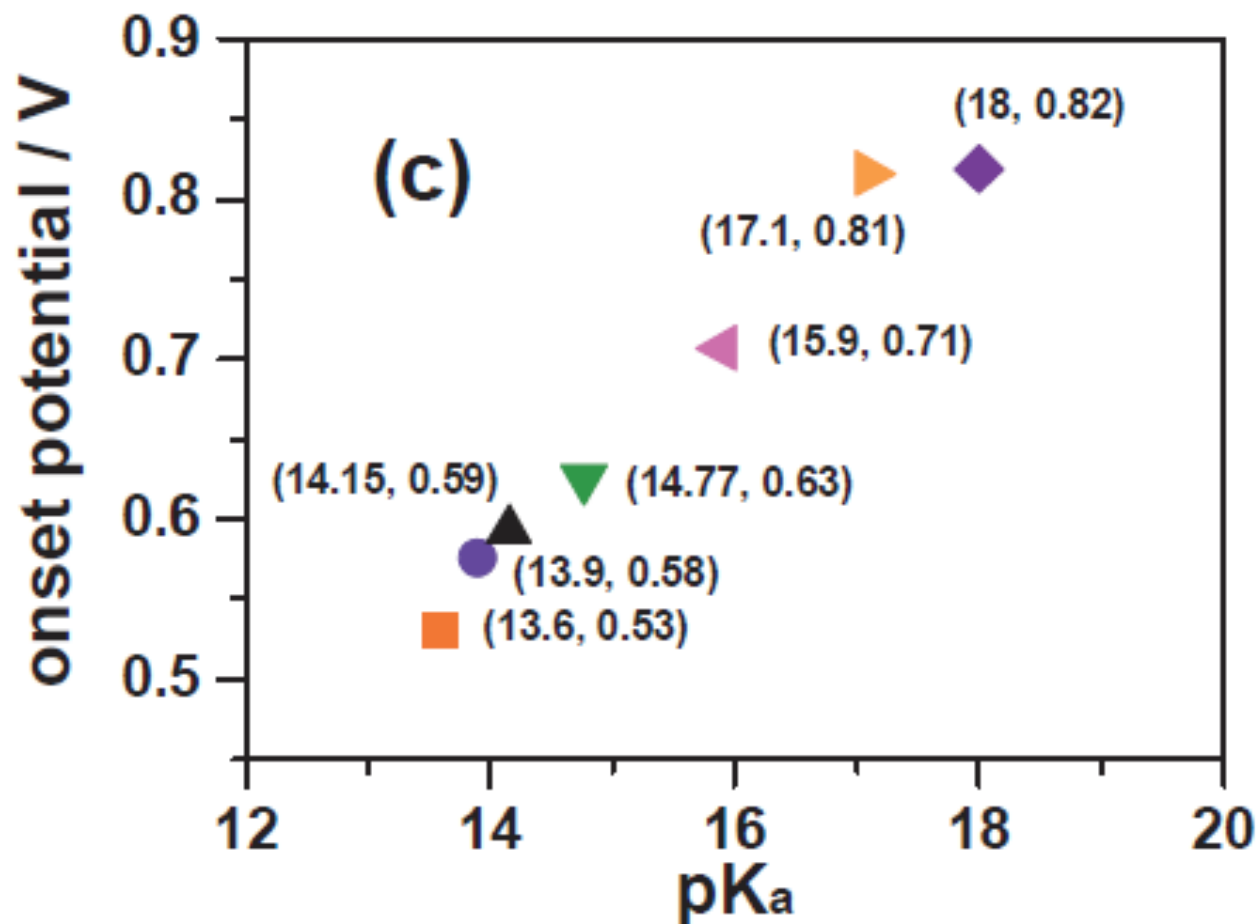
More detailed mechanism

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:

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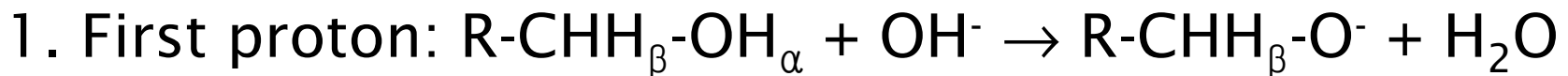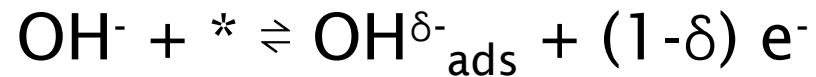
CO_{ads} favors OH_{ads} formation

3. Second proton:

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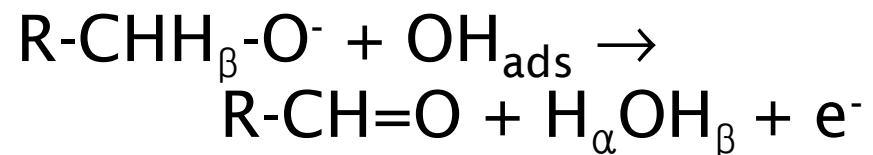
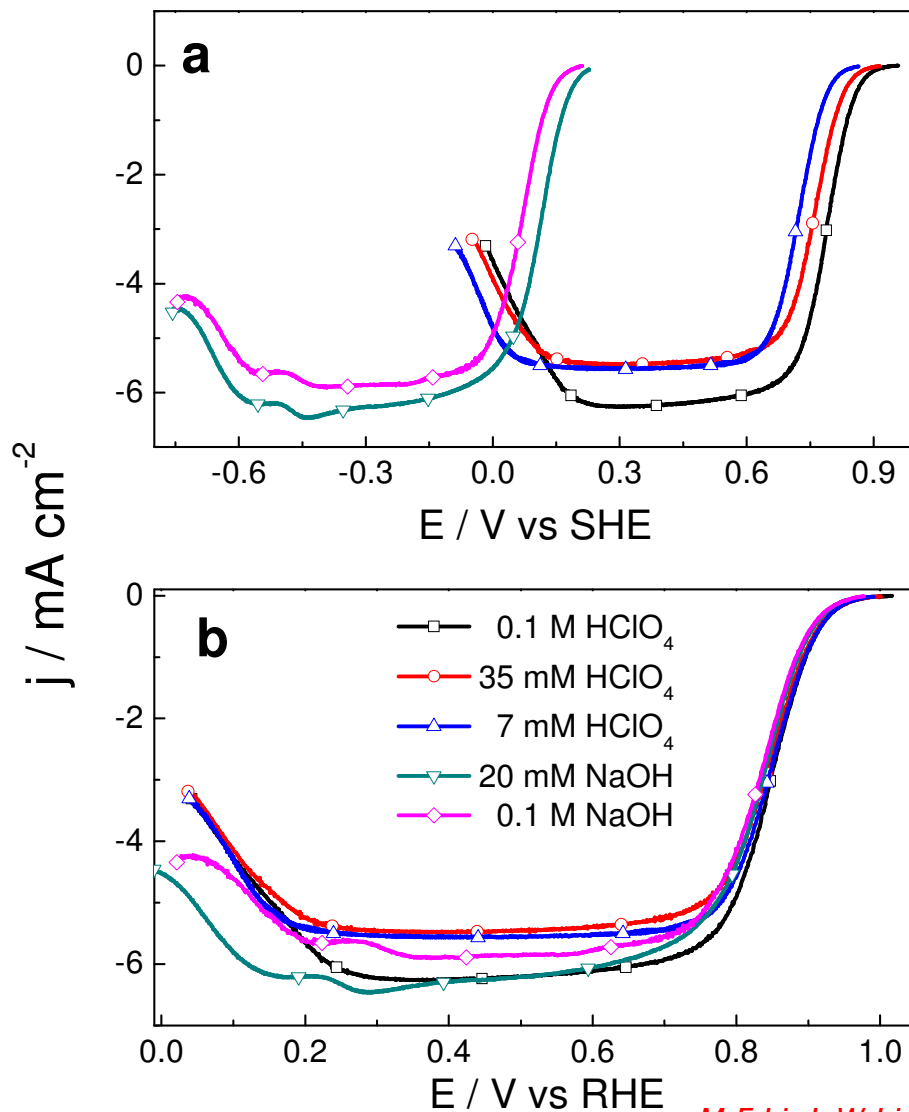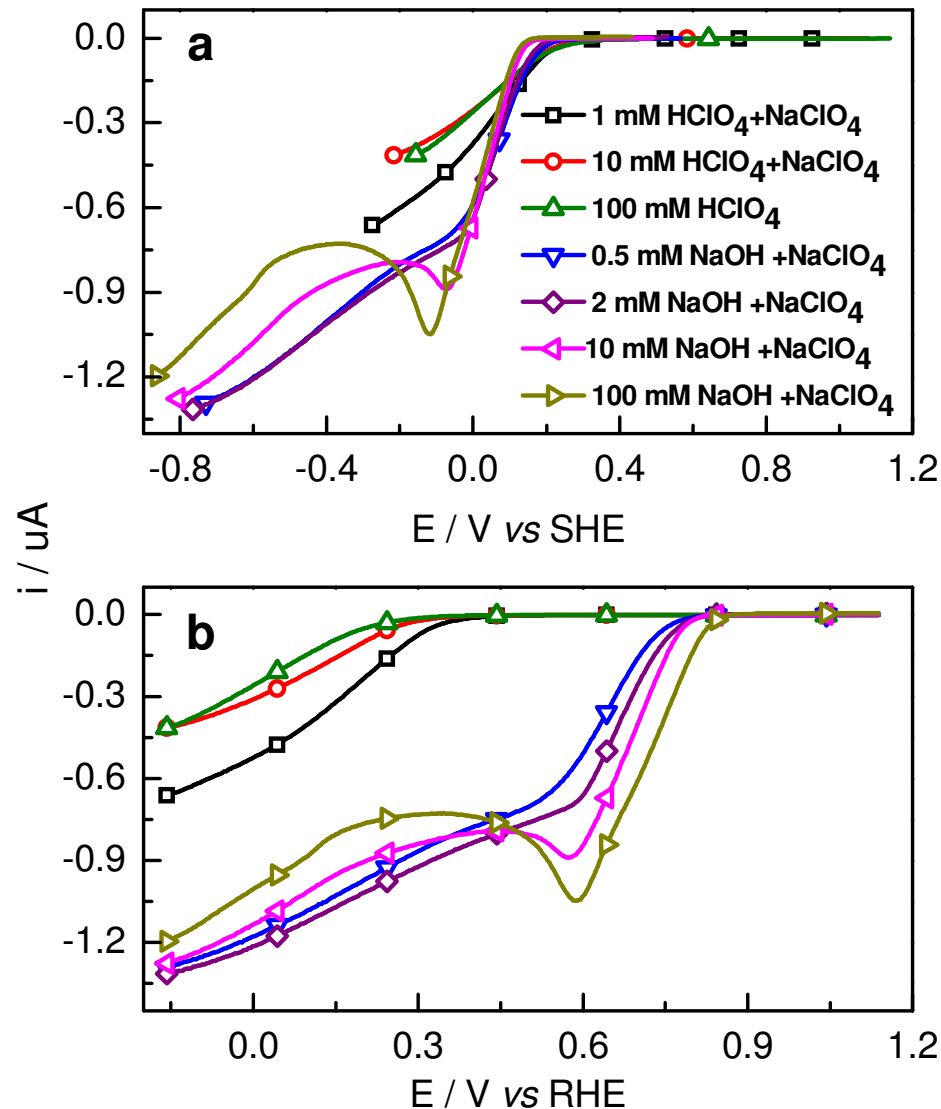*gold catalyzed*

CPET in oxygen reduction on Pt

The ORR rate on Pt is independent of pH on the RHE scale.
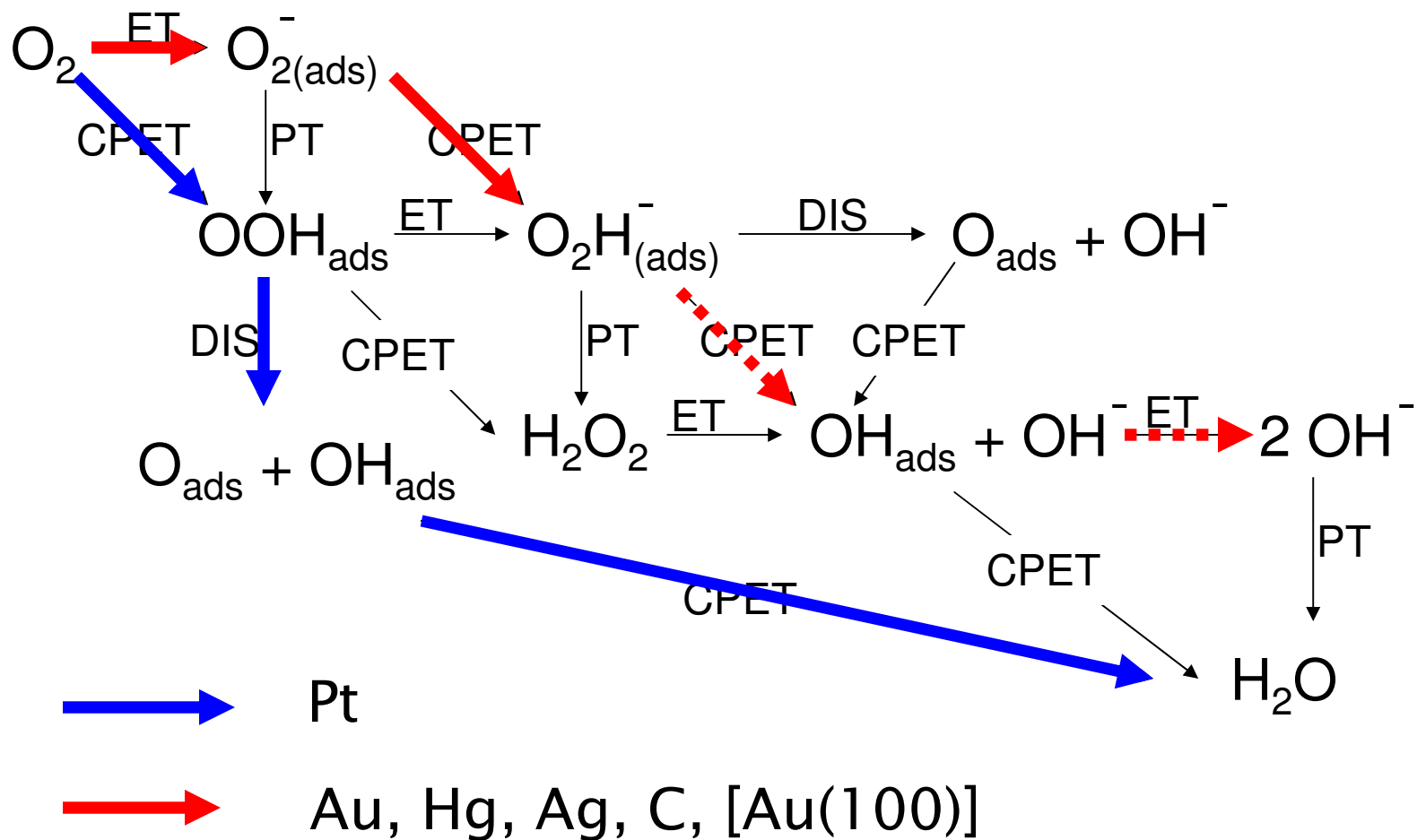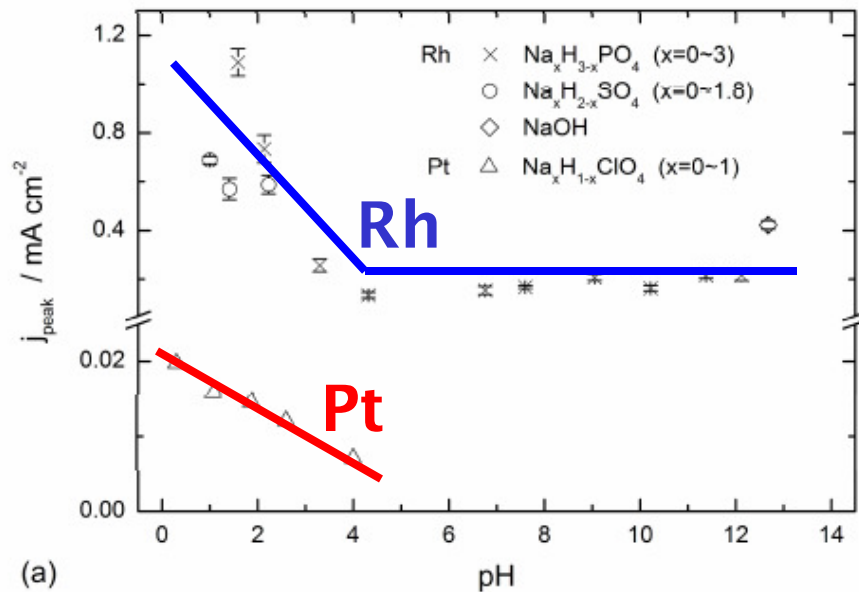
Concerted proton-electron transfer.

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

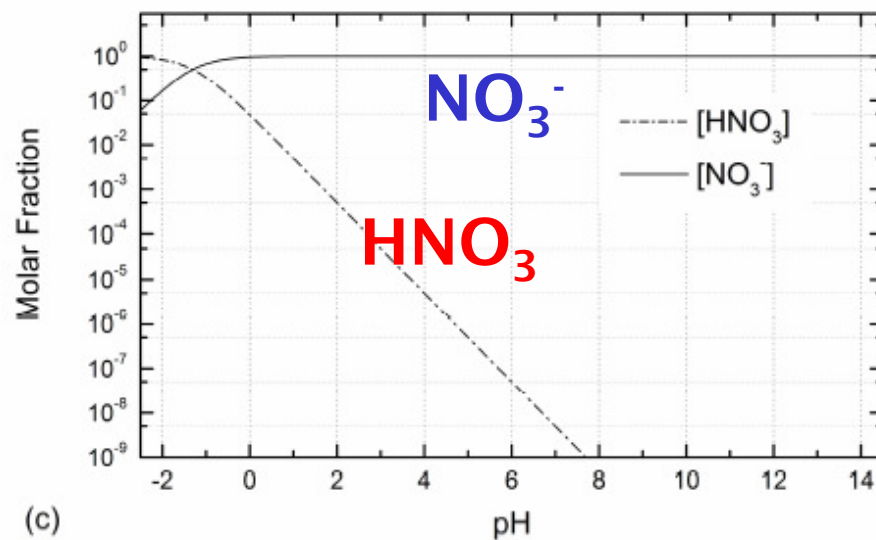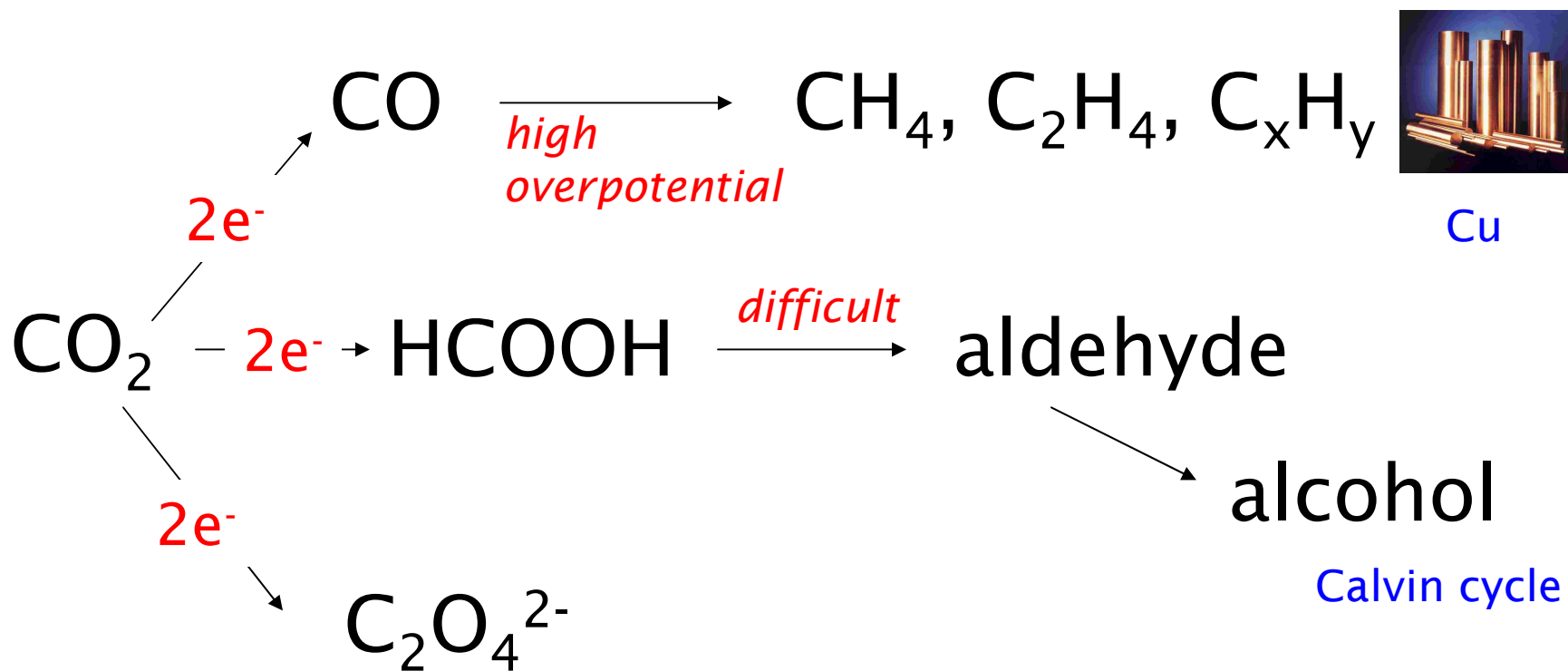# pH dependence of nitrate reduction

pK$_a$[HNO$_3$] = -1.3

Two reactive forms of nitrate:

HNO$_3$ is the only reactive species on Pt.

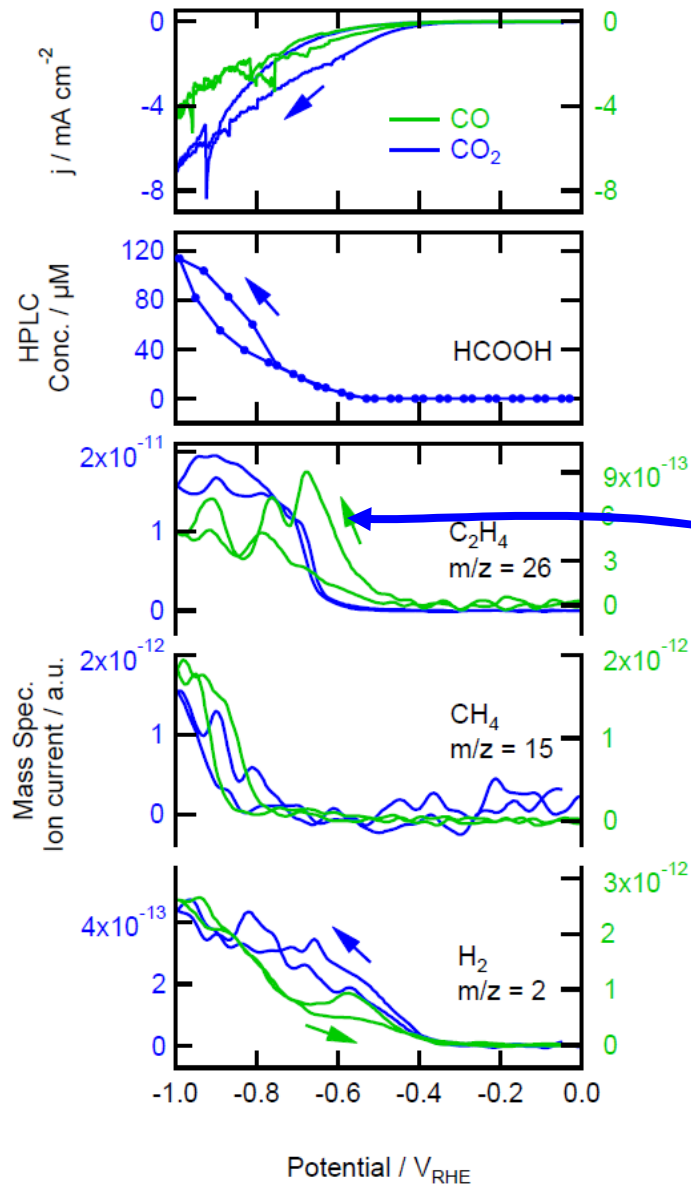Both HNO$_3$ and NO$_3^-$ can be reduced on the more reactive Rh.

J.Yang, P.Pascual, M.Duca, M.T.M.Koper, submitted

Electrocatalytic CO_2 reduction

CO_2

$2e^-$ → CO $\xrightarrow{\text{\textit{high overpotential}}}$ CH_4, C_2H_4, C_xH_y

Cu

CO_2 $\xrightarrow{2e^-}$ HCOOH $\xrightarrow{\text{\textit{difficult}}}$ aldehyde

alcohol
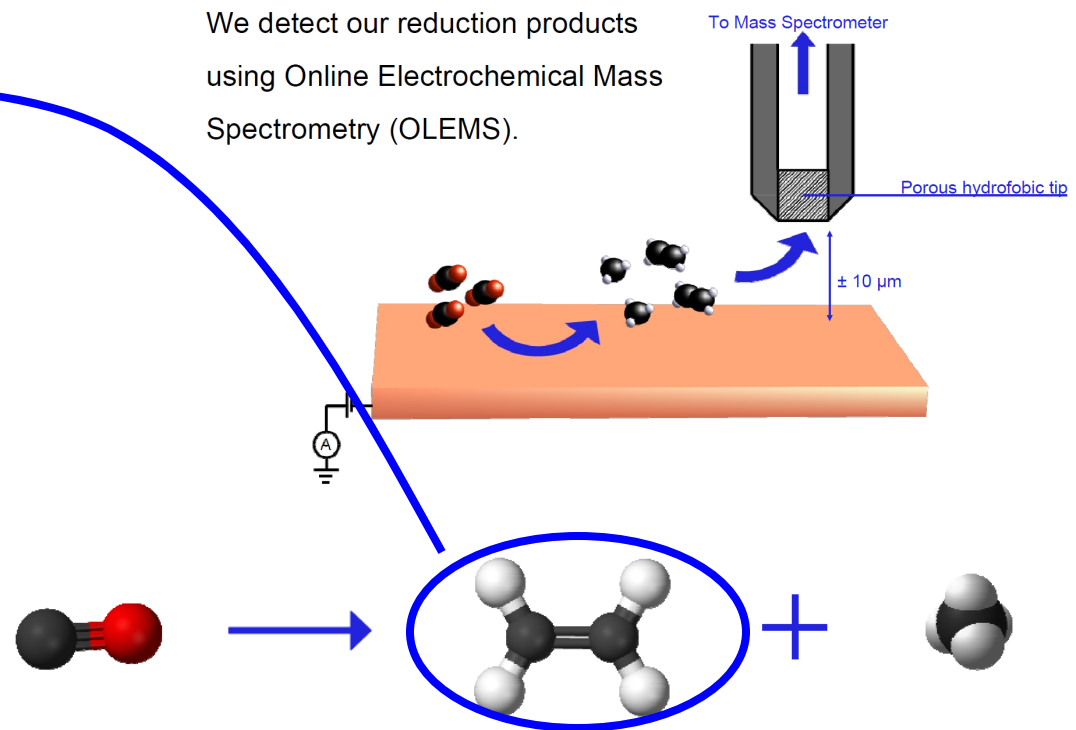
Calvin cycle

$2e^-$ → $C_2O_4^{2-}$
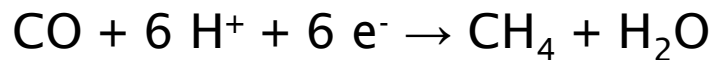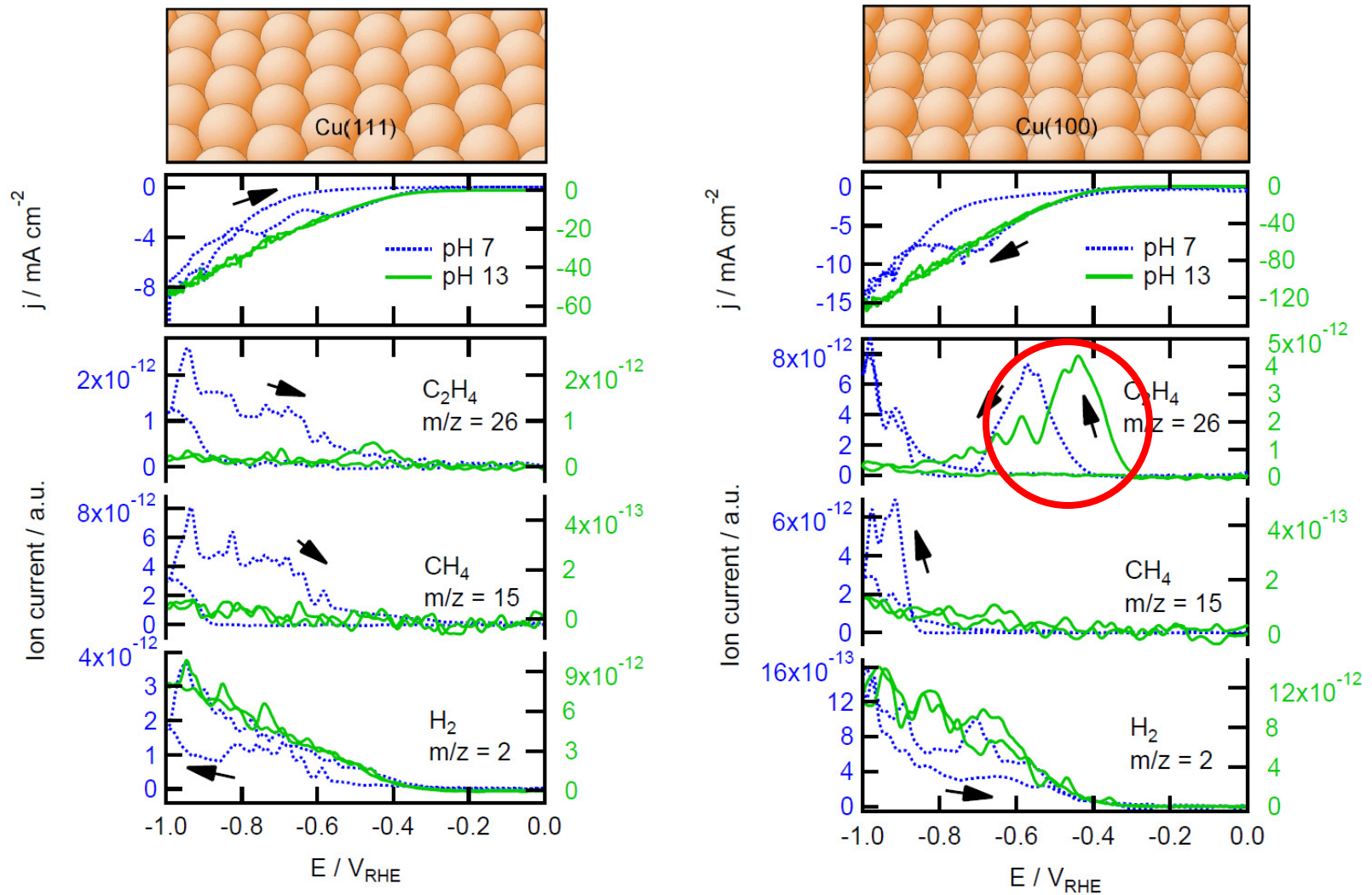
CO and CO$_2$ reduction on copper

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).

To Mass Spectrometer

Porous hydrofobic tip

± 10 μm

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)

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

$$2\,CO + 8\,H^+ + 8\,e^- \rightarrow C_2H_4 + 2\,H_2O$$
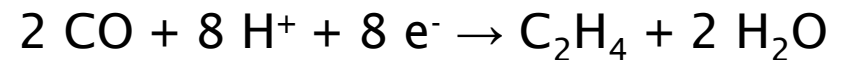
(100) terraces - not (100) steps

A consistent mechanism

HCOOH

$HCHO \longrightarrow CH_2OH_{ads} \longrightarrow CH_3OH$

$2H^+,2e^-$

$HCO_{ads} \longrightarrow HC_{ads} \longrightarrow CH_4$

$2H^+,2e^-$

H^+,e^-

$CO_2 \longrightarrow CO_{ads}$

e^-

O   O⁻
C C

HC=CH
O   O

CH$_2$
O   CH

HC = CH

C$_2$H$_4$

?

reductive CO coupling
McMurry coupling
epoxide reduction

7.91 e⁻   3.52 e⁻
2.03 e⁻   7.48 e⁻

K.J.P.Schouten, Y.Kwon, C.J.M.van der Ham, Z.Qin, M.T.M.Koper, Chem.Sci. 2 (2011) 1902
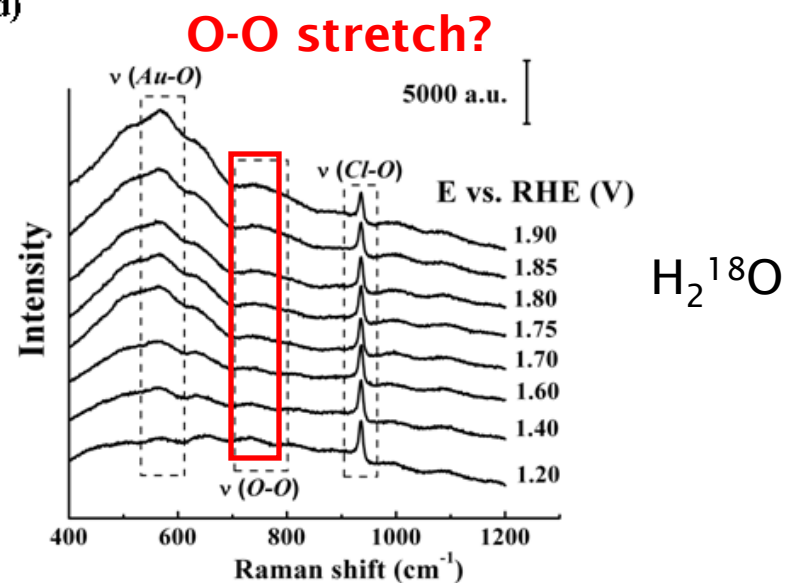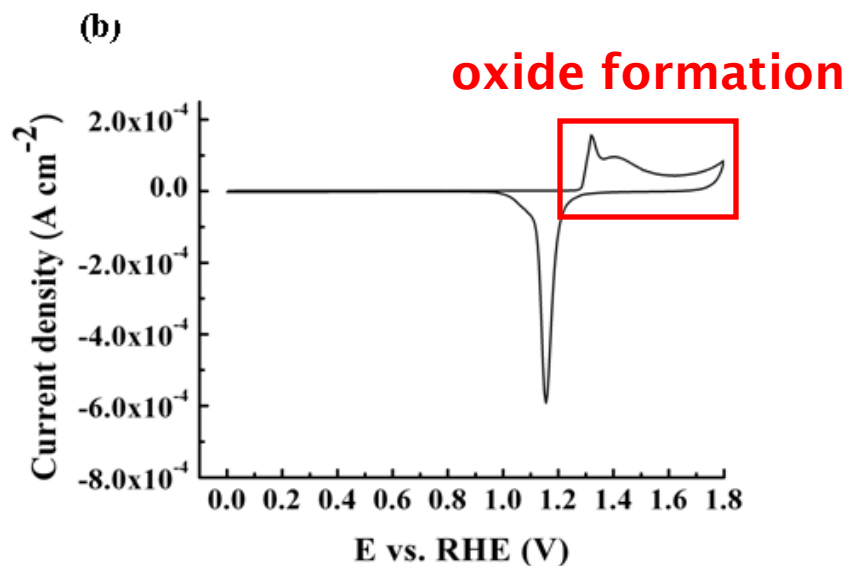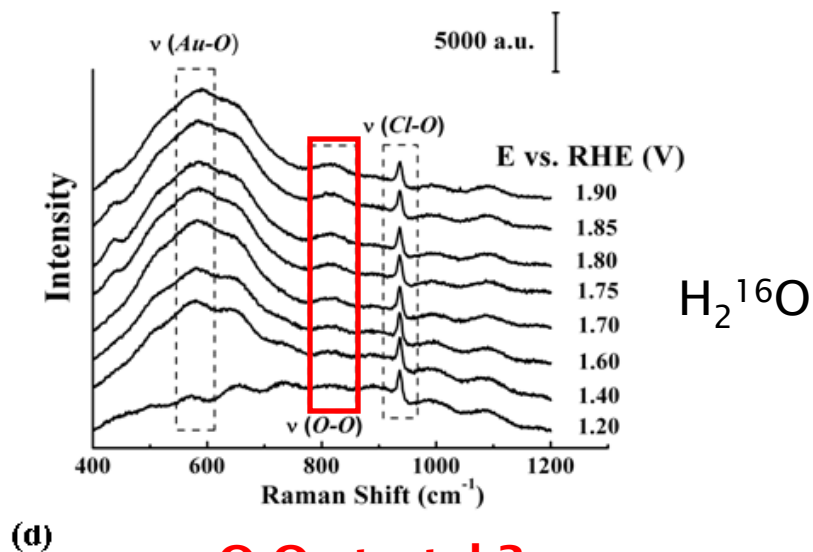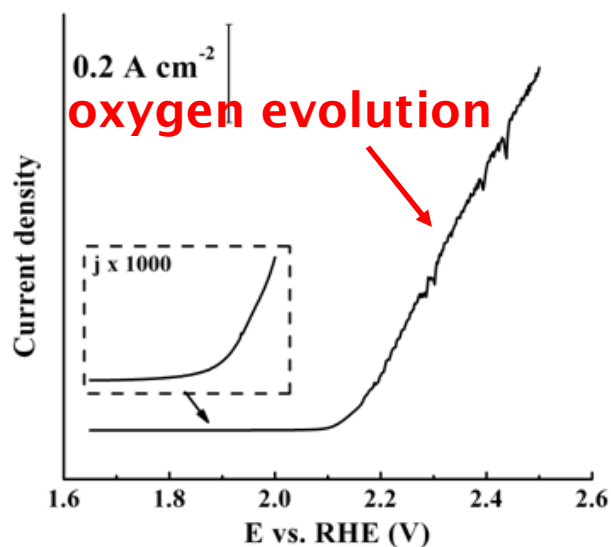F.Calle Vallejo, M.T.M.Koper, Angew.Chem.Int.Ed 52 (2013) 7282
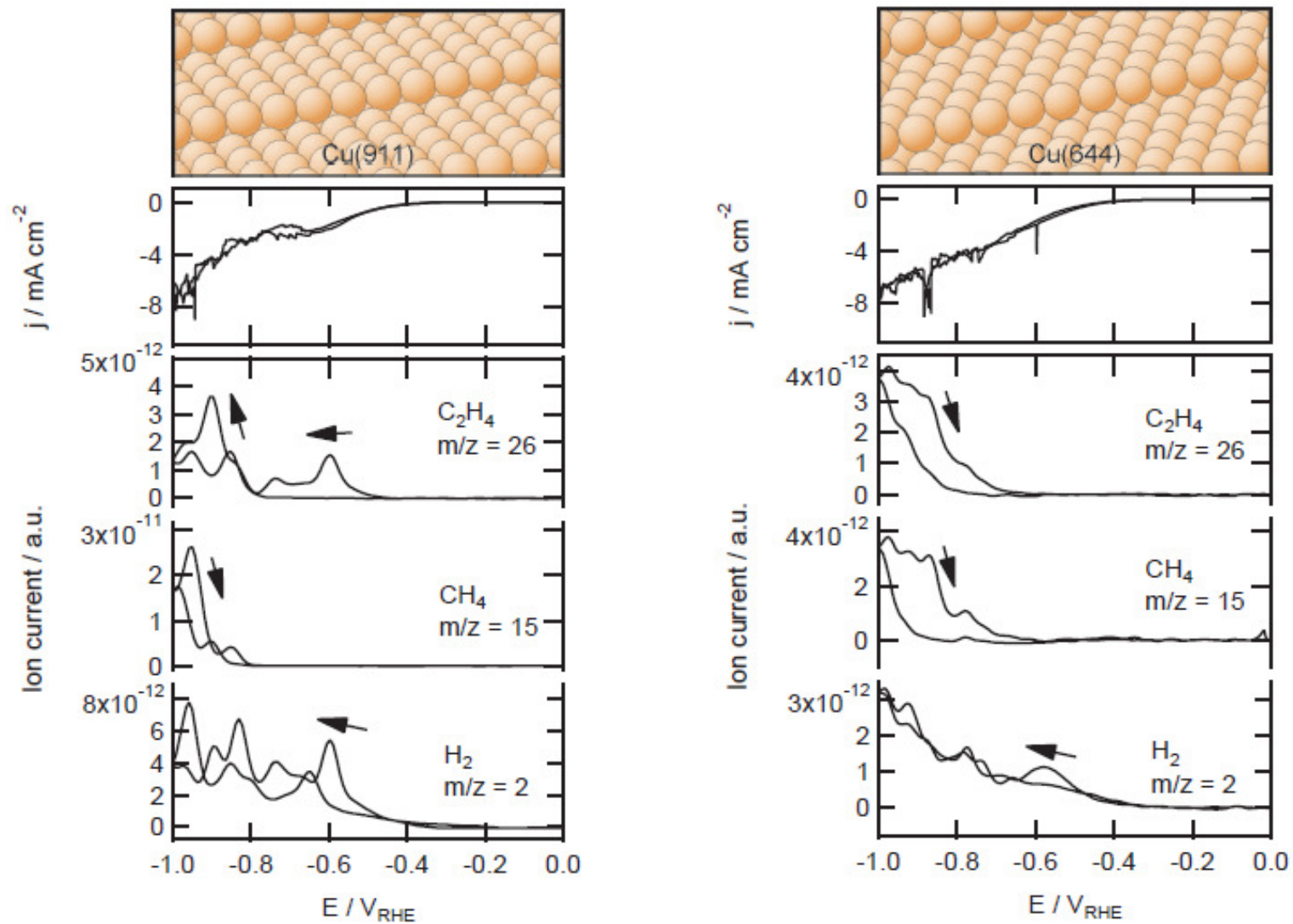
1789: birth of water splitting
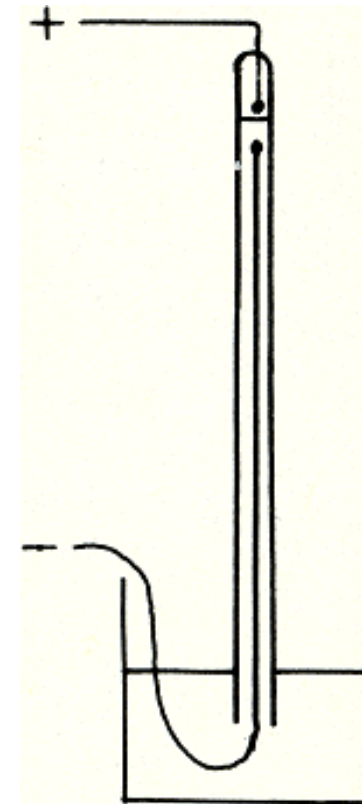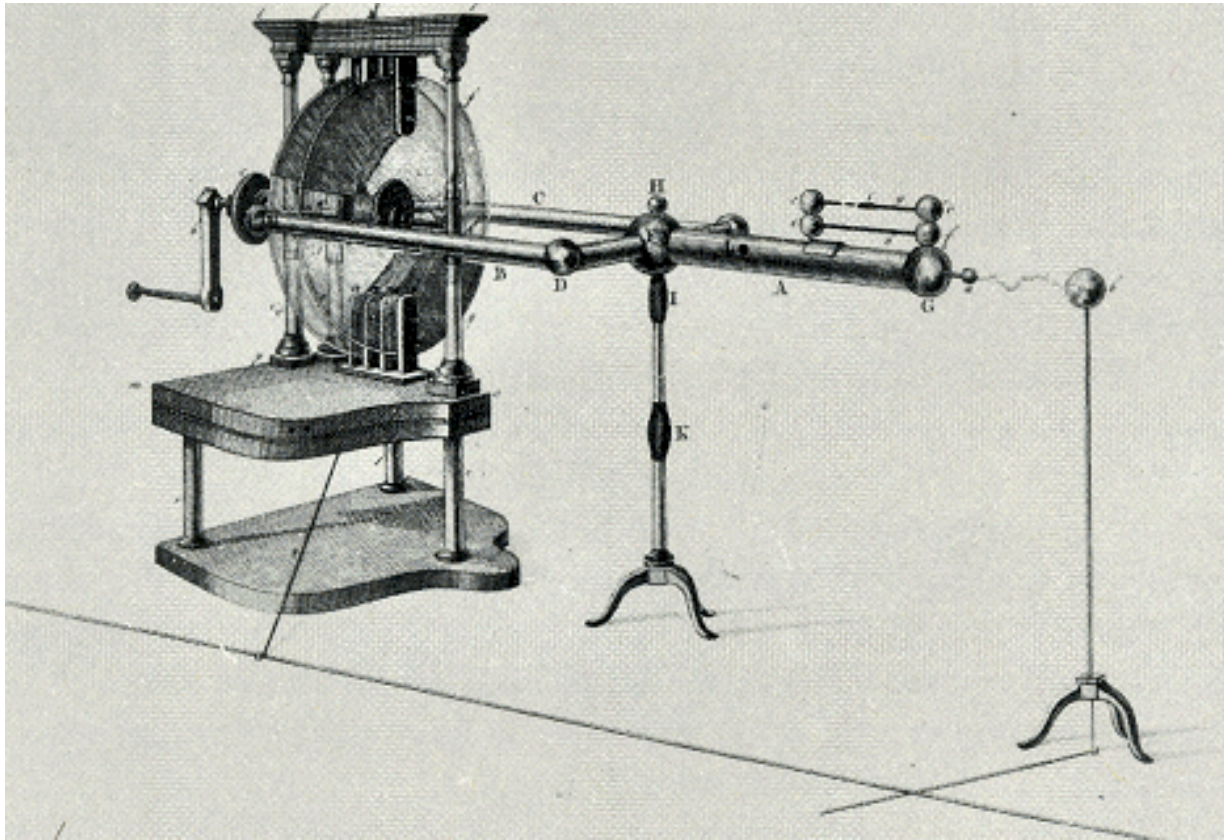
"Sur une manière de décomposer l'Eau en Air inflammable et en Air vital"

A. Paets van Troostwijk, J.R. Deiman, Obs. Phys. 35 (1789) 369.
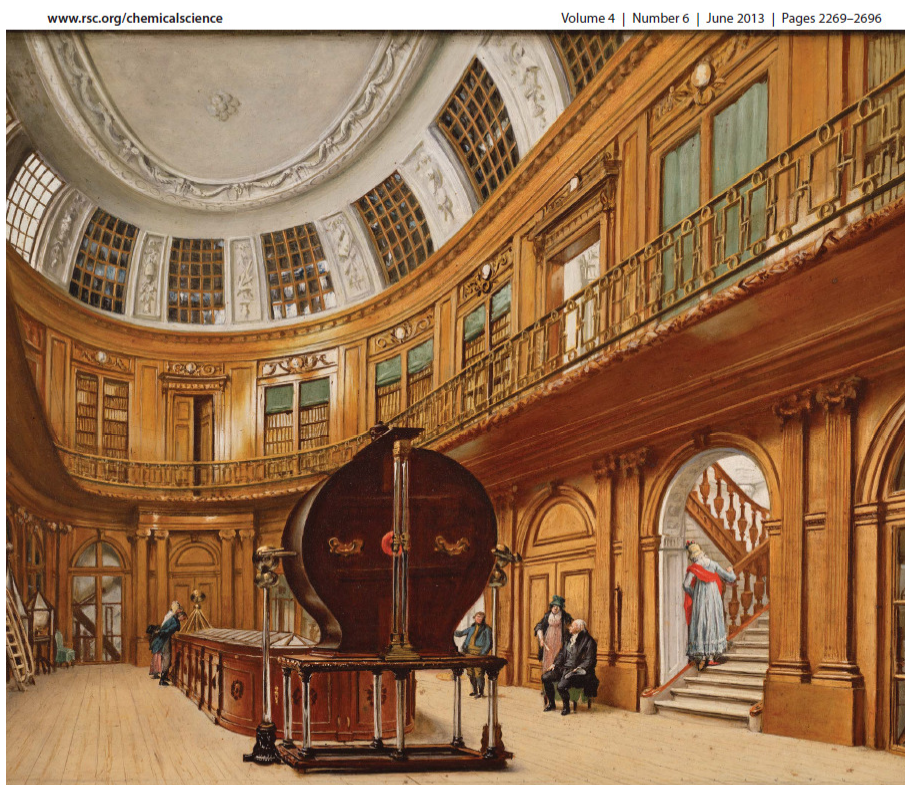
Oxygen evolution on gold: SERS

$H_2{}^{16}O$

$H_2{}^{18}O$

oxygen evolution

oxide formation

O-O stretch?

O.Diaz-Morales, F.Calle-Vallejo, C.de Munck, M.T.M.Koper, Chem.Sci. 4 (2013) 2334

O$_2$ evolution on gold: online MS

Chemical Science

www.rsc.org/chemicalscience — Volume 4 | Number 6 | June 2013 | Pages 2269–2696

Oxygen evolution from a Au electrode with an oxide layer formed in ^{18}O-water: ^{36}O$_2$ is evolved first.

Suggests an oxide decomposition/dispropor-tionation mechanism

Teyler's Museum, Haarlem (NL)

ISSN 2041-6520

RSC Publishing

EDGE ARTICLE
Marc T. M. Koper et al.
Electrochemical water splitting by gold: evidence for an oxide decomposition mechanism

2041-6520(2013)4:6;1-P

O.Diaz-Morales, F.Calle-Vallejo, C.de Munck, M.T.M.Koper, Chem.Sci. 4 (2013) 2334

Conclusions

- 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
- Many important electrocatalytic reactions are pH dependent

Acknowledgements

- Paramaconi Rodriguez, Youngkook Kwon, Klaas Jan Schouten, Zhisheng Qin, Elena Perez Gallent, Stanley Lai, Federico Calle-Vallejo, Oscar Diaz-Morales, Jian Yang
- Jiyong Joo, Masatoshi Osawa (Sapporo)
- Netherlands Organization for Scientific Research (NWO)
- National Research School Catalysis (NRSC)
- BioSolarCells consortium (NL)
- European Commission (FP7 ELCAT Network)
- Japan Society for the Promotion of Science (JSPS)