Electrocatalysis: Experimental Techniques and Case Studies

1) Introduction (what is electrochemistry?)
    - Electric double layer
    - Electrode potential

2) How to measure electrochemical reactions?
    - Cyclic voltammetry
    - Impedance spectroscopy

3) The metal/electrolyte interface
    - Surface reconstruction
    - Ion adsorption, ordered adsorption, SAMs

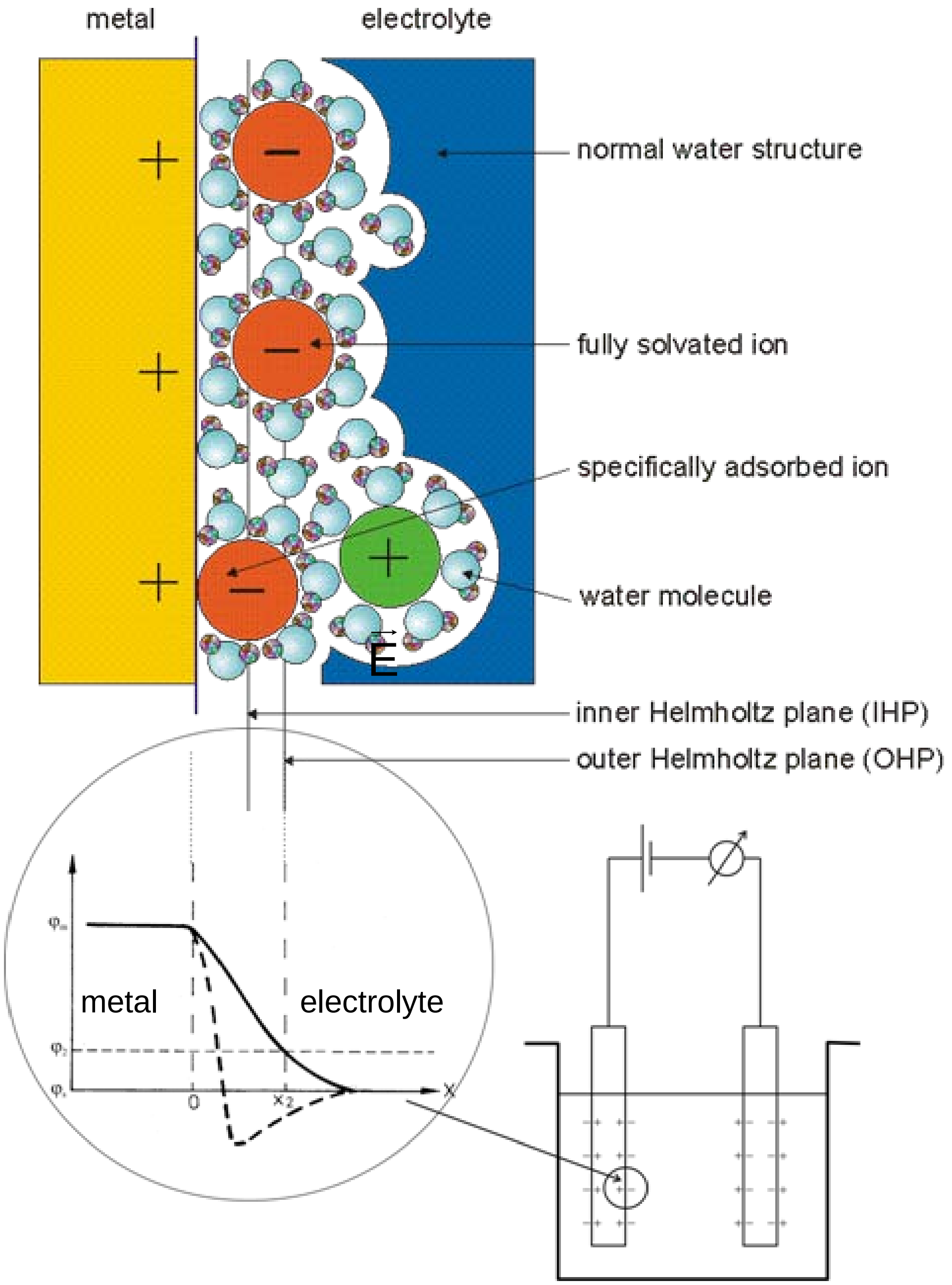
4) Electrode kinetics
    - Butler-Volmer equation

5) Structure and reactivity
    - Surface defects
    - Surface strain
    - Bimetallic surfaces

$C = 20 – 50\ \mu F cm^{-2}$

$\vec{E} = 10^{7}\ V cm^{-1}$

$\Delta q = 0.2\ e^{-}$/ surface atom



The Thermodynamic Equilibrium

$$^{S}\tilde{\mu}_i = {}^{E}\tilde{\mu}_i$$

S: Solution
E: Electrode
$\tilde{\mu}_i = \mu_i + zF\varphi$

$$\mathrm{Me}^{Z^+} + \mathrm{ze}^- \leftrightarrow \mathrm{Me}$$

$$\tilde{\mu}_{\mathrm{Me}^{Z^+}} + z\tilde{\mu}_{e^-} = \mu_{\mathrm{Me}}$$

$$\tilde{\mu}_{\mathrm{Me}^{Z^+}} = \mu_{\mathrm{Me}} - z\tilde{\mu}_{e^-}$$

$$z\tilde{\mu}_{e^-} = \mu_{\mathrm{Me}} - \tilde{\mu}_{\mathrm{Me}^{Z^+}}$$

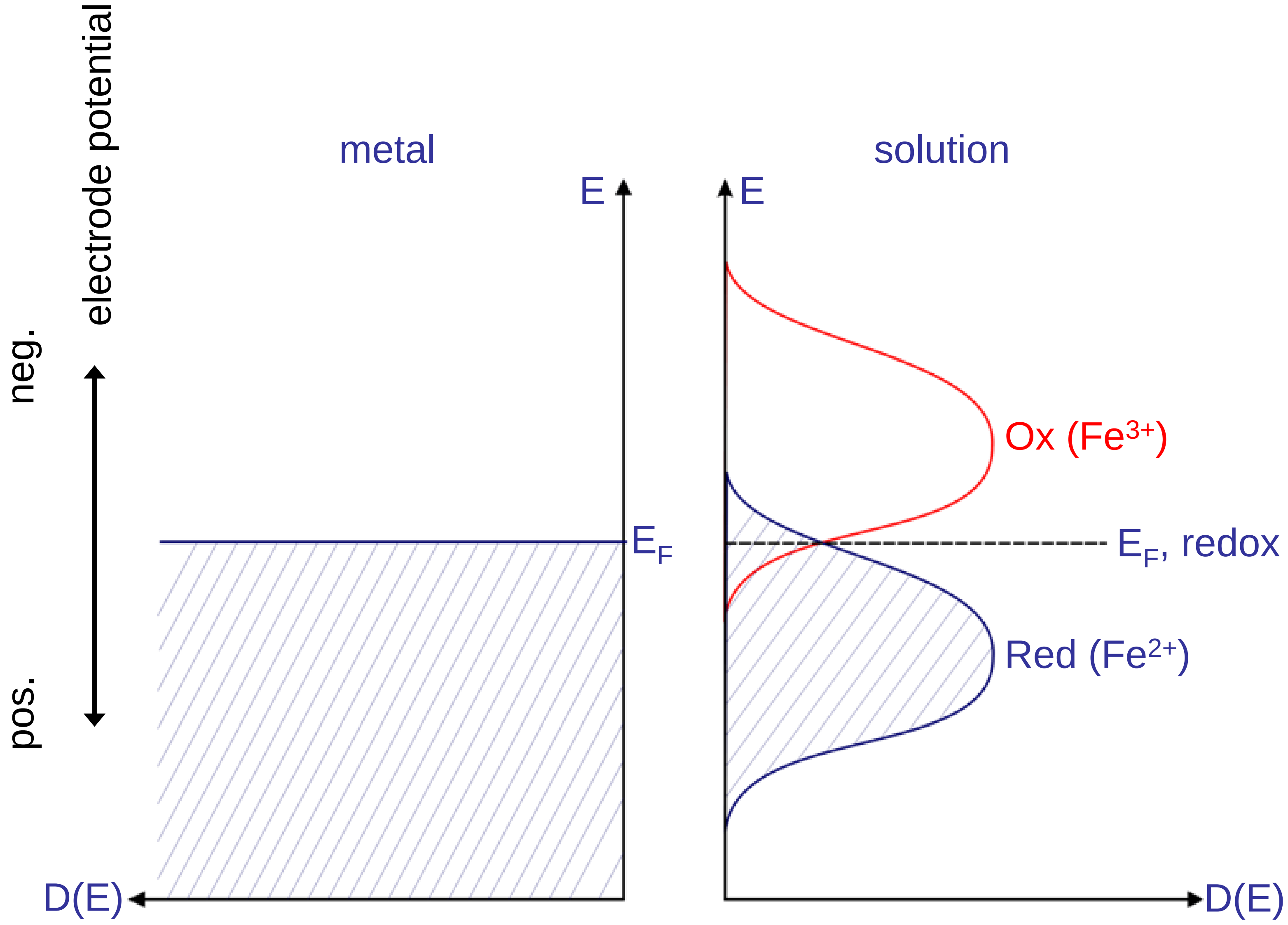
$$\tilde{\mu}_{e^-} = \mu_{e^-} - F\varphi$$

$$\tilde{\mu}_{e^-} = F \cdot (E_F - K)$$

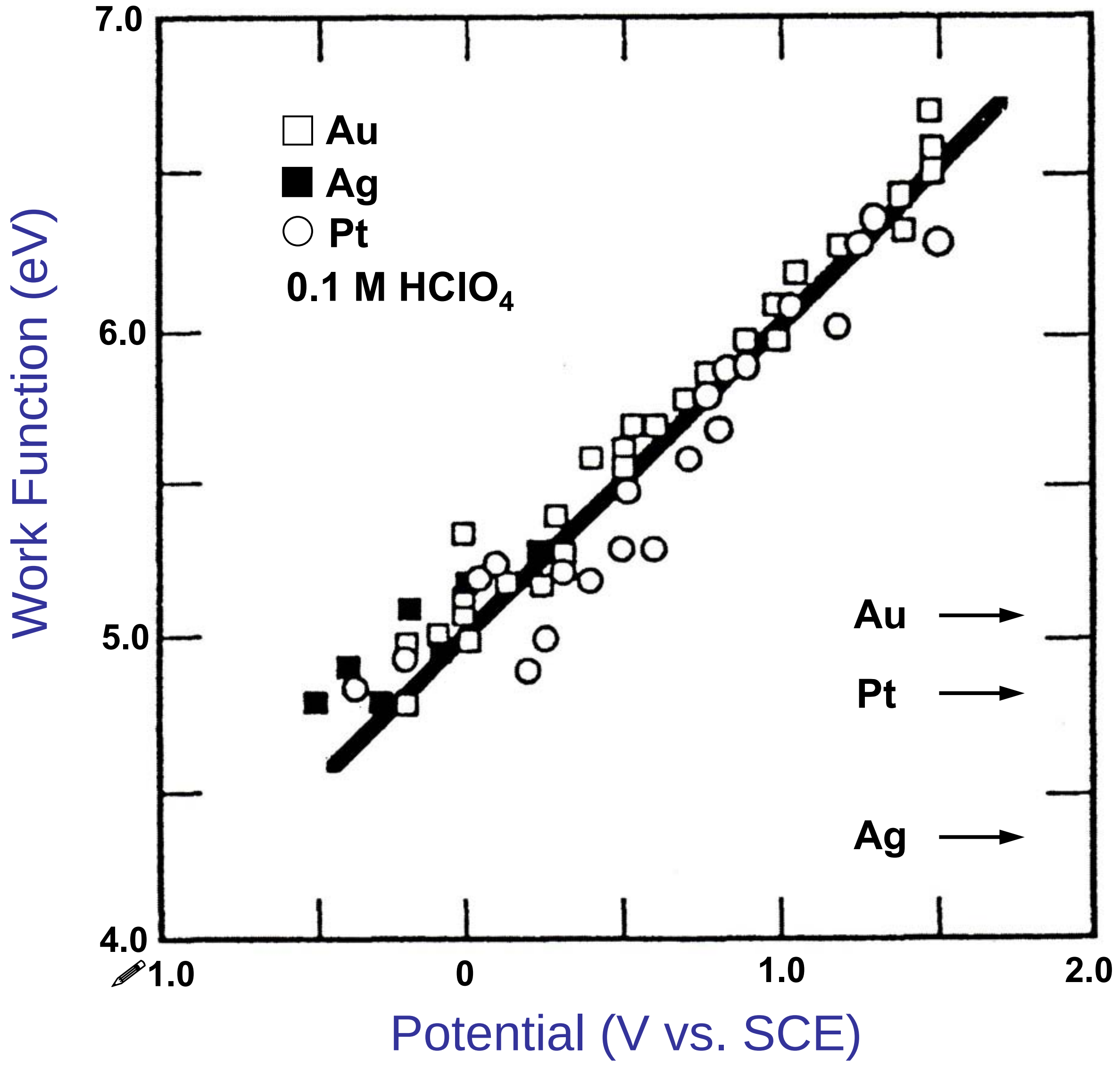
$K \approx 4.5$ eV

for $\tilde{\mu}_{e^-}$ vs NHE

The electrode potential is the electrochemical potential of the electrons in the metal

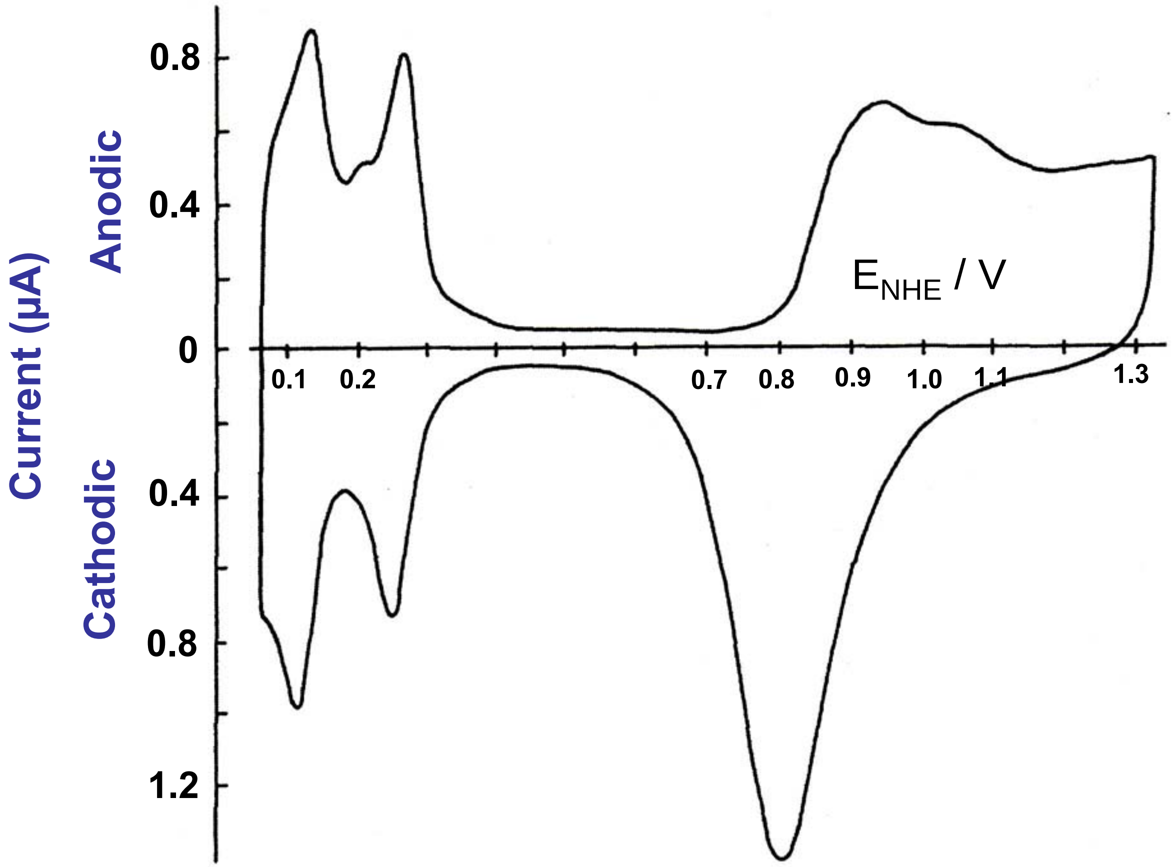


The electronic equilibrium between metal electrode and redox electrolyte



Work functions of Au, Pt and Ag electrodes emersed from 0.1 M HClO$_4$ at different potentials. Arrows indicate work functions of clean surfaces.

From R. Kötz



Electrochemical spectrum of clean Pt electrode in 0.5 M H_2SO_4 solution. From Conway et al.

In equilibrium or in steady state (E_{dc} and I_{dc} are constant in time)

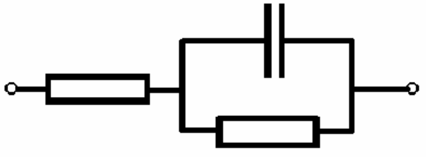
Stimulus: $E(t) = E_{dc} + E_{ac} \sin(\omega t)$

Response: $I(t) = I_{dc} + I_{ac} \sin(\omega t + \varphi)$

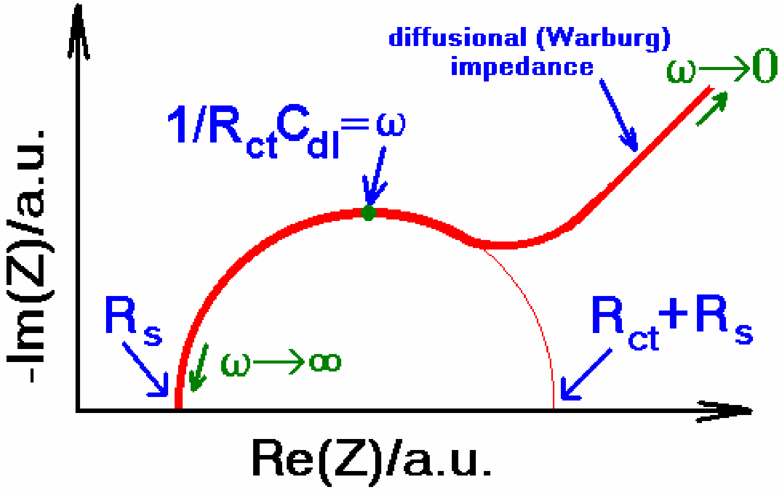
Impedance:

- is a complex quantity,
  $Z \equiv Z_{abs} \exp(i\varphi) = Z_{abs} \cos \varphi + i \cdot Z_{abs} \sin \varphi$ with $Z_{abs} \equiv E_{ac}/I_{ac}$
- is a spectrum (typically 1 mHz<ω<1MHz);
- is usually interpreted in terms of *equivalent circuits* containing R (resistance), C (capacitance) and other (e.g. W: diffusional impedance) elements.

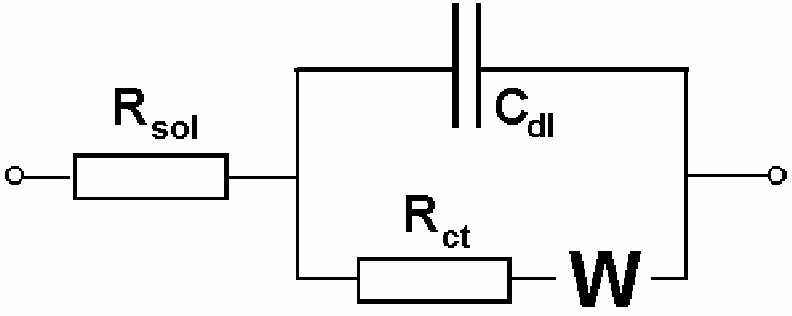
Example No.1: charge transfer across a metal/electrolyte interface

(an  equivalent circuit is expected)

1: measurement of impedance spectrum



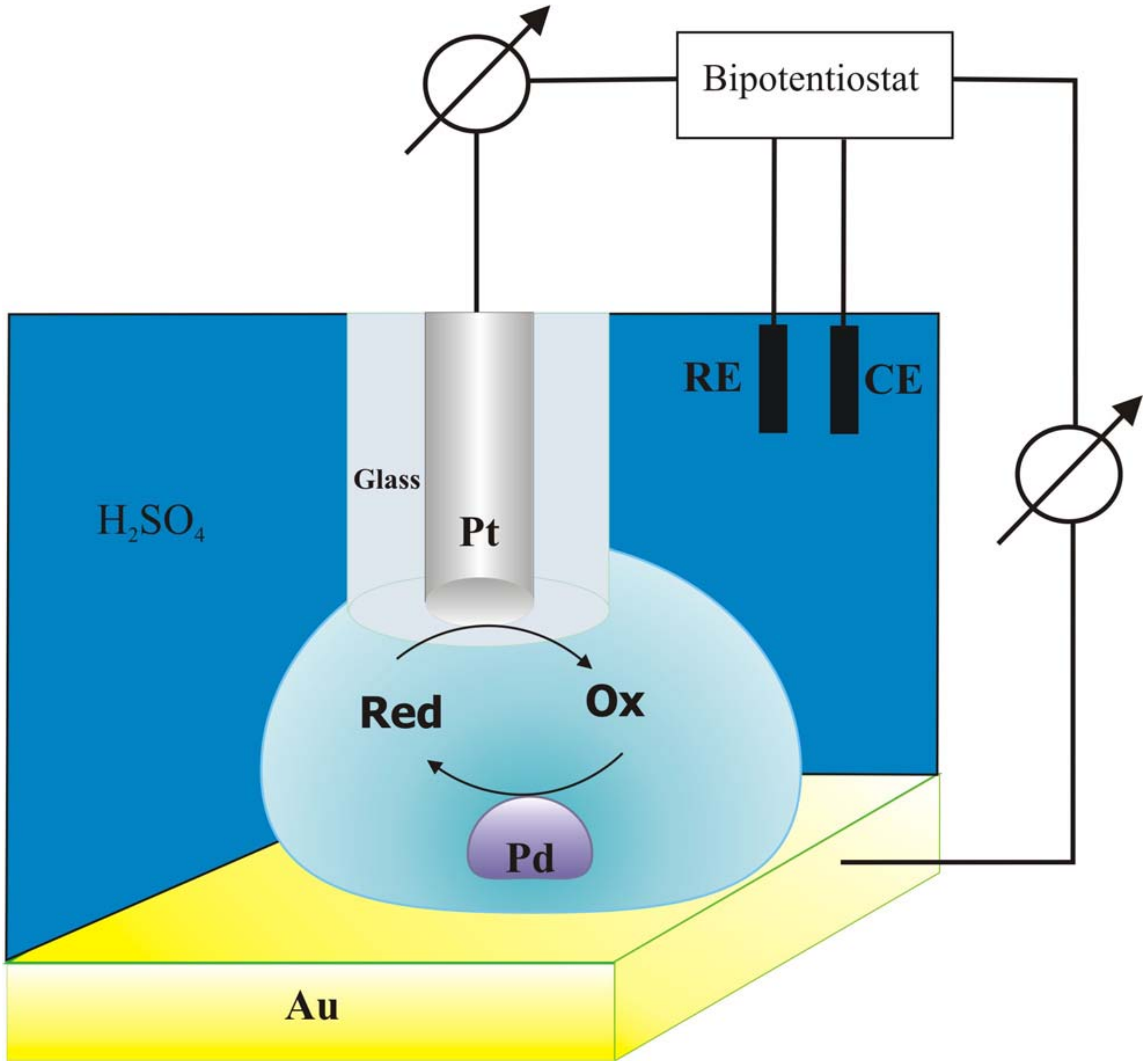
2: determination of equivalent circuit parameters



3: calculation of kinetic parameters from the equivalent circuit parameters

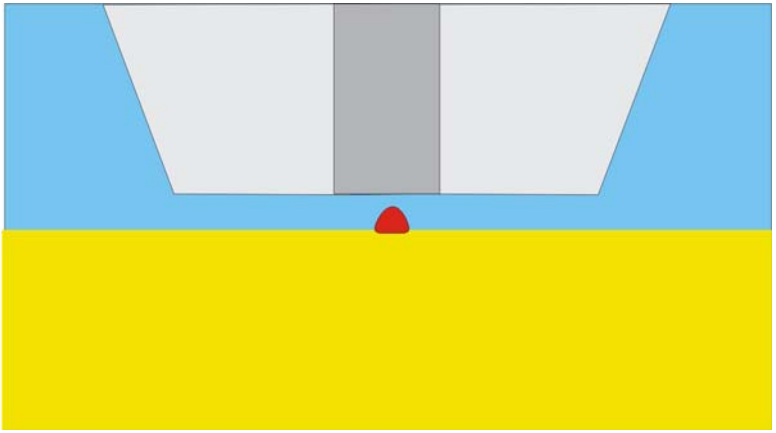
$$\frac{\delta I}{\delta E} \equiv \frac{1}{R_{ct}} = nFA\left(c_{red,surf}\frac{\partial k_{ox}}{\partial E} + c_{ox,surf}\frac{\partial k_{red}}{\partial E} \right)$$

Scanning electrochemical microscopy (SECM)



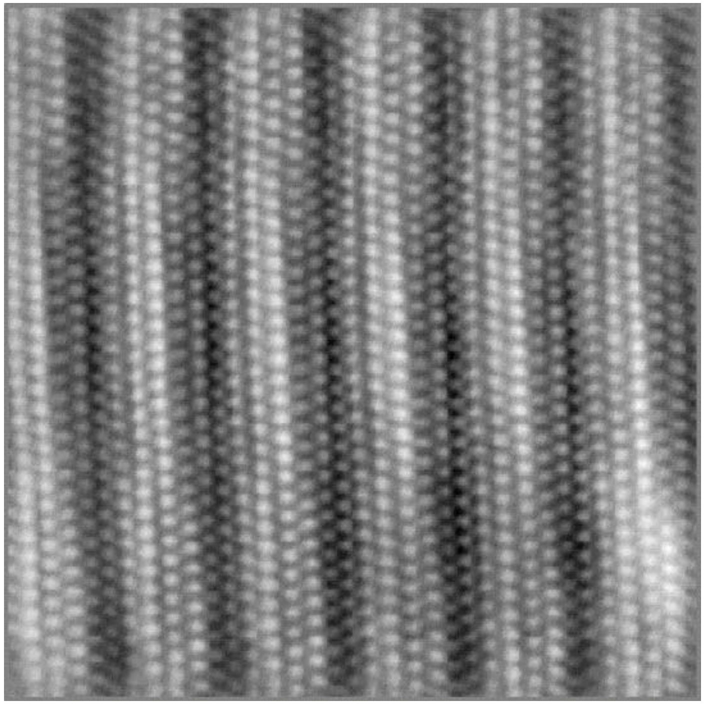
From J. Heinze

Principal of SECM



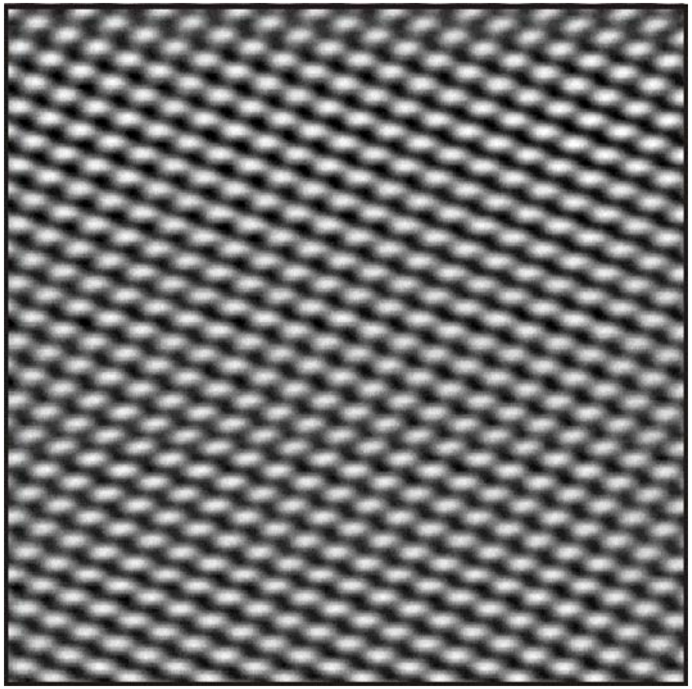
Surface reconstruction of Au(100) in 0.1 M H_2SO_4

10 nm x 10 nm



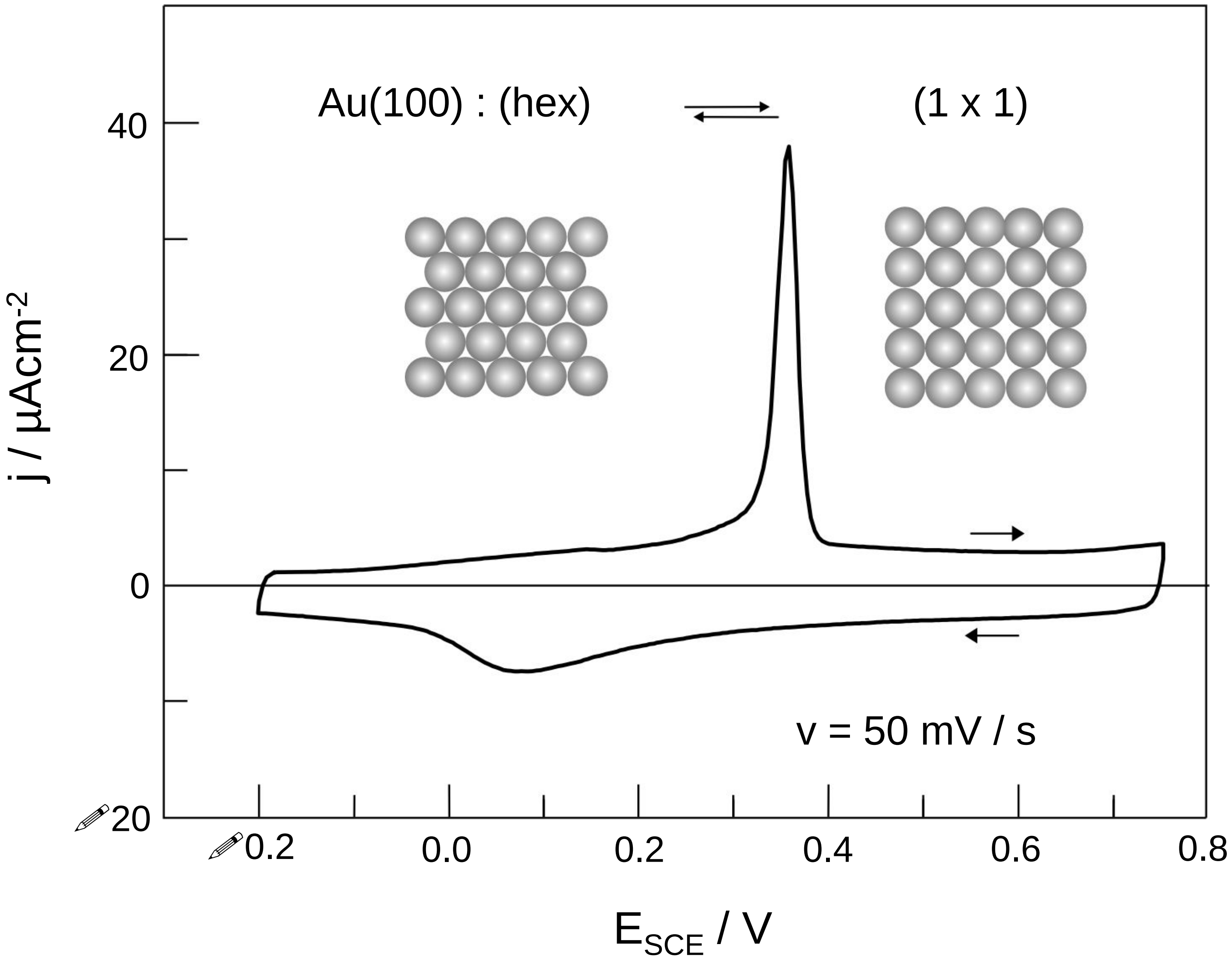
E_{SCE} = ✐200 mV

8 nm x 8 nm

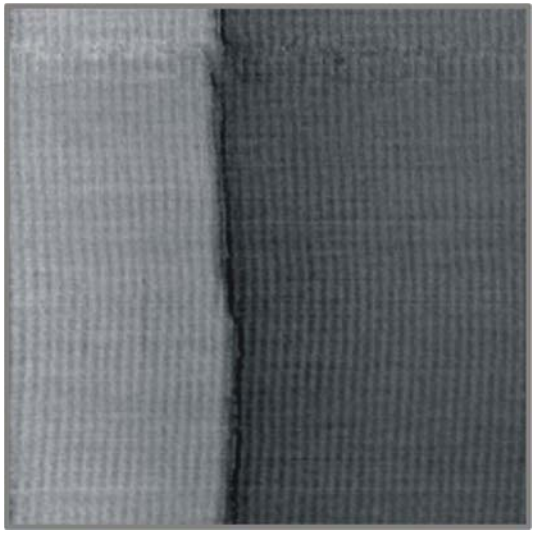


E_{SCE} = 630 mV

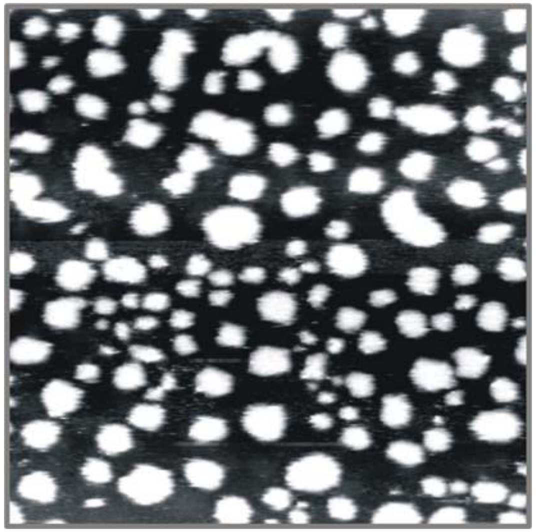
Cyclic voltamogramme of Au(100) in 0.1 M H_2SO_4

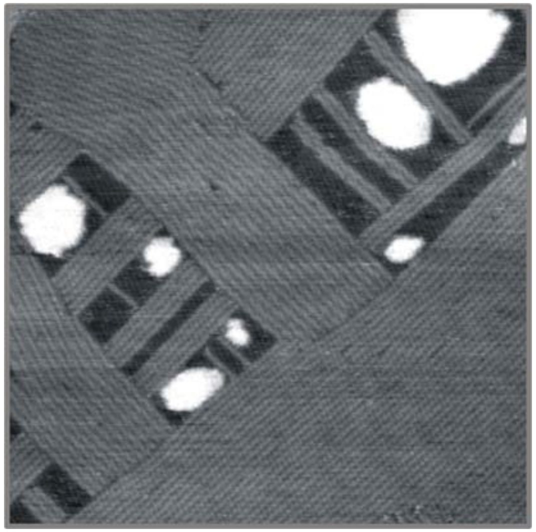


63 nm x 63 nm E_{SCE} = -0.24 V

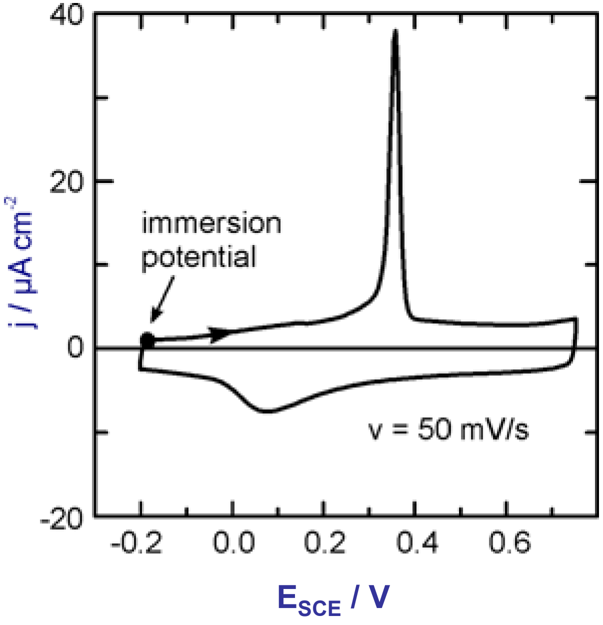


84 nm x 84 nm +0.5 V



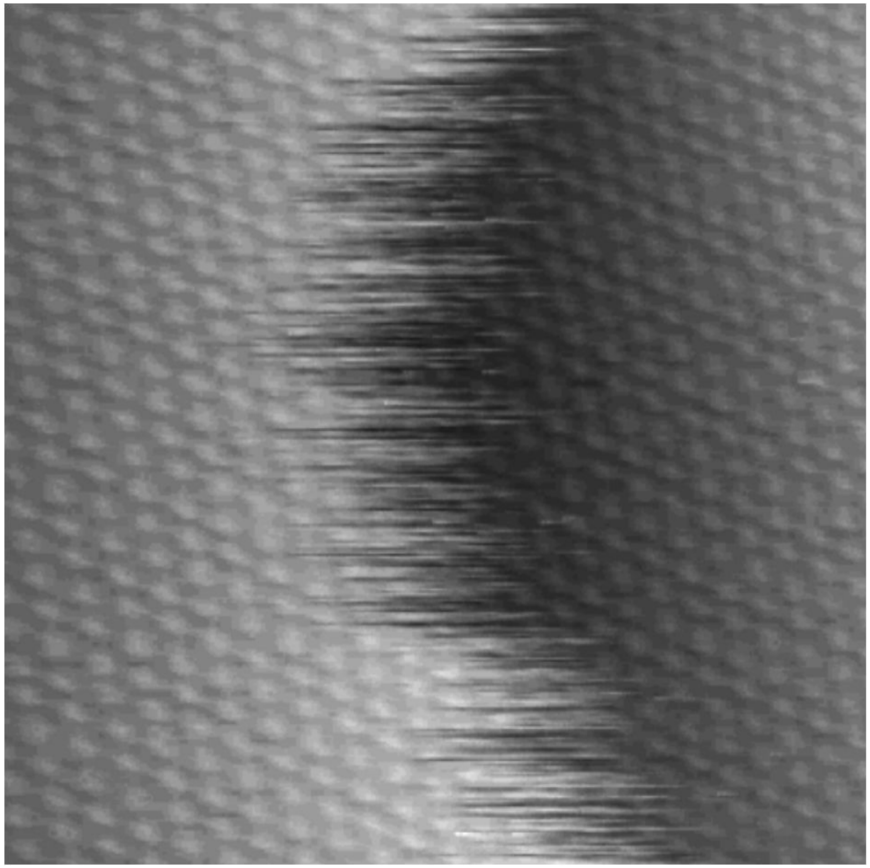


92 nm x 92 nm E_{SCE} = -0.19 V



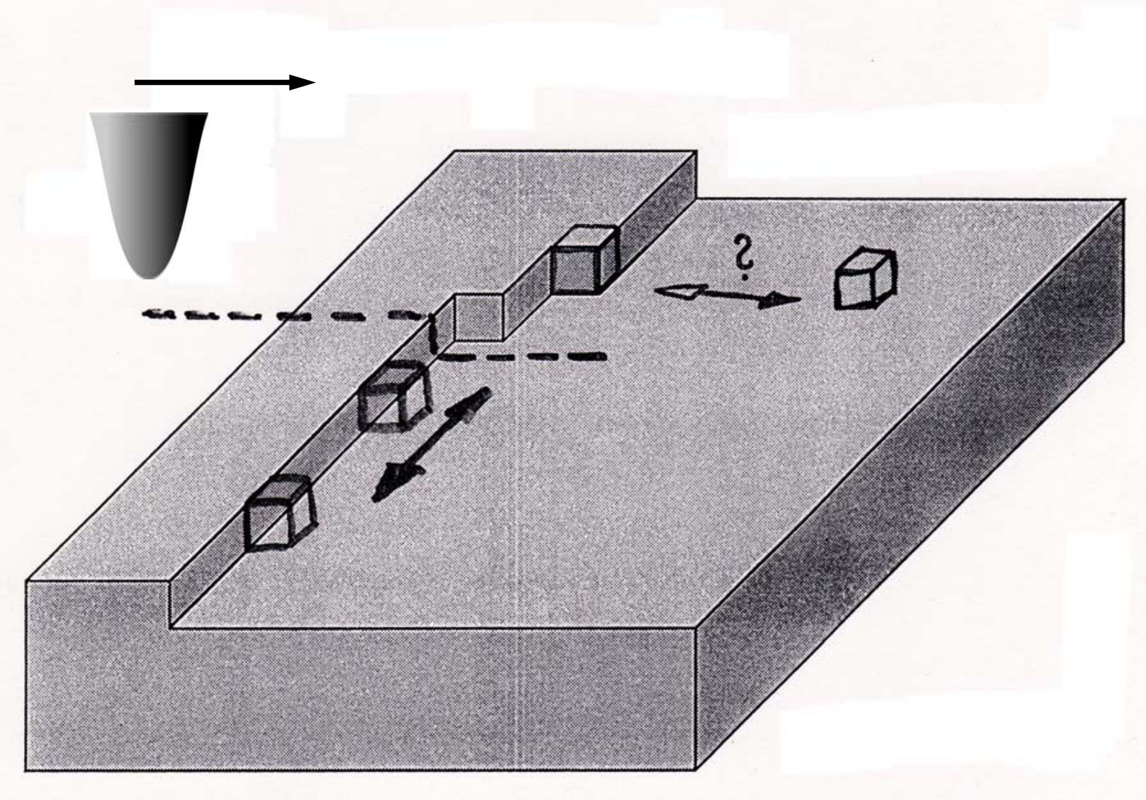
Potential-induced surface reconstruction of Au(100)

Ag(111) in 0.05 M H_2SO_4 + 0.1 mM $CuSO_4$



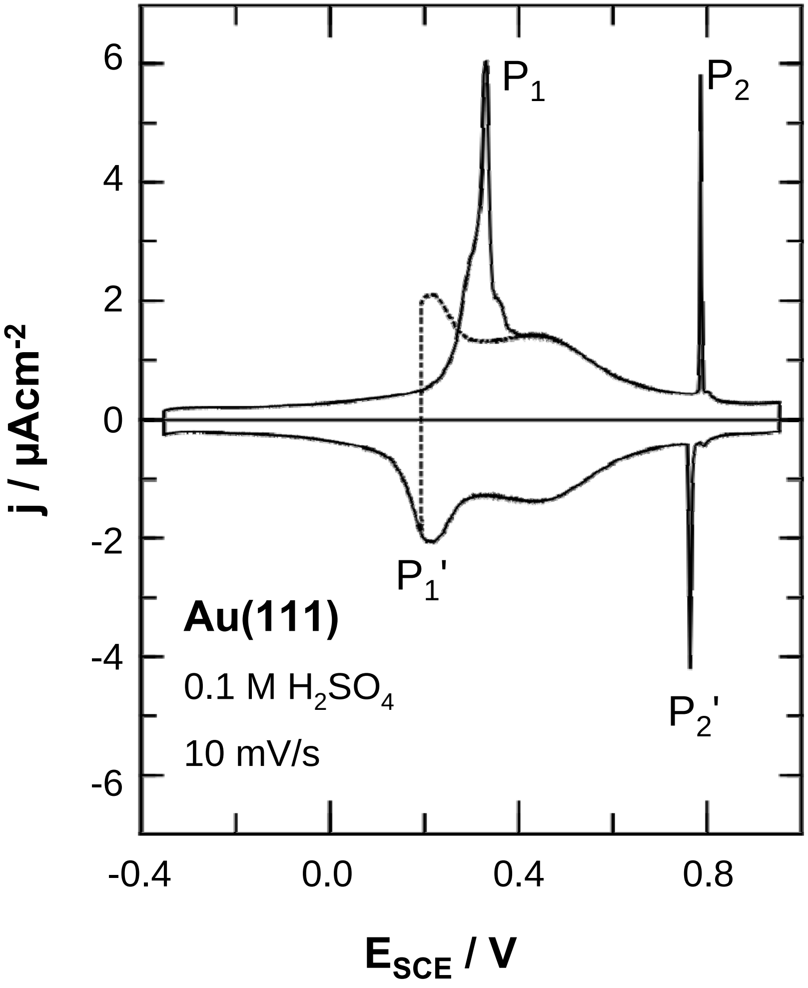
+60 mV vs. SCE **73 Å**

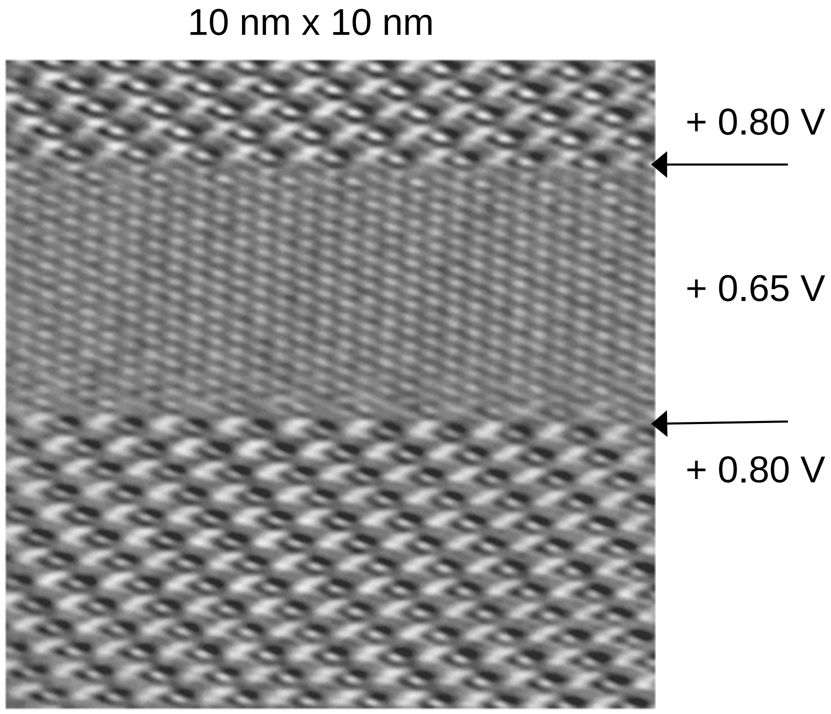
"frizzy step“ on Ag(111)



Literature:
M. Dietterle et al., Surf. Sci. 327 (1995) L 495
M. Giesen et al., Surf. Sci. 468 (2000) 149

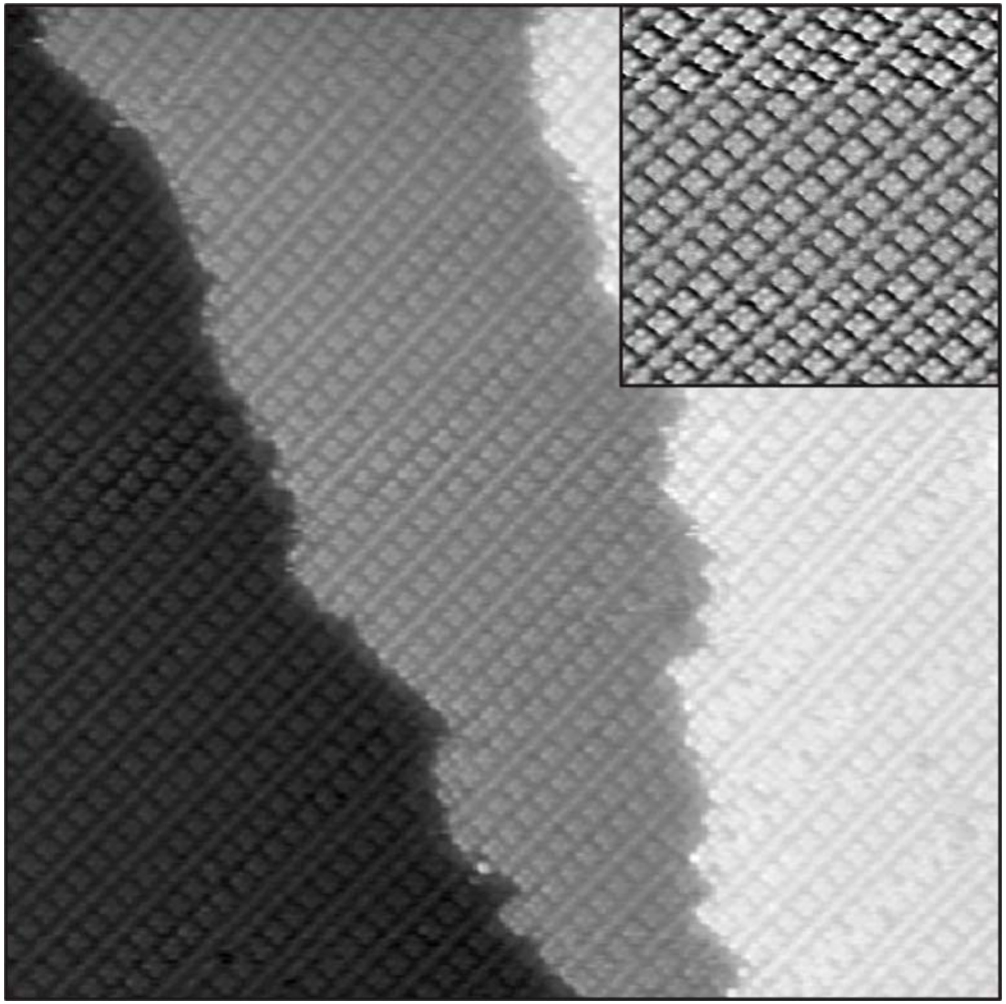
Ordered adsorption of sulfate on Au(111):



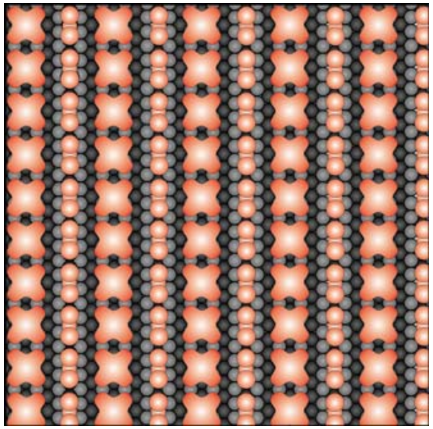


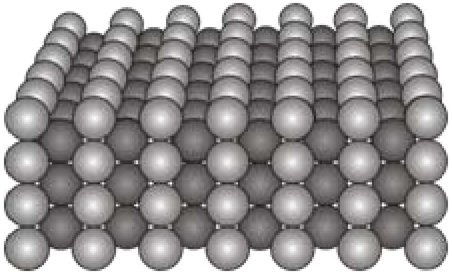
$E_{SCE} = +0.8\ V \rightleftharpoons E_{SCE} = +0.65\ V$

Au(110) / 0.1 M H_2SO_4 + 0.1 mM $[PdCl_4]^{2-}$

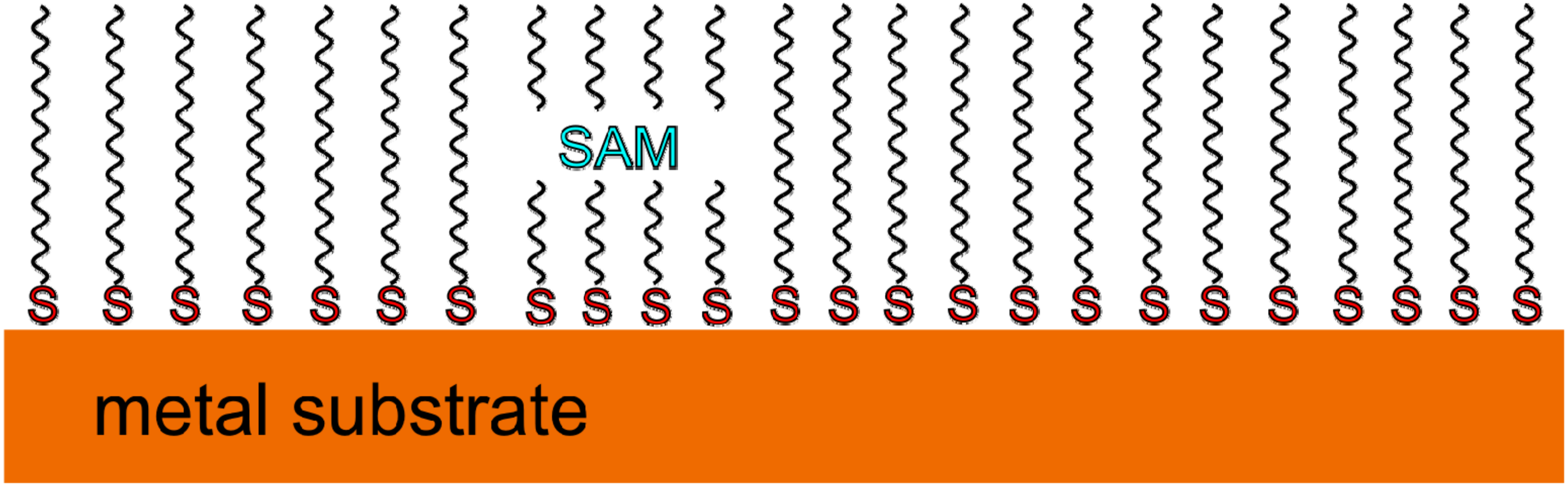


E_{SCE} = 0.55 V



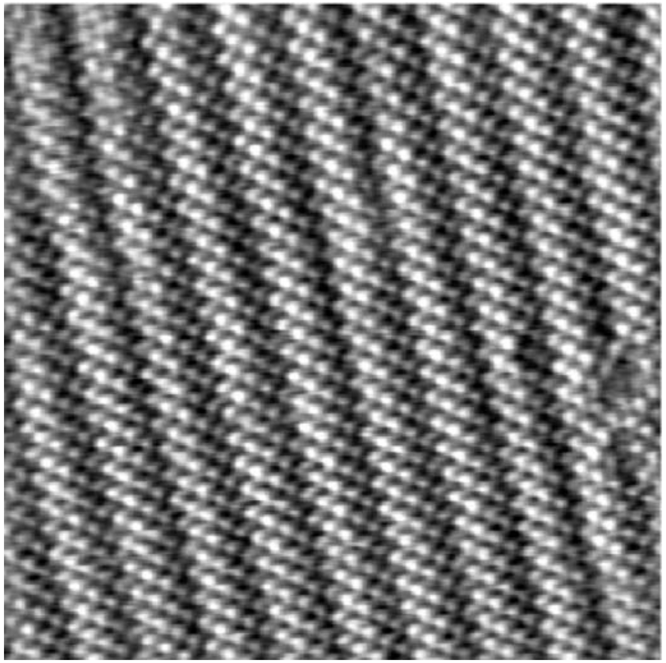


Alkanethiol Self Assembled Monolayer



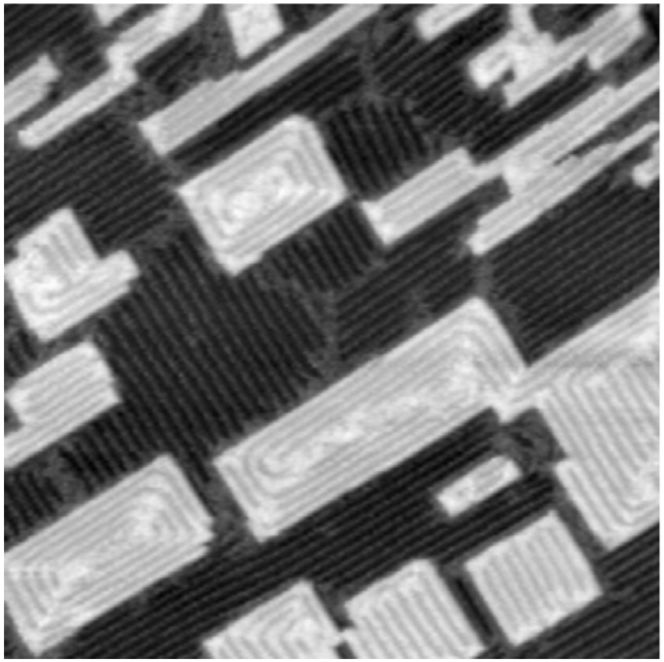
Butanthiol – SAM on Au(100) in 0.1 M H_2SO_4

15 x 15 mm^2



E_{SCE} = +0.55 V

70 x 70 mm^2



E_{SCE} = +0.55 V

Electrode Kinetics

rate constant $k = k_0 \cdot \exp\left(-E_a / kT\right) = \frac{k_B T}{h} \cdot \exp\left(-\Delta^0 G^{\ddagger} / RT\right)$

$$\Delta^0 G^{\ddagger} = \Delta^0 G^{\ddagger}{}_{\text{chem}} + \alpha F \Delta\varphi$$

$$A^+ + e^- \rightarrow D$$

reaction rate $\nu_- = k \cdot c_{A^+}$

current density $j = F \cdot \nu$

$$j_- = -F \cdot \overrightarrow{k}_{\text{chem}} \cdot c_{A^+} \cdot \exp\left[-\alpha \cdot F\Delta\varphi / RT\right]$$

$$j_+ = F \cdot \overleftarrow{k}_{\text{chem}} \cdot c_D \cdot \exp\left[(1-\alpha) \cdot F\Delta\varphi / RT\right]$$

At equilibrium: $|j_+| = |j_-| = j_0$ (exchange current density)

$$j = j_+ + j_- = 0$$

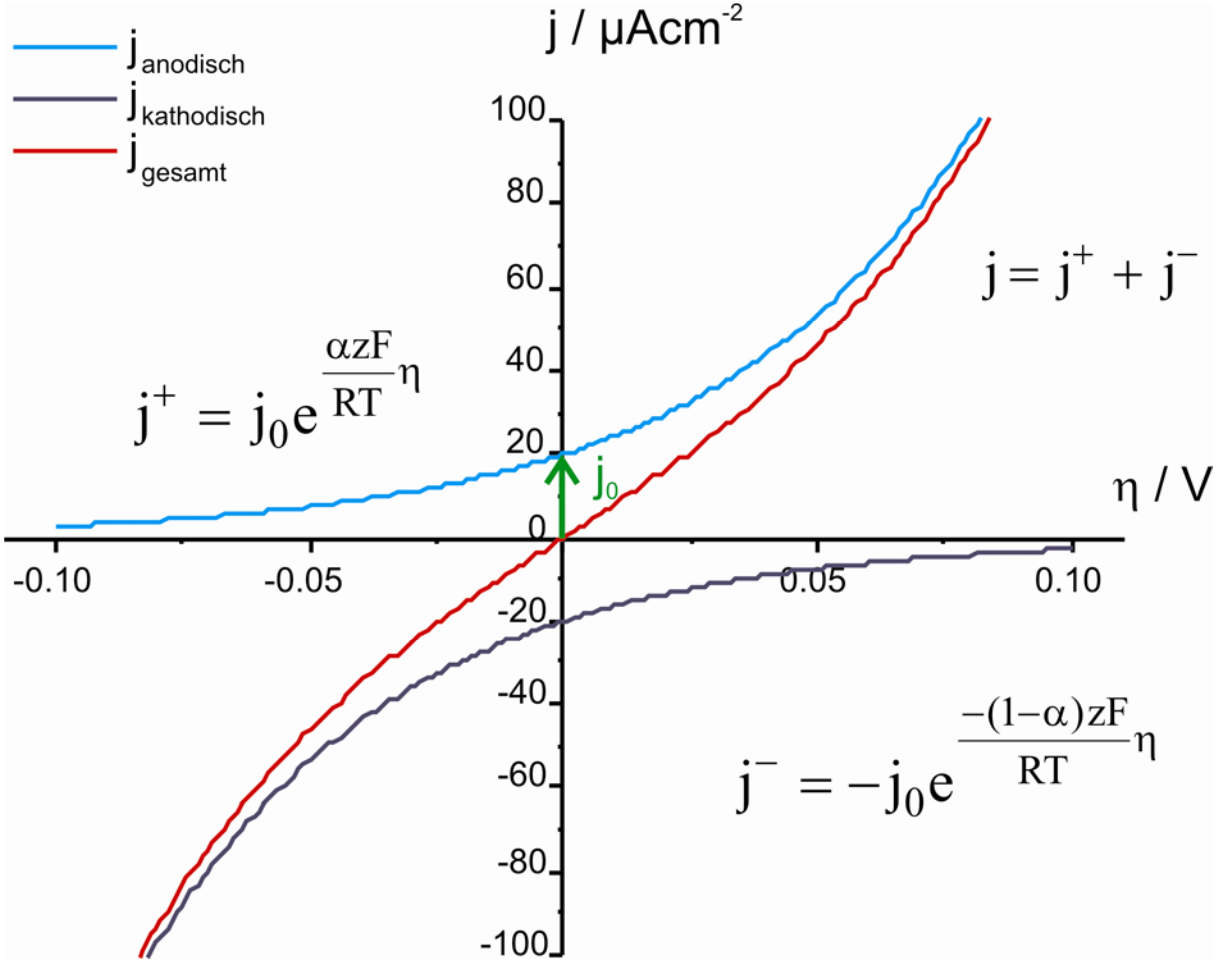
At an overpotential $\eta = \Delta\varphi - \Delta\varphi_{eq}$ a net current j is flowing

$$j = j_0 \left\{ \exp\left[(1-\alpha)\cdot F\eta / RT\right] - \exp\left[-\alpha \cdot F\eta / RT\right] \right\}$$

Butler-Volmer equation

Die Butler-Volmer-Gleichung

(die Austauschstromdichte j_0)



$$j = j^{+} + j^{-}$$

$$j^{+} = j_0 e^{\frac{\alpha z F}{RT}\eta}$$

$$j^{-} = -j_0 e^{\frac{-(1-\alpha) z F}{RT}\eta}$$

Hydrogen Evolution Reaction (HER)

$H_3O^+ + e^- \leftrightarrow 1/2\, H_2 + H_2O$ (acidic solution)

$H_2O + e^- \leftrightarrow 1/2\, H_2 + OH^-$ (basic solution)

Volmer – Tafel mechanism

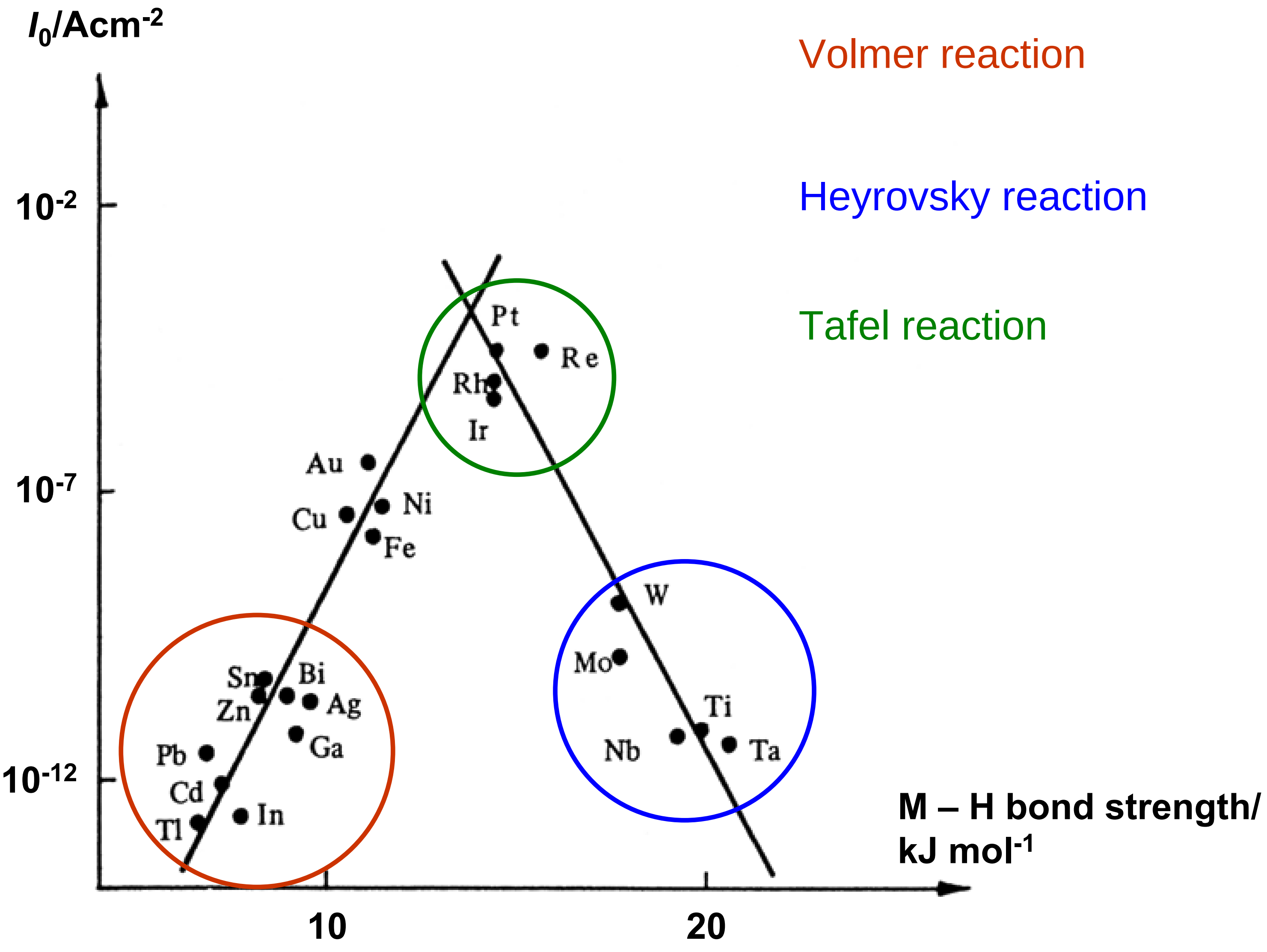
I) $H_3O^+ + e^- \leftrightarrow H_{ads} + H_2O$ (Volmer reaction)

II) $2H_{ads} \leftrightarrow H_2$ (Tafel reaction)

Volmer – Heyrovsky mechanism

I) $H_3O^+ + e^- \leftrightarrow H_{ads} + H_2O$ (Volmer reaction)

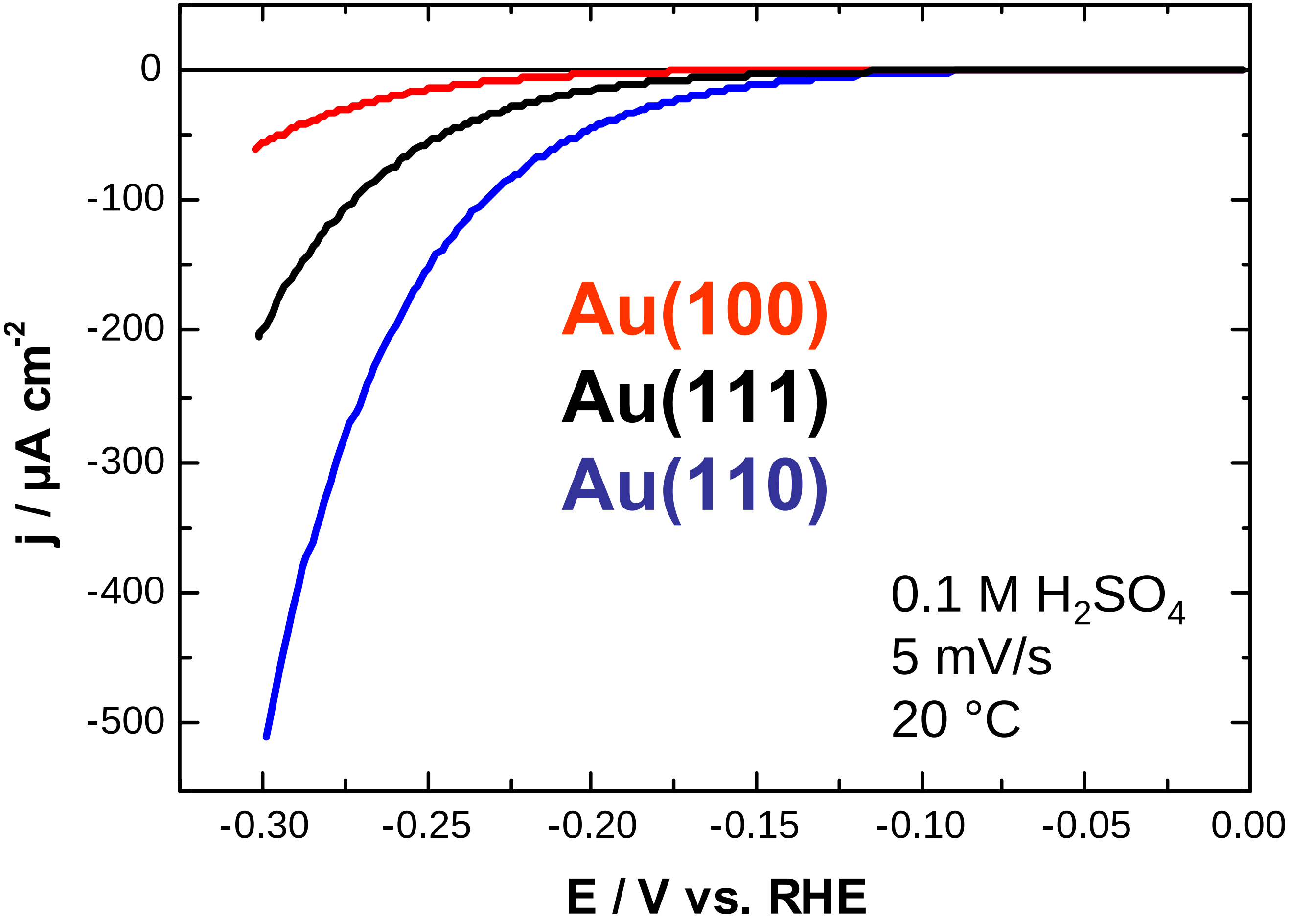
III) $H_{ads} + H_3O^+ + e^- \leftrightarrow H_2 + H_2O$ (Heyrovsky reaction)



Exchange current density for HER as a function of metal - hydrogen bond strength.
From S. Trasatti

HER on Au single crystal surfaces

crystallographic orientation



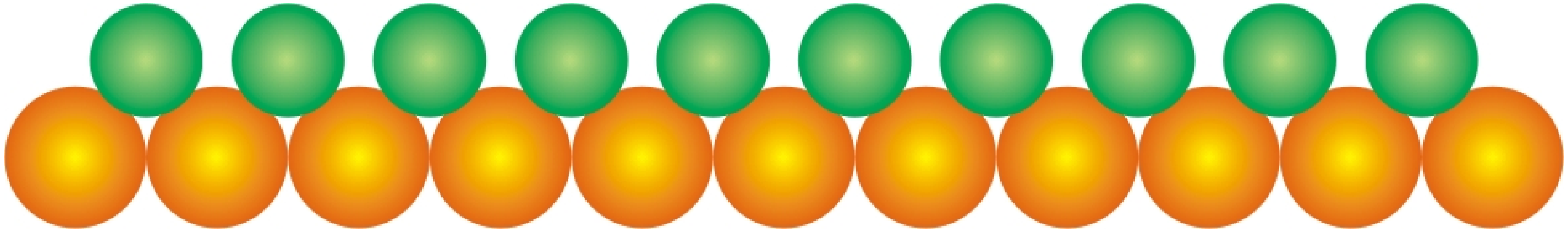
HER on Au single crystal surfaces

trends for exchange current density

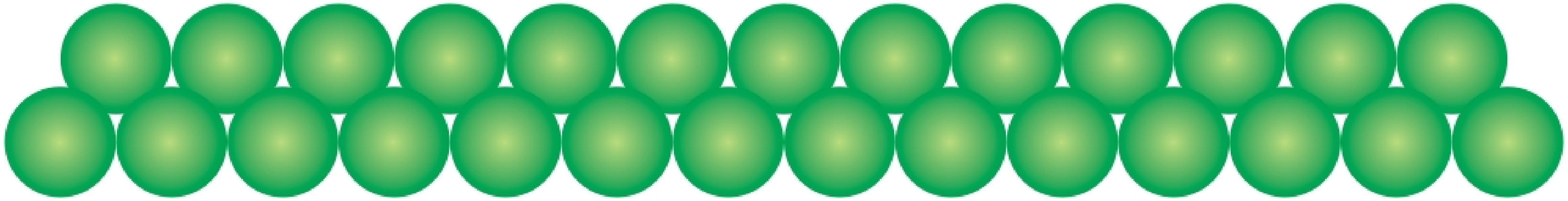
	j_0 / µA cm^{-2}	
Au(111)	0.12	thermally induced reconstruction
	0.20	potential-induced reconstruction
Au(100)	0.05	thermally induced reconstruction
	0.10	potential-induced reconstruction
	1 - 2	(1 x 1), unreconstructed

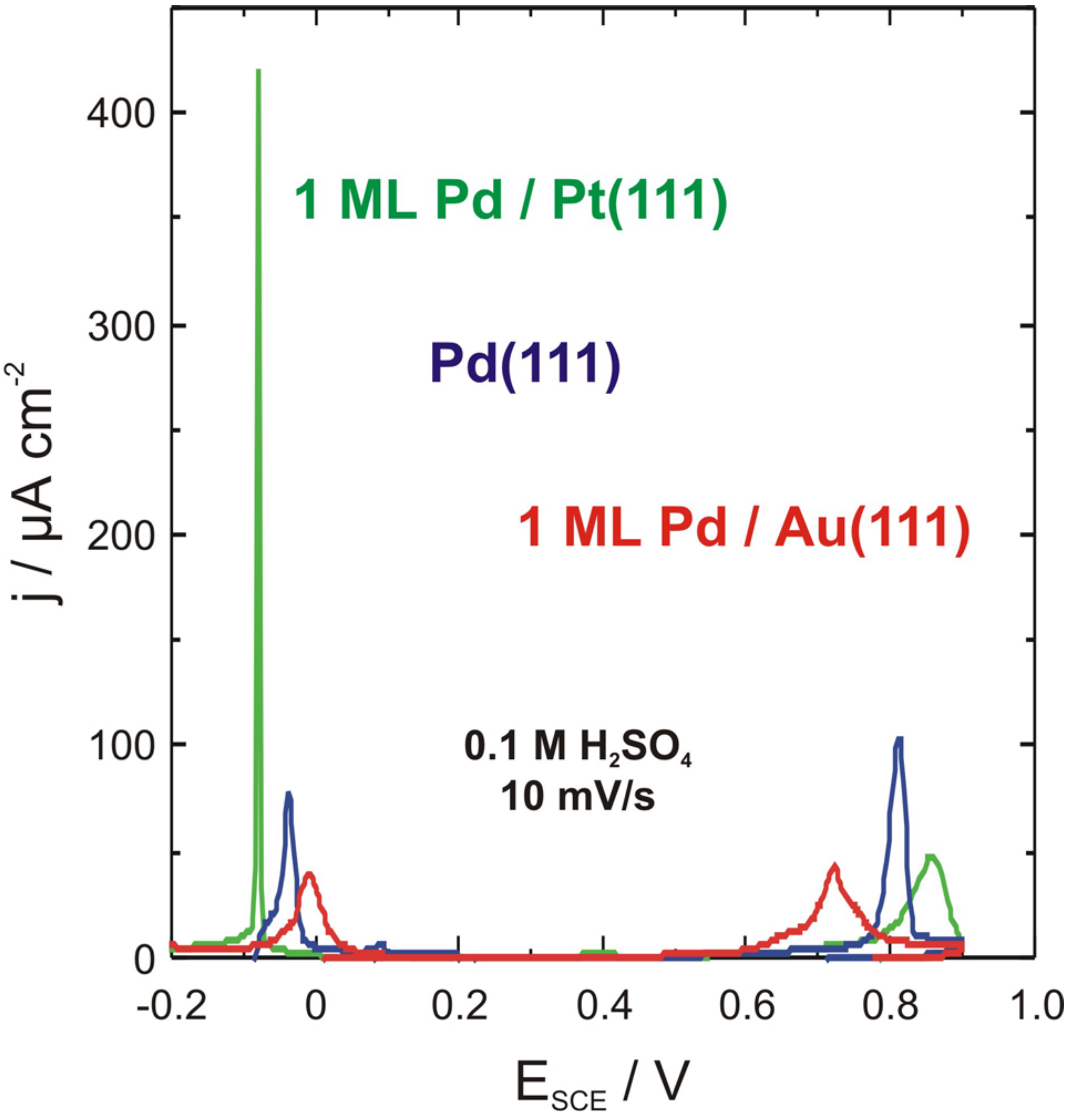
$\alpha \sim 0.4$

pseudomorphic overlayer



massive metal

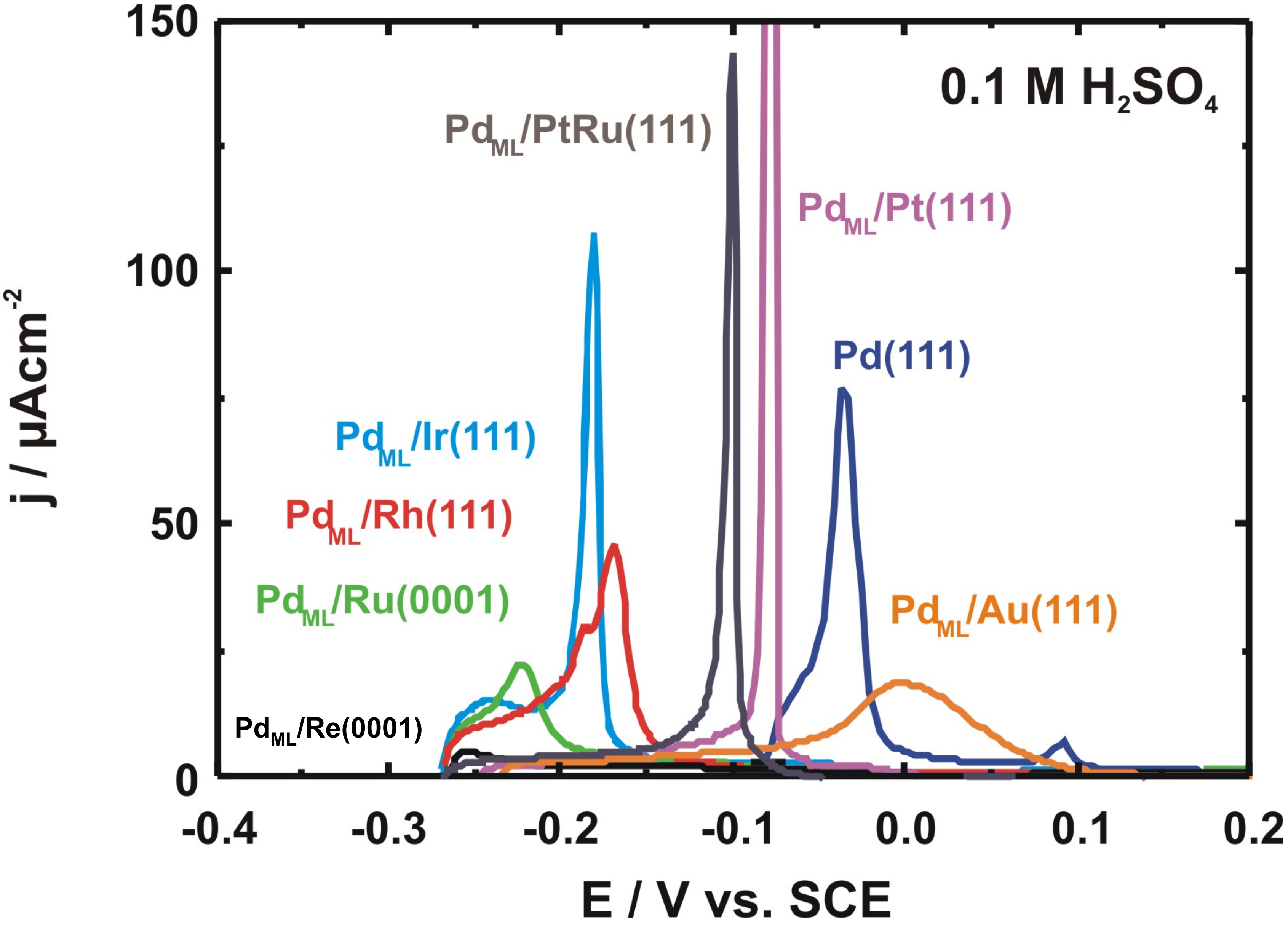



1 ML Pd / Pt(111)
Pd(111)
1 ML Pd / Au(111)
0.1 M H_2SO_4
10 mV/s
j / μA cm^{-2}
E_{SCE} / V
0
100
200
300
400
-0.2
0
0.2
0.4
0.6
0.8
1.0

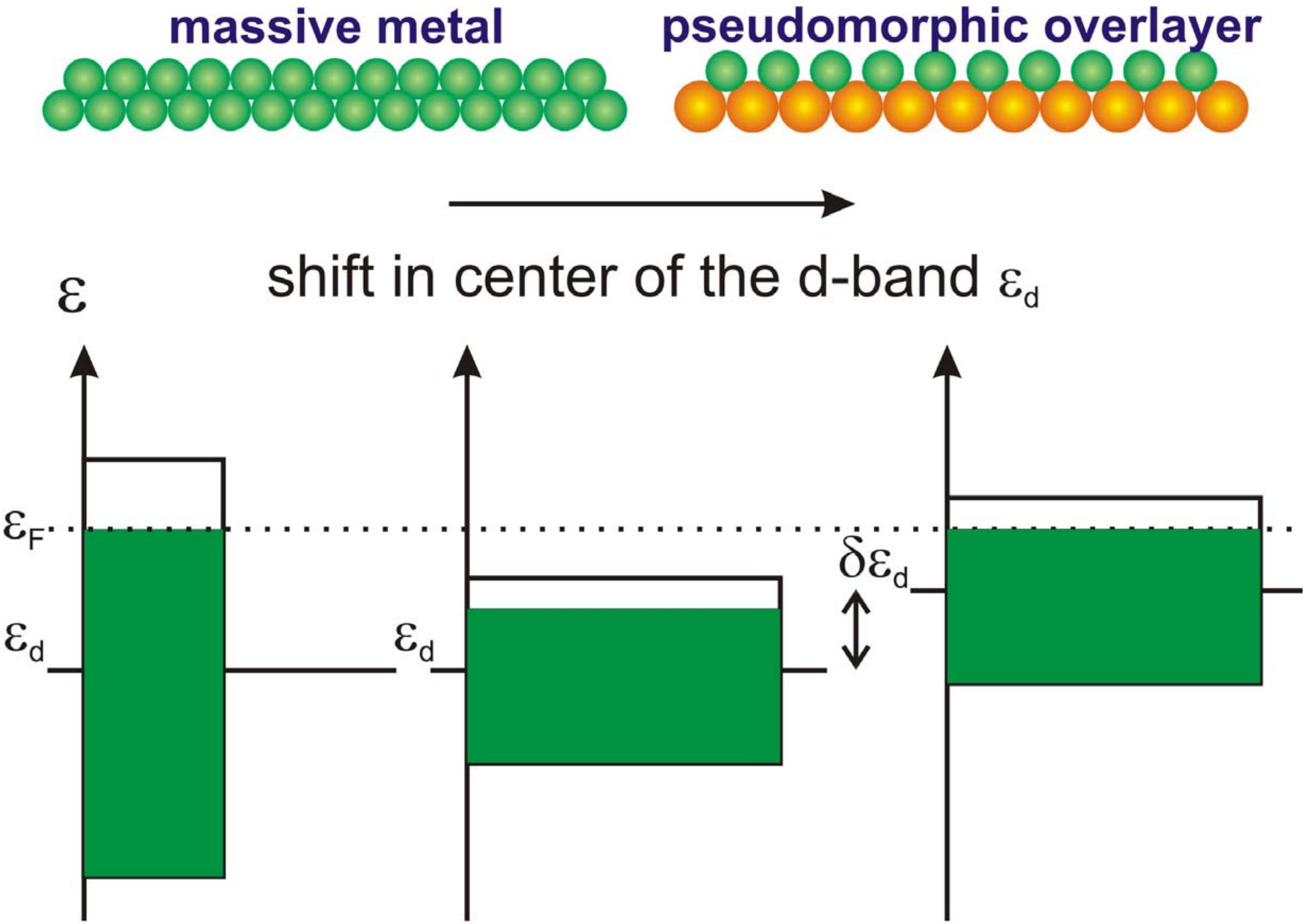
Pd-Pd distance / Å

Pd$_{ML}$ / Au(111)	2.88	+4.7%
Pd$_{ML}$ / Pt(111)	2.77	+0.7%
Pd$_{ML}$ / Re(0001)	2.76	+0.4%
Pd(111)	2.75	0
Pd$_{ML}$ / Ir(111)	2.72	-1.1%
Pd$_{ML}$ / Ru(0001)	2.70	-1.8%
Pd$_{ML}$ / Rh(111)	2.69	-2.2%

H-adsorption on Pd monolayers

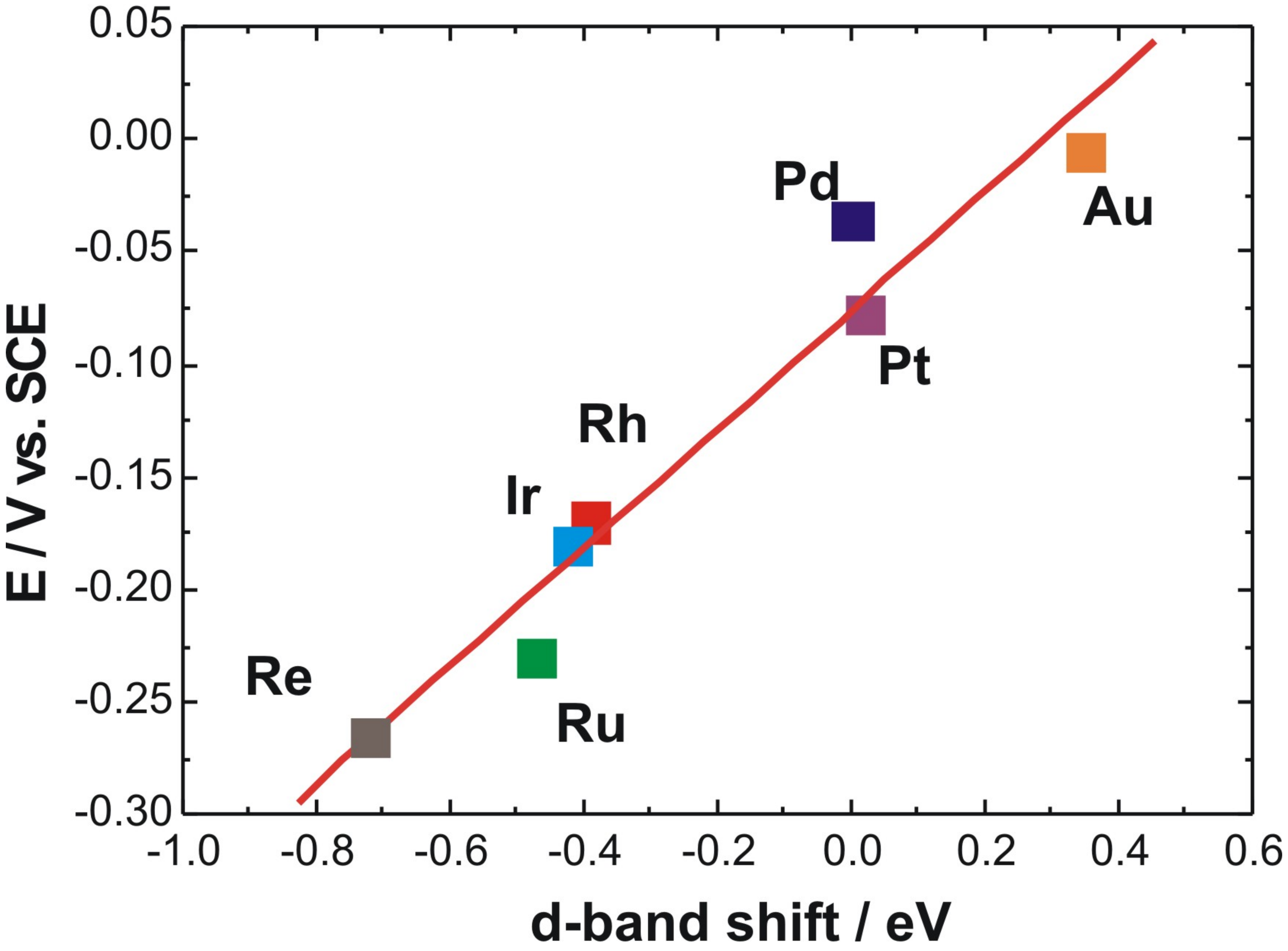


d-band model



J.K. Nørskov et al., ***J. Mol. Catal.* A 115** (1997) 421.

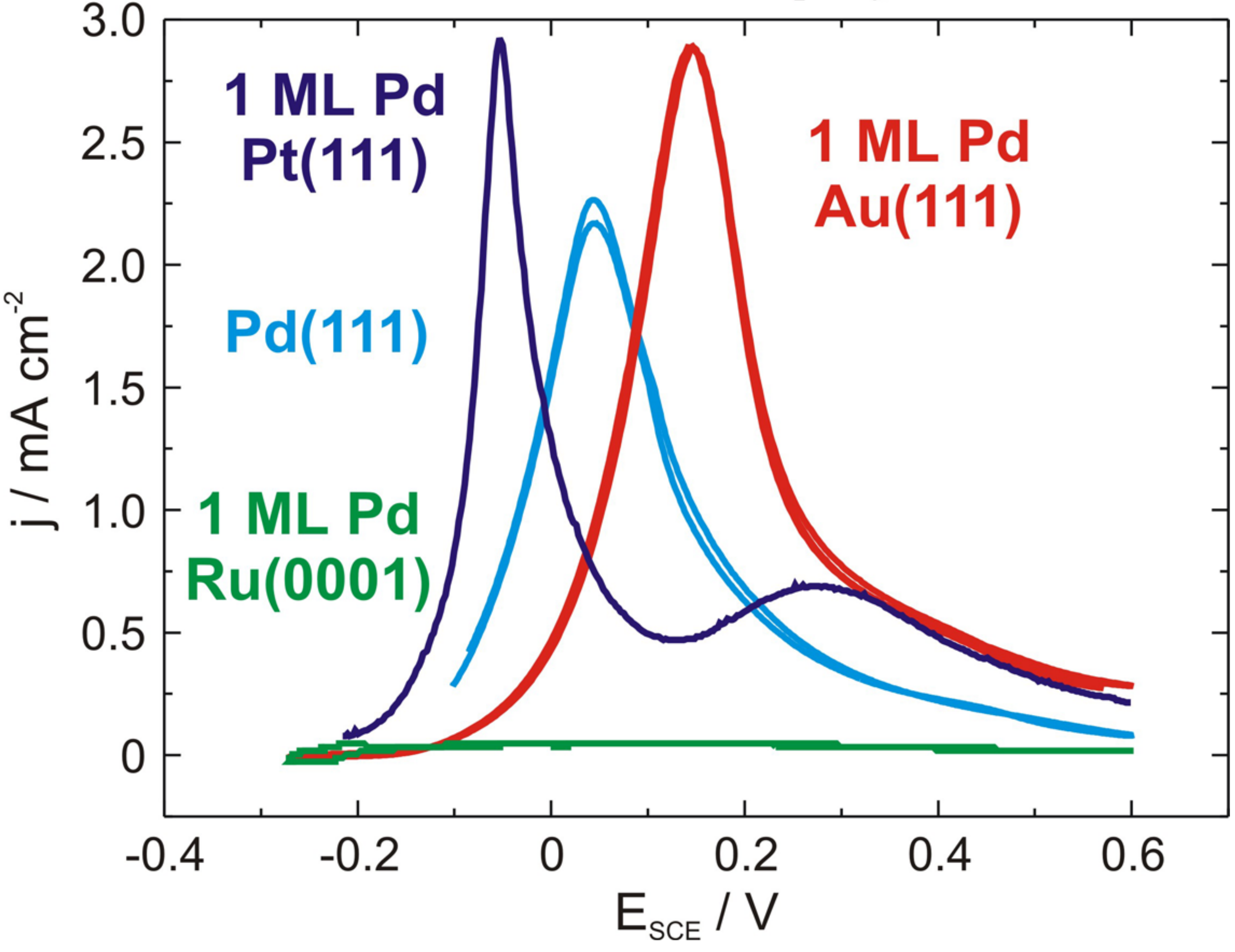
H-adsorption on Pd(111) vs. d-band shift



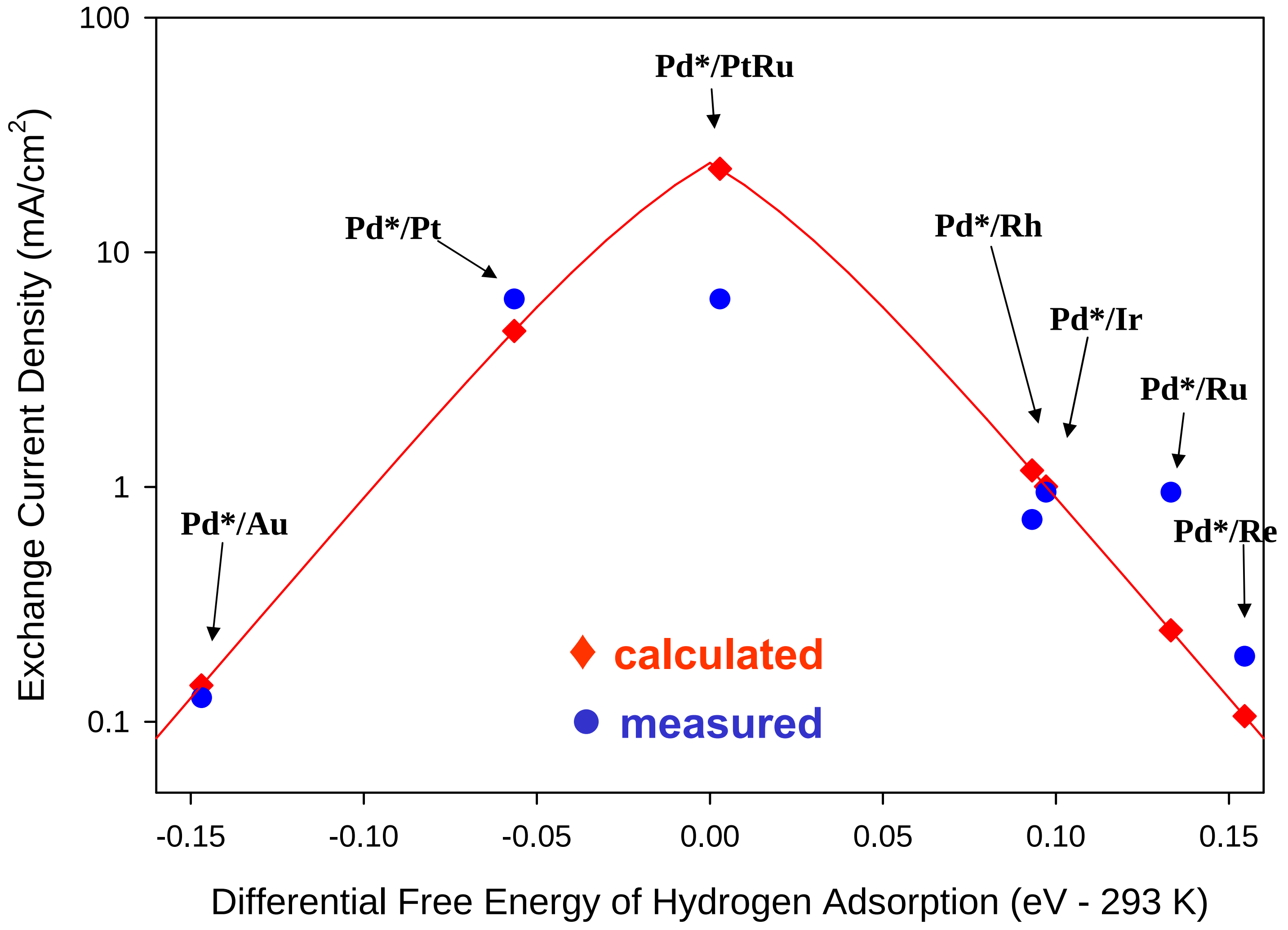
L.A. Kibler et al., Angew. Chem. Int. Ed. **44**, 2080-2084(2005).

Formic acid oxidation

0.2 M HCOOH + 0.1 M H_2SO_4, 20 mV/s

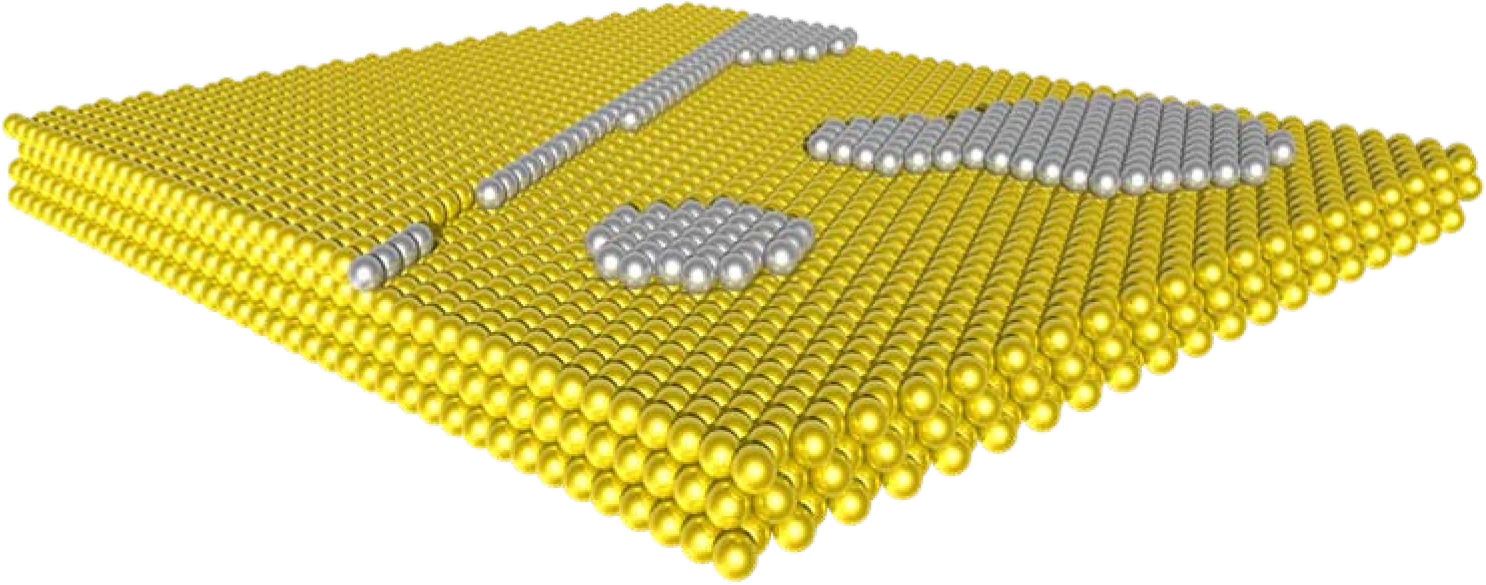


HER on Pd monolayers



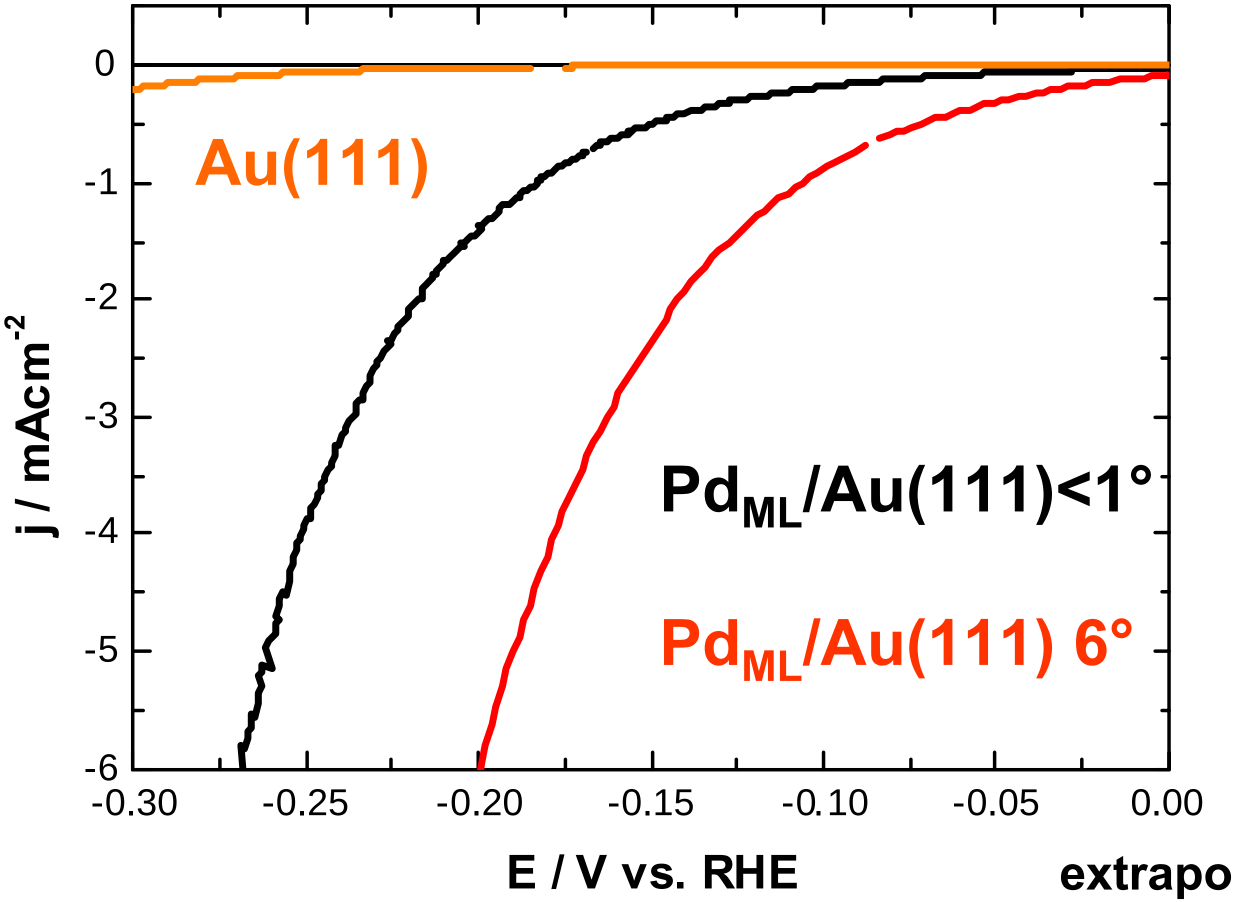
J Greeley, JK Norskov, LA Kibler, AM El-Aziz, DM Kolb, ChemPhysChem 7 (2006) 1032

HER on Pd / Au(111)



HER an Pd / Au(111)

1mV/s, 0.1M H_2SO_4



j_0 / µA cm^{-2}

0.12

30

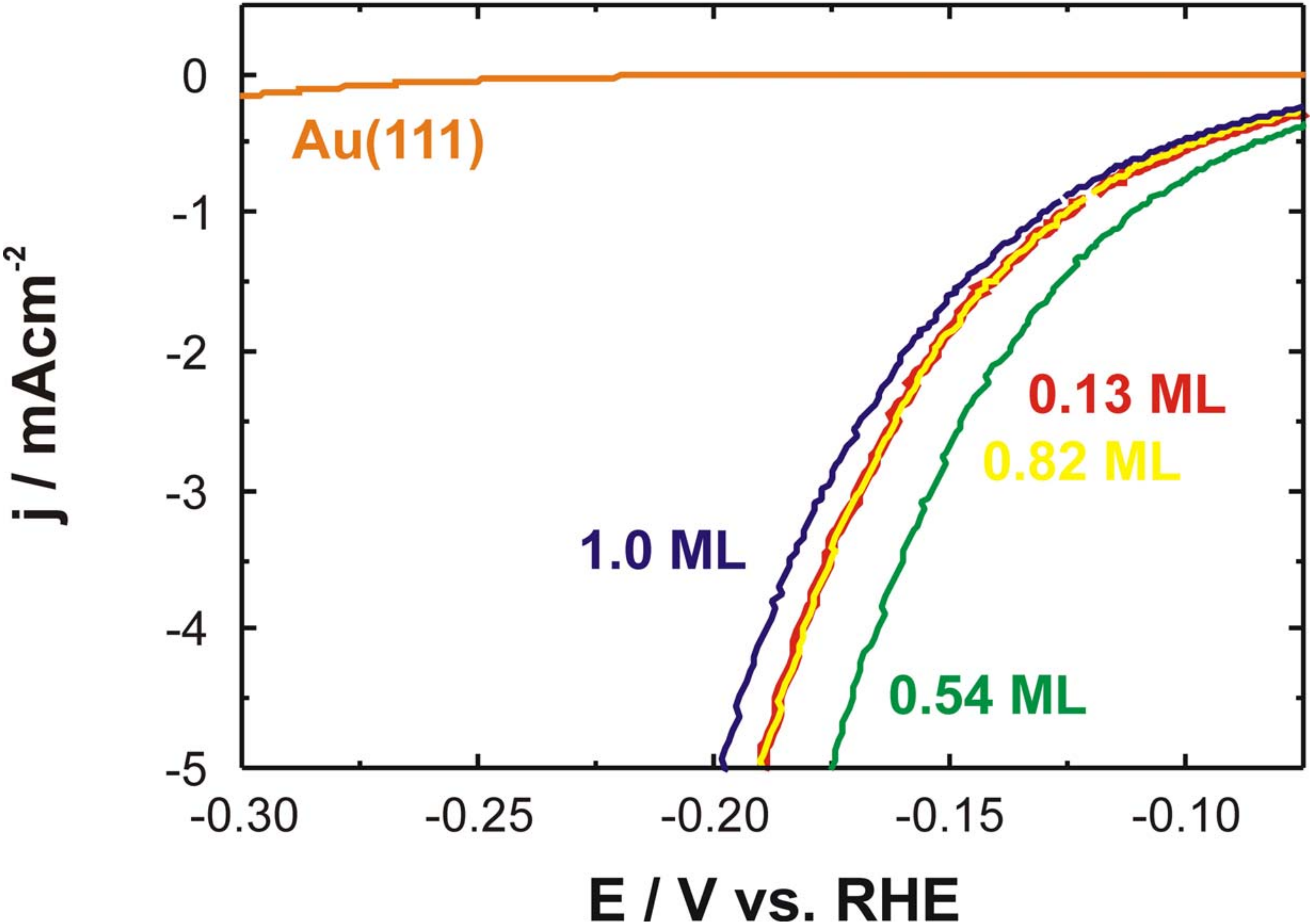
120

extrapolation to 0°:

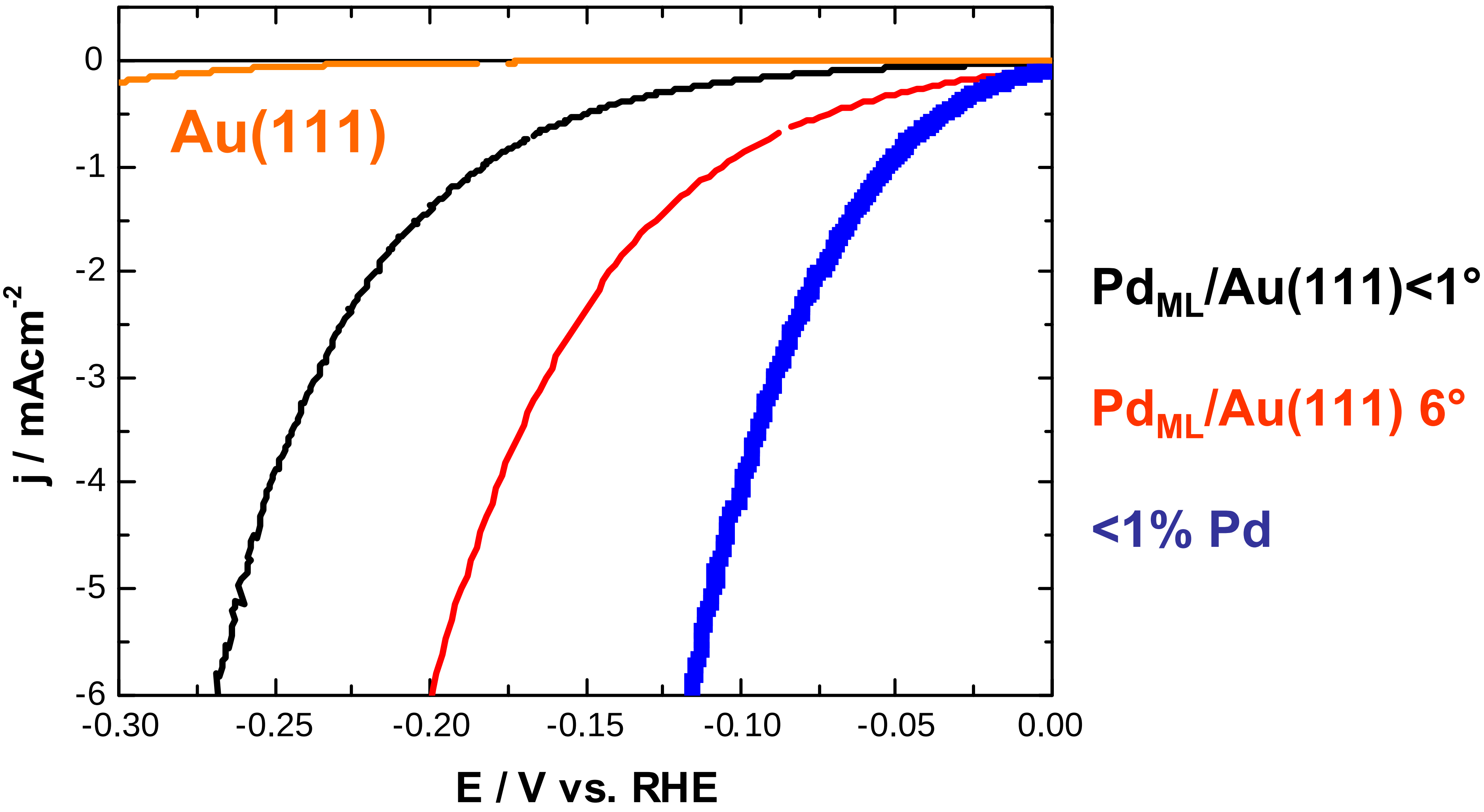
j_0 Pd_{ML}/Au(111) ~ 20 µA cm^{-2}

Hydrogen evolution

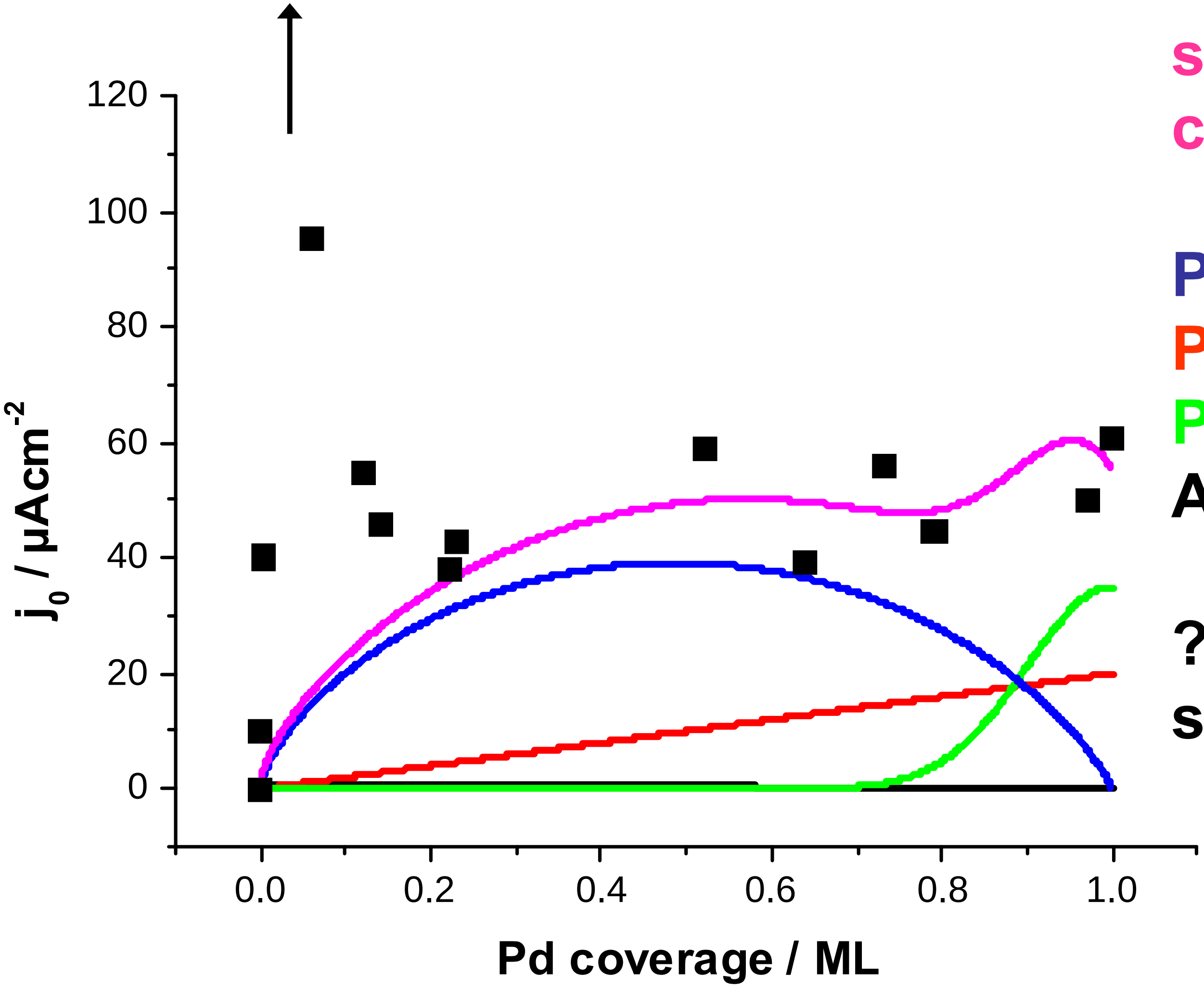
0.1 M H_2SO_4, 1 mV/s



High activity for small Pd coverages



Active sites for HER on Pd / Au(111)



sum of 4 contributions:

Pd-Au steps
Pd terraces
Pd-Pd steps
Au(111)

? high activity for small coverage

L.A. Kibler