Electrocatalysis in fuel cells

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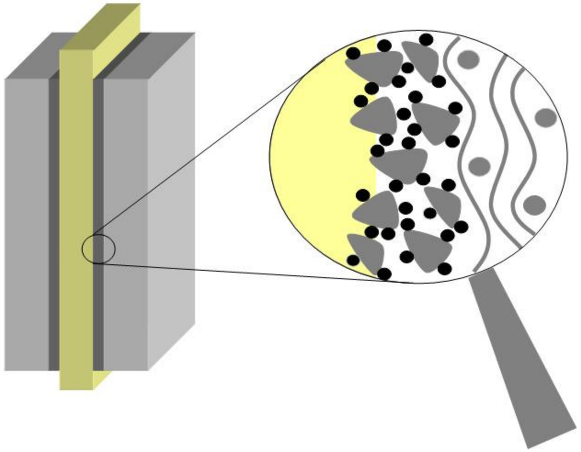
Berlin, 01.02.2008



Outline

Principles of fuel cells and electrocatalysis

Important electrocatalytic reactions:
- Oxygen reduction
- Hydrogen oxidation
- Methanol oxidation

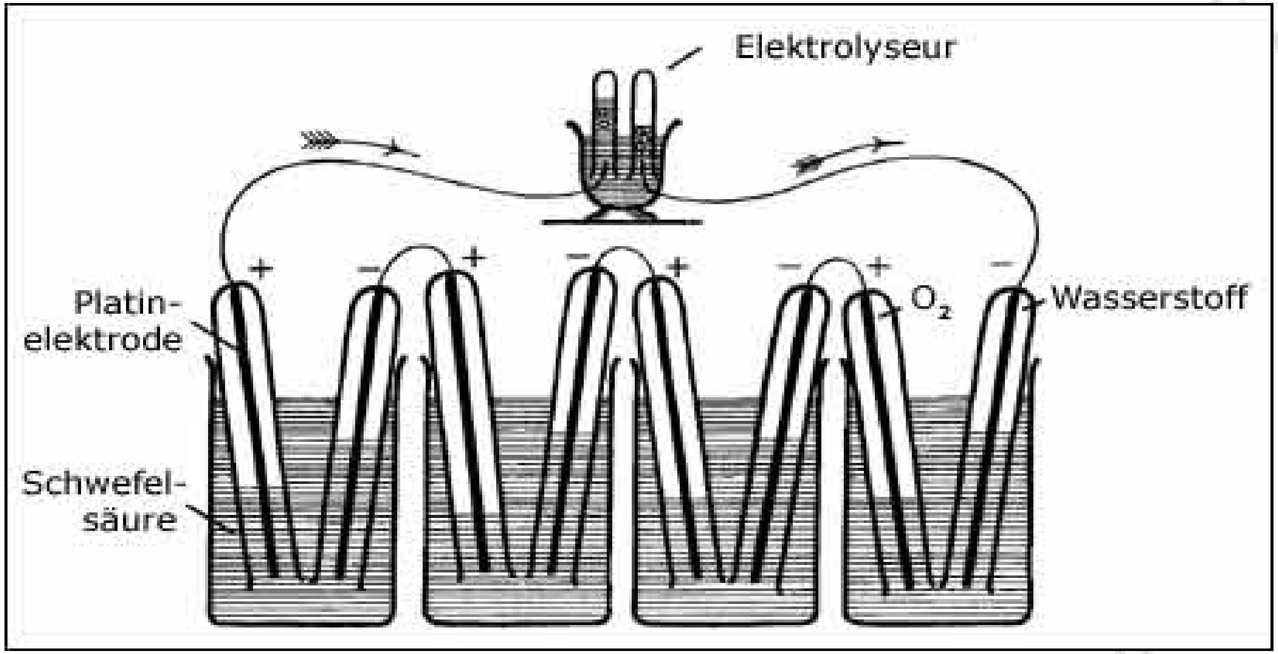
Experimental methods in electrocatalysis

Current trends in electrocatalysis and own work

The “invention” of the fuel cell

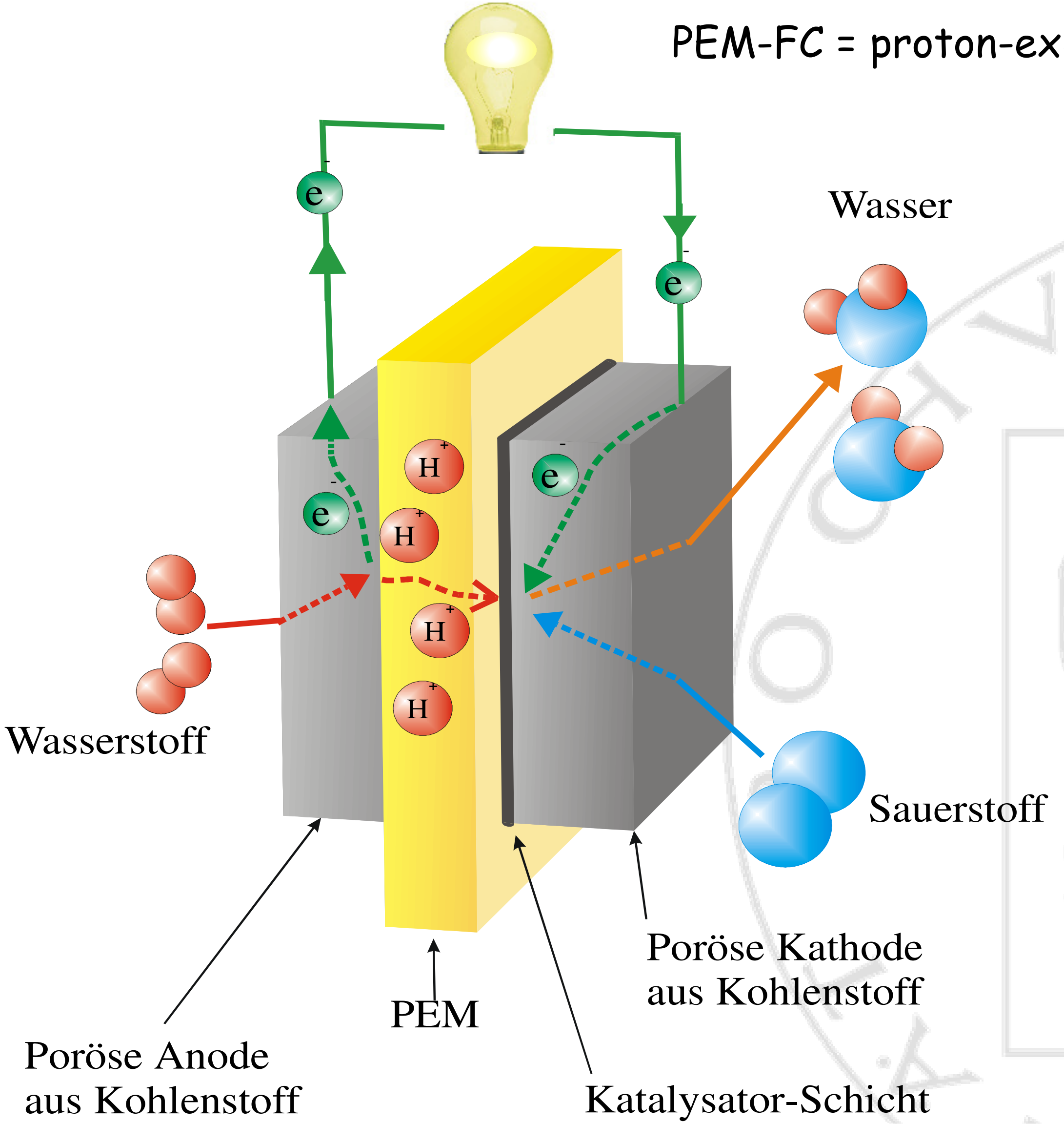
Sir William Robert Grove

Scheme of Groves fuel cell



Schematic setup of a PEM fuel cell

PEM-FC = proton-exchange membrane fuel cell



Wasser

Wasserstoff

Sauerstoff

Poröse Kathode
aus Kohlenstoff

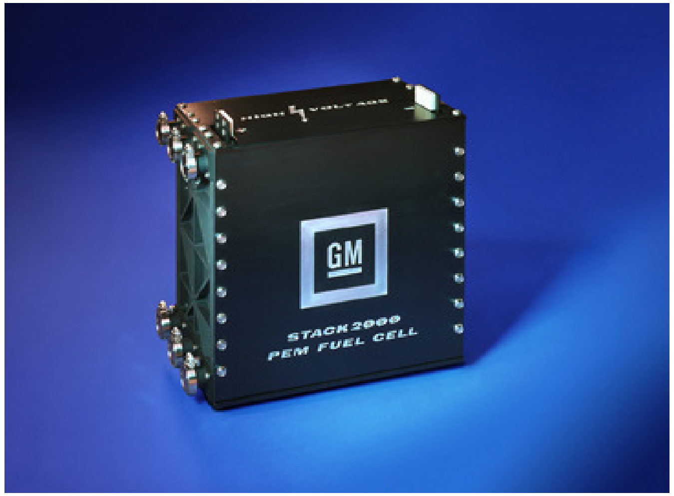
PEM

Poröse Anode
aus Kohlenstoff

Katalysator-Schicht

“HydroGen3”, Opel/GM

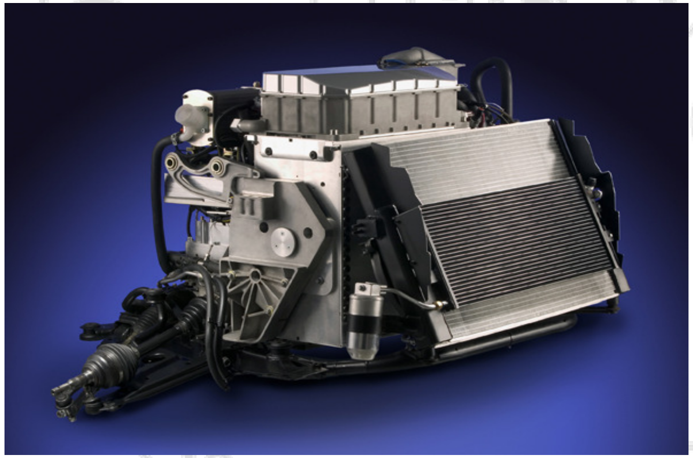
Components of the "HydroGen3", Opel/GM



FC-Stack

Liquid hydrogen tank

Pressure tank

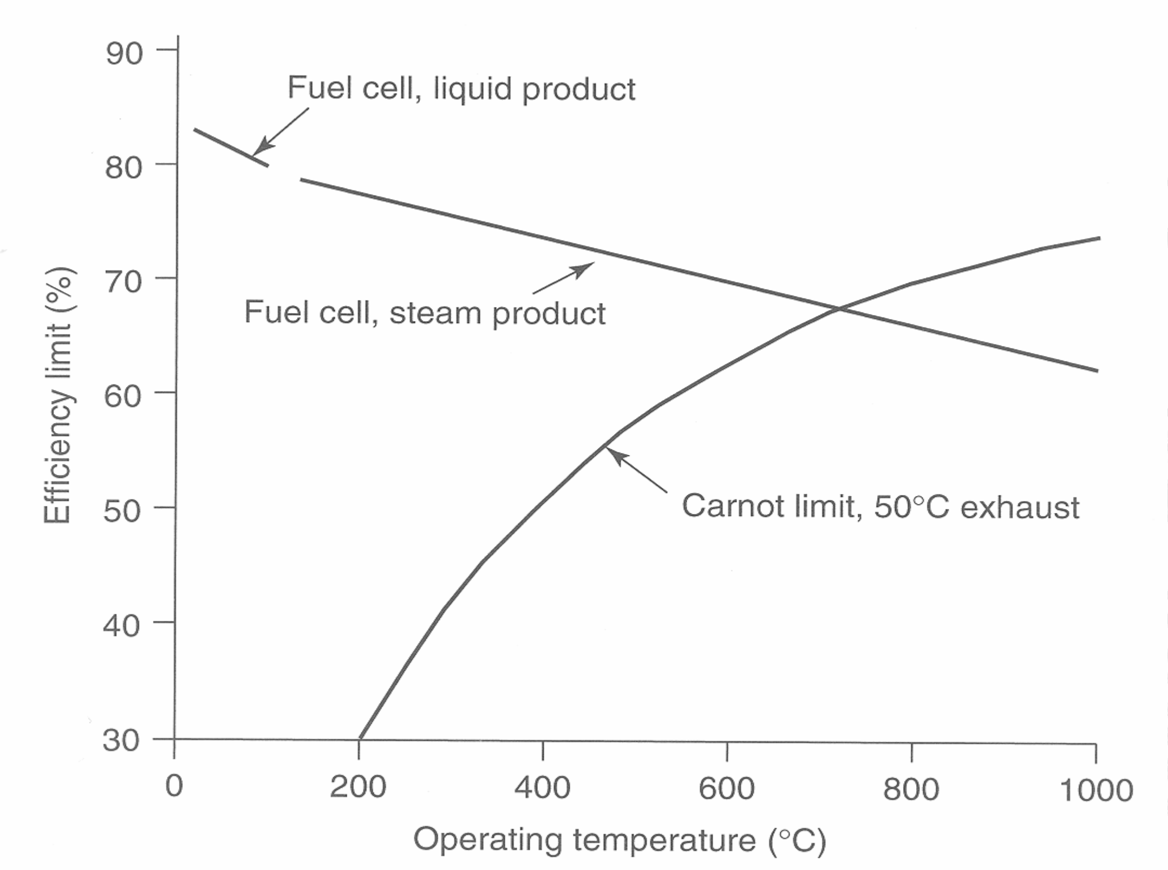


Fuel cell

Direct methanol fuel cell (DMFC)
12 V/25 W
120 ml MeOH-cartridges
> 7 h power supply
1.1 kg overall/150 g per cartridge

www.smartfuelcell.de

Comparison: Efficiency limit of Carnot process and fuel cell

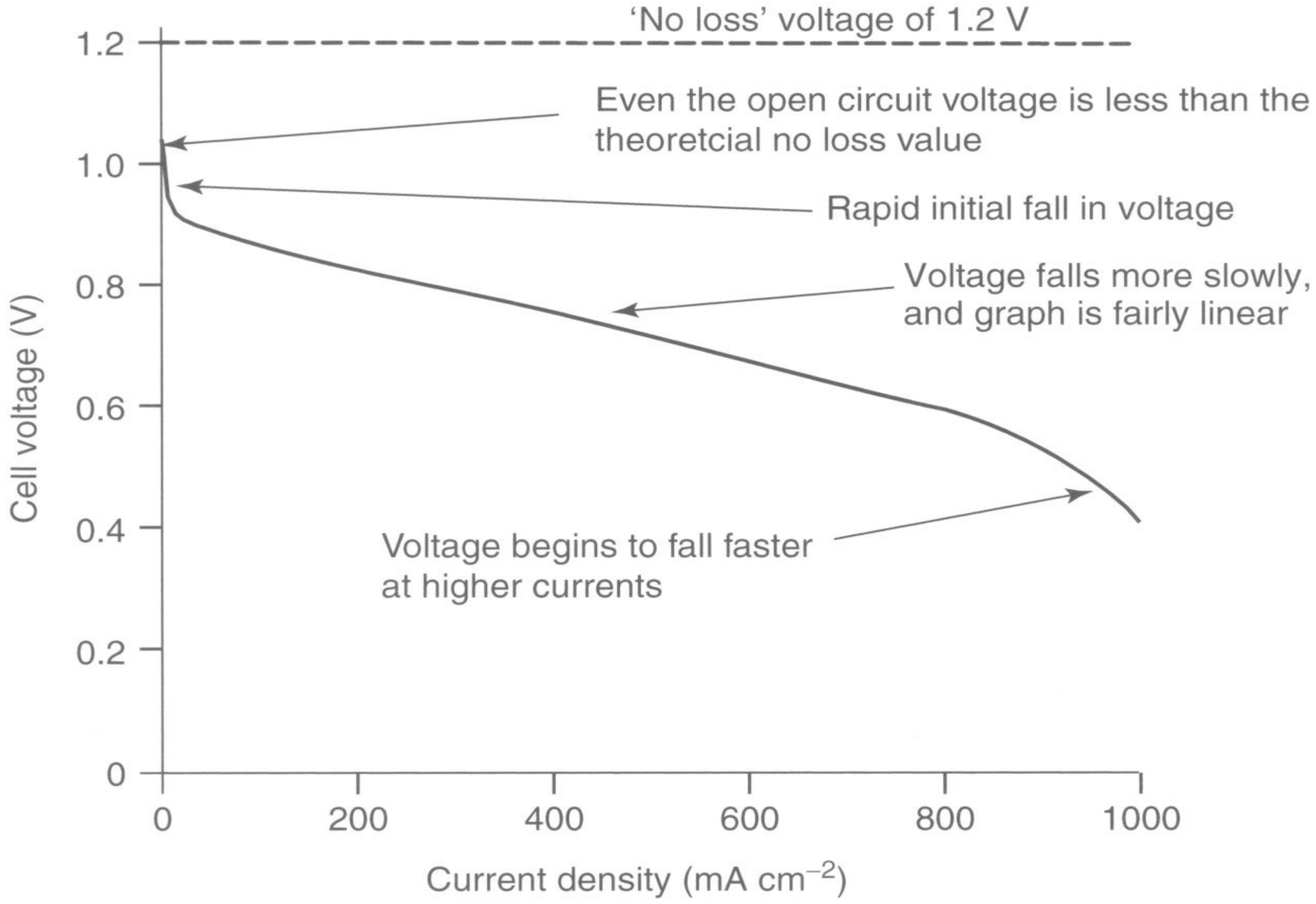


Taken from: “Fuel Cell Systems Explained”, J. Larminie, A. Dicks, Wiley 2003

Overview: different types of fuel cells

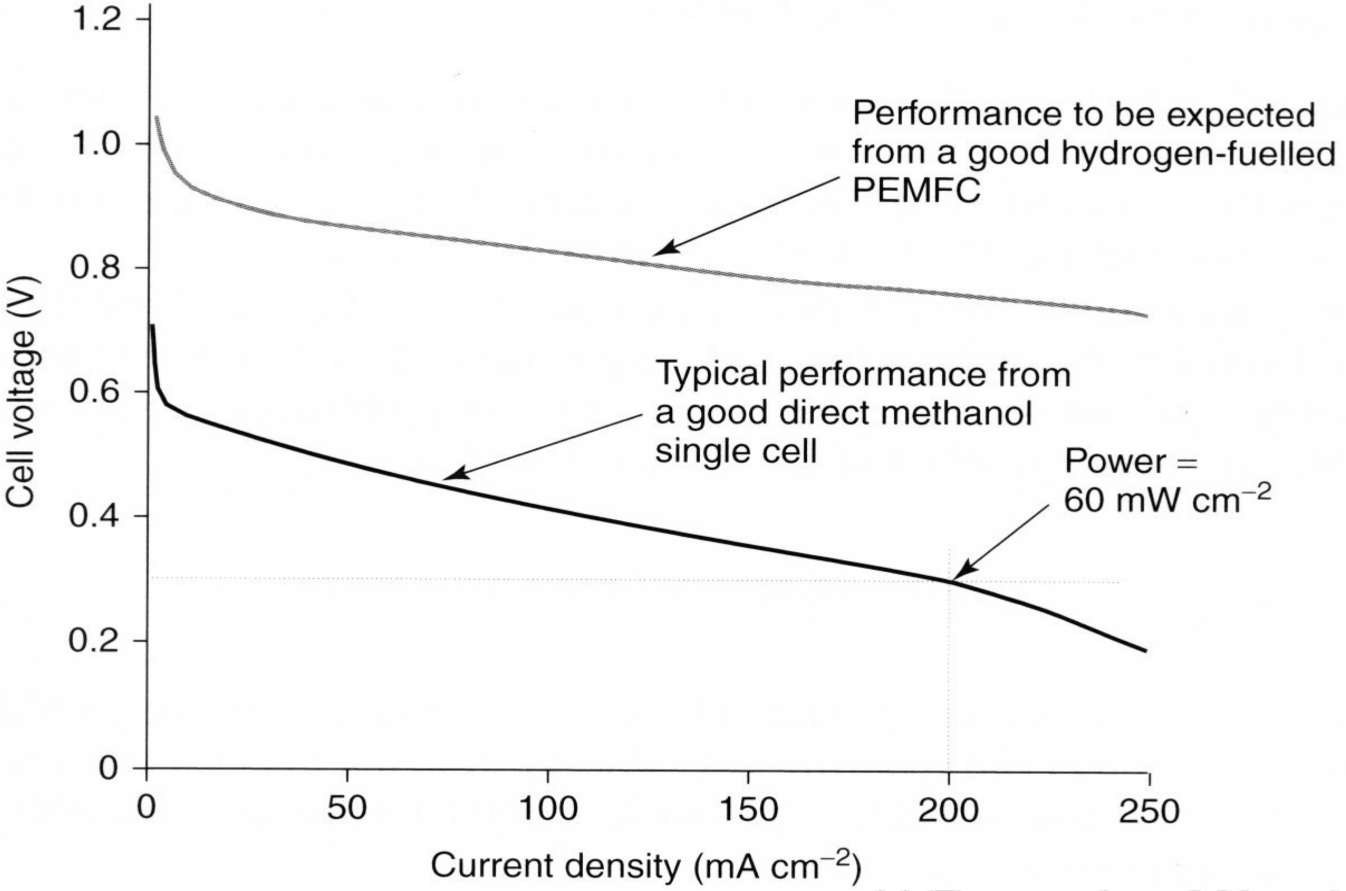
Name	Alkaline Fuel Cell (**AFC**)	Polymer Electrolyte Membrane Fuel Cell (**PEM-FC**)	Direct Methanol Fuel Cell (**DMFC**)	Phosphoric Acid Fuel Cell (**PAFC**)	Molten Carbonat Fuel Cell (**MCFC**)	Solid Oxide Fuel Cell (**SOFC**)
Electrolyte	KOH	Proton-Exchange-membrane	PEM	H_3PO_4 (immobilis.)	$LiKCO_3$	$Zr(Y)O_2$
Operating temperature	50-200 ℃	30-100 ℃	20-90 ℃	190-220 ℃	650 ℃	800-1000 ℃
Reactands	H_2, NH_2 NH_2, O_2	H_2 O_2/Luft	MeOH O_2/Luft	H_2 O_2/Luft	H_2, CH_4.... O_2/Luft	H_2, CH_4.... O_2/Luft
Catalysts	A: Raney-Ni K: Ag	A: Pt/C K: Pt/C	A: PtRu/C K: Pt/C	A: Pt/C K: Pt/C	A: NiCr-Leg. K: LiNiO	A: $NiZrO_2$ K: $LaSrMnO_3$
Electrical Efficiency	60 %	55 %		40 %	55 %	55 %
Area of Application	Space flight, navy	Mobile applications 50-100 kW, de-centralised energy supply few Watt to 10 kW	Mobile/portable (100 mW to 100 W) applications, de-centralised energy supply	Combined heat and power plants (50-500 kW) Power plants (1-100 MW)	Combined heat and power plants (50-500 kW) Power plants (1-100 MW)	Combined heat and power plants (50-500 kW) Power plants (1-100 MW)

Typical current-voltage-curve of a PEM-FC



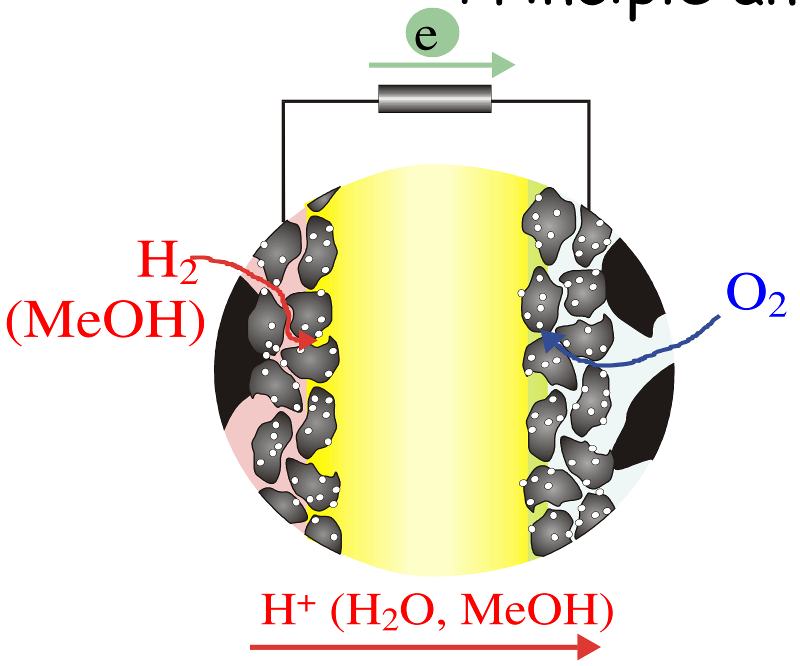
From: "Fuel Cell Systems Explained", J. Larminie, A. Dicks, Wiley 2003

Comparison: PEM-FC using MeOH or hydrogen as fuel



Aus: “Fuel Cell Systems Explained”, J. Larminie, A. Dicks, Wiley 2003

Principle and reactions of the PEM-FC



PEM-FC = proton-exchange membrane fuel cell

Hydrogen fuel cell:

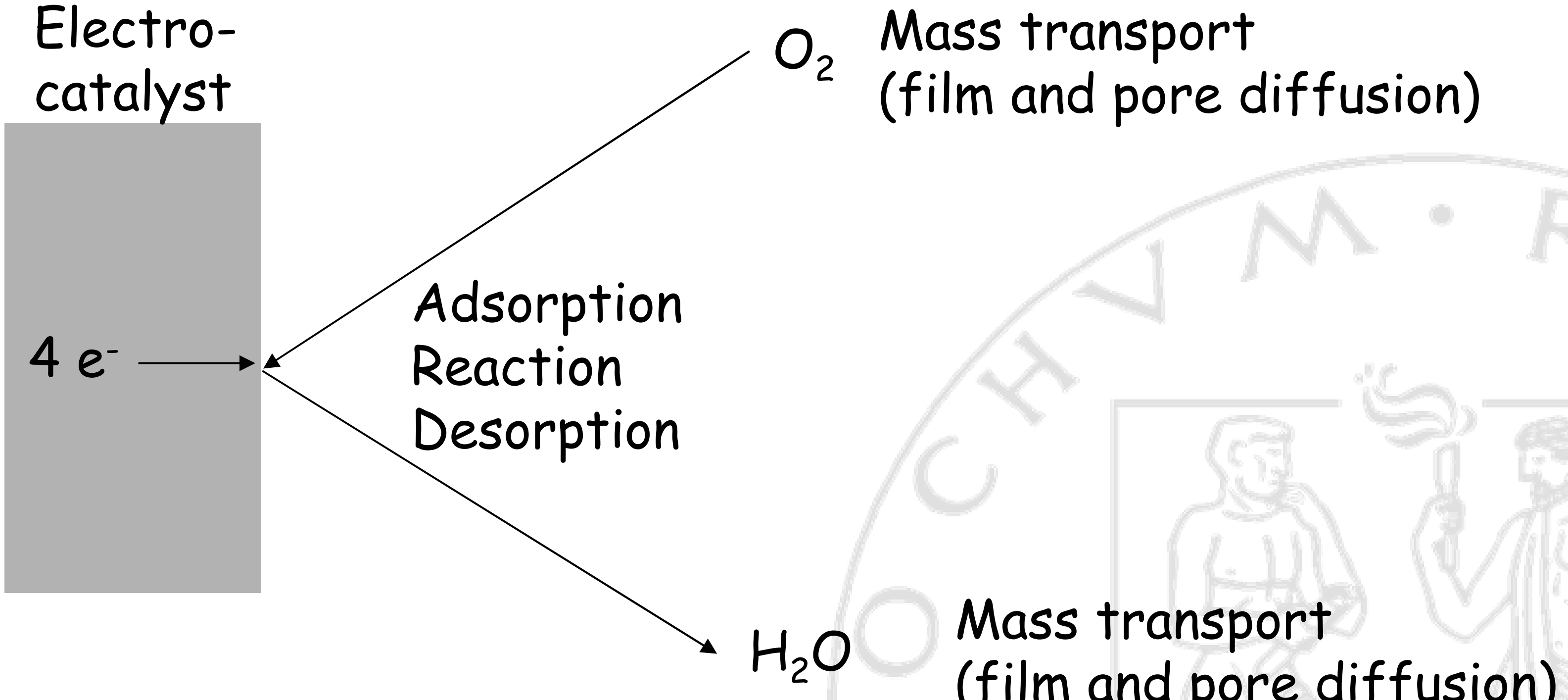
Anode $2\,H_2 \rightarrow 4\,H^+ + 4e^-$ 0 V vs. NHE
Cathode $O_2 + 4\,e^- + 4\,H^+ \rightarrow 2\,H_2O$ 1.23 V vs. NHE
Overall $2\,H_2 + O_2 \rightarrow 2\,H_2O$ $E_0 = 1.23$ V

$\Delta G^R = -nFE_0$

Efficiency losses due to
- mass transport problems in the porous electrode
- high overpotential of orr (oxygen reduction reaction)
- (ohmic losses)

Demand for efficient (and cheap) electrocatalysts

Comparison heterogeneous catalysis/electrocatalysis



Electro-
catalyst

$4\,e^-$

O_2 Mass transport
(film and pore diffusion)

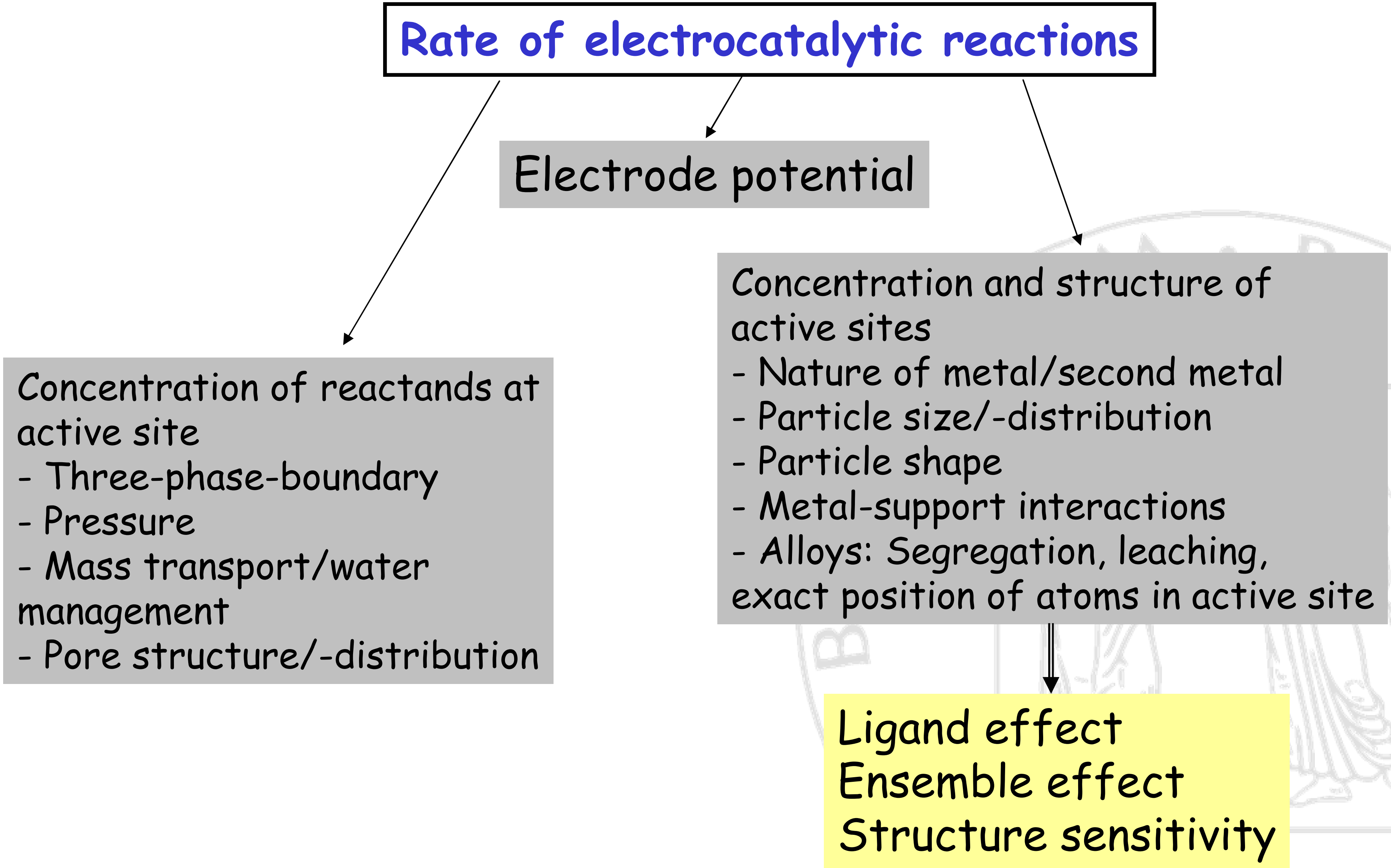
Adsorption
Reaction
Desorption

H_2O Mass transport
(film and pore diffusion)

Additionally in electrocatalysis:

- Charge transfer (electron, ion) through phase boundary

- Mass transport (migration)
- Potential-dependent effects (e.g. adsorption)



Rate of electrocatalytic reactions

Electrode potential

Concentration of reactands at active site
- Three-phase-boundary
- Pressure
- Mass transport/water management
- Pore structure/-distribution

Concentration and structure of active sites
- Nature of metal/second metal
- Particle size/-distribution
- Particle shape
- Metal-support interactions
- Alloys: Segregation, leaching, exact position of atoms in active site

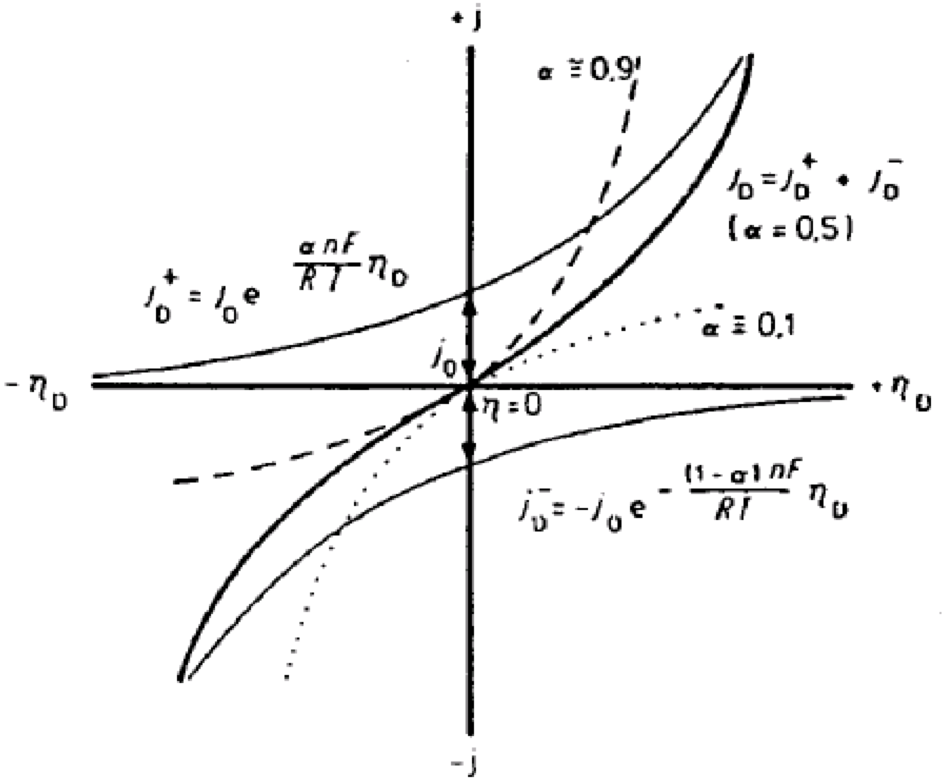
Ligand effect
Ensemble effect
Structure sensitivity

Electrode kinetics: Butler-Volmer equation

(see also talk of Prof. D. Kolb)

$$i = i_o\left[\exp\left(\frac{\alpha_A nF}{RT}\eta\right) - \exp-\left(\frac{\alpha_C nF}{RT}\eta\right)\right]$$

where i_o = exchange current density
η = overpotential $(= E - E_o)$
n = number of electrons
α_A = anodic transfer coefficient
α_C = cathodic transfer coefficient



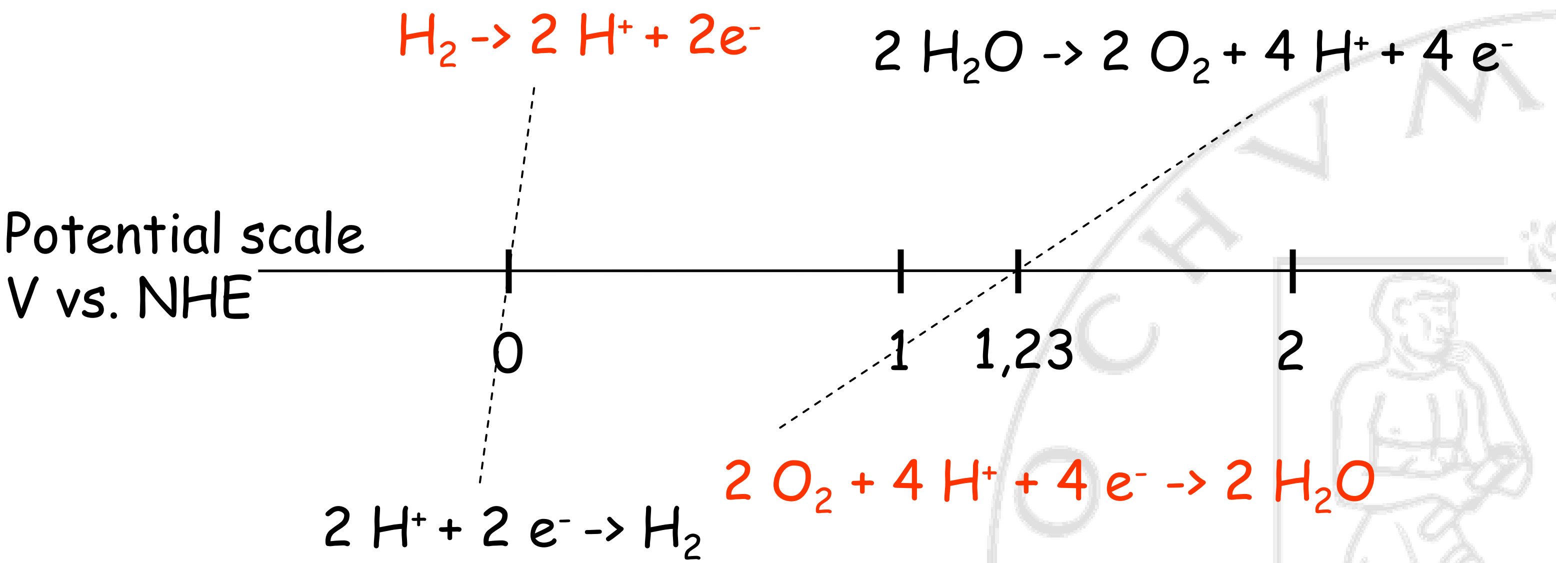
Elektrochemie Carl H. Hamann, Wolf Vielstich,
ISBN 3-527-27894-x

$i_C >> i_A$: Tafel equation

$$i = i_0 * \exp[-(\alpha_c nF/RT)\,\eta]$$

i = current
j = current density
$\alpha_C = 1-\alpha_A$

Overpotentials and cell voltages (schematic!!!!)



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

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

Potential scale
V vs. NHE

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

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

Example 1: Electrocatalytic oxygen reduction

4-electron-reduction

$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O \qquad E_0 = +\,1.229\text{ V vs. NHE}$

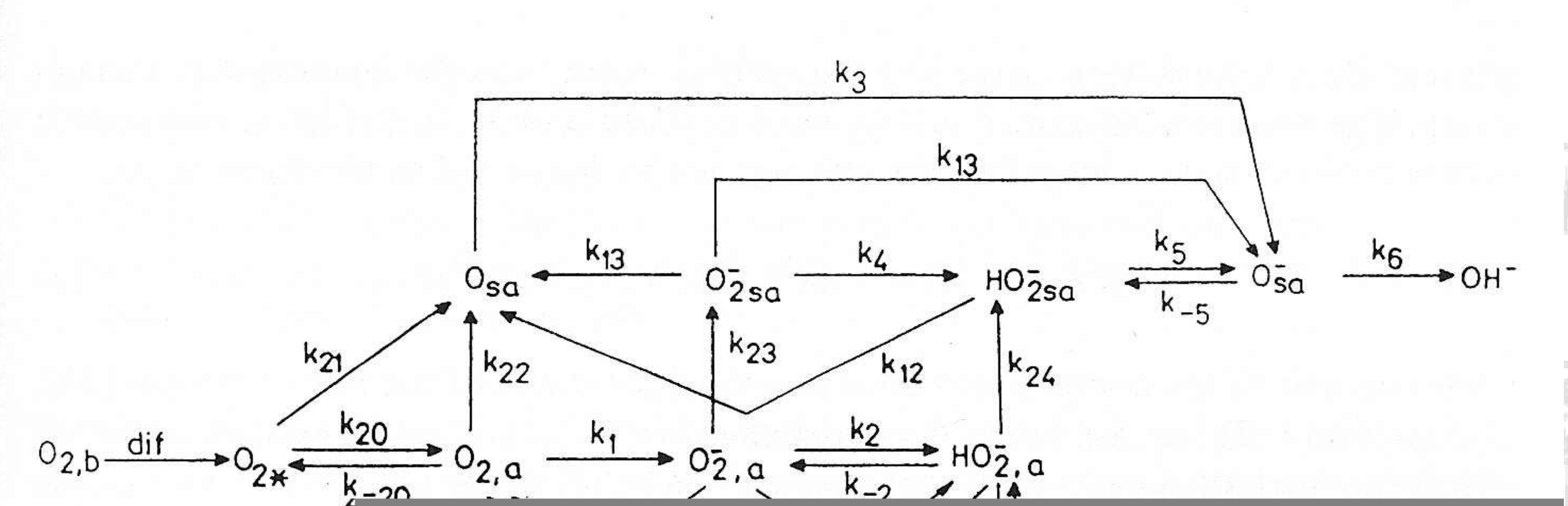
(2x)2-electron-reduction

$O_2 + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O_2 \qquad E_0 = +\,0.67\text{ V vs. NHE}$

$H_2O_2 + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O \qquad E_0 = +\,1.77\text{ V vs. NHE}$

$H_2O_2 \longrightarrow H_2O + O_2$ Catalytic decomposition

General scheme of electrocatalytic oxygen reduction

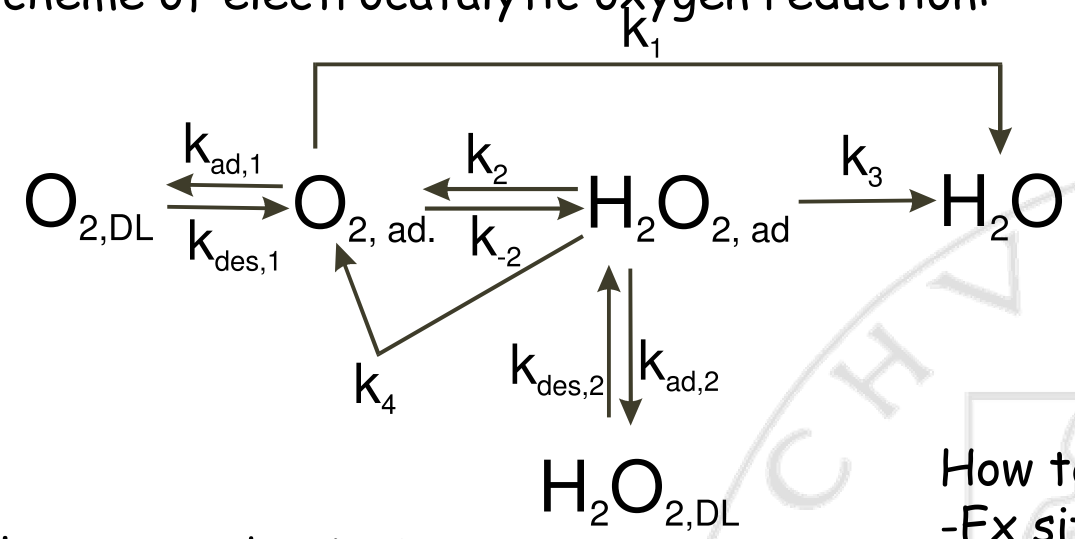


[redacted]

From: “Electrocatalysis”, J. Lipkowski, P.N. Ross, Eds.; Wiley VCH, New York 1998.

Electrocatalytic oxygen reduction

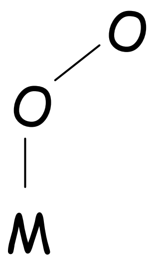
- Simplified scheme of electrocatalytic oxygen reduction:



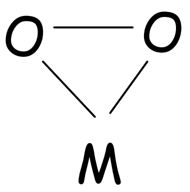
How to investigate in situ?
-Ex situ: e.g. EELS, LEED, NEXAFS, XPS

2-electron- or 4-electron-reduction?

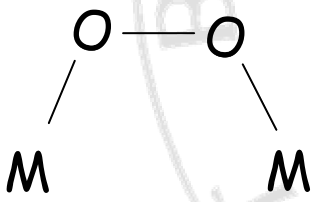
- Adsorbate geometries



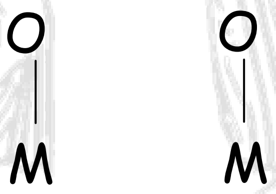
Pauling



Griffith



bridged



dissociative

Catalysts for oxygen reduction in PEM fuel cells

State of the art oxygen reduction catalyst:
Platinum
- Direct four-electron reduction
- Exact mechanism still not clarified
- Still large overpotential

Platinum alloys (Co, Fe, Ni, Cr,….)

Alternatives:
- Iron (and cobalt) based catalysts
- Catalysts based on ruthenium
- Surface modified ruthenium catalysts

Pt-alloy catalysts for oxygen reduction: structural and electronic characterisation

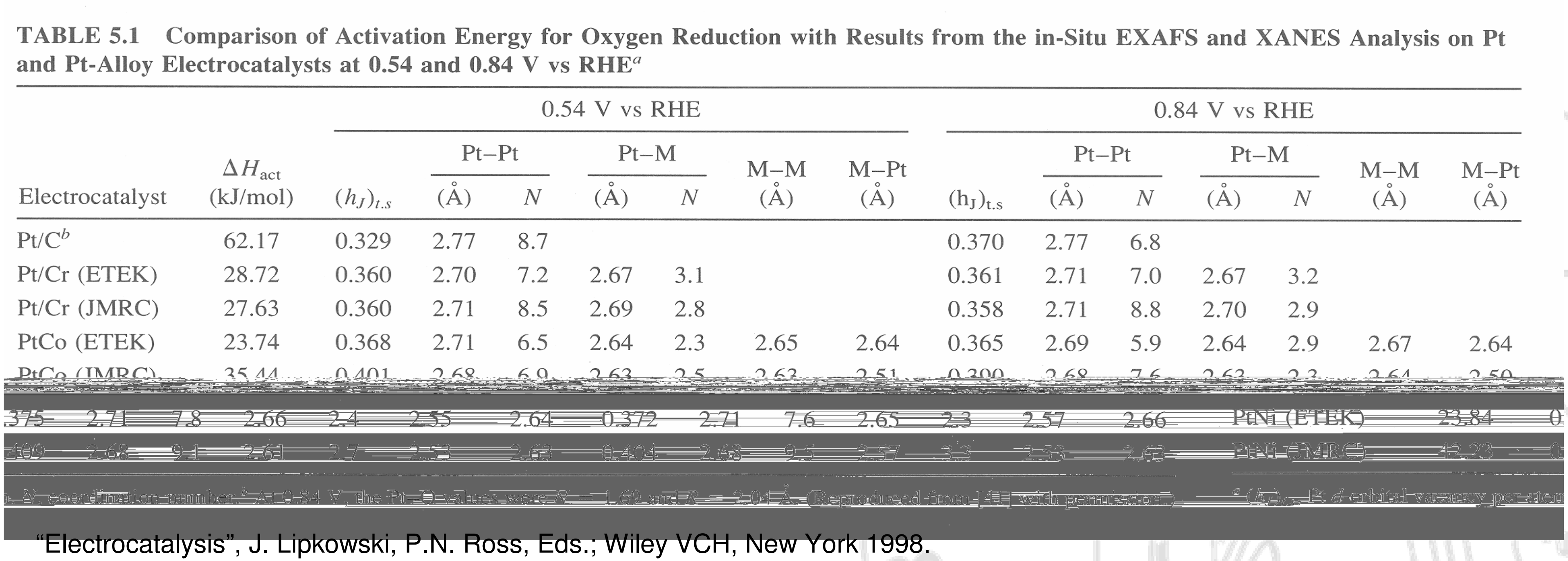


TABLE 5.1 Comparison of Activation Energy for Oxygen Reduction with Results from the in-Situ EXAFS and XANES Analysis on Pt and Pt-Alloy Electrocatalysts at 0.54 and 0.84 V vs RHE[a]

		0.54 V vs RHE							0.84 V vs RHE						
			Pt–Pt		Pt–M		M–M	M–Pt		Pt–Pt		Pt–M		M–M	M–Pt
Electrocatalyst	ΔH_{act} (kJ/mol)	$(h_J)_{t.s}$	(Å)	*N*	(Å)	*N*	(Å)	(Å)	$(h_J)_{t.s}$	(Å)	*N*	(Å)	*N*	(Å)	(Å)
Pt/C[b]	62.17	0.329	2.77	8.7					0.370	2.77	6.8				
Pt/Cr (ETEK)	28.72	0.360	2.70	7.2	2.67	3.1			0.361	2.71	7.0	2.67	3.2		
Pt/Cr (JMRC)	27.63	0.360	2.71	8.5	2.69	2.8			0.358	2.71	8.8	2.70	2.9		
PtCo (ETEK)	23.74	0.368	2.71	6.5	2.64	2.3	2.65	2.64	0.365	2.69	5.9	2.64	2.9	2.67	2.64
PtCo (JMRC)	35.44	0.401	2.68	6.9	2.63	2.5	2.63	2.51	0.390	2.68	7.6	2.63	2.3	2.64	2.50
PtNi (ETEK)	23.84	0.375	2.71	7.8	2.66	2.4	2.55	2.64	0.372	2.71	7.6	2.65	2.3	2.57	2.66
PtNi (JMRC)	42.23	0.409	2.68	9.1	2.61	2.7	2.53	2.63	0.404	2.68	9.5	2.57	3.3	2.53	2.62

[a] *N*, coordination number. [b] At 0.84 V, the Pt–O values were *N* = 1.69 and *R* = 2.04 Å. (Reproduced from [11] with permission.) [c] $(h_J)_{t.s}$, Pt *d*-orbital vacancy per at

"Electrocatalysis", J. Lipkowski, P.N. Ross, Eds.; Wiley VCH, New York 1998.

electronic factors (electronic structure of surface atoms) and geometric factors (exact position of surface atoms)

here: geometric factors seem to be dominating

Crystallite size effects in oxygen reduction over Pt

Structure sensitive activity:

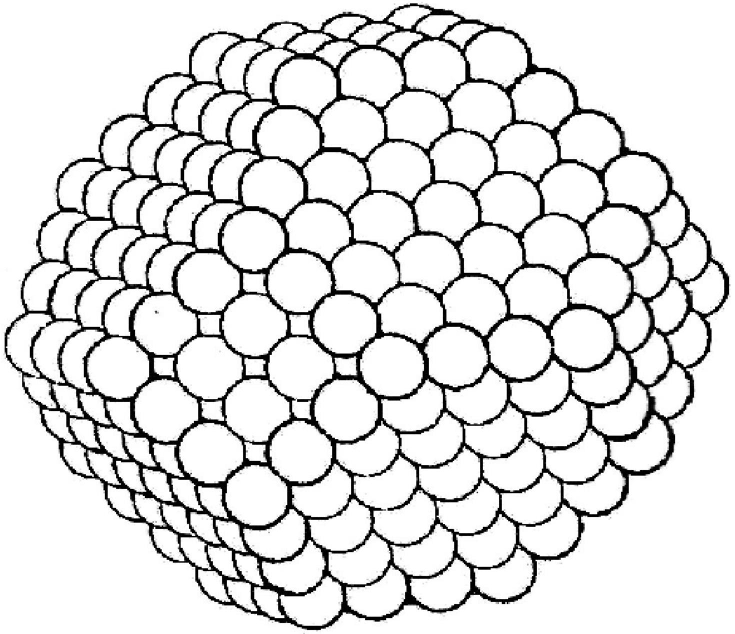
(111), (110) > 100 in aqueous $HClO_4$

(111) << (100) < (110) in aqueous H_2SO_4

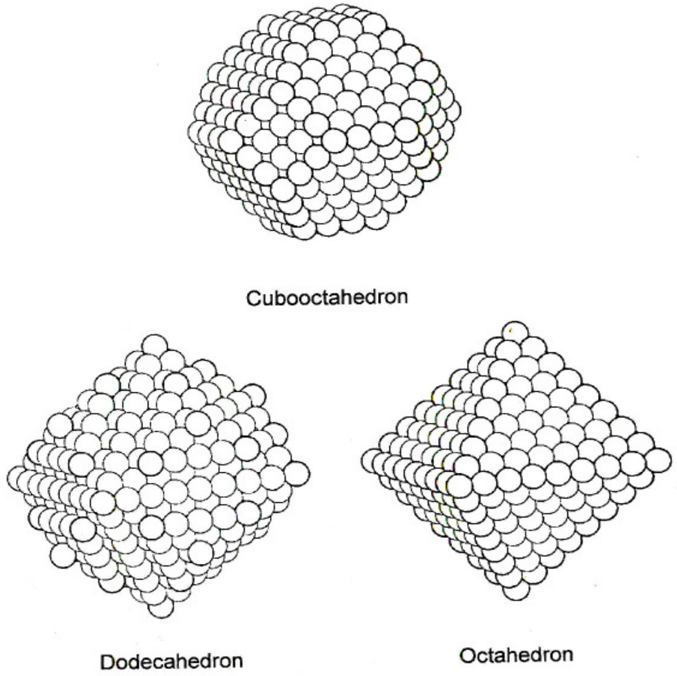
Explanation includes structure sensitive anion adsorption!

(N. Markovich, P. Ross, 1997)

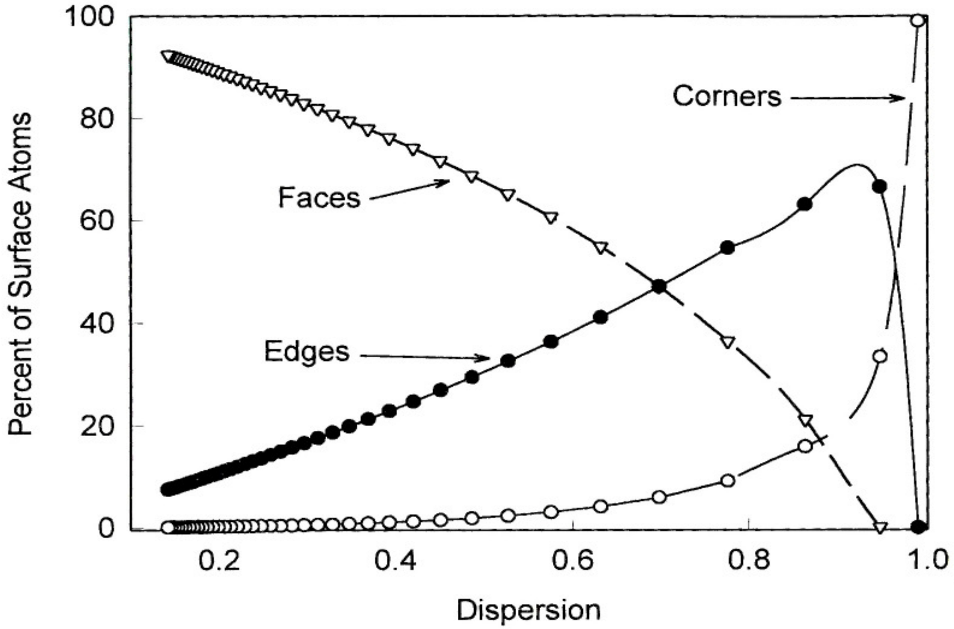
Particle < 6 nm: (111)-surface dominating,
< 1.8 nm: (111) is nearly the only surface

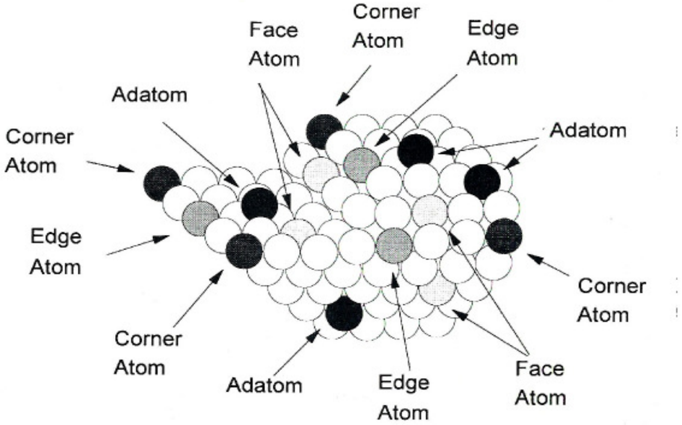


Structure sensitivity: particle size



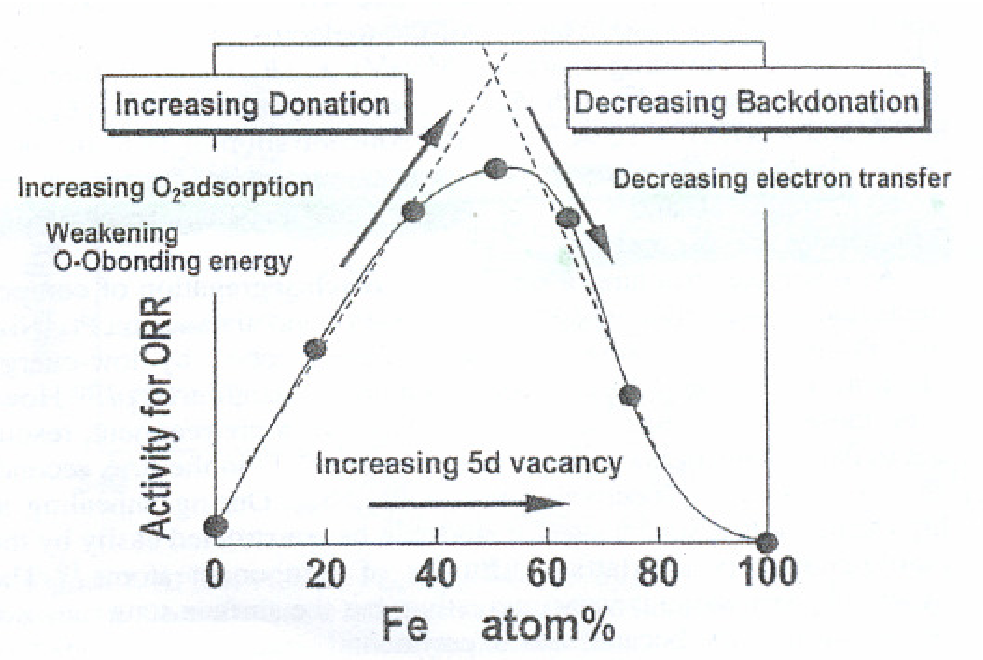
Idealized crystal shapes

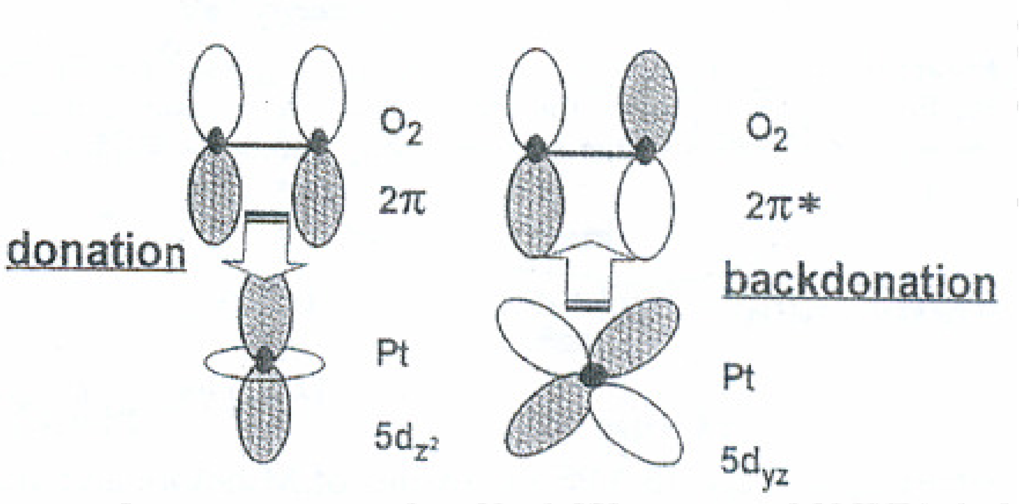




different types of surface atoms

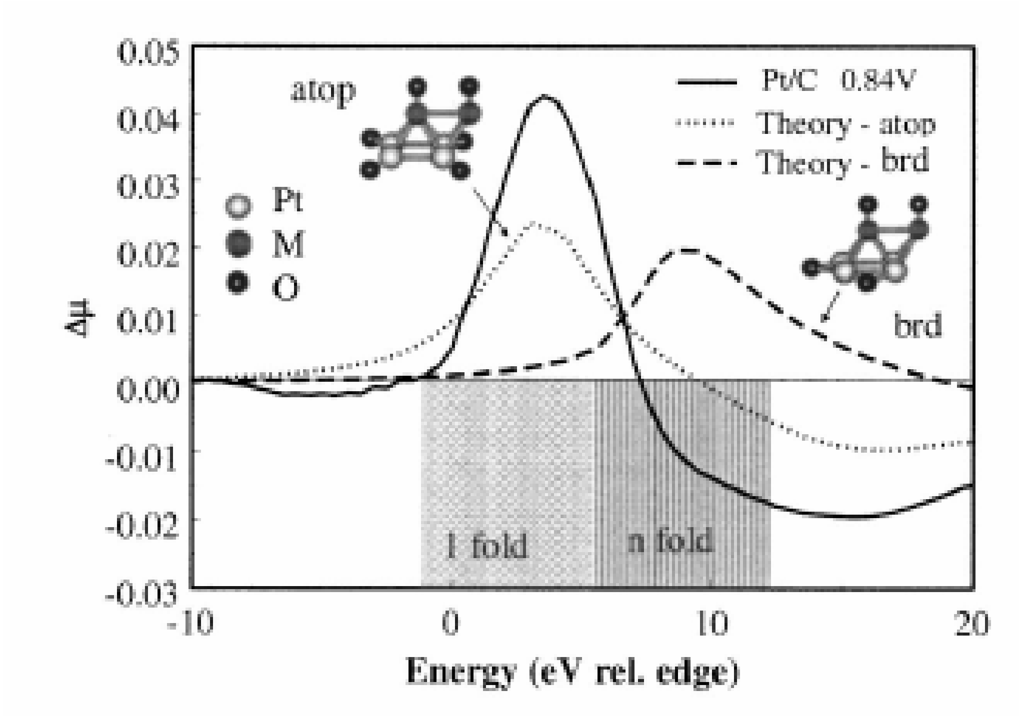
Another view: simplified model of donation-backdonation

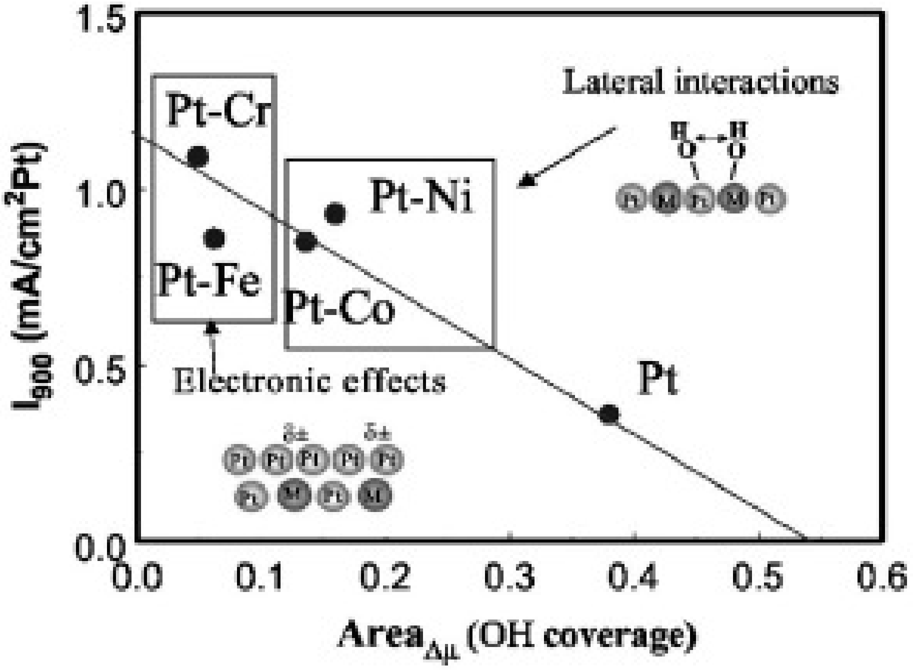




T. Toda, H. Igarashi, H. Uchida, and M. Watanabe, *J. Electrochem. Soc.*, *146*, 3750 – 3756, 1999

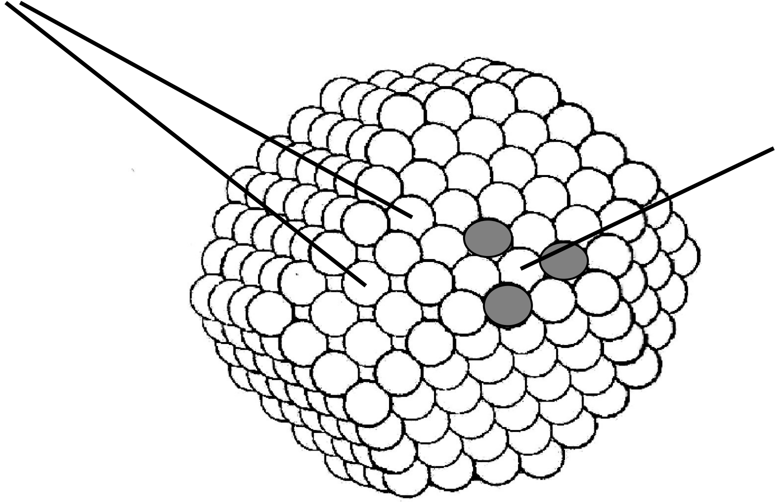
Inhibition of oxygen reduction by adsorbed species





From: Teliska et al. J. Electrochem. Soc. 152 (2005) A2159-A2169.

Influence of OH-adsorption

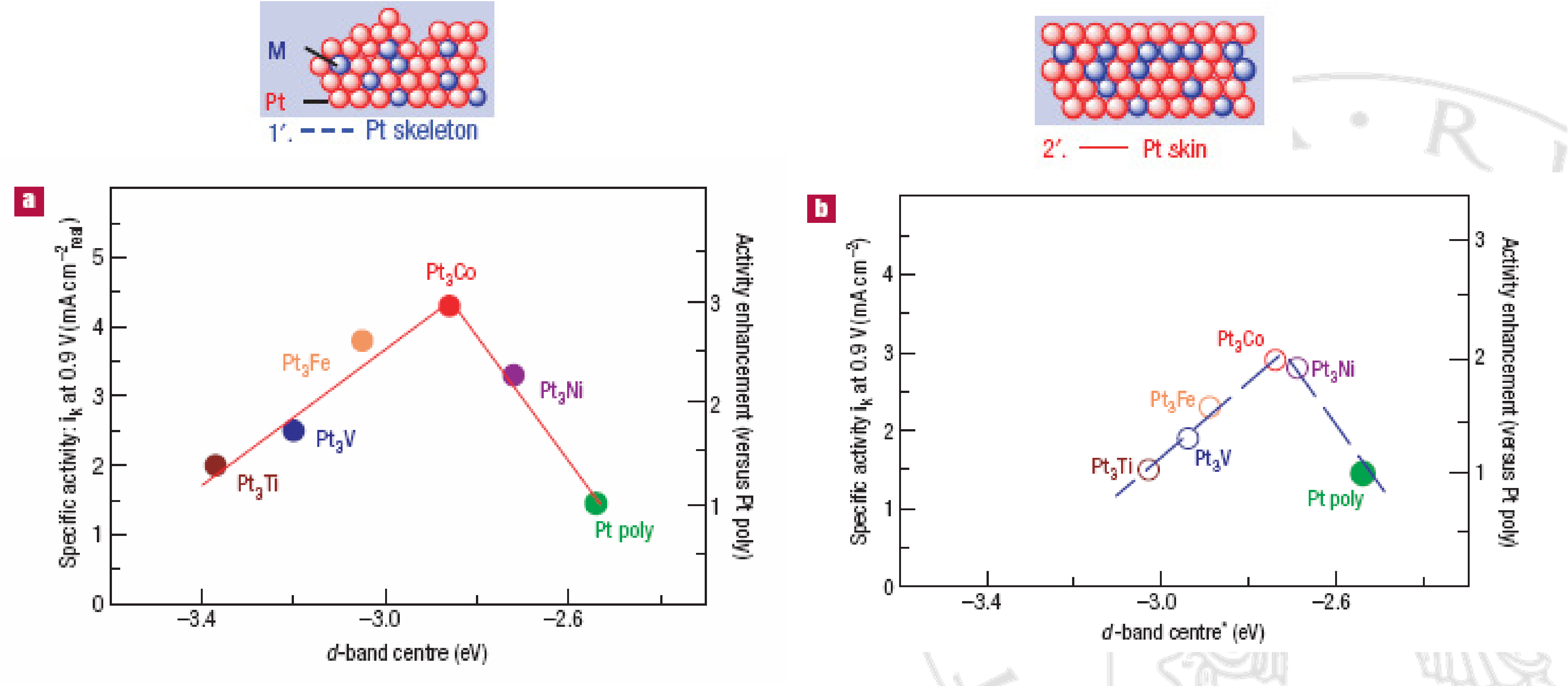


geometrical structure sensitivity
due to OH-adsorption

OH adsorption depends on
electronic structure (alloy)

optimum particle size (larger particles: less OH adsorption but less surface area)

Volcano behaviour: Oxygen activation/inhibition



Stamenkovic et al., NatureMaterials 6 (2007) 242

Stability of Pt(alloy) electrocatalysts

Pt-alloy:
- leaching of less noble metal
- poisoning of membrane
- kind of core-shell structure forms
- sintering

What is really present under reaction conditions
(i.e., in a membrane electrode assembly of a working fuel cell) ?

→ Real in situ-measurements to establish true structure-activity relationships

→ Development of long-term stable orr catalysts

Hydrogen electrode reactions

$H_2 + 2\,H_2O \rightleftharpoons 2\,H_3O^+ + 2\,e^-$ $\quad E_0 = 0\,V$

Volmer-reaction:

$H_3O^+ + e^- \rightleftharpoons H_{ad} + H_2O$

Tafel-reaction:

$2\,H_{ad} \rightleftharpoons H_{2,ad}$

Heyrowsky-reaction

$H_3O^+ + H_{ad} + e^- \rightleftharpoons H_{2,ad} + H_2O$

Volmer-Tafel- und Volmer-Heyrowsky-mechanism

CO as anode poison

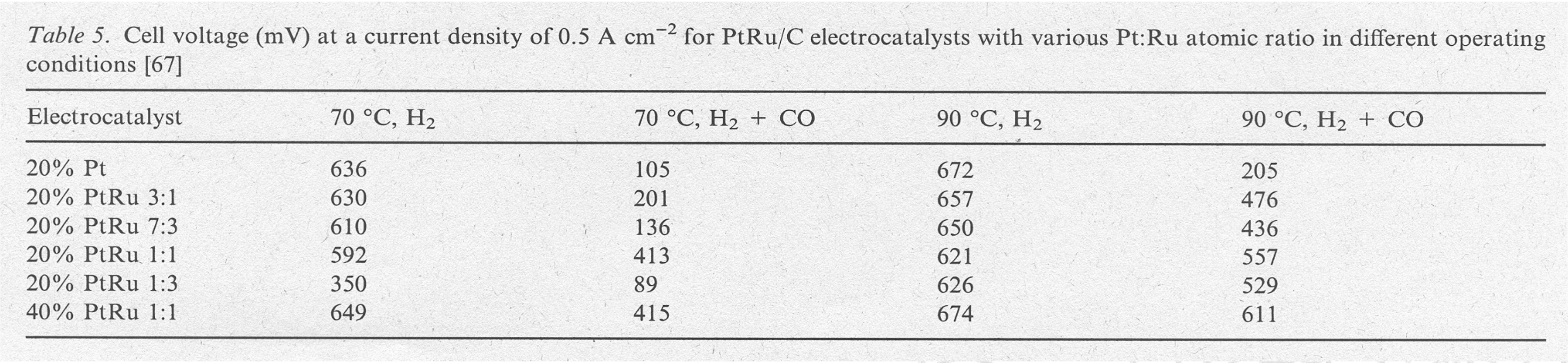


Table 5. Cell voltage (mV) at a current density of 0.5 A cm^{-2} for PtRu/C electrocatalysts with various Pt:Ru atomic ratio in different operating conditions [67]

Electrocatalyst	70 °C, H_2	70 °C, H_2 + CO	90 °C, H_2	90 °C, H_2 + CO
20% Pt	636	105	672	205
20% PtRu 3:1	630	201	657	476
20% PtRu 7:3	610	136	650	436
20% PtRu 1:1	592	413	621	557
20% PtRu 1:3	350	89	626	529
40% PtRu 1:1	649	415	674	611

From: E. Antolini, J. Appl. Electrochem. 34 (2004) 563-576.

CO oxidation

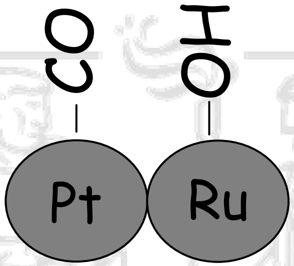
$$CO_{ad} + H_2O \longrightarrow CO_2 + 2\,H^+ + 2\,e^-$$

Bifunctional mechanism vs. electronic effect

Bifunctional mechanism:

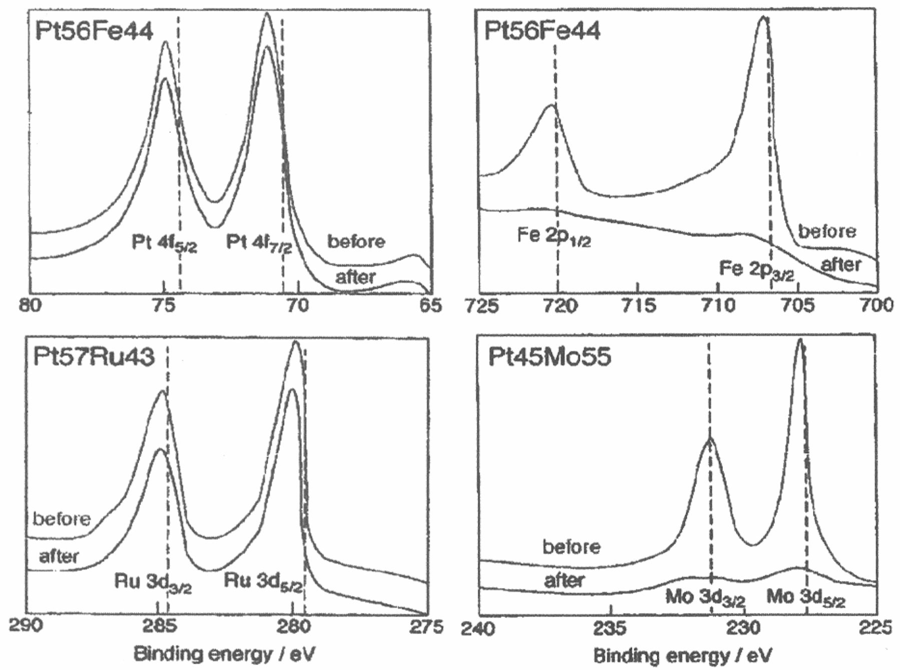
$$Ru + H_2O \longrightarrow Ru\text{-}OH_{ad} + H^+ + e^-$$

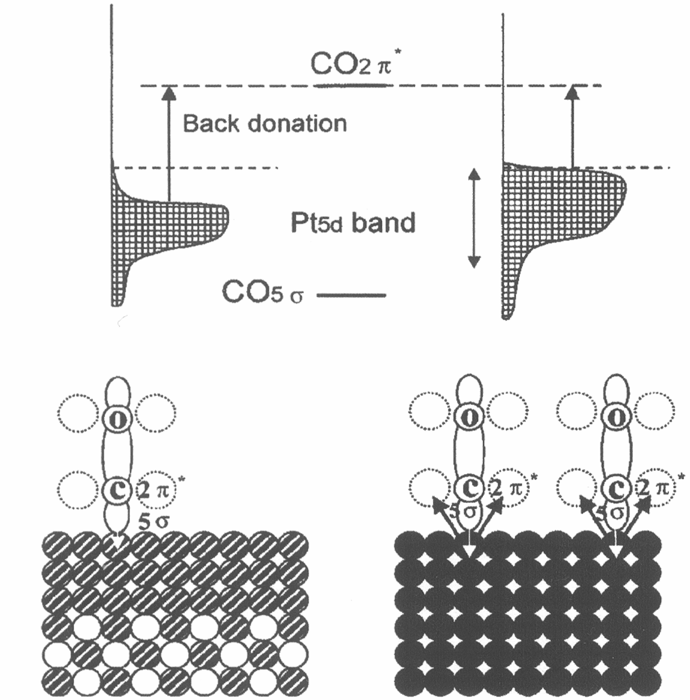
$$Pt\text{-}CO_{ad} + Ru\text{-}OH_{ad} \longrightarrow CO_2 + H^+ + e^- \ (+\,Ru + Pt)$$



50:50-alloy PtRu highly active for oxidation of adsorbed CO
CO in solution: Blocking of Ru sites by CO
high activity with e.g. Pt_3Sn

Electronic effects in CO-poisoning of fuel cell anodes





Thin Pt skin on Pt-Fe alloy (5d-vacancy)

Pure Pt (higher E_F)

Igarashi et al., Phys. Chem. Chem. Phys. 3 (2001) 306-314

Methanol oxidation

Established pathway

$CH_3OH \longrightarrow CO_{ad} + 4\ H^+ + 4\ e^- \xrightarrow{+\ H_2O} CO_2 + 6\ H^+ + 6\ e^-$

Alternative:

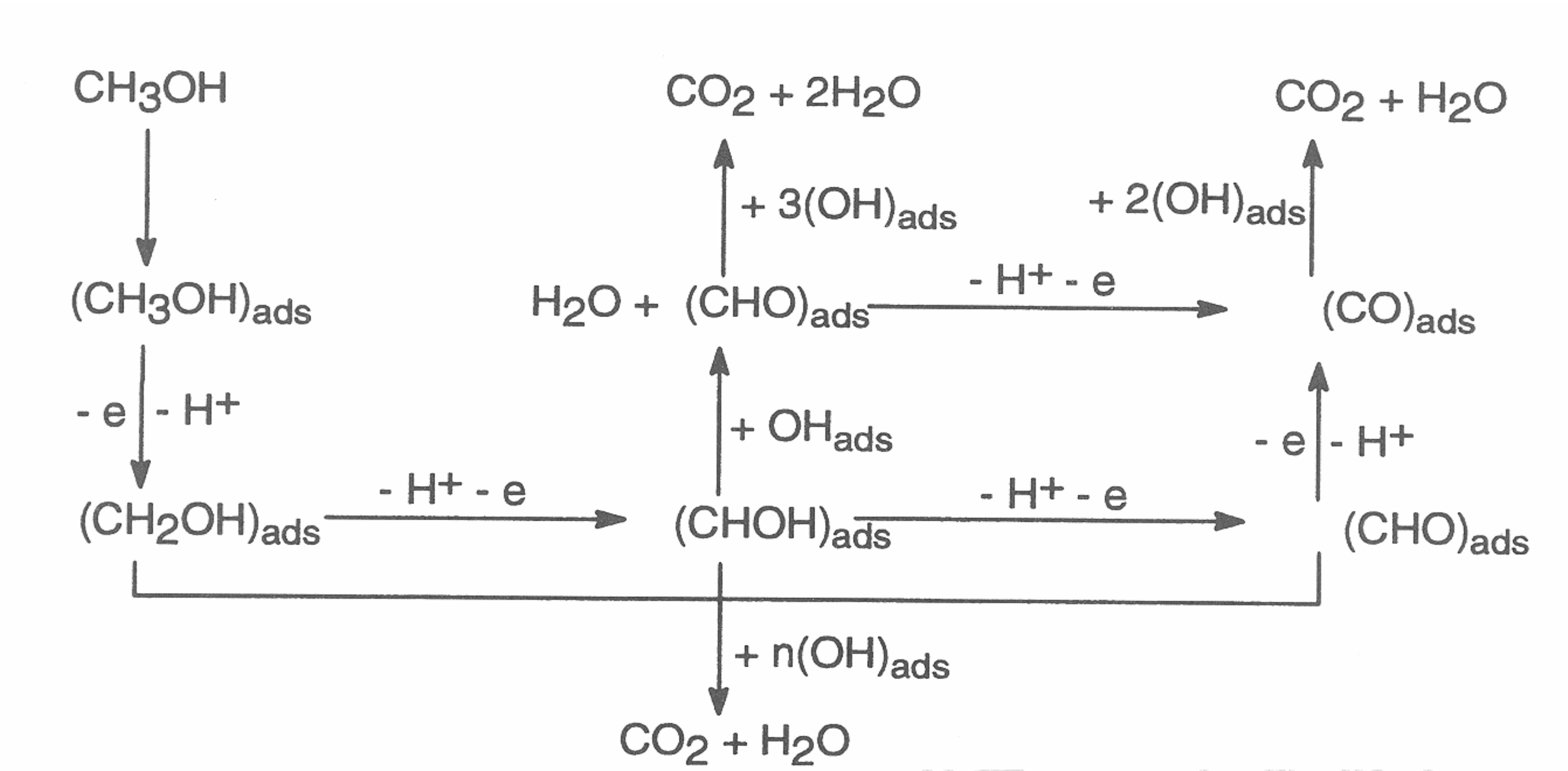
$CH_3OH \longrightarrow HCO_{ad} + 3\ H^+ + 3\ e^- \xrightarrow{+\ H_2O} CO_2 + 6\ H^+ + 6\ e^-$

(with CO formation as side reaction („spectator species“)

Catalysts:
PtRu-Allyos

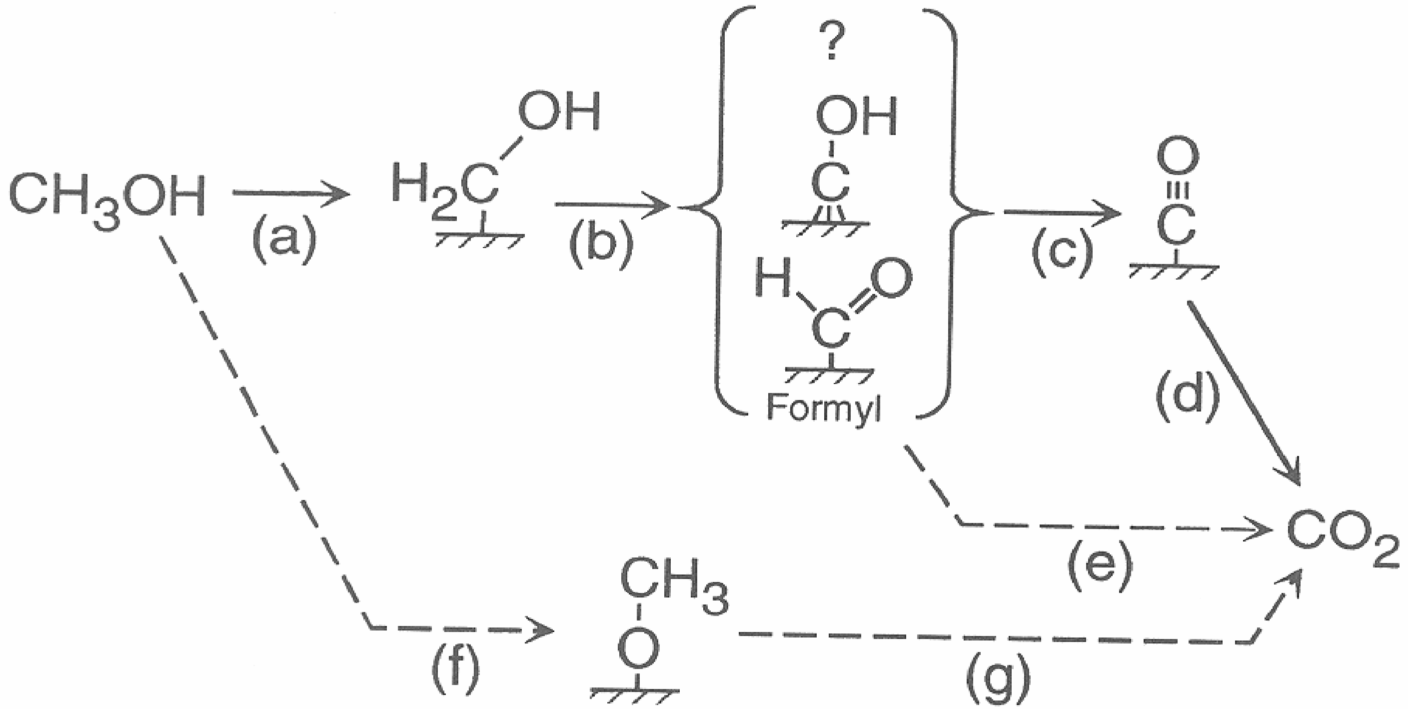
But: $PtMeO_X$ is claimed to be more active than alloys
(Me: Ru, but also W, Mo,...

Reaction network of MeOH-Oxidation on Pt electrodes



Aus: “Electrocatalysis”, J. Lipkowski, P.N. Ross, Eds.; Wiley VCH, New York 1998.

Surface species during methanol Oxidation



Aus: "Electrocatalysis", J. Lipkowski, P.N. Ross, Eds.; Wiley VCH, New York 1998.

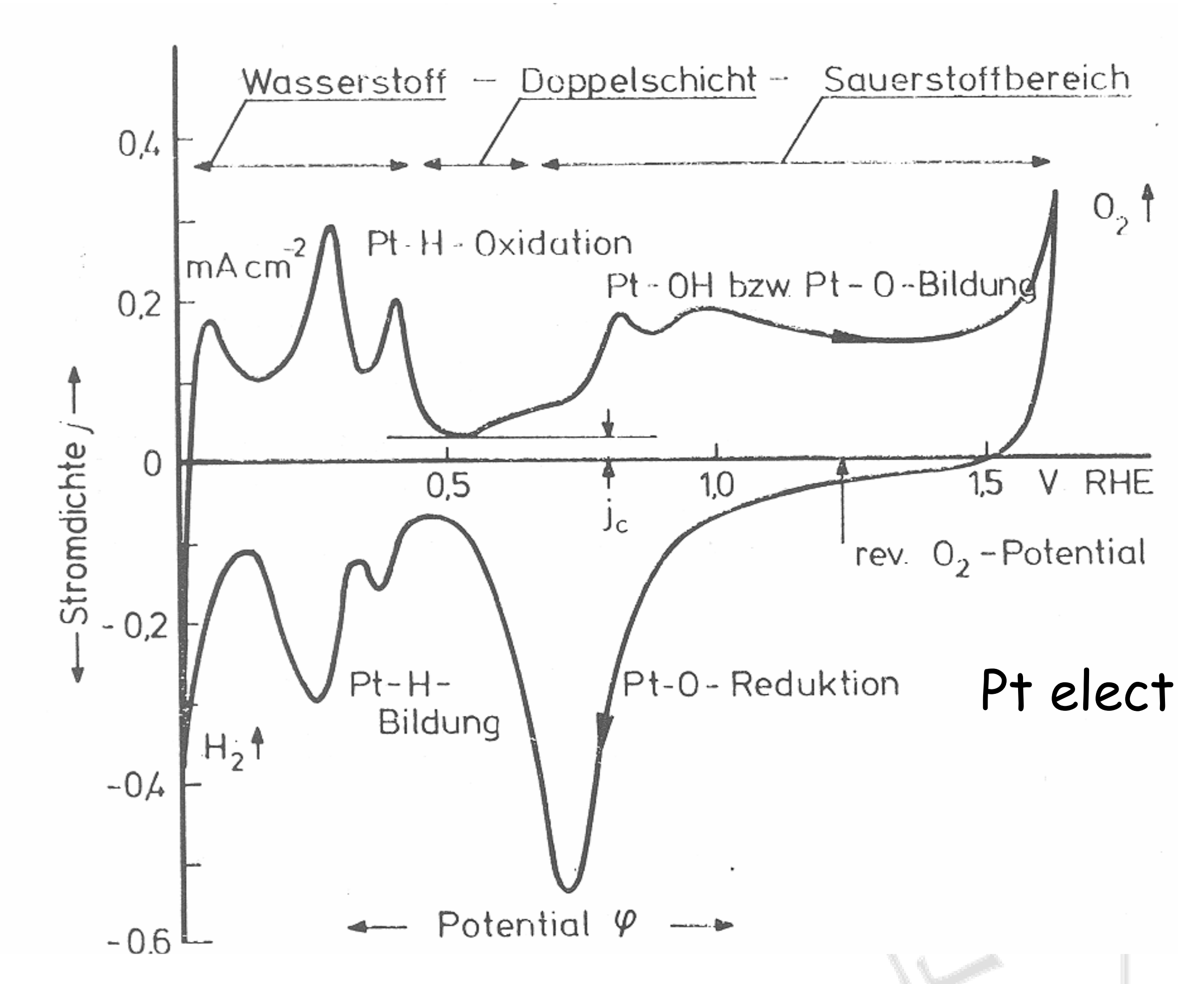
Concentration and structure of active sites
- Nature of metal/second metal
- Particle size/-distribution
- Particle shape
- Metal-support interactions
- Alloys: Segregation, leaching, exact position of atoms in active site

→

- strength of adsorption/stability of adsorbates (educts, intermediates, poisons, products, co-adsorbates)
- adsorbate geometries: occupied surface sites, binding within adsorbates)

Electrode potential → Electron transfer kinetics

Cyclic voltammetry

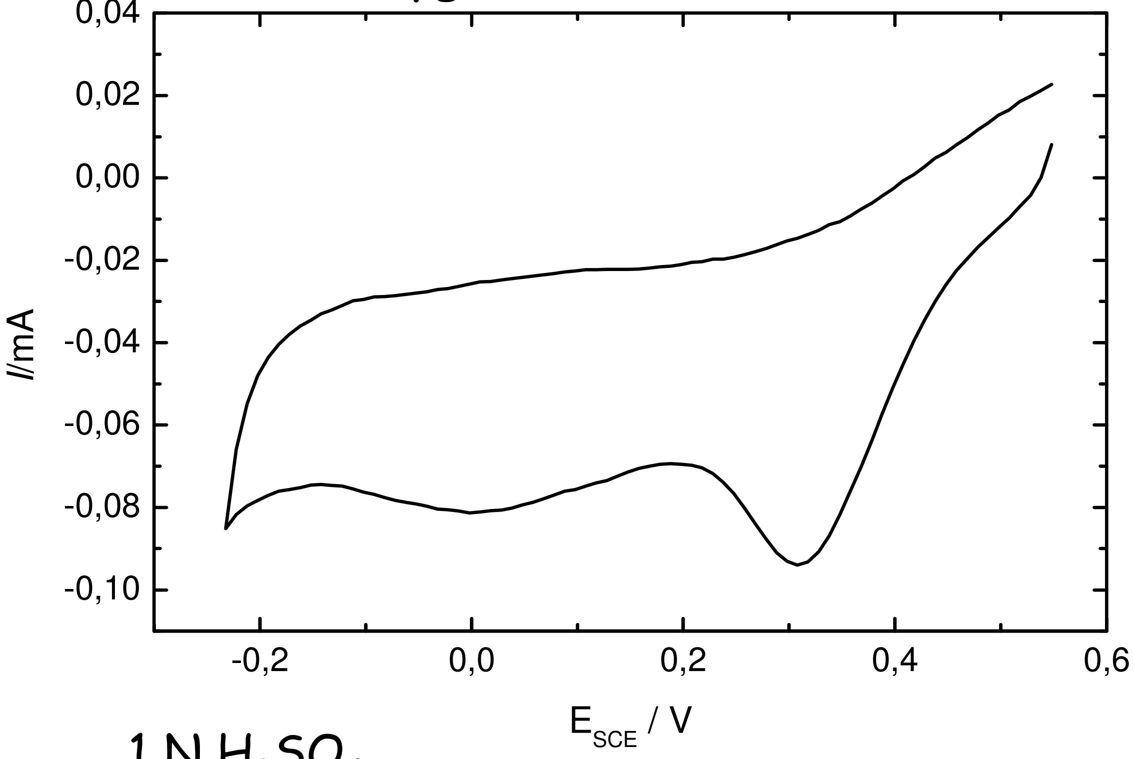


Pt electrode in 1 N KOH

From: C.H. Hamann, W. Vielstich: "Elektrochemie"

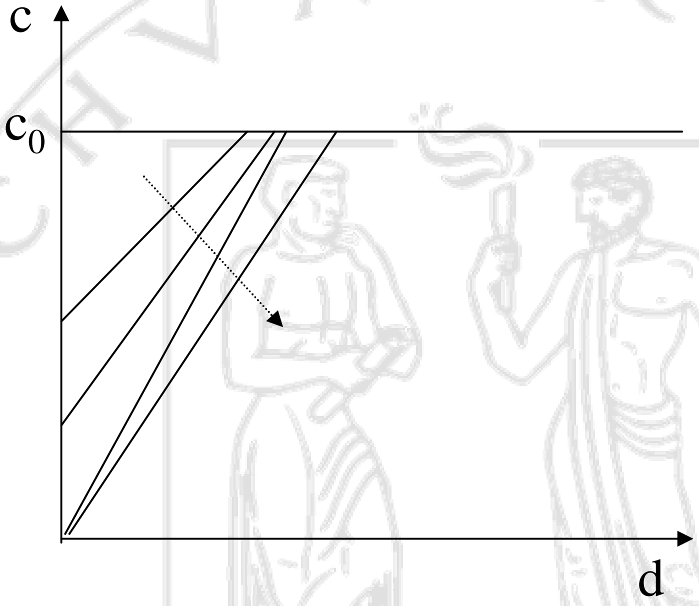
Cyclic voltammetry: influence of diffusion

CV: Oxygen reduction at Ru/C

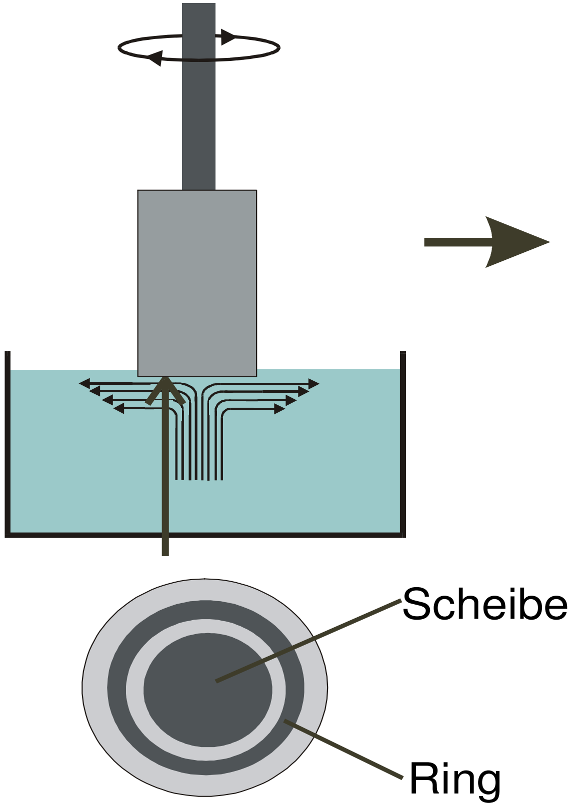


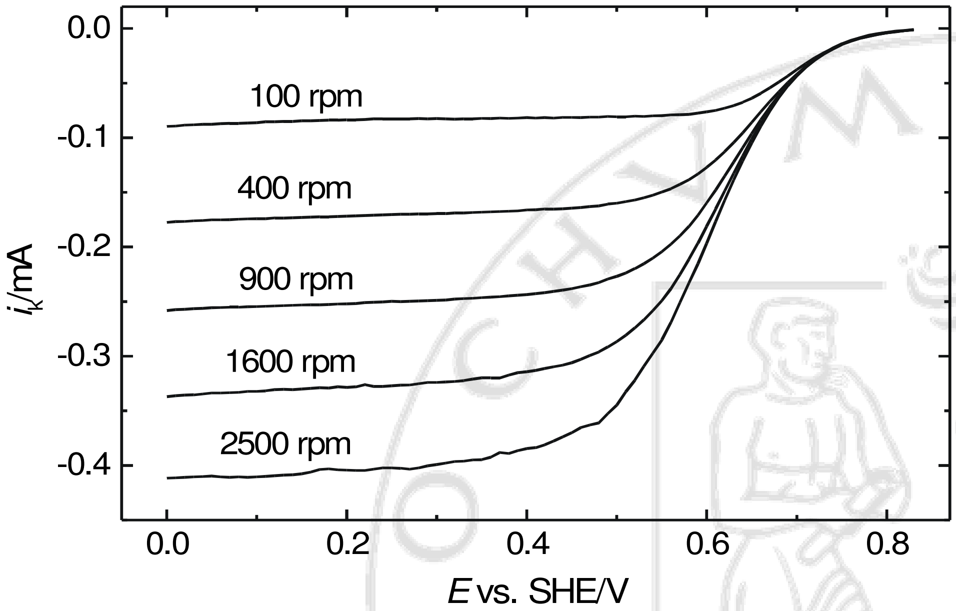
1 N H_2SO_4
100 mV s^{-1}

Schematic: Diffusion profiles during "fast" CV



Principles of Rotating Ring-Disc Electrodes

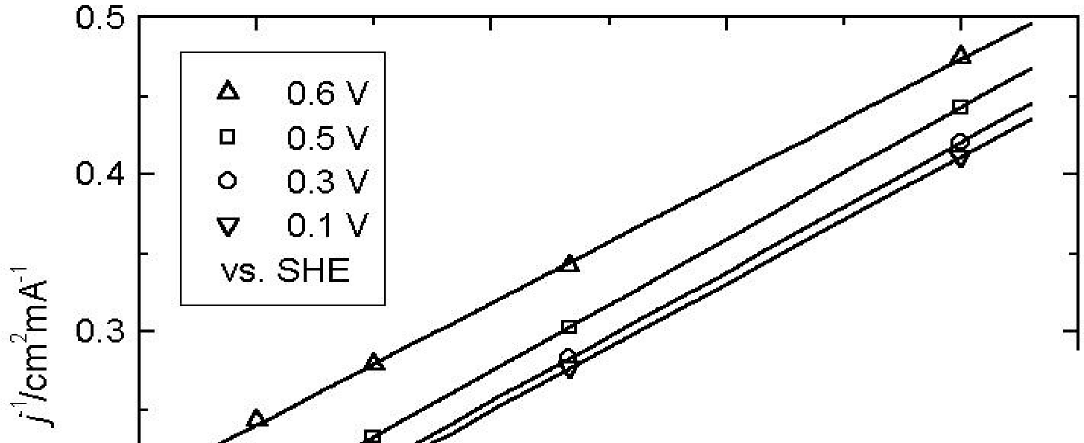




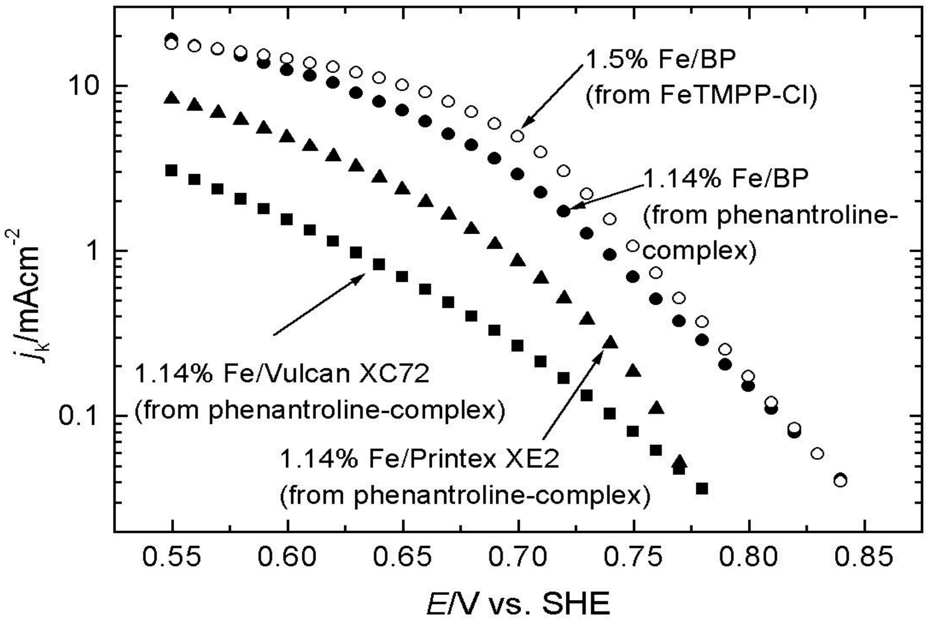
Koutecky-Levich-Analyse

$$1/i = 1/i_k + 1/i_d \quad \text{with } i_d = Bc_o\omega^{1/2}$$

Koutecky-Levich-Plot

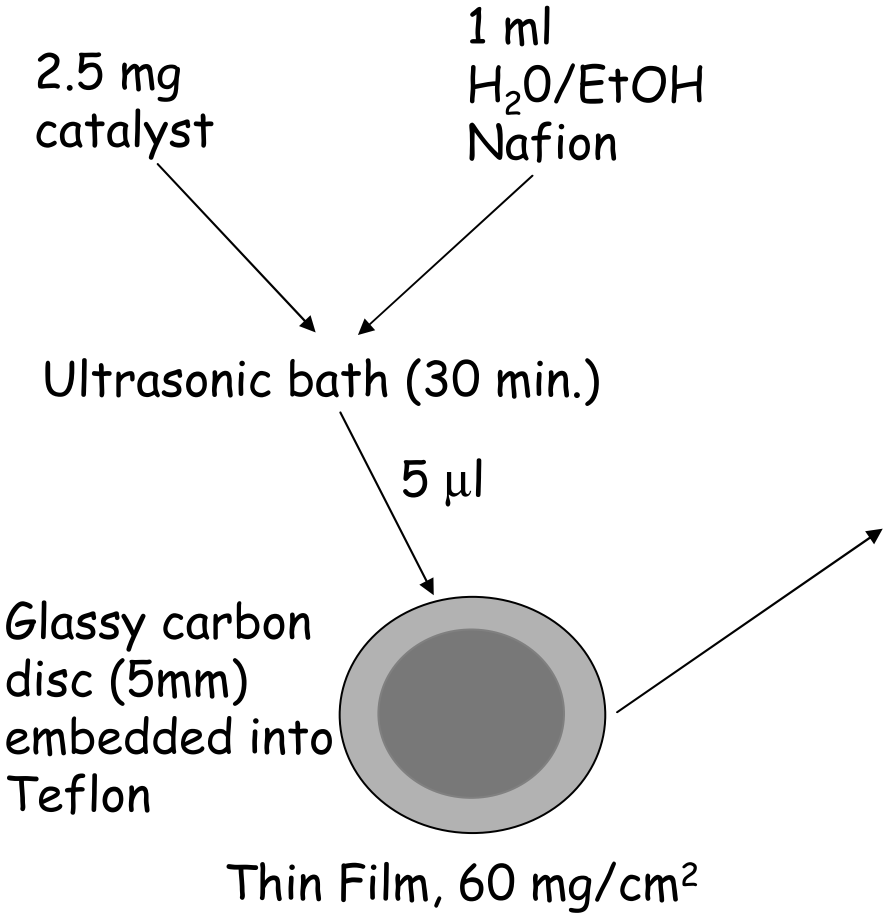


Tafel-Plot



$$1/i = 1/i_k + 1/(Bc_o\omega^{1/2})$$

Electrode preparation for powder catalysts



2.5 mg
catalyst

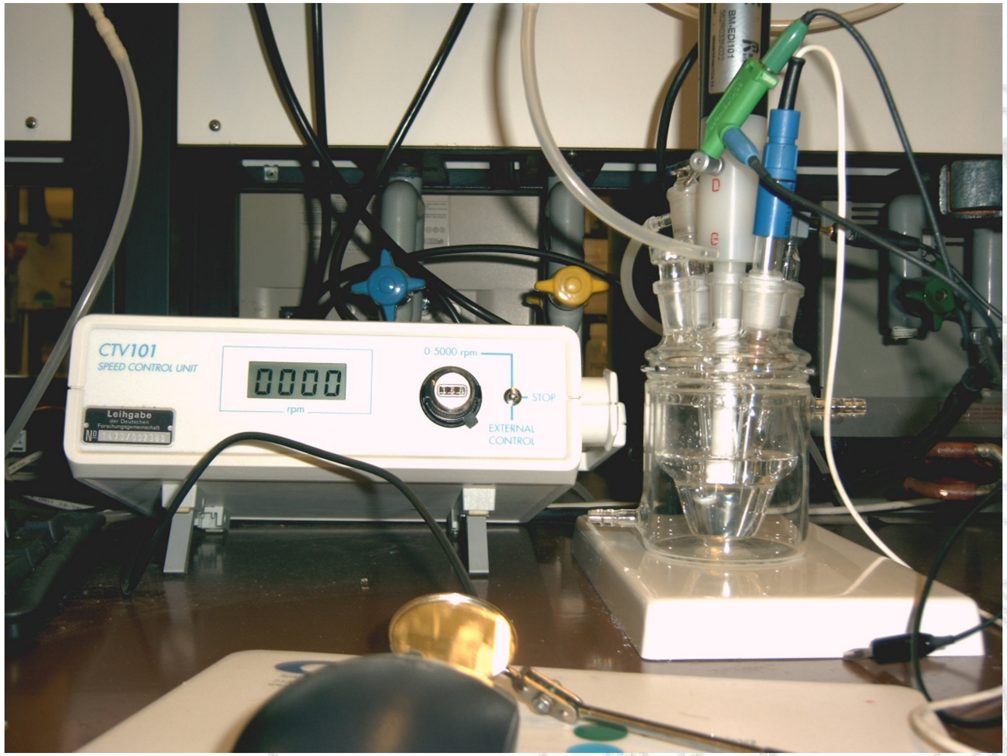
1 ml
H_2O/EtOH
Nafion

Ultrasonic bath (30 min.)

5 µl

Glassy carbon
disc (5mm)
embedded into
Teflon

Thin Film, 60 mg/cm²

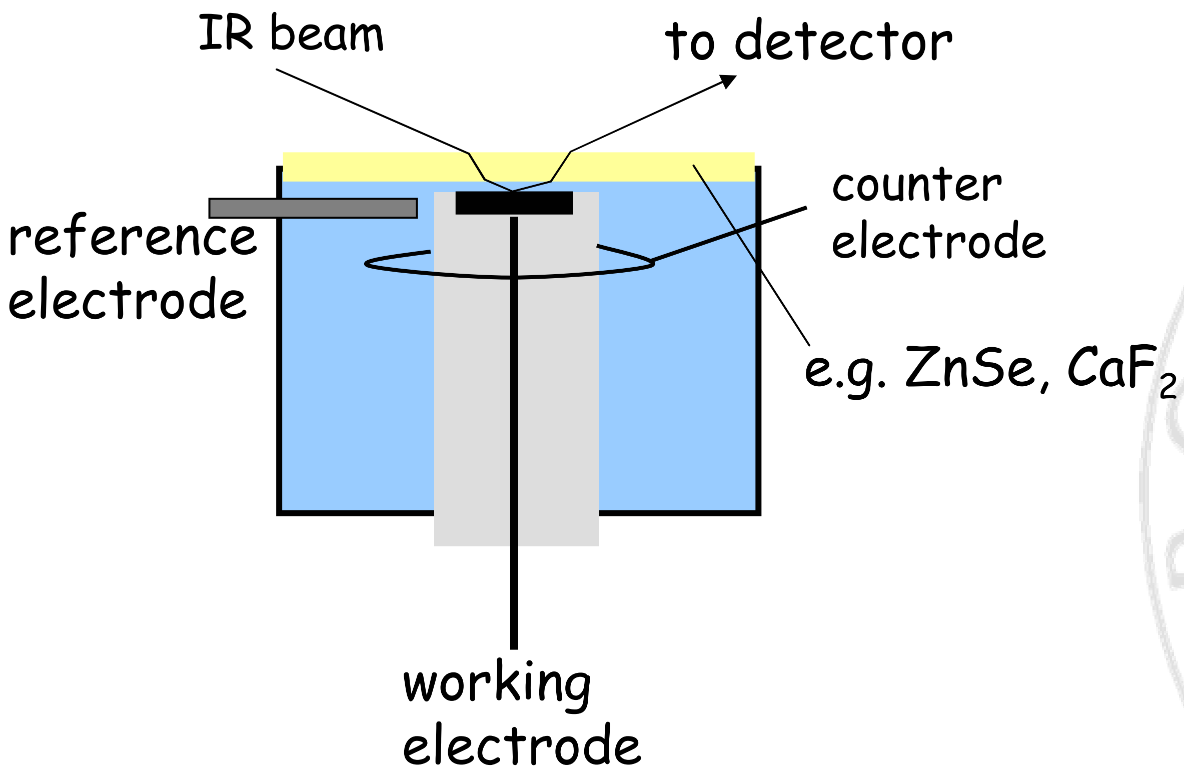


CV, RDE, Impedance

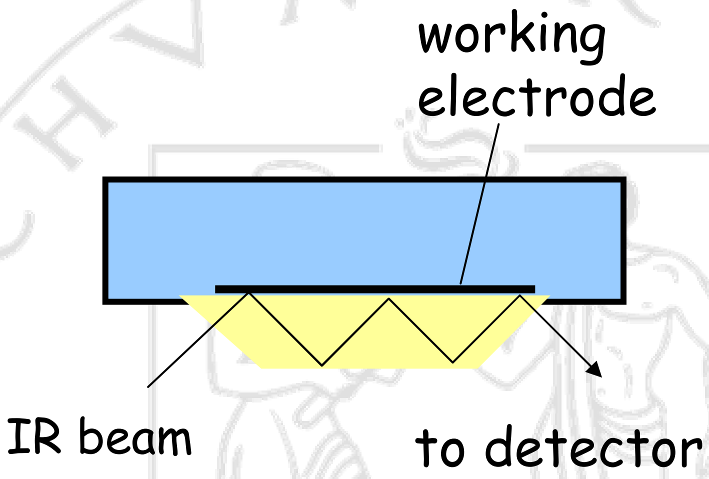
T.J. Schmidt et. al., J. Electrochem. Soc. 145 (1998) 2354.
M. Bron et al., J. Electroanal. Chem. 517 (2001) 85.

Electrochemical Infrared spectroscopy ("spectroelectrochemistry")

External reflection



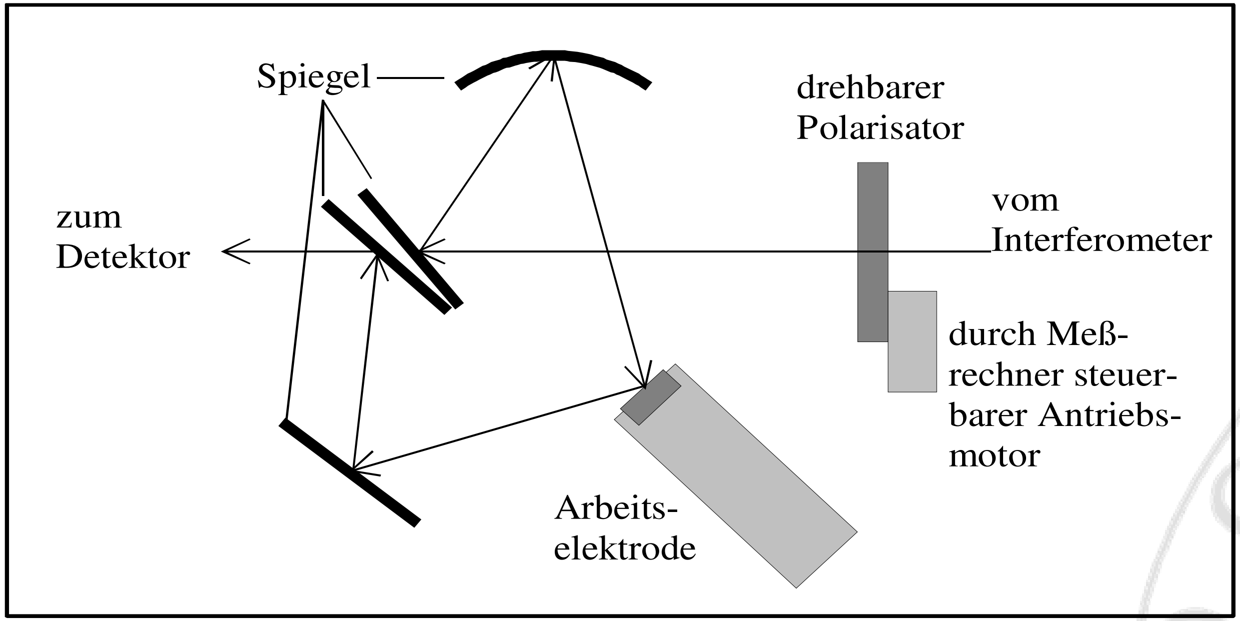
Internal reflection (ATR)



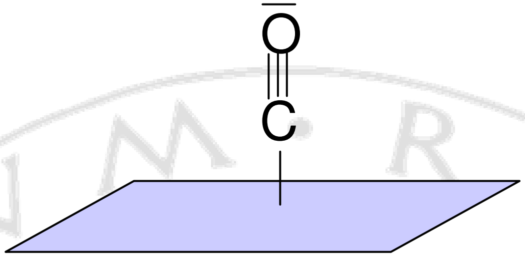
Evanescent wave interacting with adsorbates

Gap electrode - window: < 10 µm

Setup for in situ-IR-spectroscopic experiments

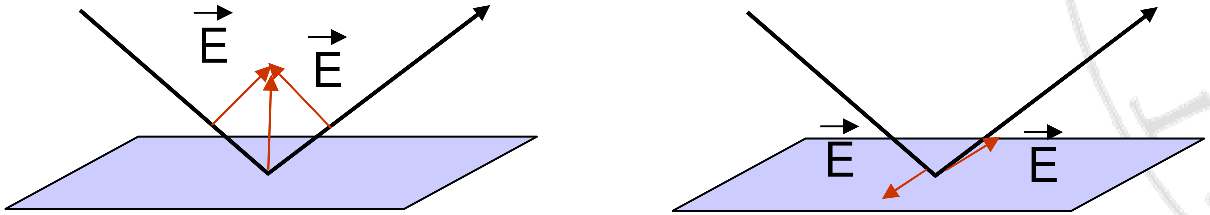


Potential modulation



Adsorption strength depends on electrode potential

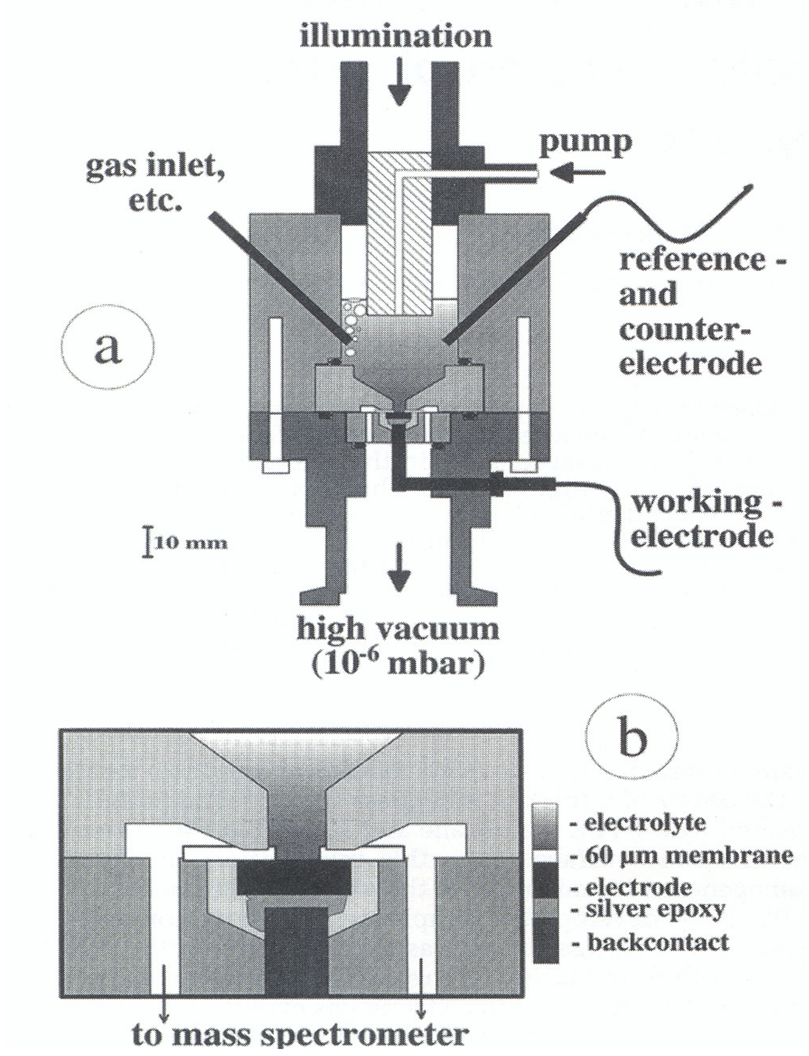
Polarisation modulation



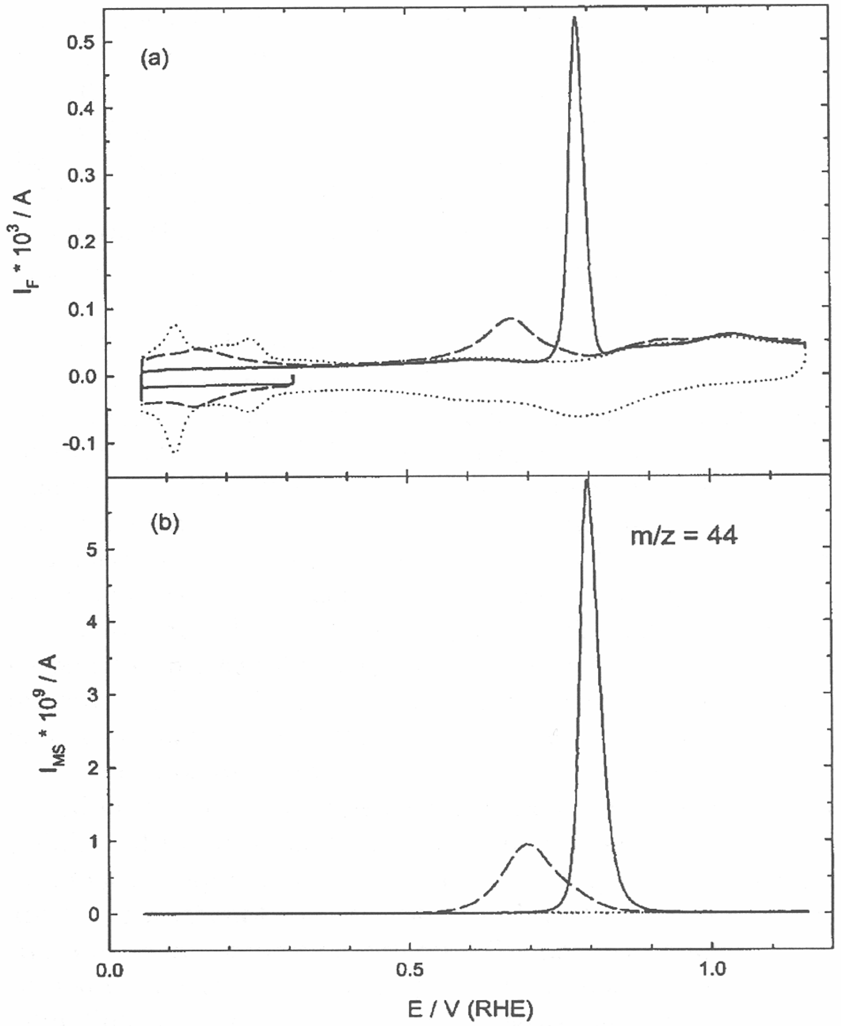
Adsorbate orientations:

Surface selection rule

Differential electrochemical mass spectrometry DEMS

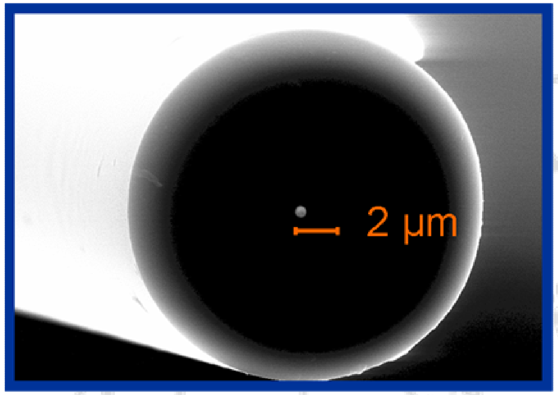


From: Bogdanoff et al., J. Electrochem. Soc. 145 (1998) 576.

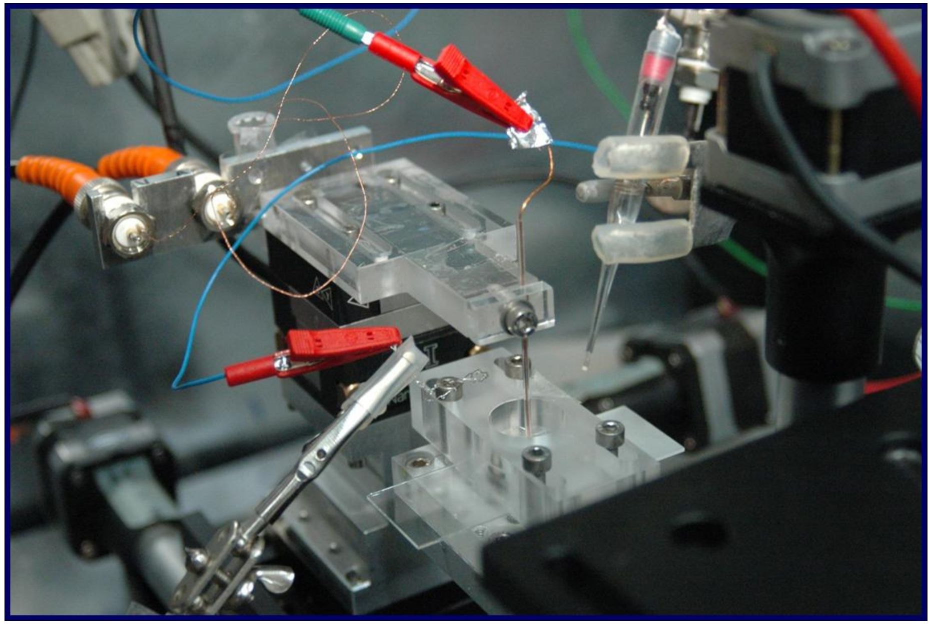


From: Jusys and Behm, J. Phys. Chem. B 105 (2001) 1874.

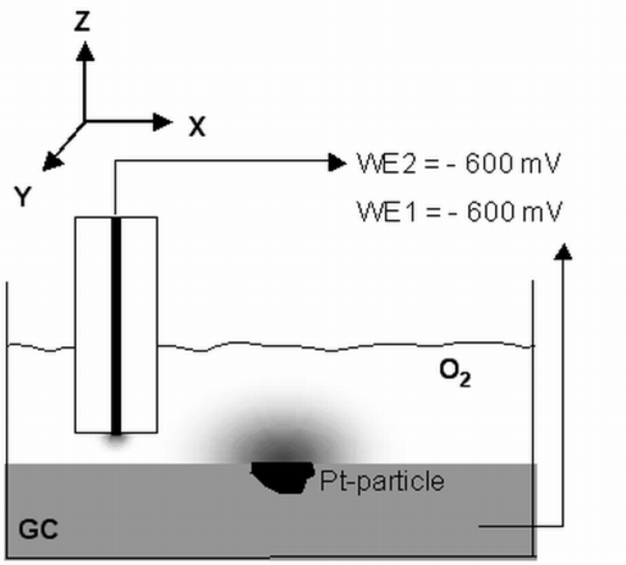
Scanning electrochemical microscope: monitoring catalytically active surfaces



SECM tip

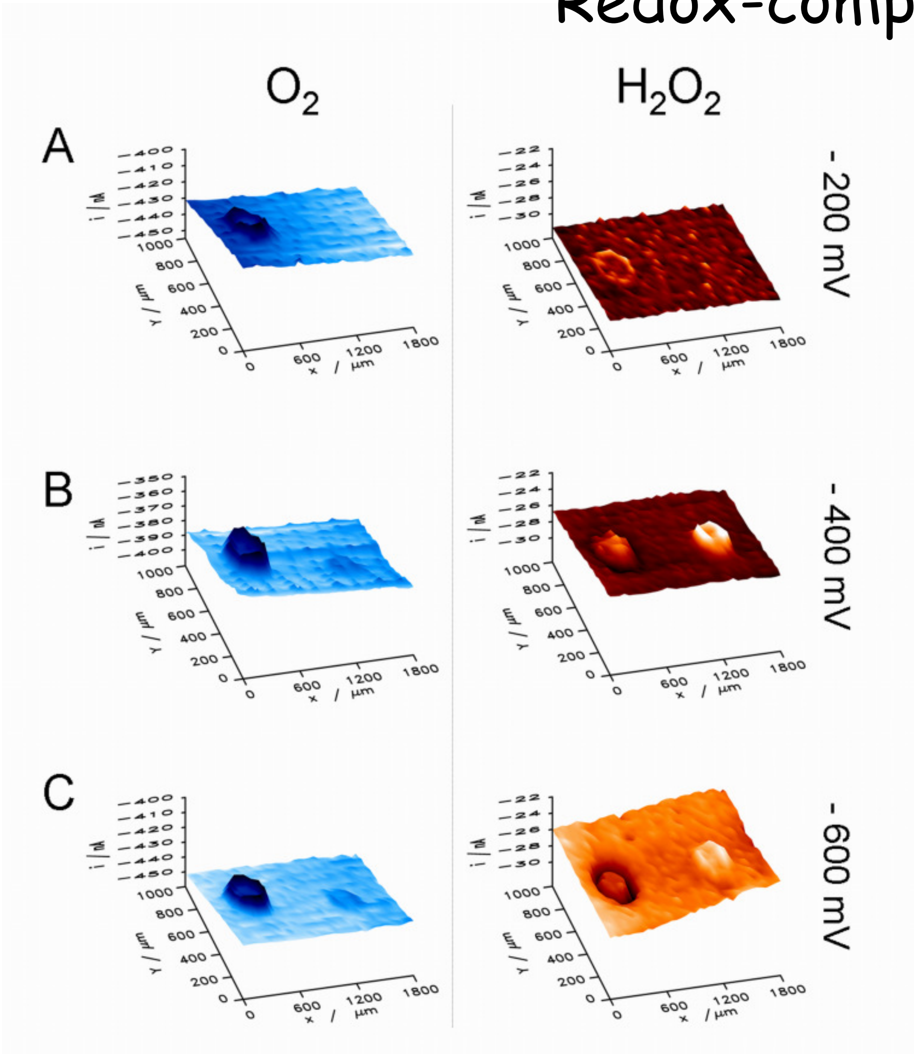


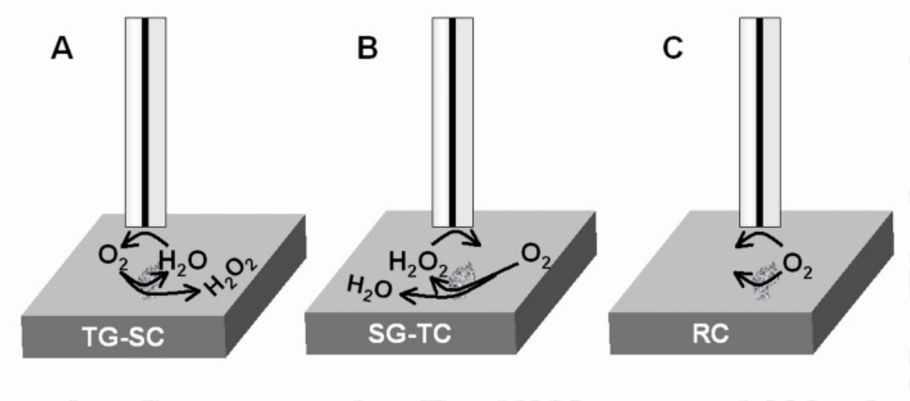
SECM setup



Thanks to K. Eckhard, Bochum

Redox-competition SECM

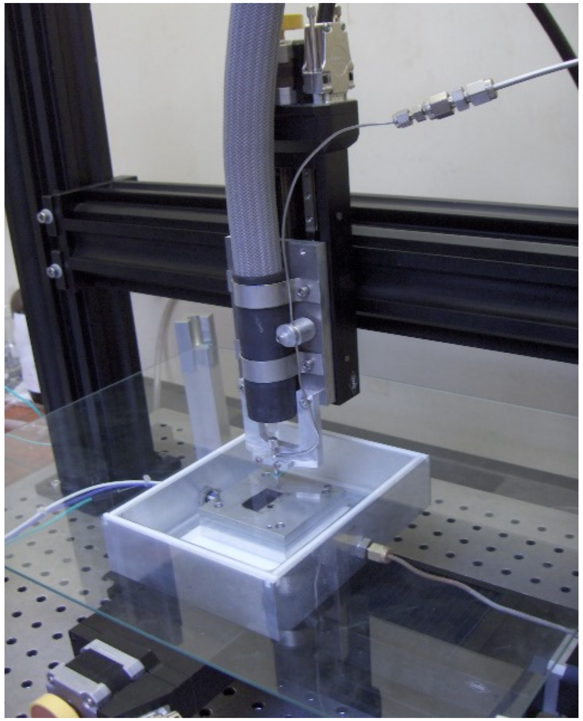




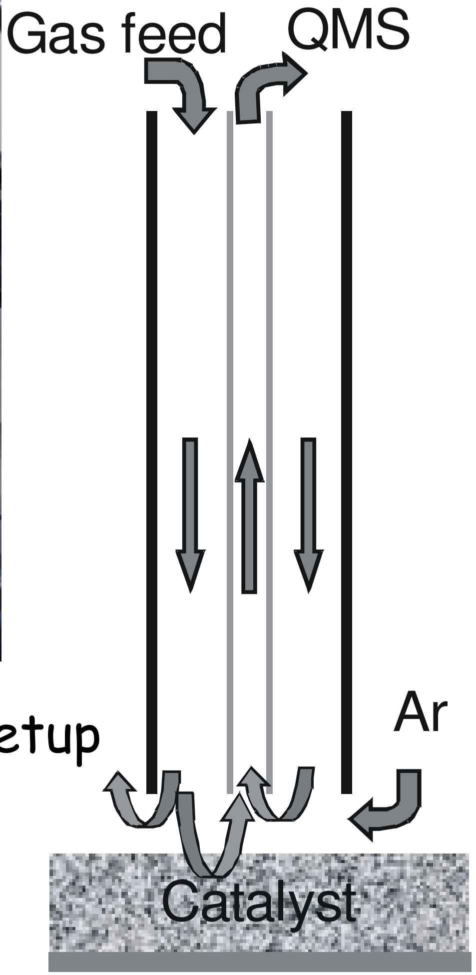
Visualising the activity of a Pt (left) and an Au (right) catalyst

K. Eckhard, Dissertation, Bochum 2007

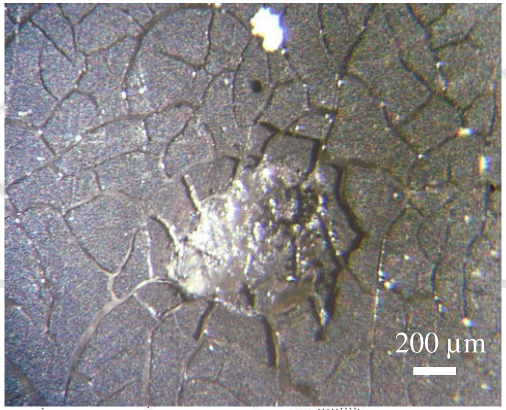
Scanning mass spectrometry

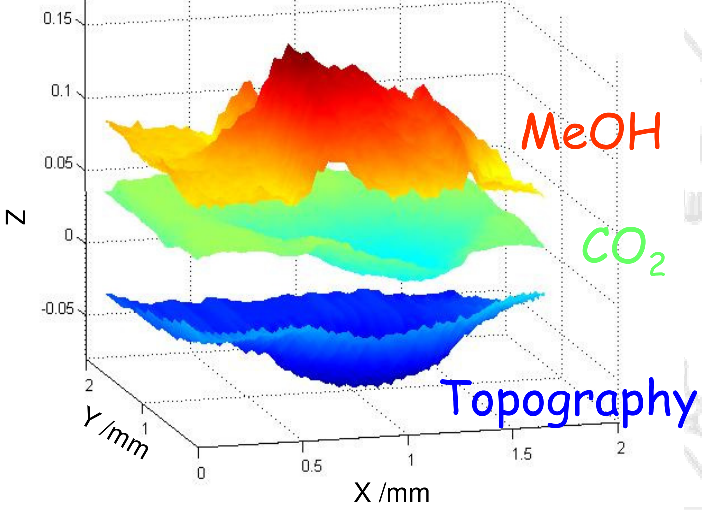


The scanning MS setup



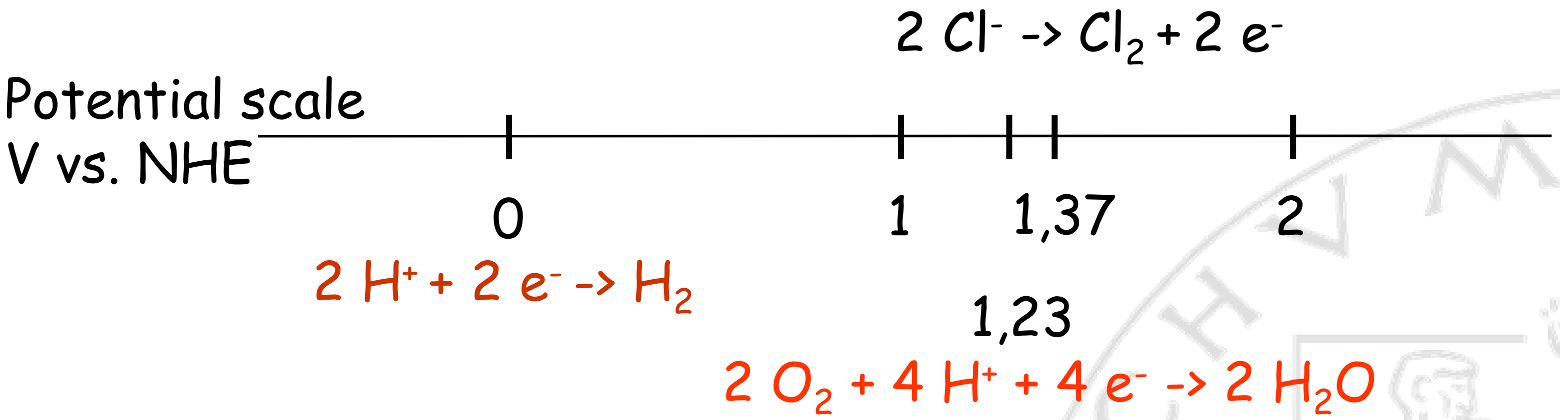
MeOH oxidation over a damaged GDE





Nan Li, Dissertation, Bochum 2008

A „new trend“ in electrocatalysis: chlorine production



$2\ Cl^- \rightarrow Cl_2 + 2\ e^-$

Potential scale
V vs. NHE

0 1 1,37 2

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

1,23

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

NaCl-electrolysis: cell voltage under operation: 3.1 V

NaCl with ODC: Cell voltage under operation: ca. 2 V (industrial goal)

ORR catalyst: Silver
Alternatively: HCl electrolysis (recycling); ORR catalyst: RhS/C

Literature

Electrochemical textbooks

Hamann, Carl H.; Vielstich, Wolf: Elektrochemie 3., überarb. u. erw. Aufl., Wiley-VCH (available also in english)

Bard, Allen J., Faulkner, Larry R.: Electrochemical Methods - Fundamentals and Applications, John Wiley & Sons, Januar 2001

D. Pletcher, R. Greff, R. Peat, L.M. Peter, J. Robinson: Instrumental Methods in Electrochemistry, Albion/Horwood Publishing House September, 2002

Electrocatalysis:

J. Lipkowski, P.N. Ross, Eds.; Electrocatalysis, Wiley VCH, New York 1998.