Electrochemical methods for electrocatalysis

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Outline

- **Introduction**

- **Potentiostatic techniques (DC)**

- **Potentiodynamic techniques (DC)**

- **Methods involving forced convection**

- **Electrochemical impedance spectroscopy**

- **Summary**

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System investigation

Probing signal 2

Probing signal 1

BLACK BOX

Response

Modeling

Properties of the "black box"

Probing signal 3
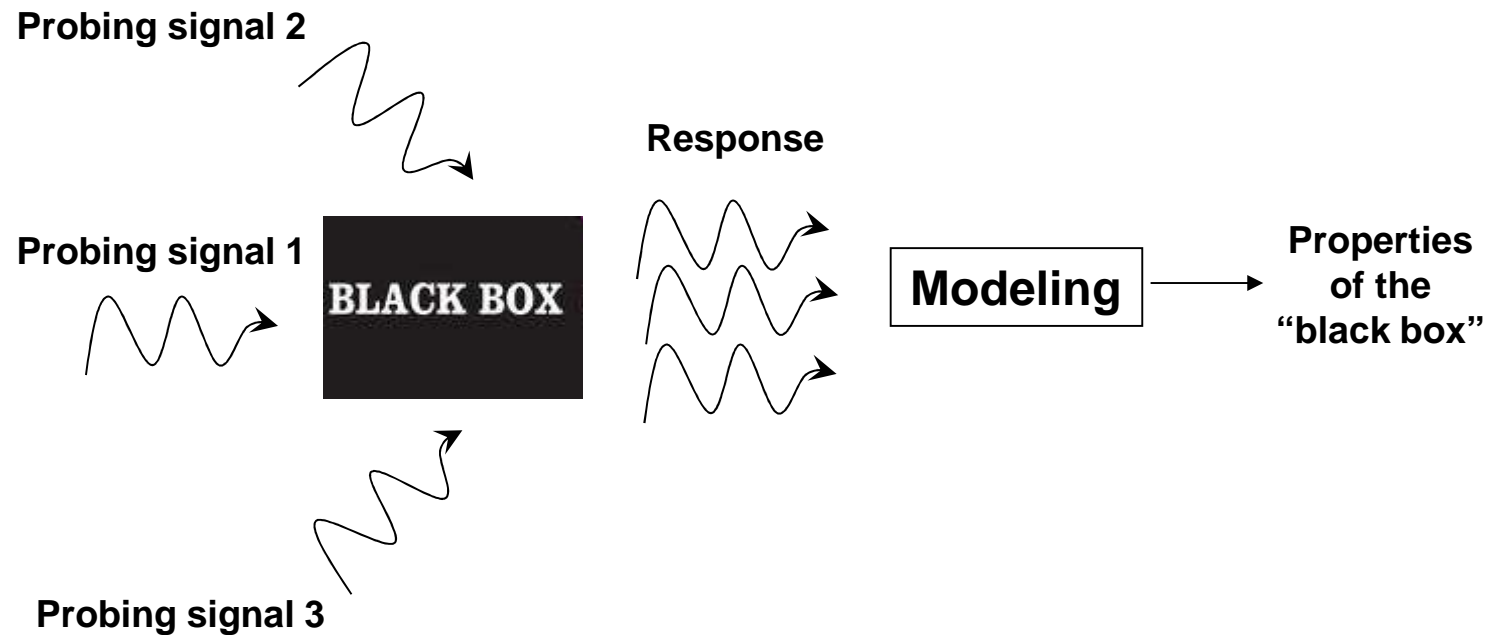
„Classical" electrochemical techniques:

Change the electrode potential / apply a bias → measure current

Change / apply the current → measure the electrode potential

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An electrochemical system

Electrode (an electron conductor)

Electrode (an electron conductor)

$\bar{e}$

$\bar{e}$

Electrolyte (an ionic conductor)

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Introduction •

Potentiostatic

Potentiodynamic

RDE

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$$H_2O \leftrightarrow H^+ + OH^-$$

$4H^+$

$+4\bar{e}$

$2H_2$

$2OH^-$

$-4\bar{e}$

$O_2 +$

Response of the electrolyte

Response of the interface 1

Response of the interface 2

A reference electrode

Electrode (an electron conductor)

Electrode (an electron conductor)

$\bar{e}$

$\bar{e}$

Electrolyte (an ionic conductor)

V

i

- +

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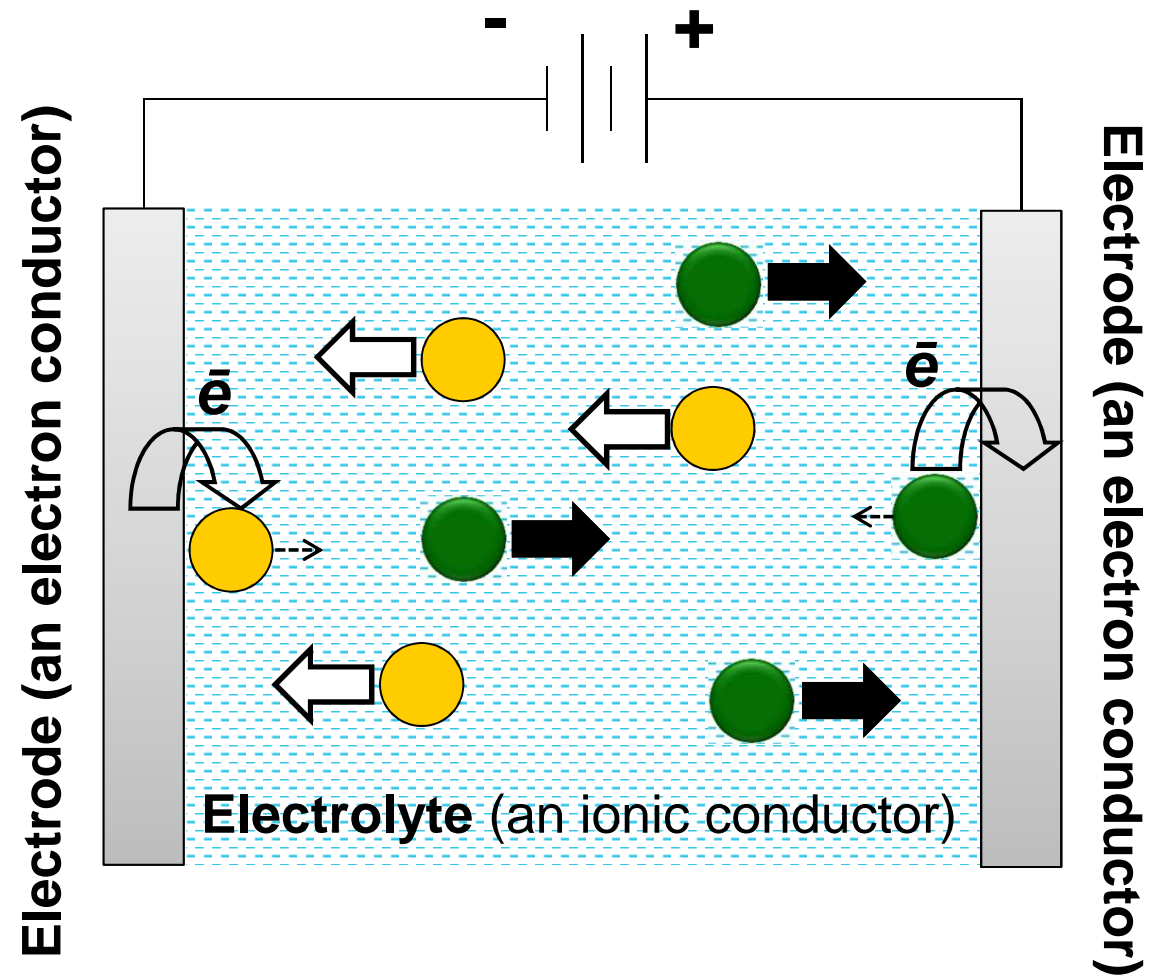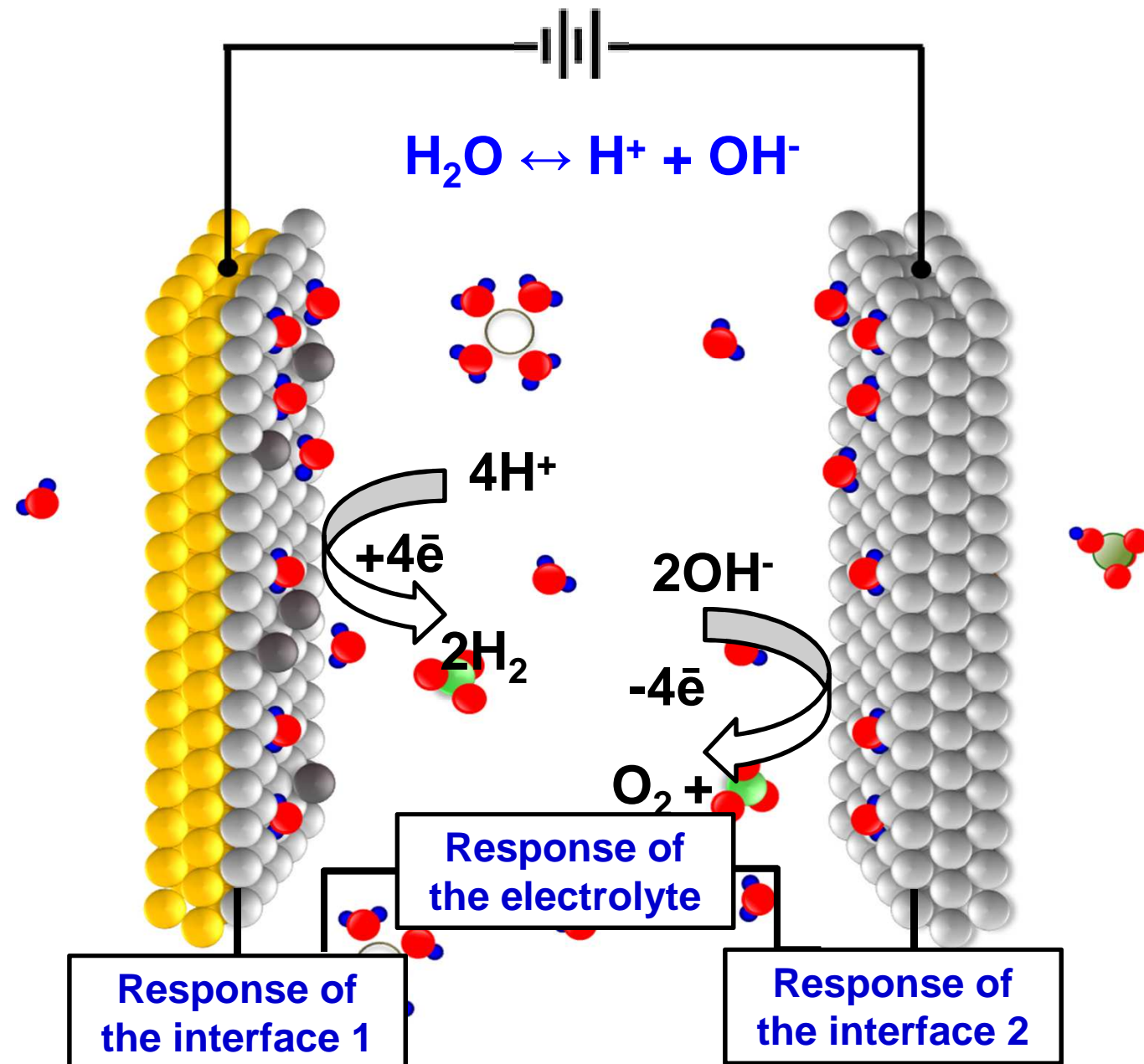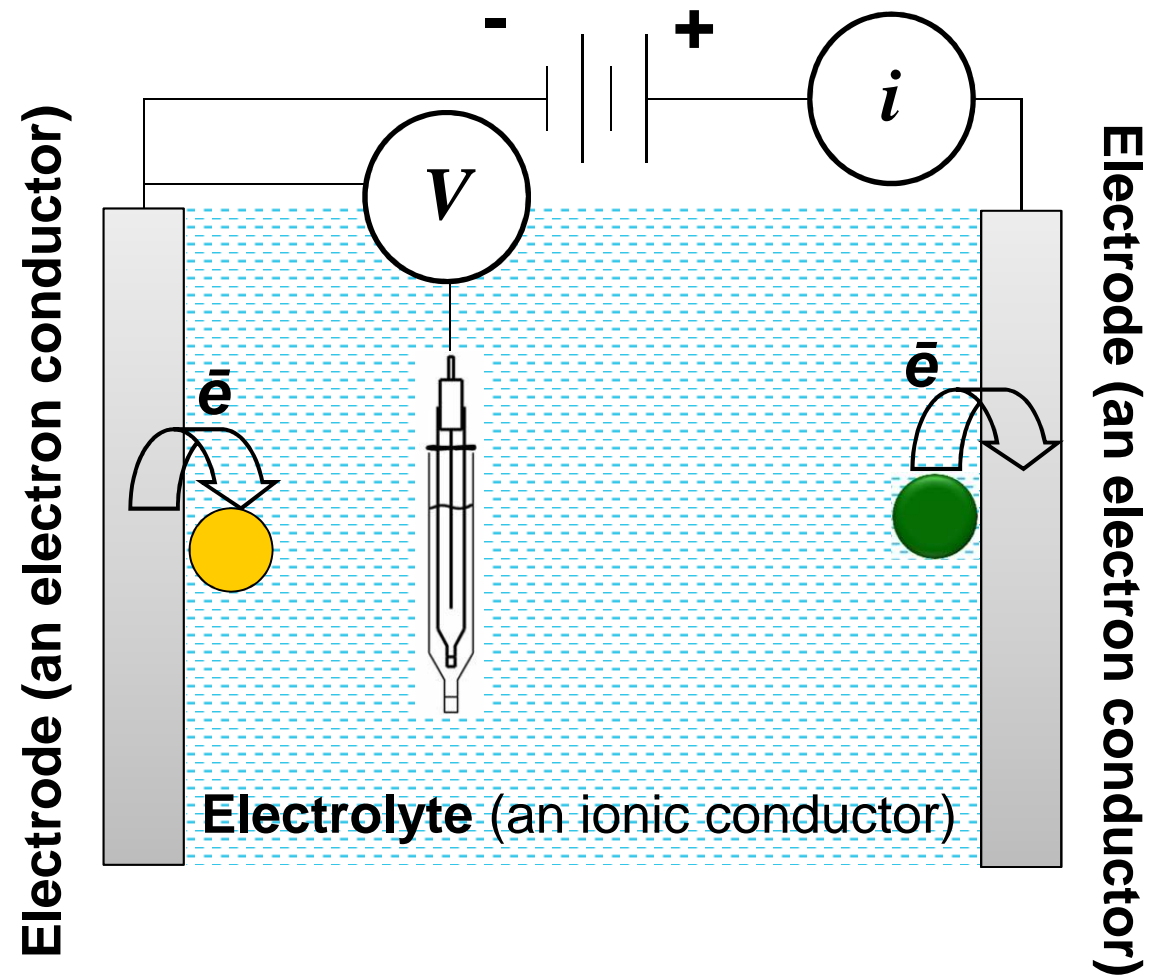
A reference electrode

Potentiostat (invented by Hickling, 1941)
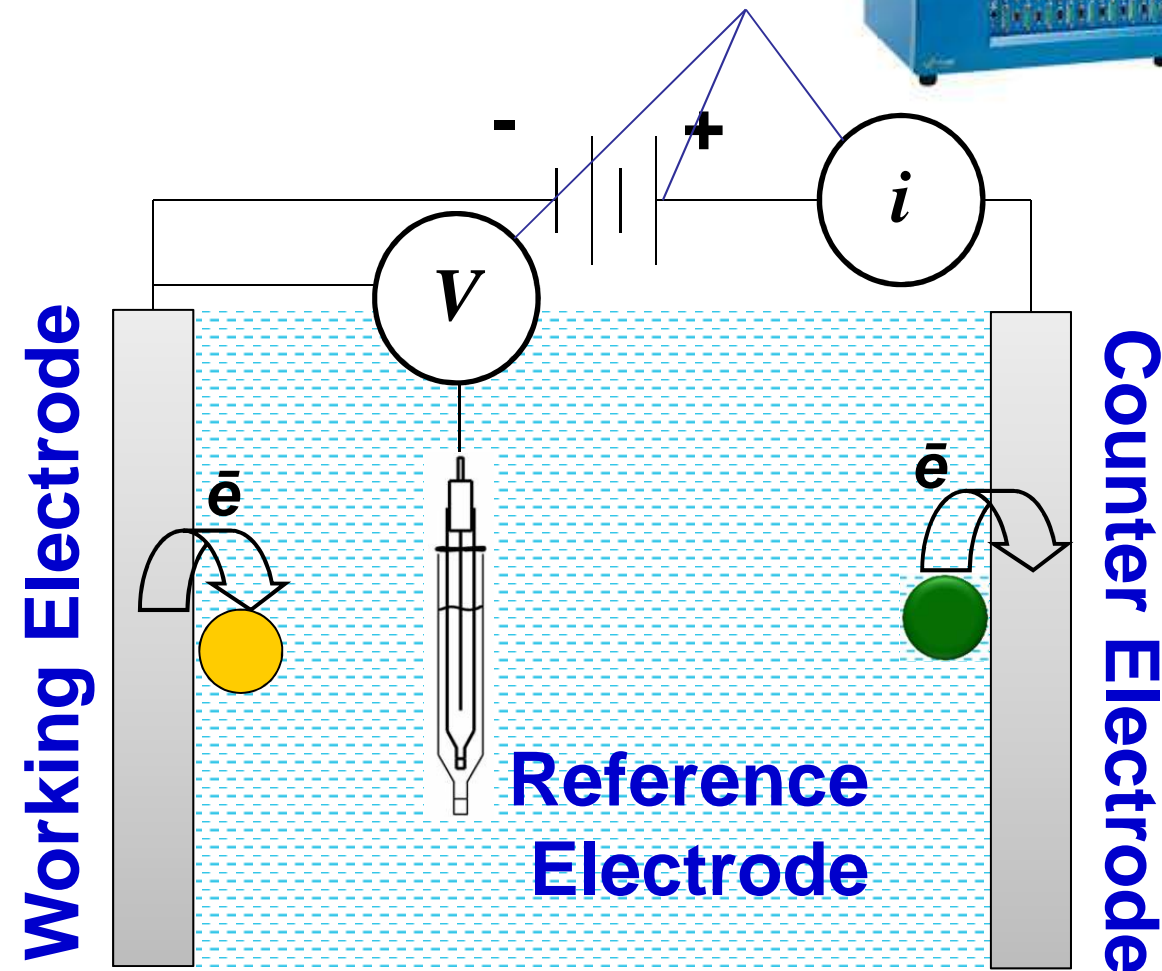
− +

V i

Working Electrode

ē

Reference Electrode

ē

Counter Electrode

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Modelling of the system in case of a 3-electrode setup
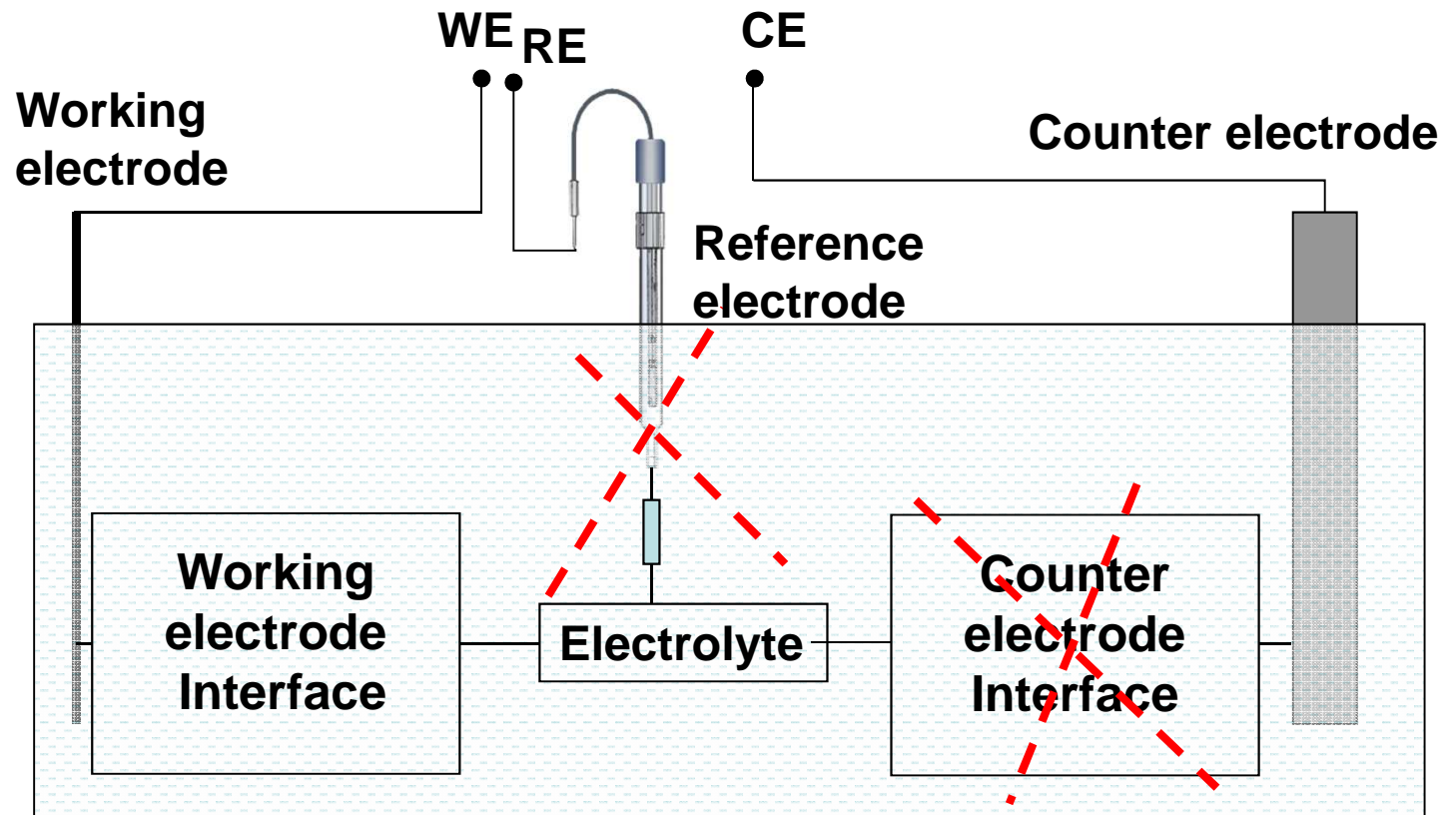
Working electrode. A general model

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Response of the electrolyte

Z_{el}

Response of the EDL

Z_i

Z_F

Response due to Faradaic (electro-catalytic) reactions

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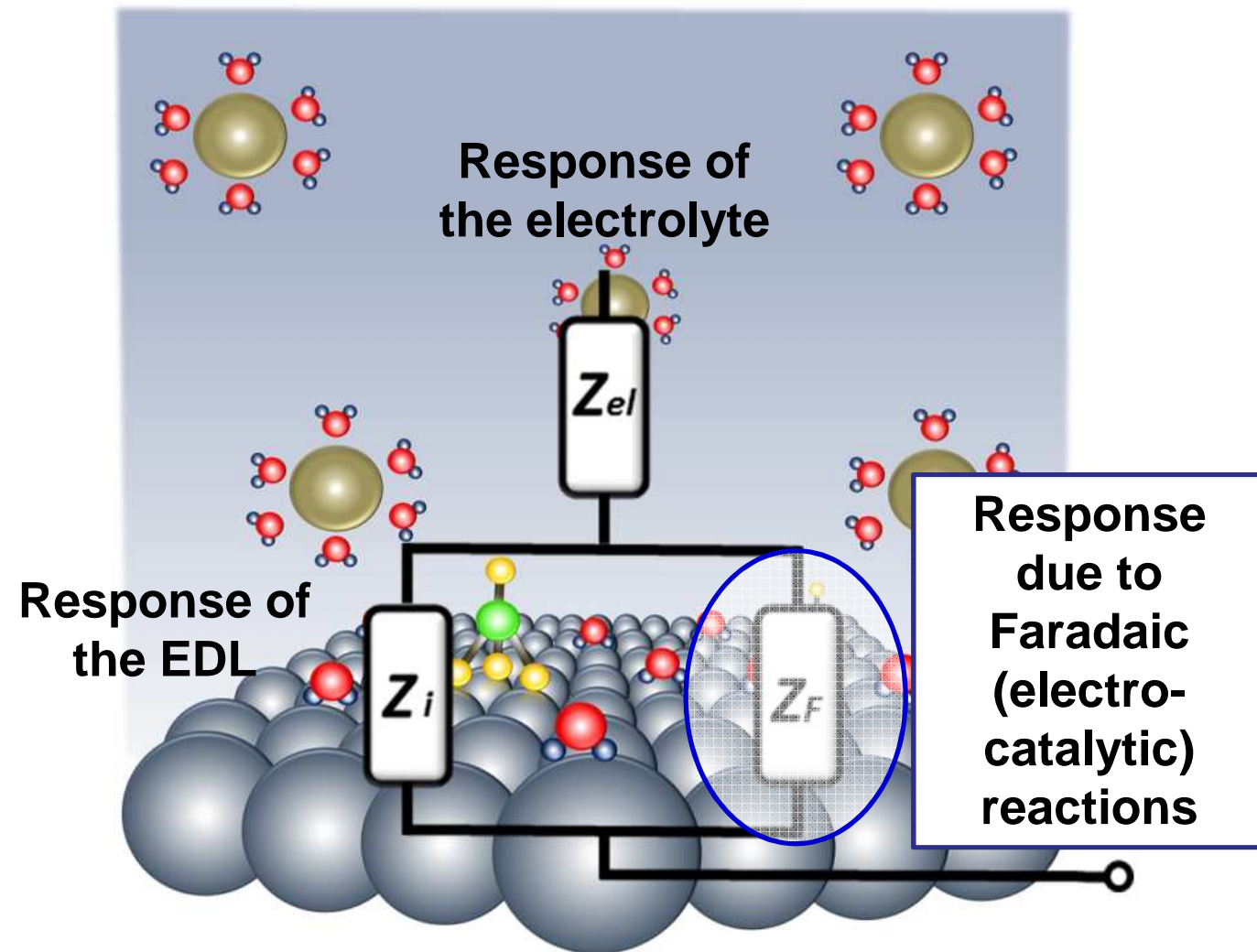
Potentiostatic techniques

Stationary electrodes

In these kind of techniques the electrode potential is often kept constant for relatively long time while the current is measured

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Oxygen evolution

Current / A

0.1

Counter
electrode

Reference
electrode   Working electrode

Electrolyte

Overpotential (η)   **Overpotential (η)**

0

1.23   **Electrode potential / V vs RHE**

Hydrogen evolution

-0.1

Historically probably the first techniques to investigate one of the simplest electrocatalytic reaction, the **Hydrogen Evolution Reaction**

Measurement scheme

Chronoamperometry

$I_{Faradaic}$ = const

„Activity"

$I_{capacitive}$ = 0

More complicated measurement scheme
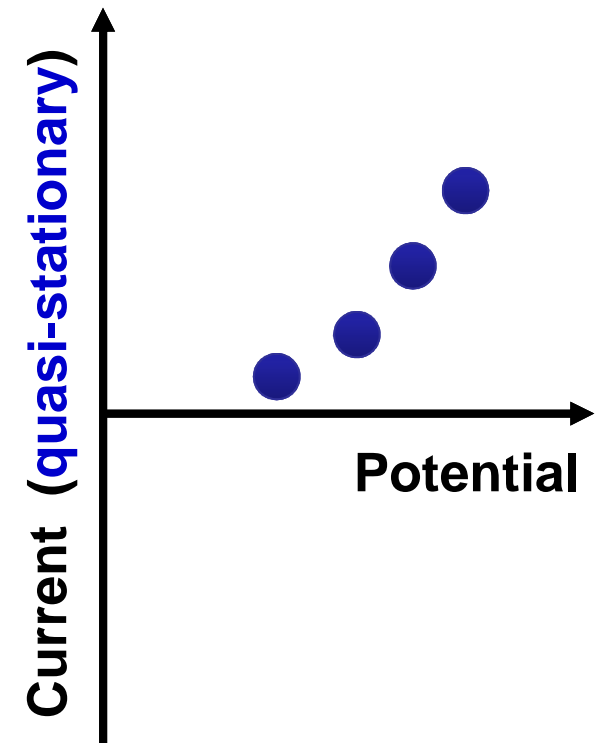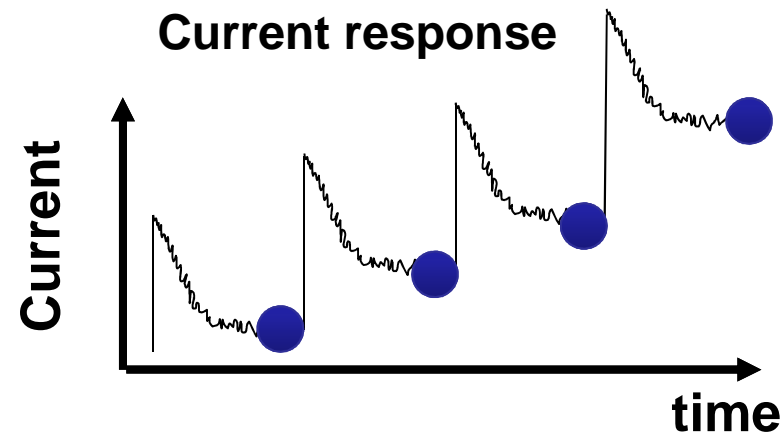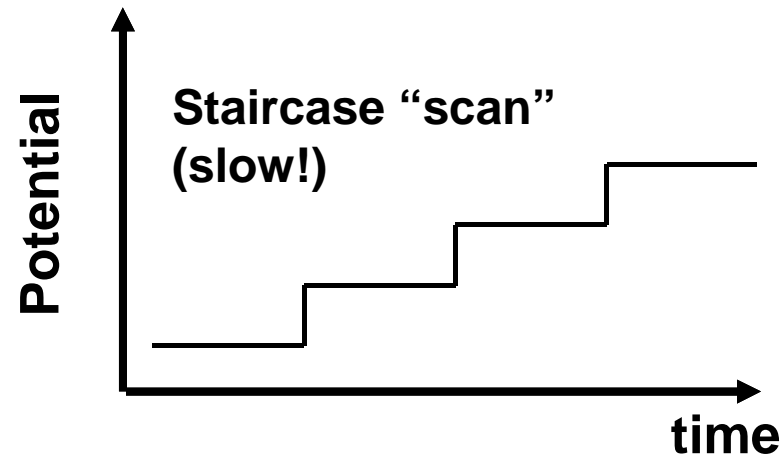
Staircase "scan" (slow!)

Potential

time

Current response

Current

time

Current (quasi-stationary)

Potential

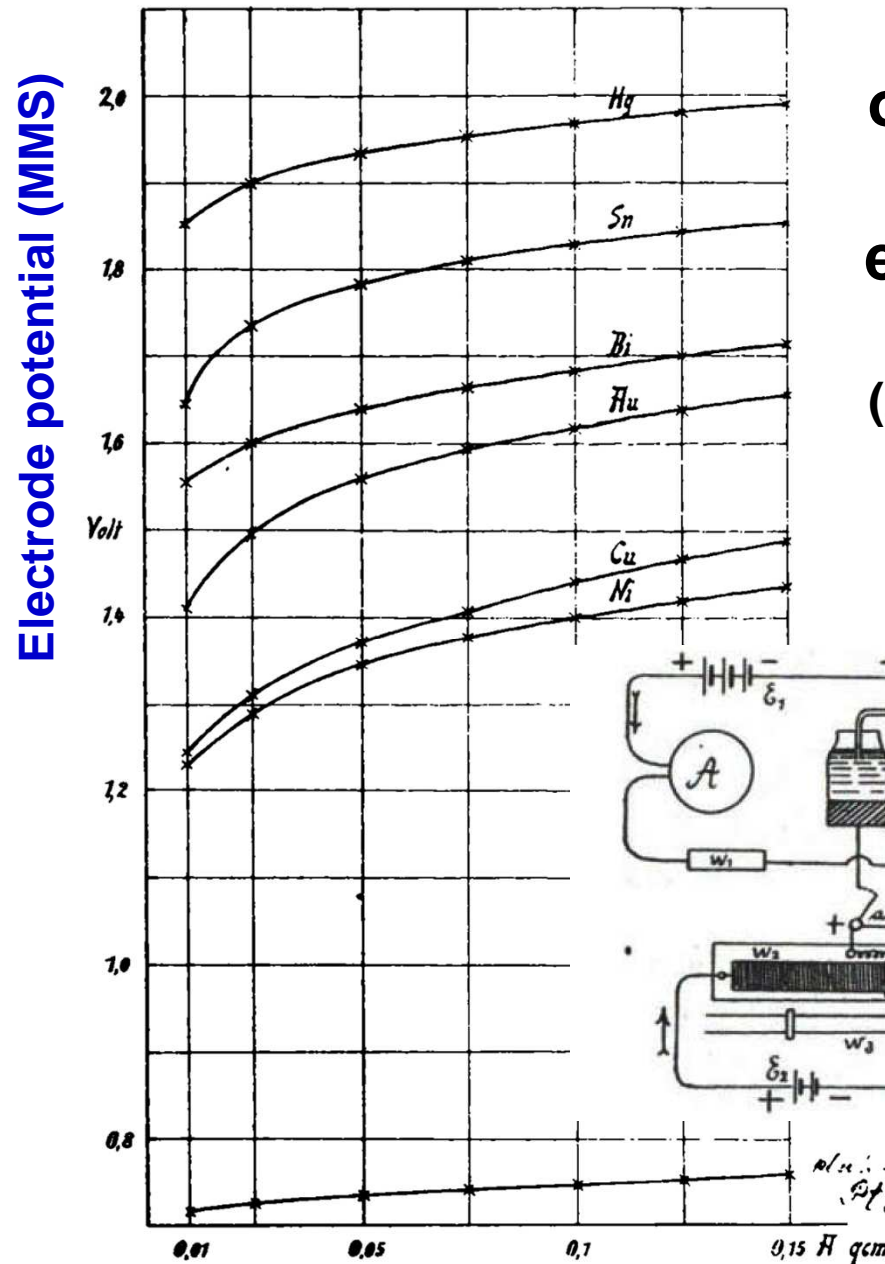Physik-Department

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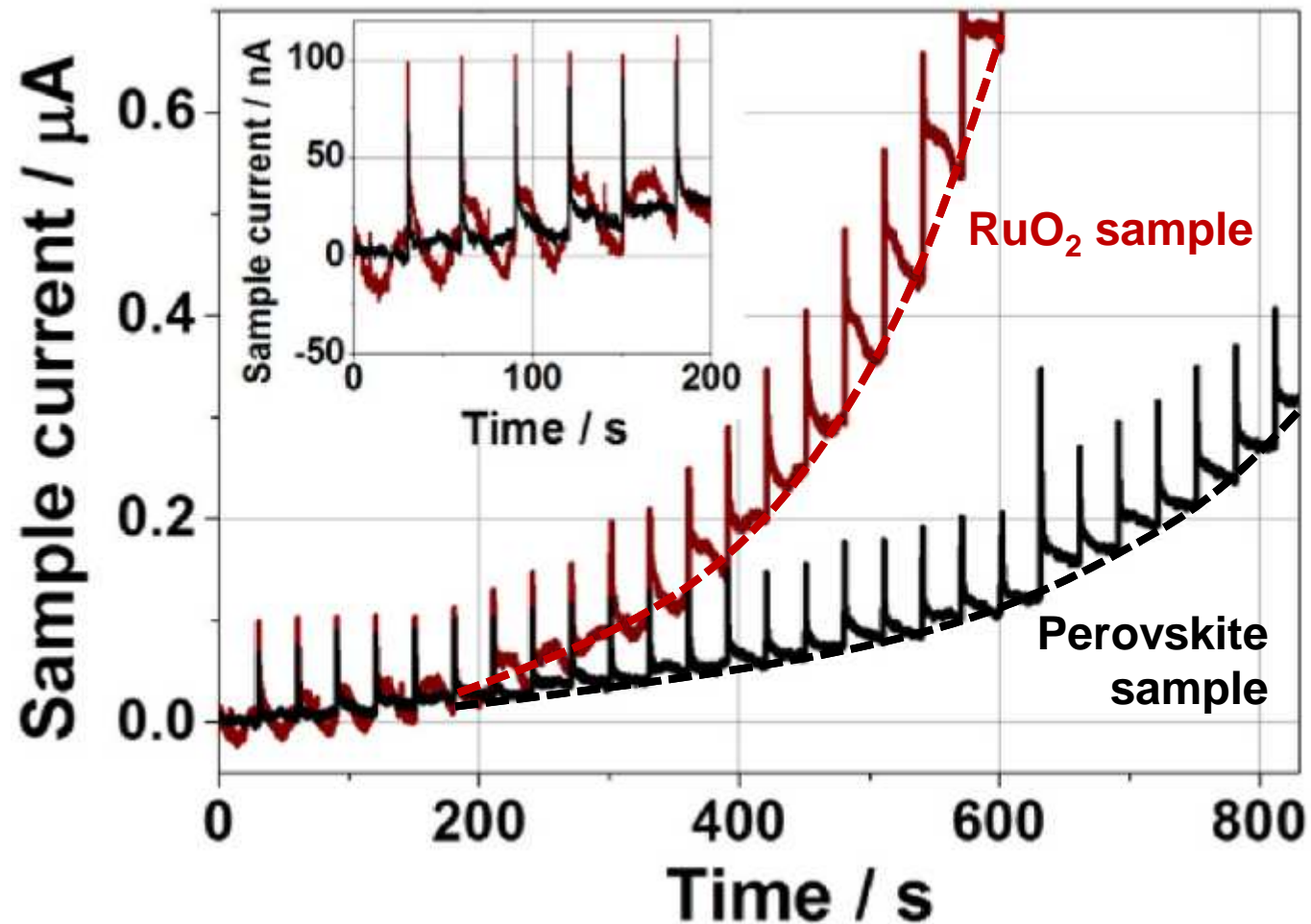Technische Universität München

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Results for HER obtained by J. Tafel for different metal electrodes in H_2SO_4 in 1905
(Zeitschrift fur physikalische Chemie", Vol. 50, pp 641-712, 1905)

Electrode potential (MMS)

Stationary DC current

Oxygen Evolution at RuO_2 and a Perovskite Sample

RuO₂ sample

Perovskite sample

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Electrochemistry Communications 38 (2014) 142

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Possible comparison of different catalysts. Particular case of the oxygen evolution

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Catalyst 1

Catalyst 2

Some reference current

Reference potentials (overpotentials)

Current (quasi-stationary)

Potential vs RHE
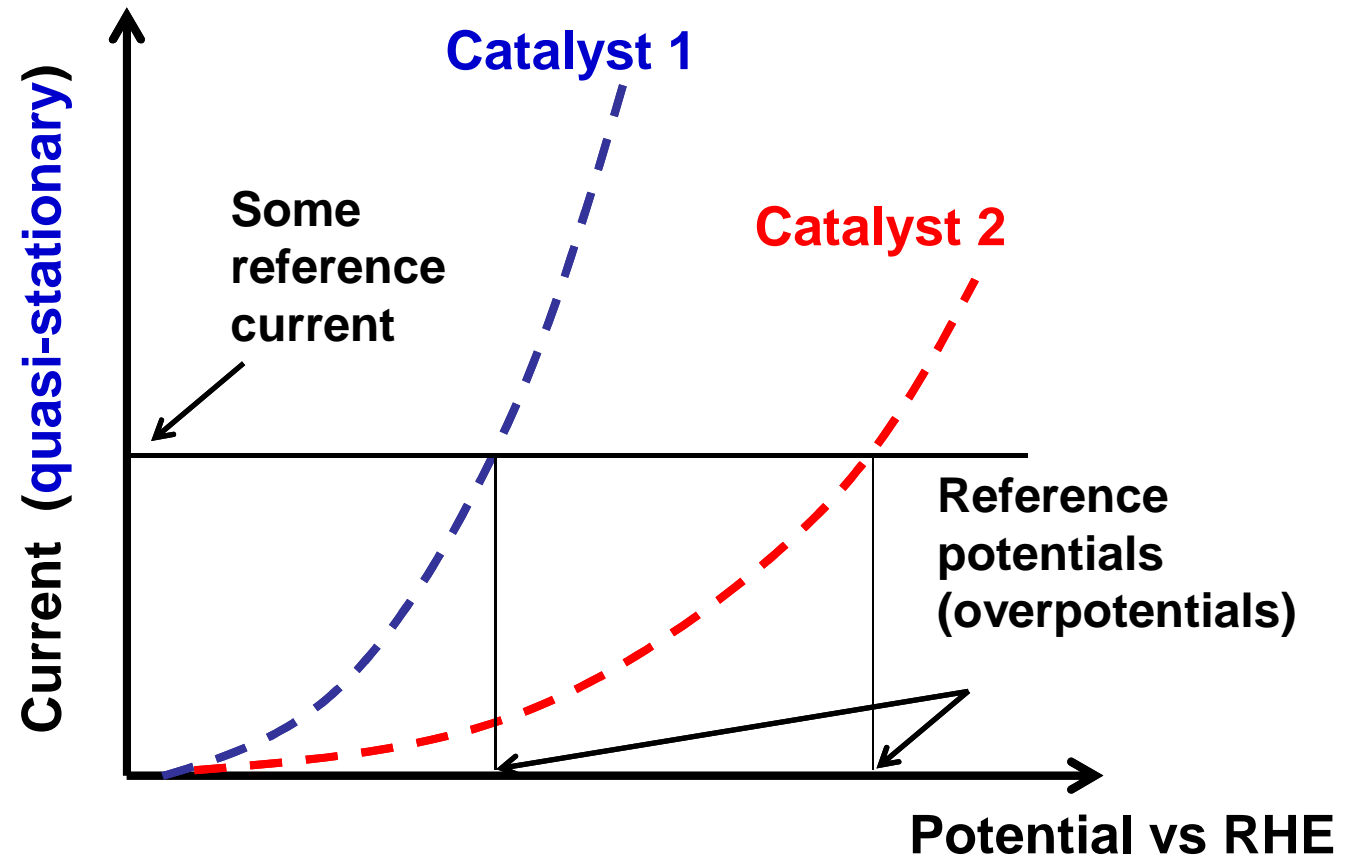
The lower the overpotential the better is the catalyst

Main advantages and disadvantages

Advantages:

Probably the most straightforward techniques in sense of the response interpretation, which is important for the comparison of different catalysts

Disadvantages:

Do not distinguish different Faradaic processes, which occur simultaneously

Relatively slow, rather stationary systems are required

A lot of *a priori* known information should be taken into account: e.g. oxide growth on the surface of a metal

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Potentiodynamic techniques

Stationary electrodes

In these kind of techniques the electrode potential is constantly changed while the current is measured

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(Cyclic) voltammetry

The most widely used technique for acquiring qualitative and quantitative information about electrochemical (electrocatalytic) reactions

Provides information on redox processes, i.e. interfacial electron transfer including adsorption processes

Gives a quick overview on electrode potentials where electrochemical processes take place

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Cyclic voltammetry. Measurement scheme
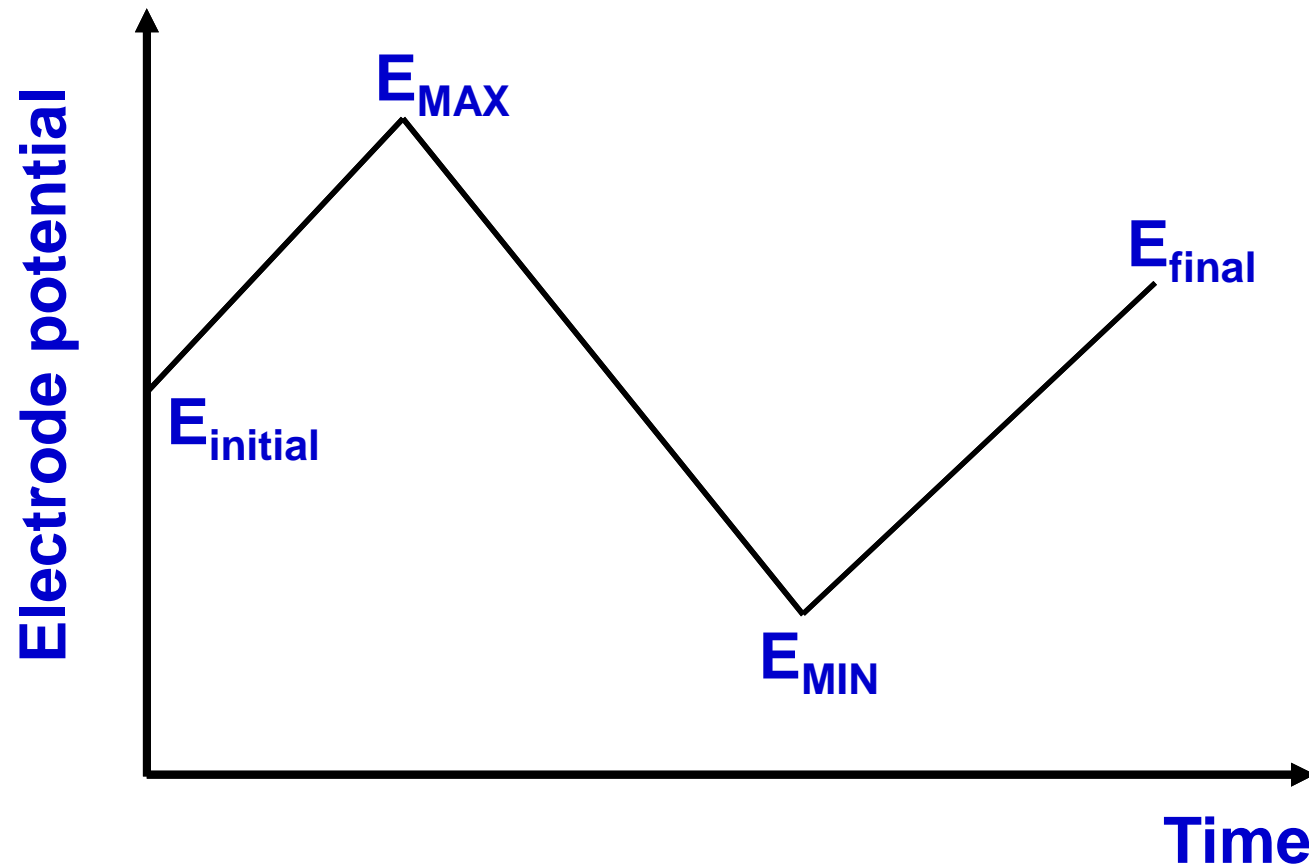
- Sweep direction
- Sweep rate

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Cyclic voltammetry. Measurement scheme

Pt(111) in 0.1M $HClO_4$, Ar-saturated
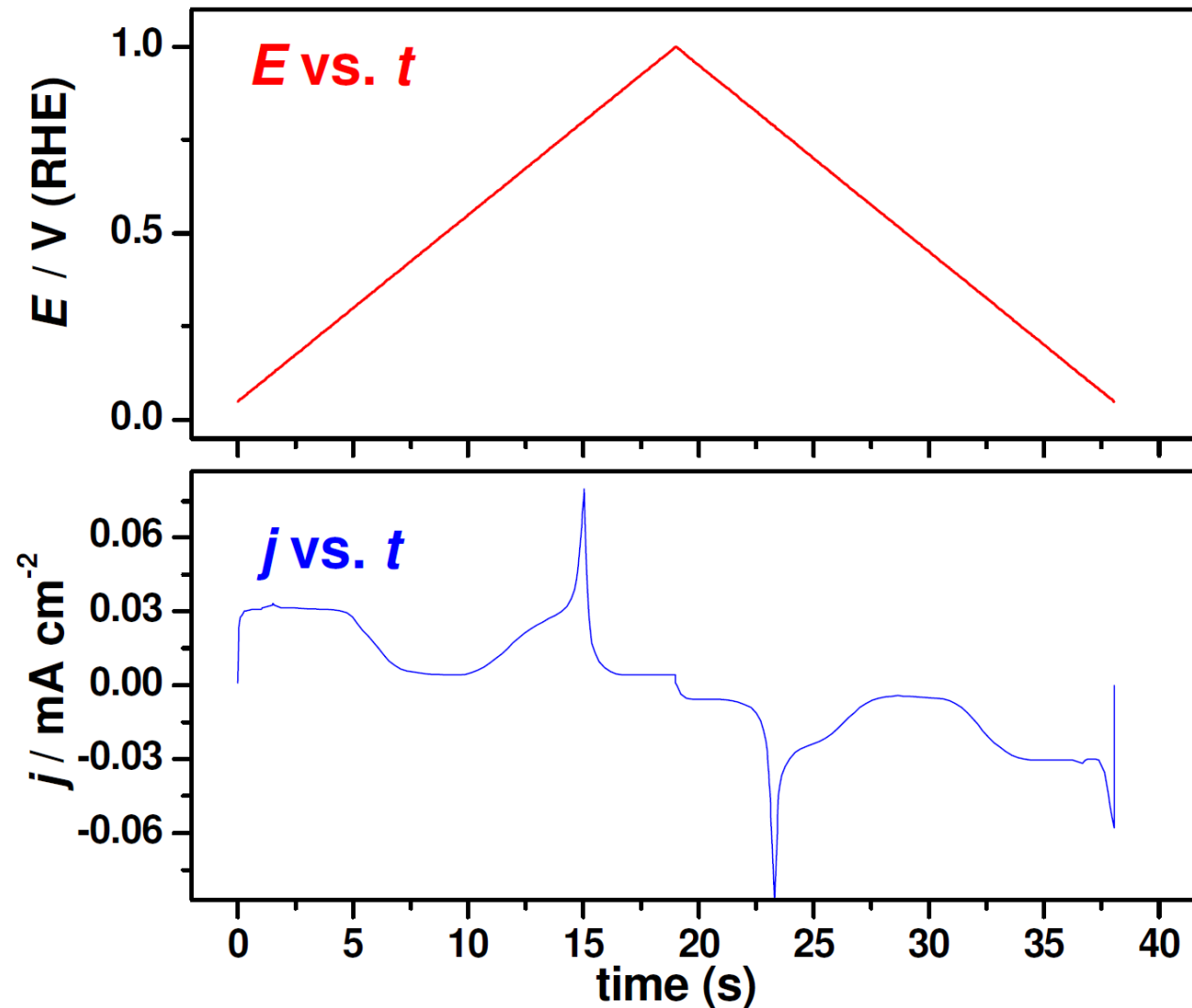
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Cyclic voltammogram

$$j = F(E)$$
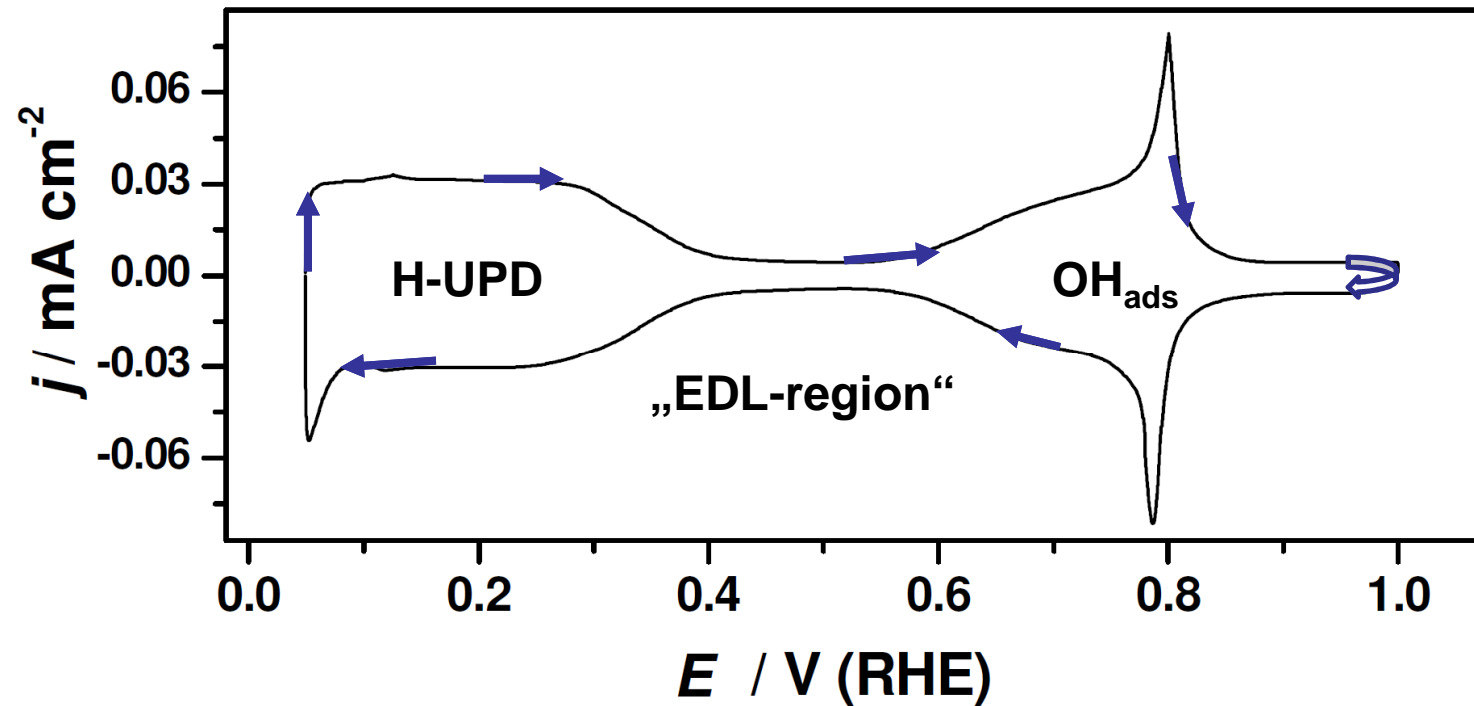
H-UPD

OH$_{ads}$

„EDL-region"

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Pt(111) in 0.1M HClO$_4$, Ar-saturated

A voltammogram of CO-monolayer oxidation
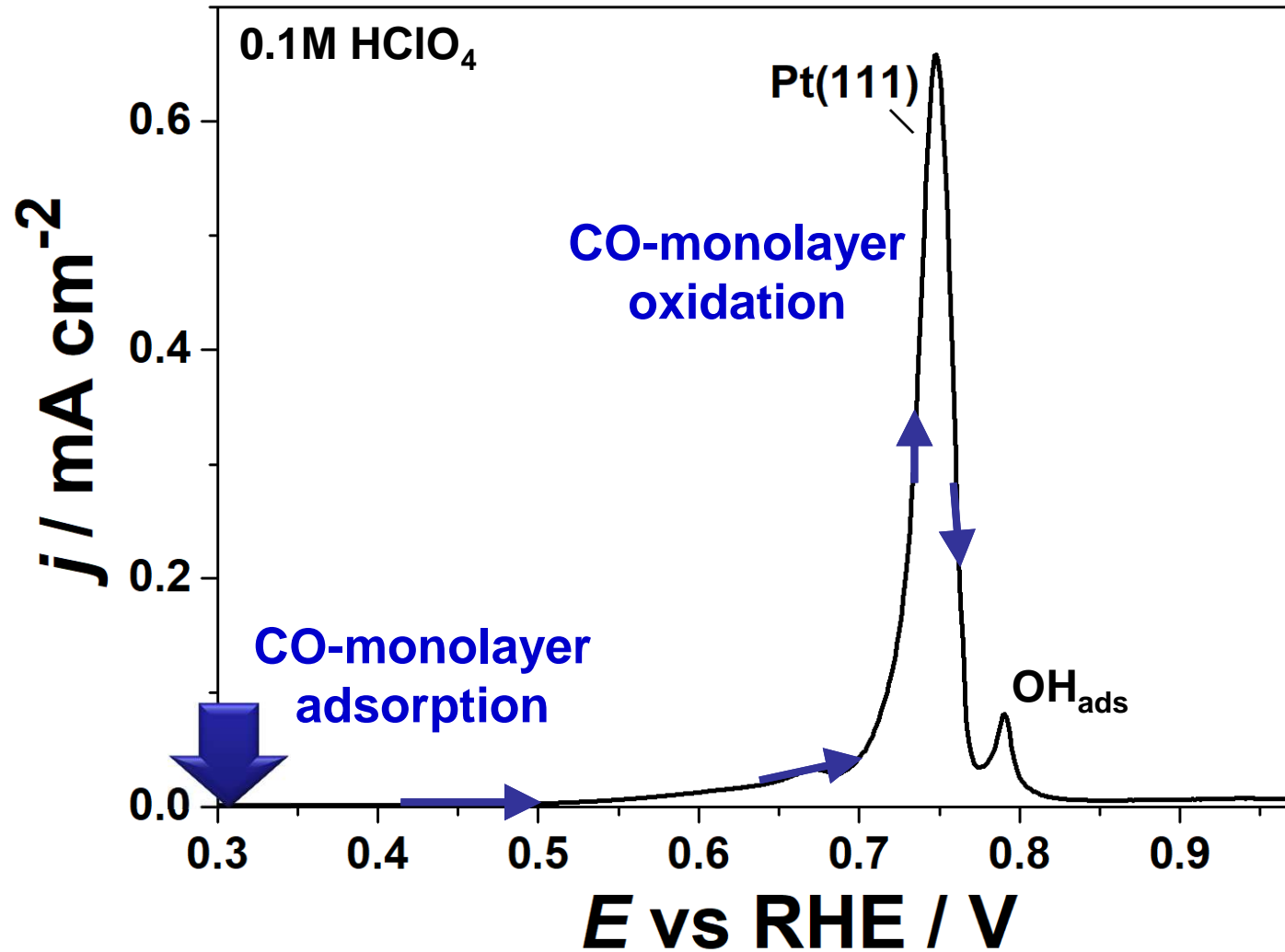
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Voltammograms of CO-monolayer oxidation

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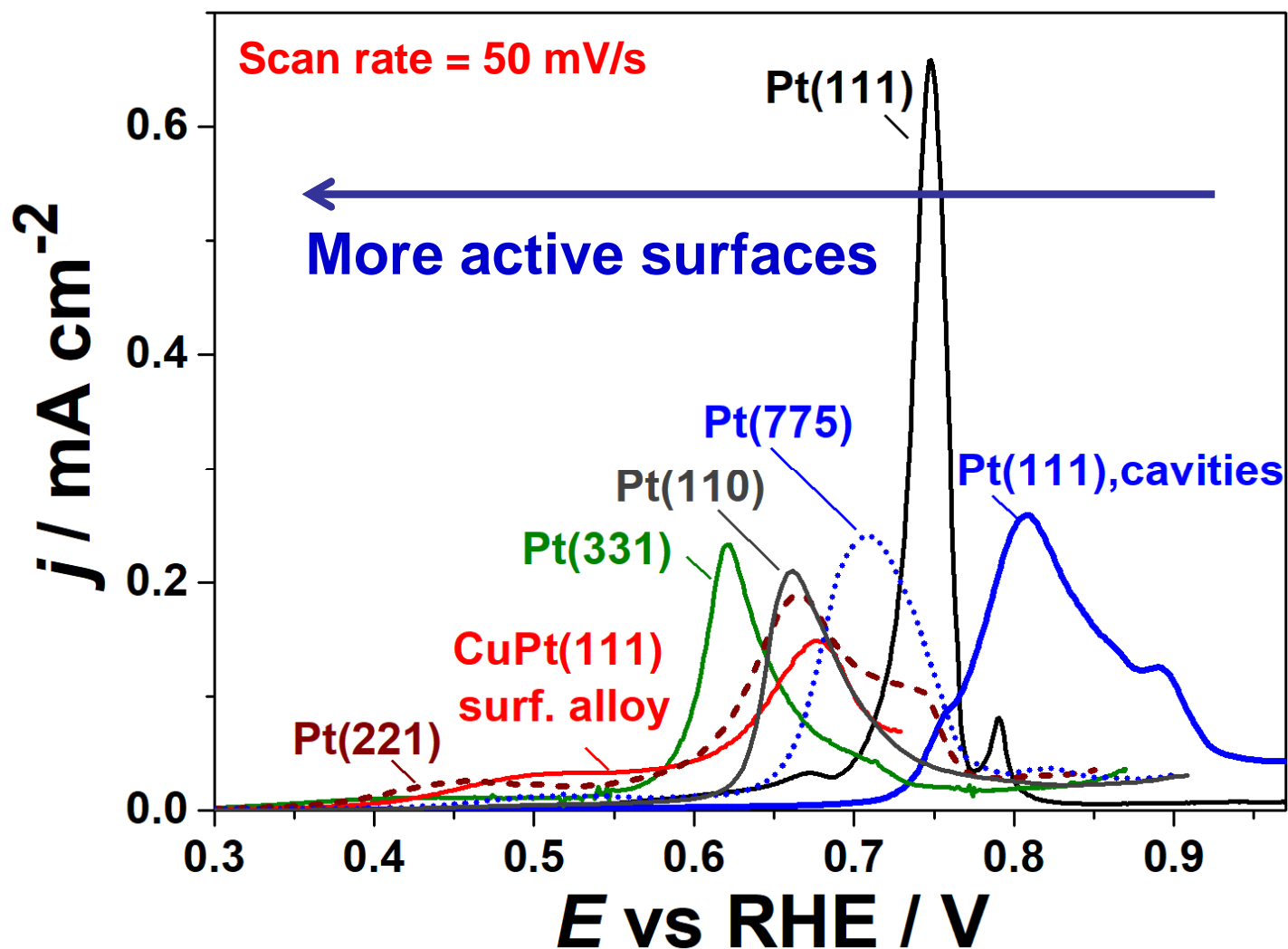
ACS Catalysis 7 (2017) 4355

Main advantages and disadvantages

Advantages:

Non-stationary electrocatalytic systems can be investigated

Relatively fast and robust technique

Disadvantages:

Does not distinguish different Faradaic processes, which occur simultaneously

Often difficult to separate Faradaic and the double layer currents

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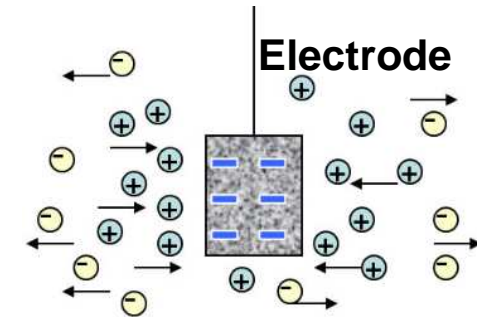# Methods involving forced convection

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# There are three typical modes of ion transport in ionic conductors

Migration - charged particles move to equalize potential gradients in the electrolyte.

Electrode

Convection - material is moved by an external force such as flow, or rotation of the electrode.

Electrode

Electrolyte
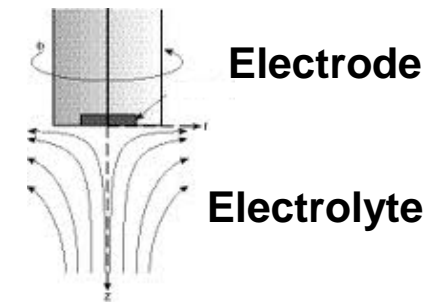
Diffusion - Movement of a species under the influence of a gradient of chemical potential (practically, a concentration gradient).

C

C_b

$\bar{e}$

$C_{ox}(x)$ profile

$C_{red}(x)$ profile

0

0

x
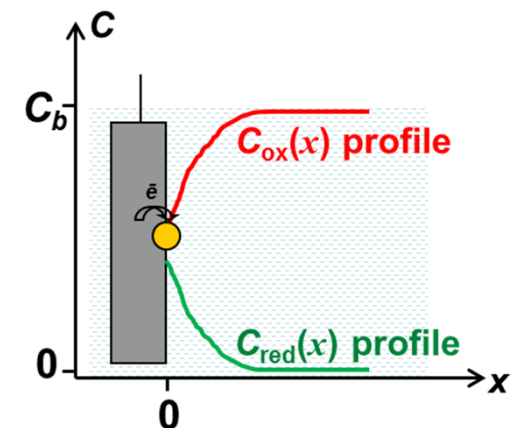
Why hydrodynamic methods?

Mass transfer rates are larger than just by diffusion alone, therefore the relative contribution of mass transfer to electron transfer kinetics is relatively small

Rather quick steady-state can be reached; the double-layer charging can be excluded at steady-state

Insulating parts

Rotating disk electrode

One of few convective electrode systems for which the hydrodynamic equations and the convective-diffusion problem have been solved analytically
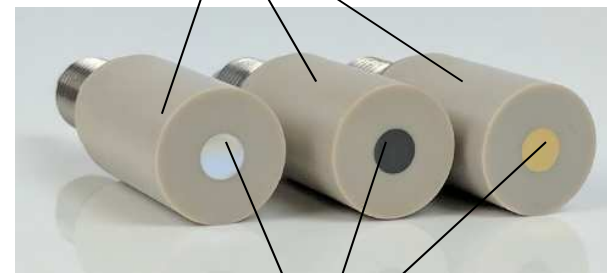
Disk electrodes

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Why hydrodynamic methods?

Side view

Top view

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Rotating disk electrodes

Electrode

Electrolyte
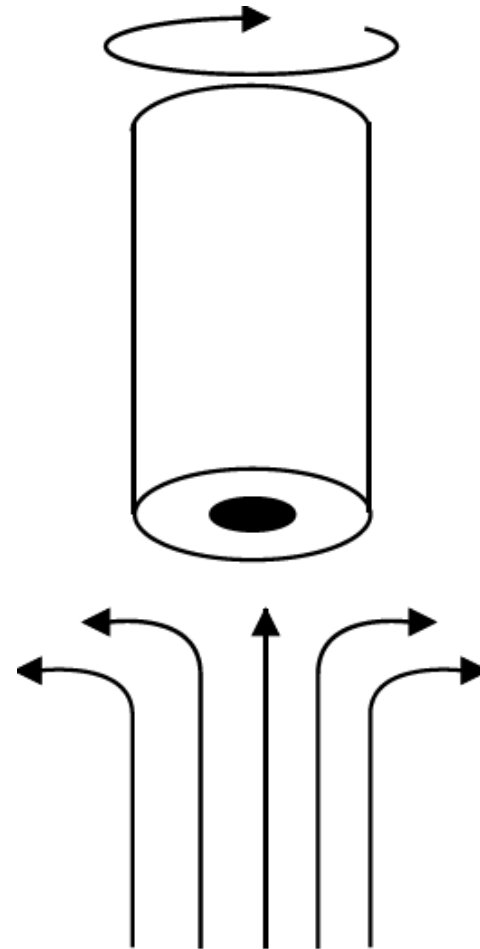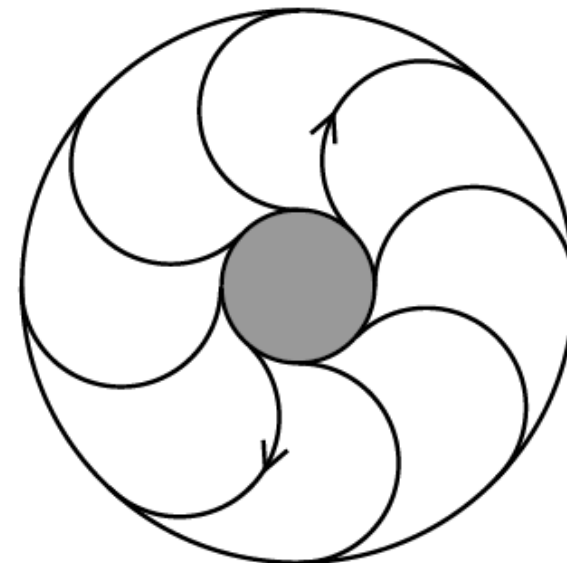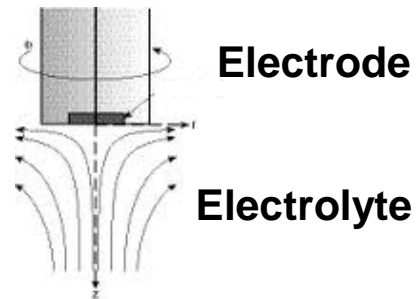
Potentiostatic experiments
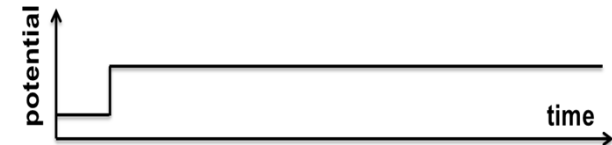
Potentiodynamic experiments
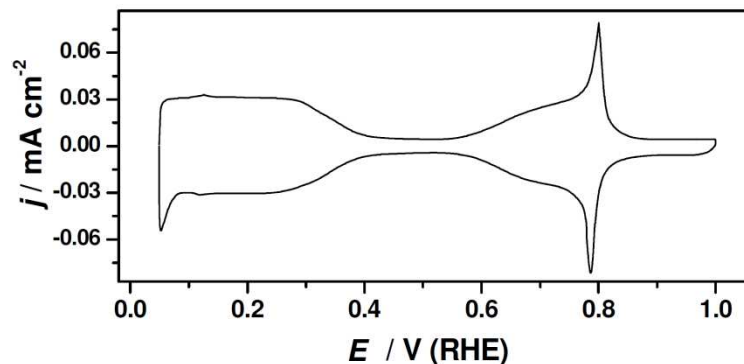
Examples:
Oxygen reduction
Hydrogen oxidation

Oxygen evolution
Hydrogen evolution

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Rotating disk electrodes

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Rotating disk electrodes

$$j_{lim} = BS_{electrode}C_0\omega^{1/2}$$

$$\frac{1}{j} = \frac{1}{j_{kinetic}} + \frac{1}{j_{lim}}$$
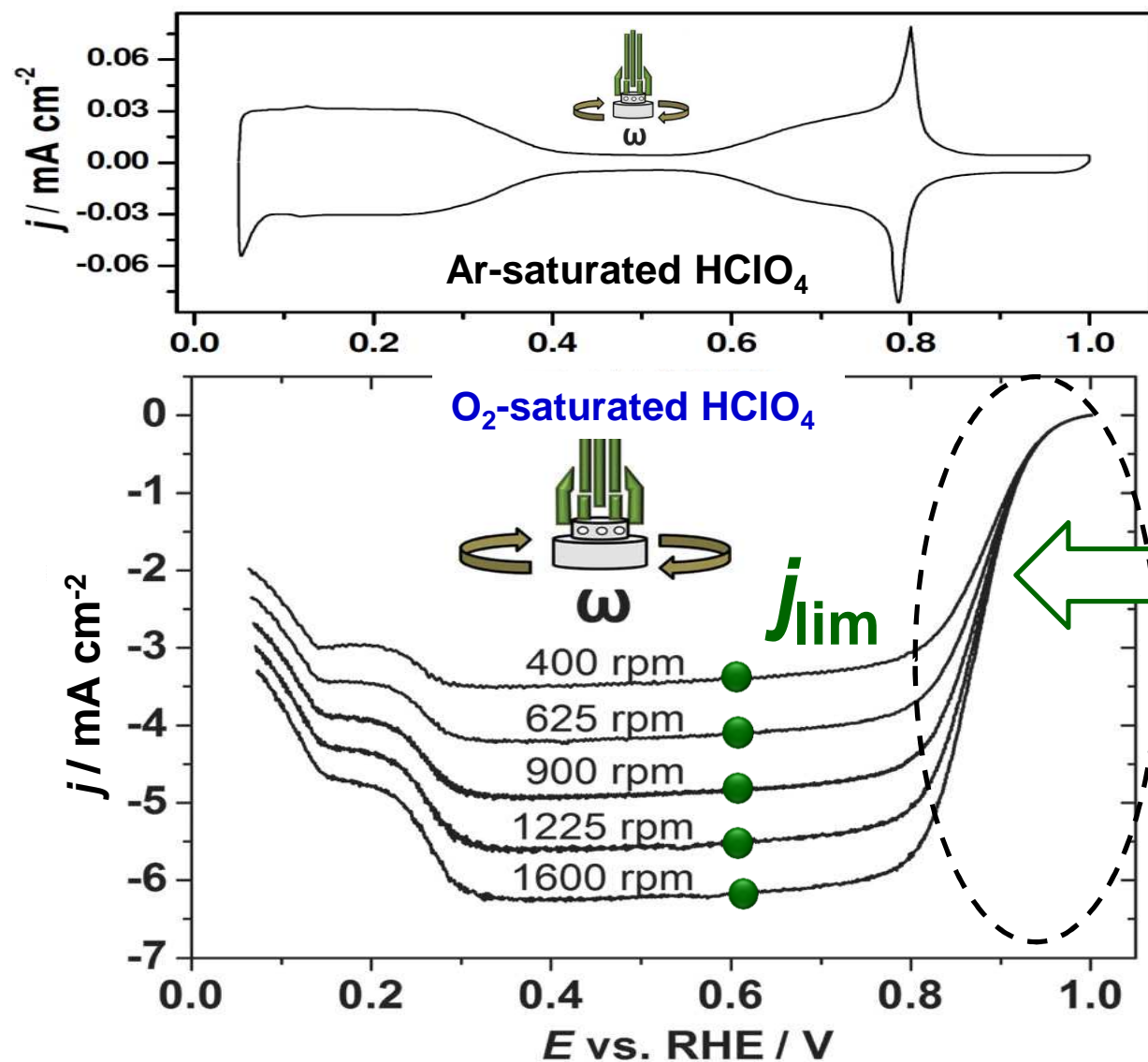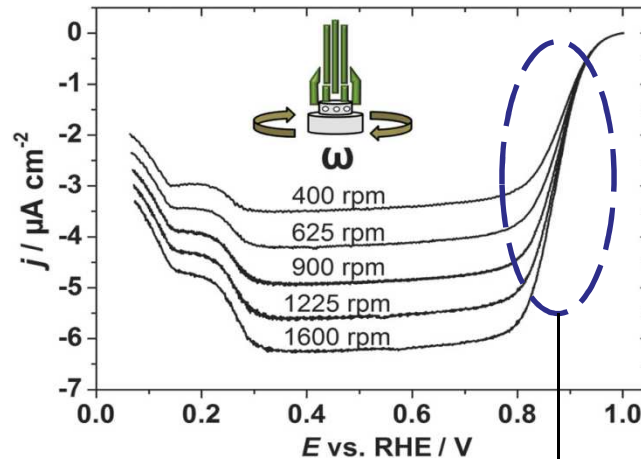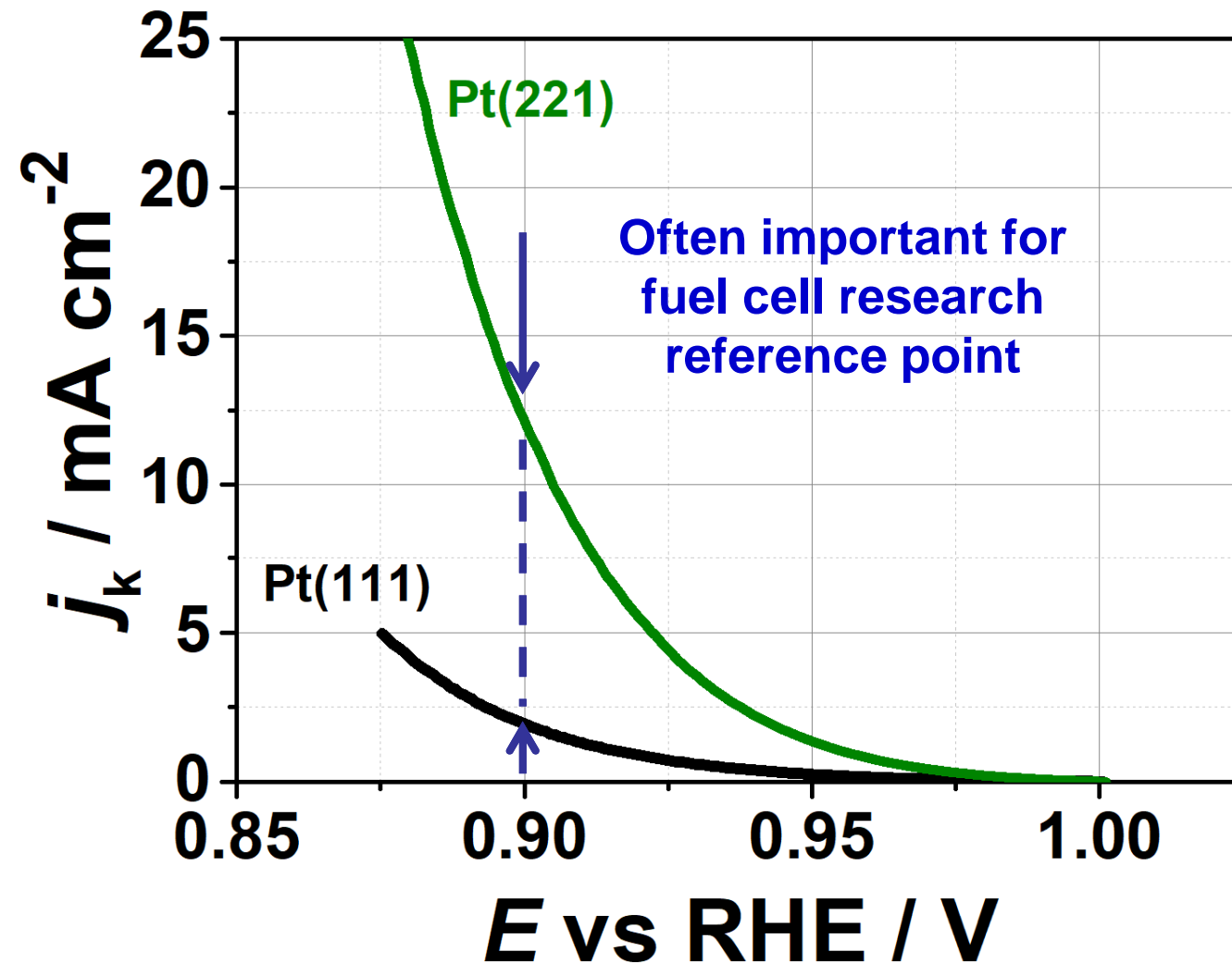
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Rotating disk electrodes. O$_2$ reduction

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Pt(221)

Pt(111)

j_k / mA cm^{-2}

E vs RHE / V

Often important for fuel cell research reference point

Chemical Science 8 (2017) 2283

Rotating disk electrodes.
O_2 reduction activity ranking
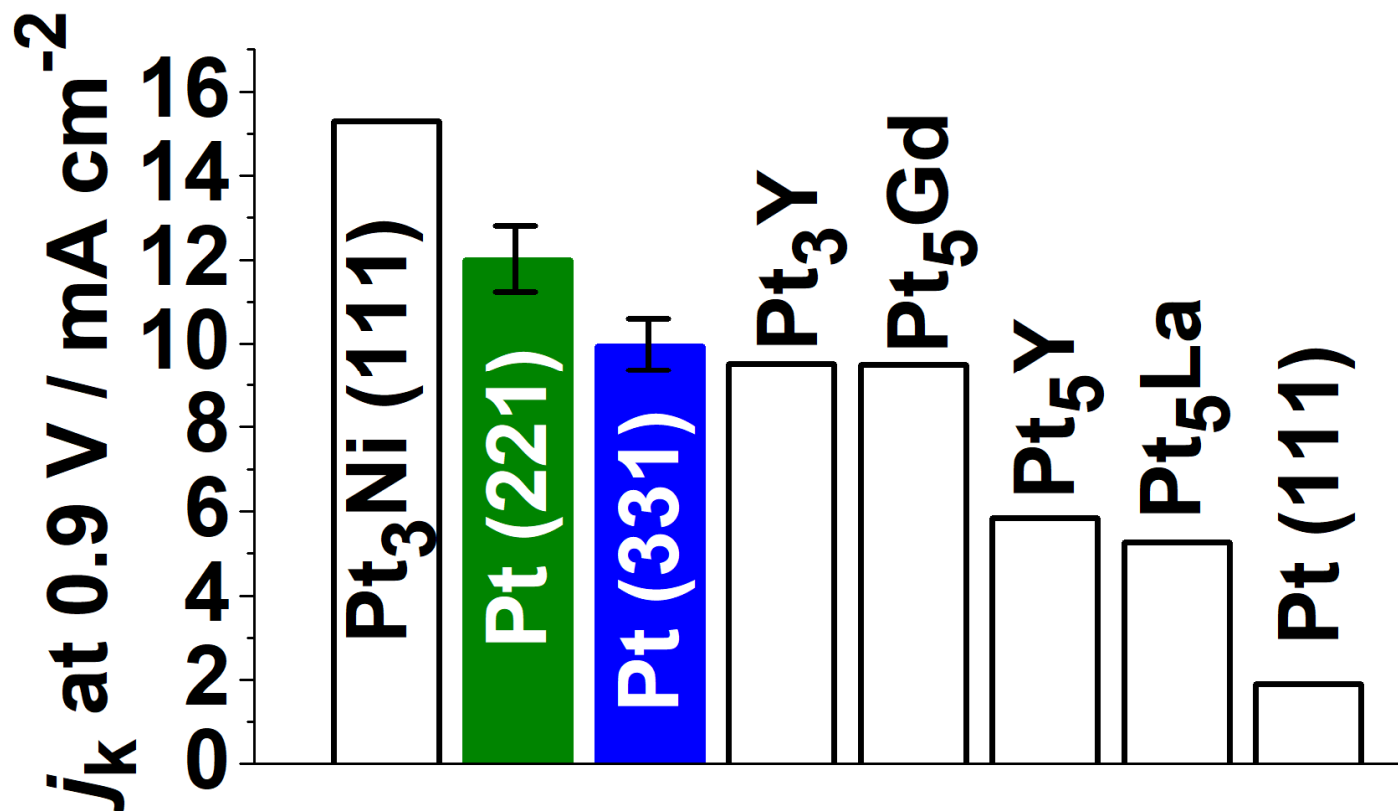
Chemical Science 8 (2017) 2283

Main advantages and disadvantages

Advantage:

Fast. Powerful tool to investigate kinetics of electrochemical reactions and test catalytic activities when mass transport plays an important role

Disadvantages:

Acquisition of the integral response. Difficult to distinguish between different Faradaic constituents

Problems with fast accumulation of impurities at the electrode surface during the experiments

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Electrochemical Impedance Spectroscopy

Basics of EIS: data acquisition

Electrochemical system

CE RE

WE

10mV

probing signal

$$E = E_{bias} + E_{ac} sin(\omega_i t)$$

at different *ac* frequencies ω_i

phase-shift

response

$$I = I_0 + I_{ac} sin(\omega_i t + \boldsymbol{\theta})$$
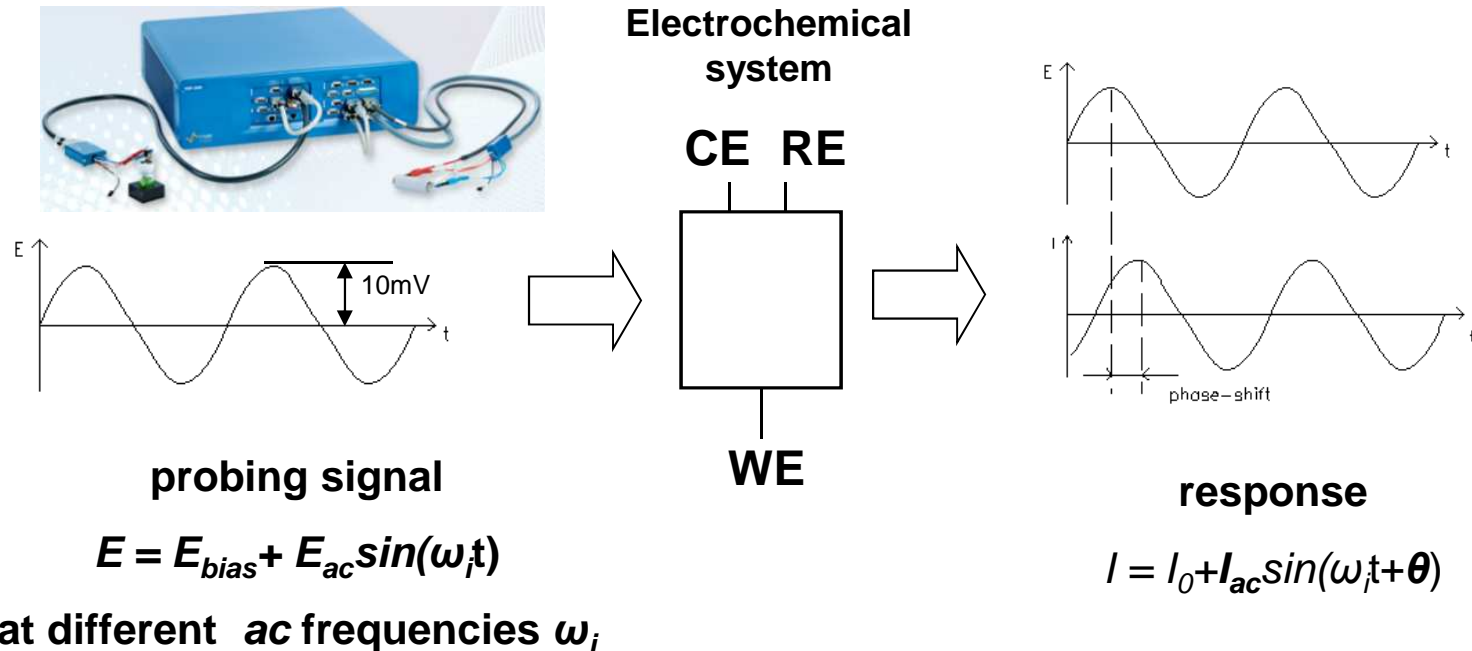
The "output" is:

1. Modulus of impedance $|Z_\omega|$, i.e. the ratio E_{ac} / I_{ac}

2. A value of the phase shift θ_ω between the probing signal *E* and the current response *I*

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Typical impedance spectra

$$ImZ = |Z|\sin(\theta) \qquad ReZ = |Z|\cos(\theta)$$

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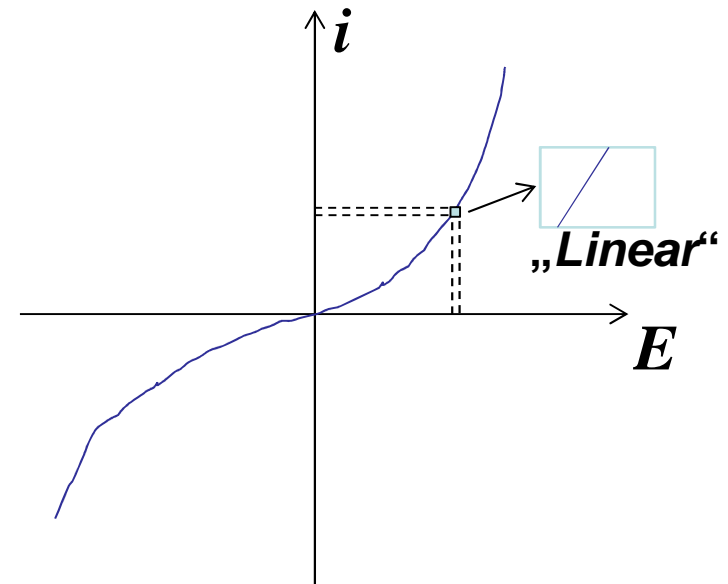
38
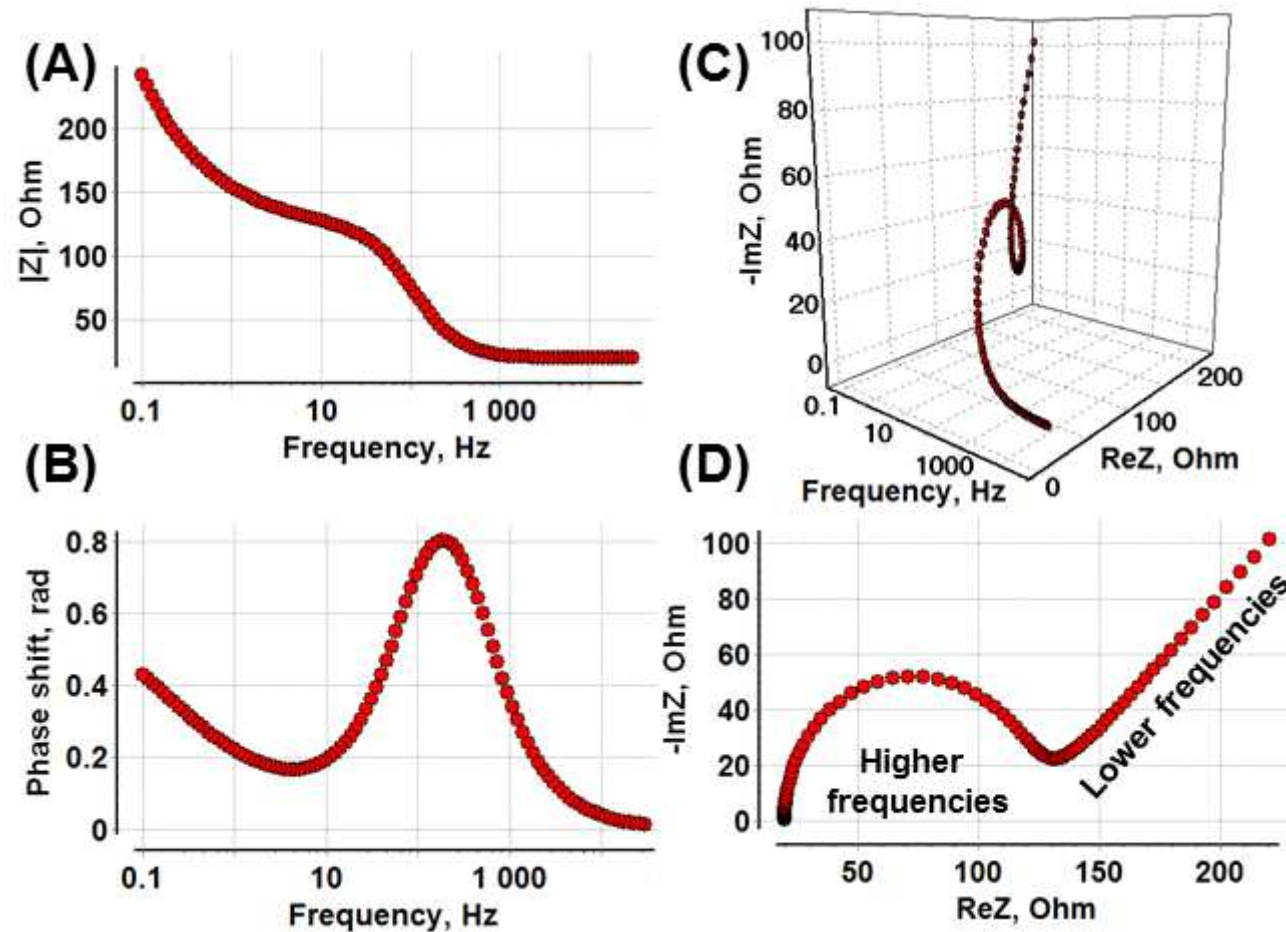
Linearity (*determines probing signal amplitude*)
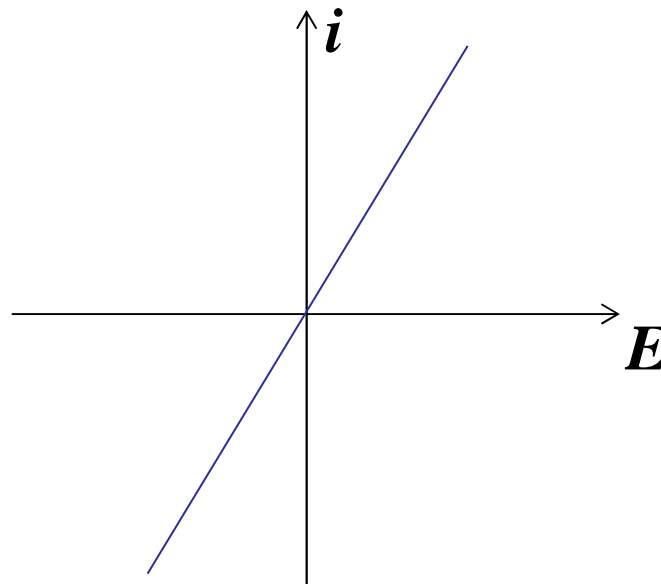
a resistor   *an electrochemical system*

The amplitude of the ac probing signal in EIS experiments should be small in order to consider our system (quasi) linear.

Depending on the system, the amplitude of <u>1-10 mV</u> is acceptably small
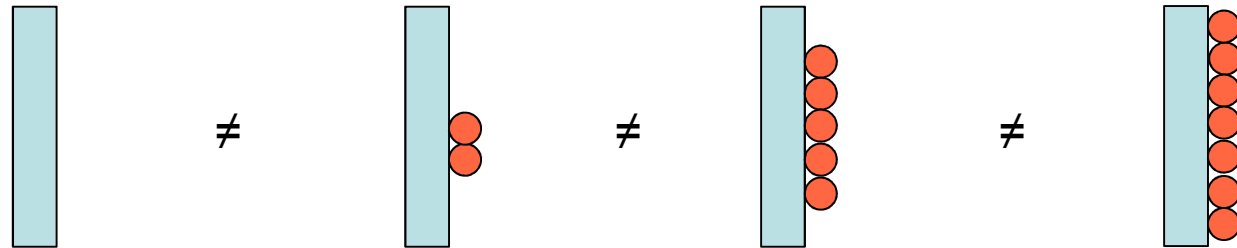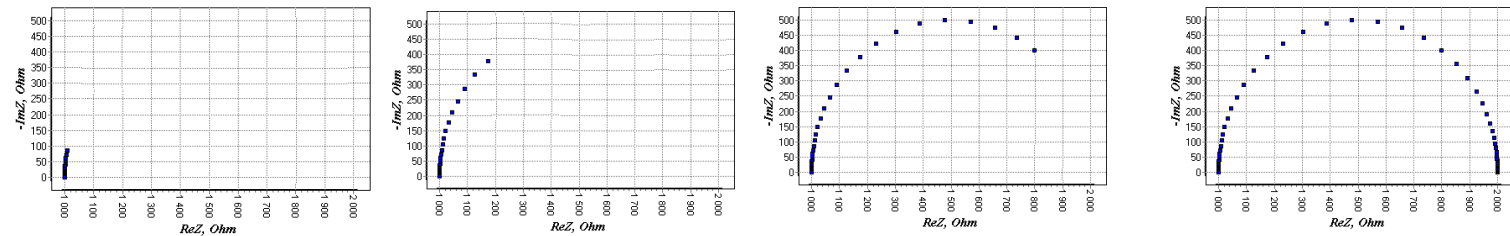
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Quasi-stationarity

Complications:

≠ ≠ ≠

time

Possible solution is to minimize the time for the measurements
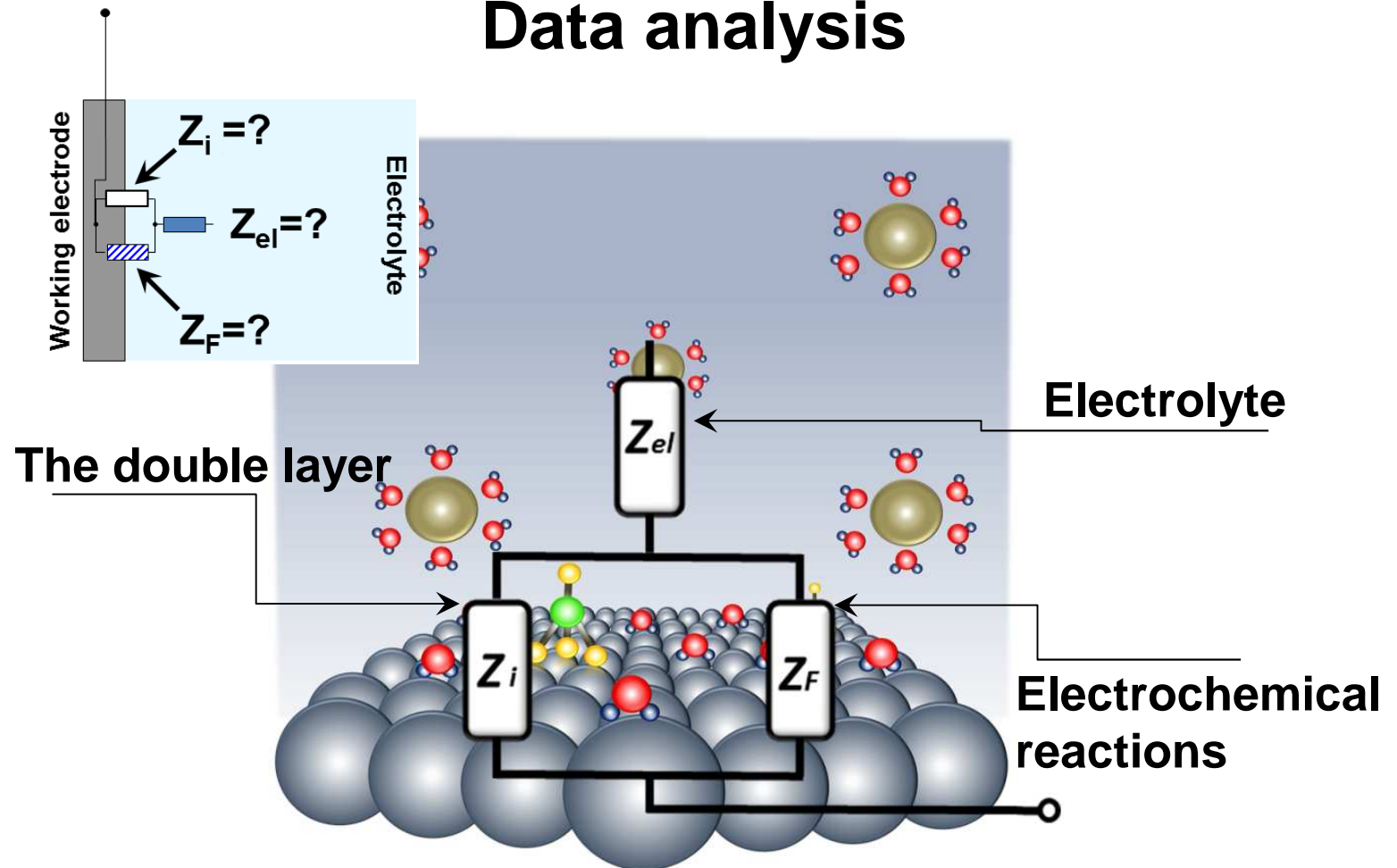
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Data analysis

Dolin-Erschler-Randles approximation (1940-1947)

Equivalent electric circuit is a schematic representation of equations describing the electrochemical system

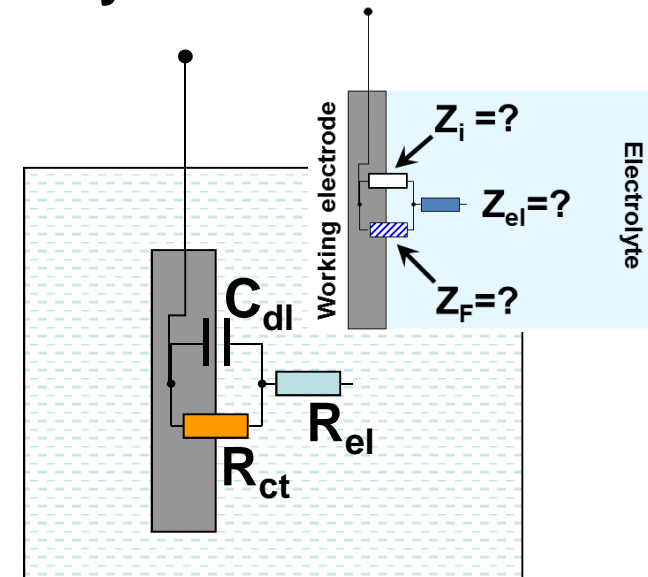q_M – excess surface charge density on the metal; $f(E, v_i....)$

i – current due to electrochemical reaction $f(E, C_s, v_i....)$

ρ – specific resistance of the electrolyte

l – distance between electrodes

s_{el} – electrode surface area

g – empirical constant depending on the cell geometry, positions of the electrodes etc.

$$Z = \underbrace{\frac{g\rho l}{s_{el}}}_{R_{el}} + \frac{\overbrace{\left(\frac{\partial i}{\partial E}\right)^{-1}}^{R_{ct}}}{1+\omega^2\underbrace{\left(\frac{\partial i}{\partial E}\right)^{-2}}_{R_{ct}}\underbrace{\left(\frac{\partial q_M}{\partial E}\right)^{2}_{\mu}}_{C_{dl}}} + j\frac{\omega\overbrace{\left(\frac{\partial i}{\partial E}\right)^{-2}}^{R_{ct}}\overbrace{\left(\frac{\partial q_M}{\partial E}\right)_{\mu}}^{C_{dl}}}{1+\omega^2\underbrace{\left(\frac{\partial i}{\partial E}\right)^{-2}}_{R_{ct}}\underbrace{\left(\frac{\partial q_M}{\partial E}\right)^{2}_{\mu}}_{C_{dl}}}$$

Solving the inverse problem: Randles circuit

EIS spectrum

$C_{dl}=20\mu F$

$R_{el}=10\Omega$

$R_{ct}=100\Omega$

$C_{dl}= (\omega R_{ct})^{-1}$

$R_{ct}=100\Omega$

$R_{el}=10\Omega$

$-ImZ, Ohm$

ReZ, Ohm

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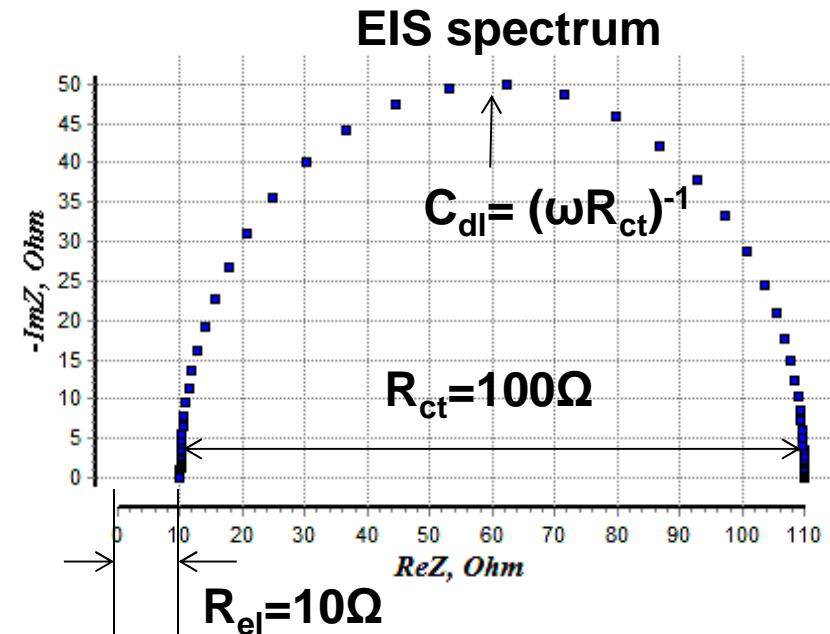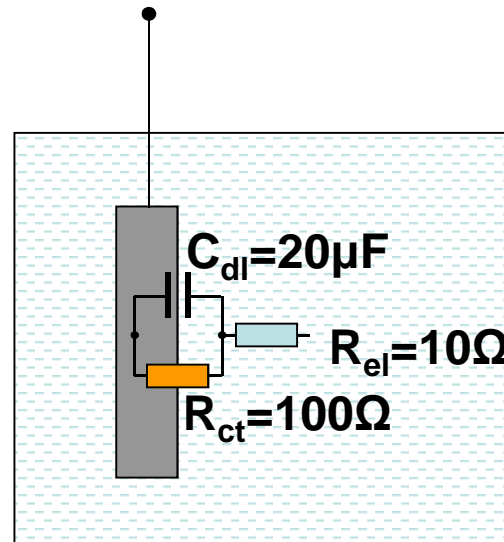
$$i(E, C_{i,s}, \theta) = nFs_{el}\left[C_{red,s} \times k_{ox}(E) \times F_1(\theta) - C_{ox,s} \times k_{red}(E) \times F_2(\theta)\right]$$

$$R_{ct}^{-1} = \left(\frac{\partial i}{\partial E}\right)_{C_{i,s},\theta} = nFs_{el}\left[C_{red,s}\frac{\partial k_{ox}}{\partial E} F_1(\theta) - C_{ox,s}\frac{\partial k_{red}}{\partial E}F_2(\theta)\right]$$

n- number of electrons; F = 96485 C/mol; C_i –surface concentrations of electroactive species, k_i- het. react. rate constants; $F_i(\theta)$- some functions of the surface coverage (e.g. θ or $1- \theta$ in case of Langmuir adsorption isotherm)

Equivalent electric circuit elements are building blocks of EIS models

Equivalent electric circuit elements

Circuit element	Element name	Expression for the element impedance $Z(j\omega)$	Optimisation parameters
R	Resistor	R	R
C	Capacitor	$(j\omega C)^{-1}$	C
L	Inductor	$j\omega L$	L
CPE	Constant phase element	$Q^{-1}(j\omega)^{-n}$	Q, n
W	Warburg element for semi-infinite diffusion	$A_w(j\omega)^{-0.5}$	A_w
W_s	Warburg element for finite length diffusion (short)	$\dfrac{W_{sr}}{\sqrt{\omega}}(1-j)\tanh\left(W_{sc}\sqrt{j\omega}\right)$	W_{sr}, W_{sc}
W_o	Warburg element for finite length diffusion (open)	$\dfrac{W_{or}}{\sqrt{\omega}}(1-j)\coth\left(W_{oc}\sqrt{j\omega}\right)$	W_{or}, W_{oc}
G	Gerischer element	$(Y_g(K_g + j\omega)^{0.5})^{-1}$	Y_g, K_g

CPE (constant phase element) is a semi-empirical element. It can describe many phenomena, however the exact interpretation of its parameters *n* and *Q* is not straightforward and will depend on system properties, models selected etc.

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- Bad news about physical impedance models:

1. It is quite difficult to derive analytical equations for the physical EIS models.
2. Many of the parameters in these equations are complex functions of the electrode potential, e.g.

$$R_{ct} = \frac{RT}{n^2 F^2} \frac{1}{\alpha k_f C_O + (1-\alpha) k_b C_R}$$

$$Z_W = \frac{RT}{n^2 F^2} \frac{\frac{k_f}{\sqrt{j\omega D_O}} + \frac{k_b}{\sqrt{j\omega D_R}}}{\alpha k_f C_O + (1-\alpha) k_b C_R}$$

$k_f = k_0 \exp[-\alpha n F(E-E_0)/RT]$

$k_b = k_0 \exp[(1-\alpha) n F(E-E_0)/RT]$

Surface concentrations C_O and C_R are normally not equal to the respective bulk concentrations c_O and c_R. Both C_O and C_R are complex functions of the electrode potential

- However the good news are:

1. For many of typical electrochemical reactions the analytical equations for the Faradaic impedance are known (someone else did this work for us). We only need to assemble the model (equivalent circuit) from the known components using some relatively simple rules.
2. There are many ways how to simplify the EIS analysis to extract valuable physico-chemical parameters.

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Picture from the past: "graphical analysis"
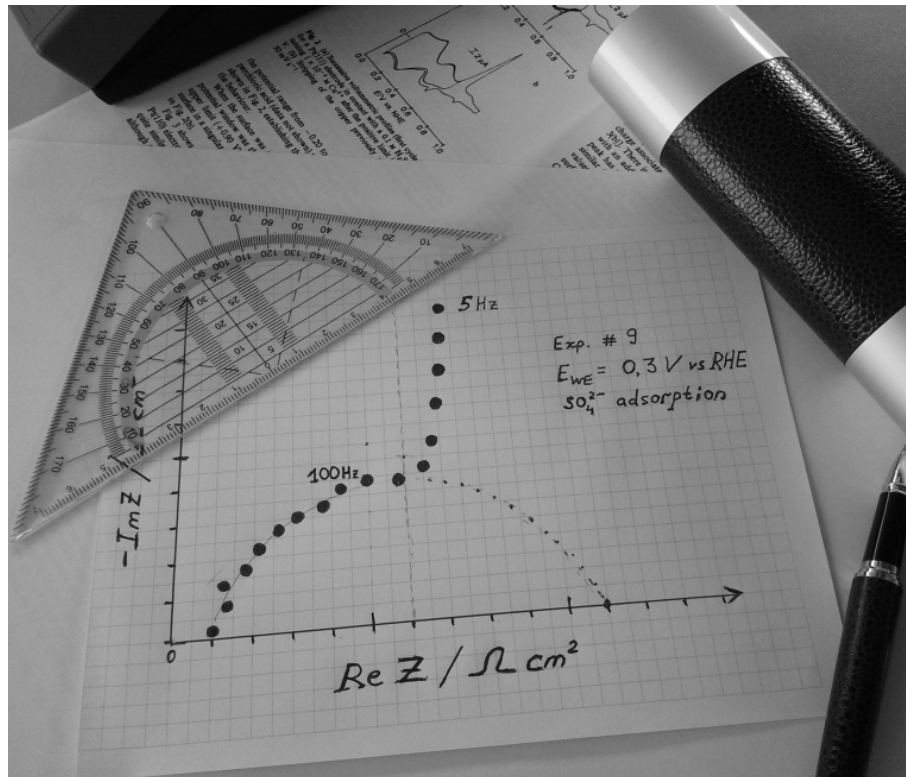
- Model postulation, e.g.
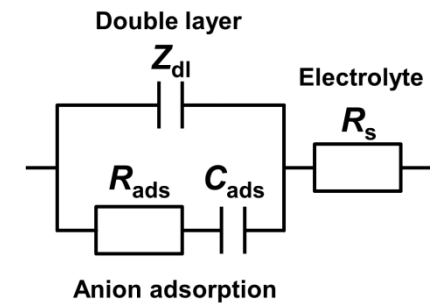
- **Model verification: just semi-quantitative or visual inspection!**

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The first software for the impedance data fitting using CNLS (1986): a new era of EIS

By Bernard A. Boukamp

Software: EQUIVCRT

Solid State Ionics, 18-19 (1986) 136

By James R. MacDonald

Software: LEVM

Solid State Ionics, 24(1) (1987) 61

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Optimisation algorithm: **Levenberg–Marquardt (iterative)**

- **Powerful algorithms for the check of data quality**
- **Careful and more objective model verification**
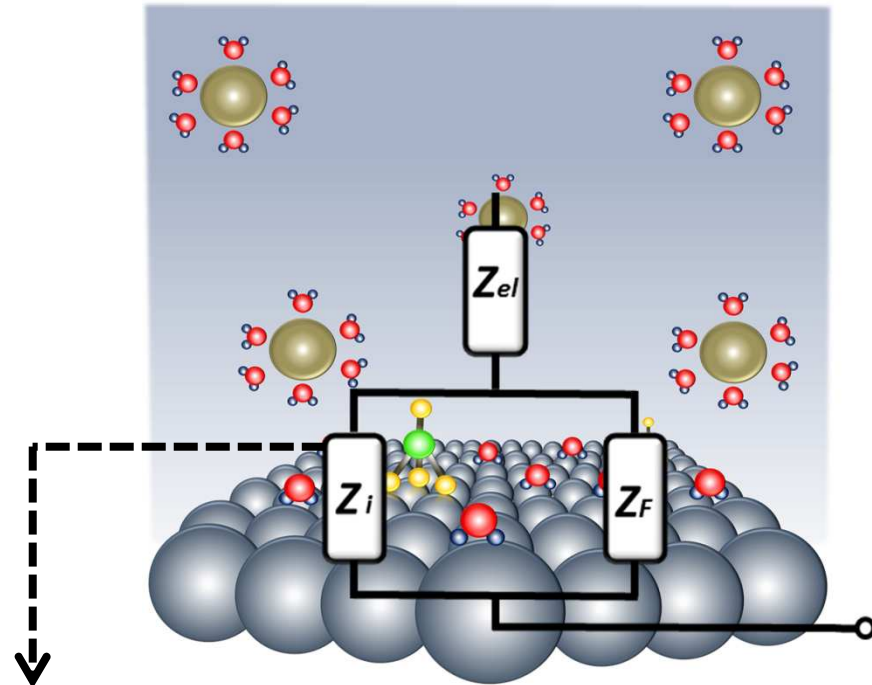- **More accurate estimation of parameters of the models**

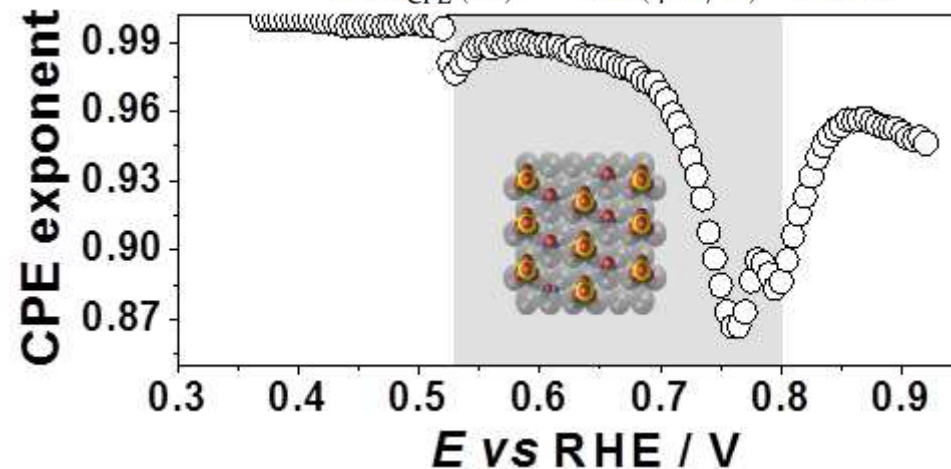# Accurate analysis of EIS data is the key
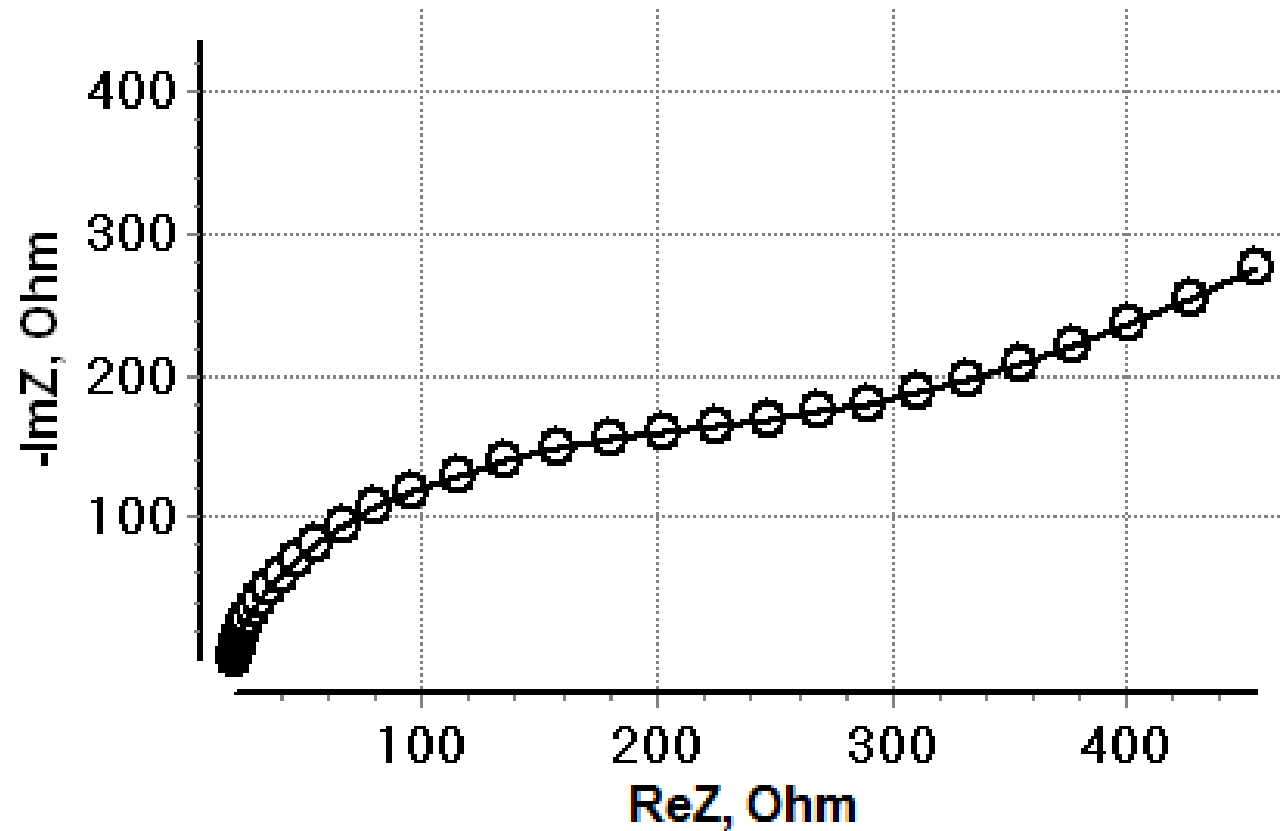
Revealing phase transitions in adsorbate layers

$$Z_i = C'_{DL}{}^{-1}(j\omega)^{-\varphi},$$

where C'_{DL} is the parameter, which is proportional to the double layer capacitance, $\varphi \leq 1$ is the CPE-exponent, which is directly related to the

$$Diss_{CPE}(\%) = \cos(\varphi\pi/2) \cdot 100\%.$$

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Revealing phase transitions in adsorbate layers

O₂-free 0.1M HClO₄

Introduction

Potentiostatic

Potentiodynamic

RDE

Impedance •

Summary

O₂-sat 0.1M HClO₄

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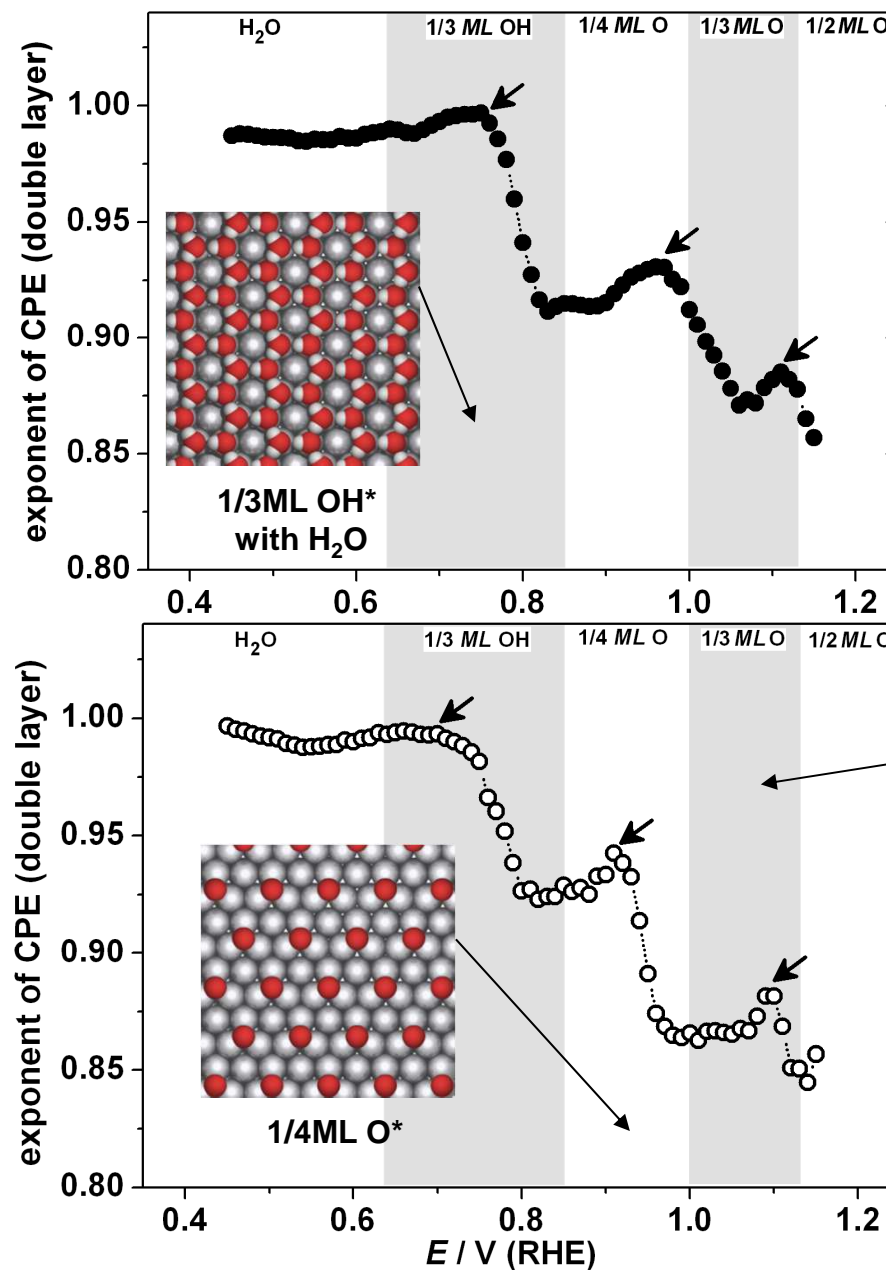
Comparison between techniques

Each technique provides information about only one or several aspects of interfacial processes

| *Techniques*	*Target aspects*	*Advantages*	*Disadvantages*
Voltammetries, static electrodes	**Averaged information about electrochemical processes at the interface**	**Fast. Creates first understanding of the system under investigation. Investigation of non-stationary systems**	**Acquisition of the integral response. Does not "distinguish" contributions from different processes**
Voltammetries, rotating disc (ring) electrodes	**Averaged information about electrochemical reactions under controllable mass transport of electroactive species**	**Fast. Powerful tool to investigate kinetics of electrochemical reactions, test catalytic activities and detect reaction intermediates**	**Acquisition of the integral response. Problems with accumulation of impurities at the electrode surface during the experiments**
Impedance spectroscopy	**Information about different constituents of simultaneously running electrochemical processes. Averaged for the electrode surface**	**Powerful tool to reveal physical models of the interface. Separates contributions from different processes which occur simultaneously**	**Relatively slow. Frequent ambiguity in the model selection: one should use *a priori* knowledge or additional information from other techniques**

Where are the most active electrocatalytic centers?

The Sabatier principle (a qualitative concept) (1911)

The interactions between the catalyst and the reaction intermediates should be just right.

**The catalyst surface should not bind them neither too strong nor too weak.**
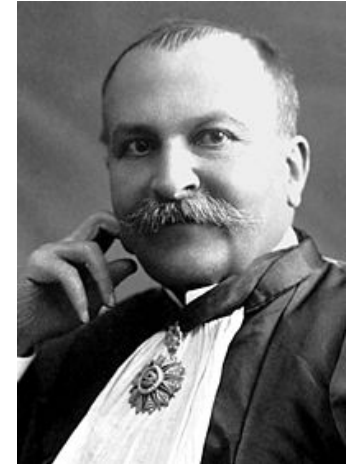
258. **Paul Sabatier: Hydrogénations et déshydrogénations par catalyse.**

[Vortrag, gehalten vor der Deutschen Chem. Gesellschaft am 13. Mai 1911.]

Messieurs.

Ma première parole doit être l'expression de ma gratitude pour le grand honneur qui m'est fait aujourd'hui par la Société Chimique Allemande, de faire entendre ma voix dans cette enceinte où les images de tant de savants illustres établissent en quelque manière une auréole de gloire, à cette place où tant de chimistes éminents sont venus apporter le résultat de leurs efforts.

Paul Sabatier
(1854-1941)
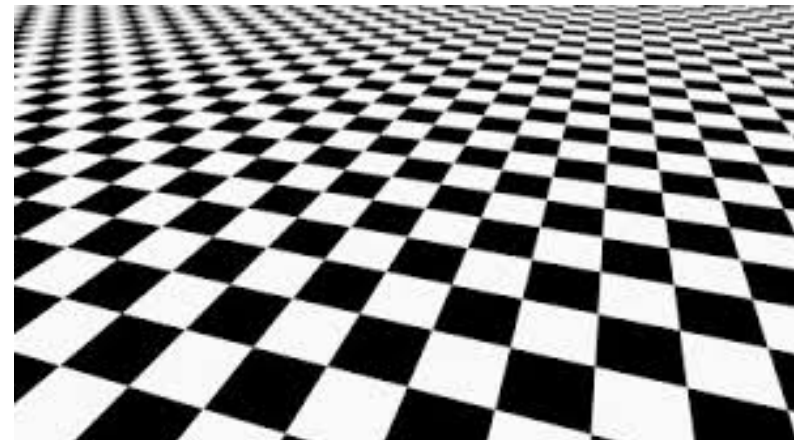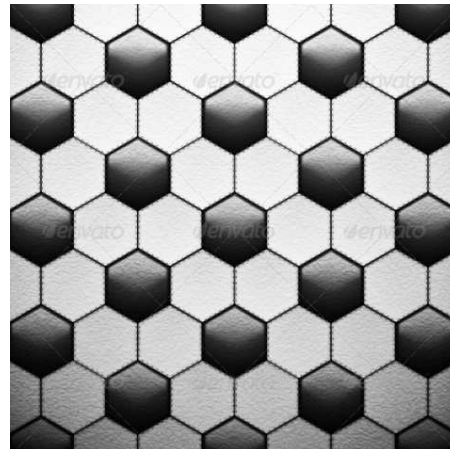
Imagination of a catalyst surface?
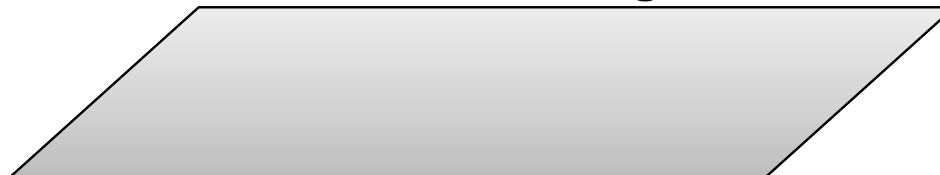
The catalyst surface is not uniform?

"**Most finely divided catalysts must have structures of great complexity. <…..> In general, we should look upon the surface as consisting of a checkerboard.**" (1922)
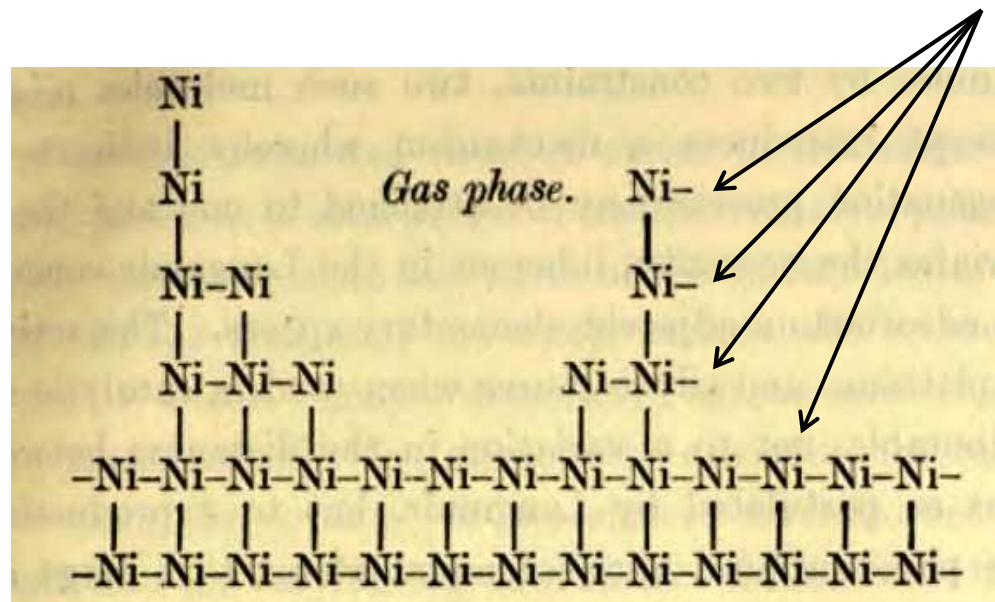
Irving Langmuir
(1881 –1957)

The concept of active sites

"A catalyzed chemical reaction is e.g. not catalyzed over the entire solid surface of the catalyst but only at certain 'active sites' or centers" (1925)
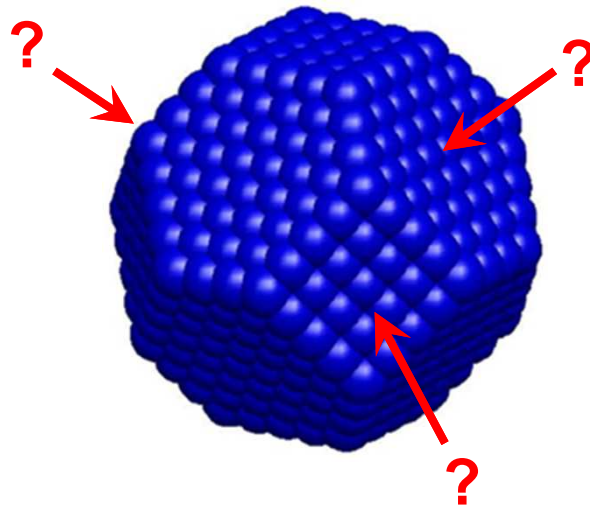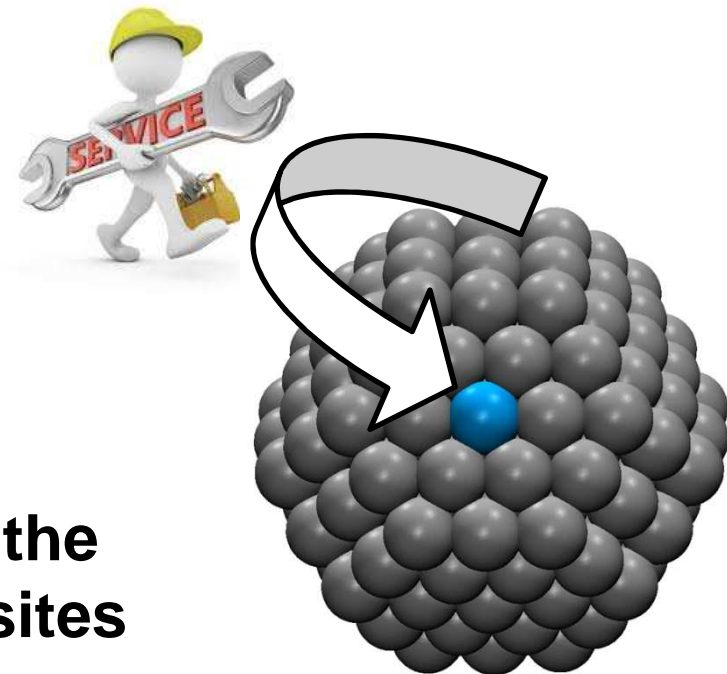

Hugh Stott Taylor
(1890-1974)

Namely the active sites at the surface should bind the intermediates "just right"

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Key initial procedures in (heterogeneous) electro-catalysis

Identification of the nature of the most active sites

Optimization of the electronic (adsorption) properties of those active sites
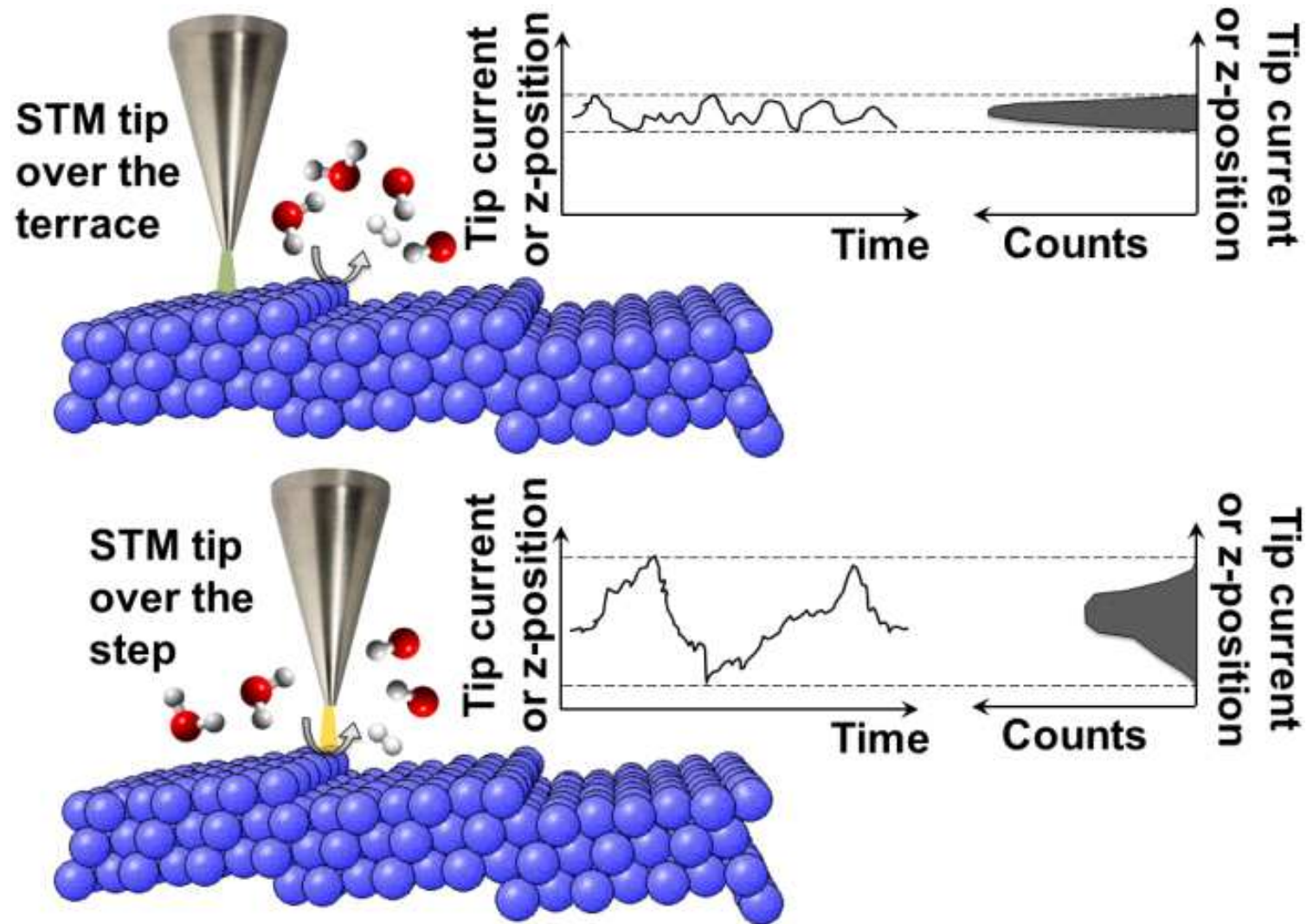
Maximisation of the density of those sites at the surface

A big problem in heterogeneous catalysis: the nature of active sites is known only for few reactions and only few types of materials
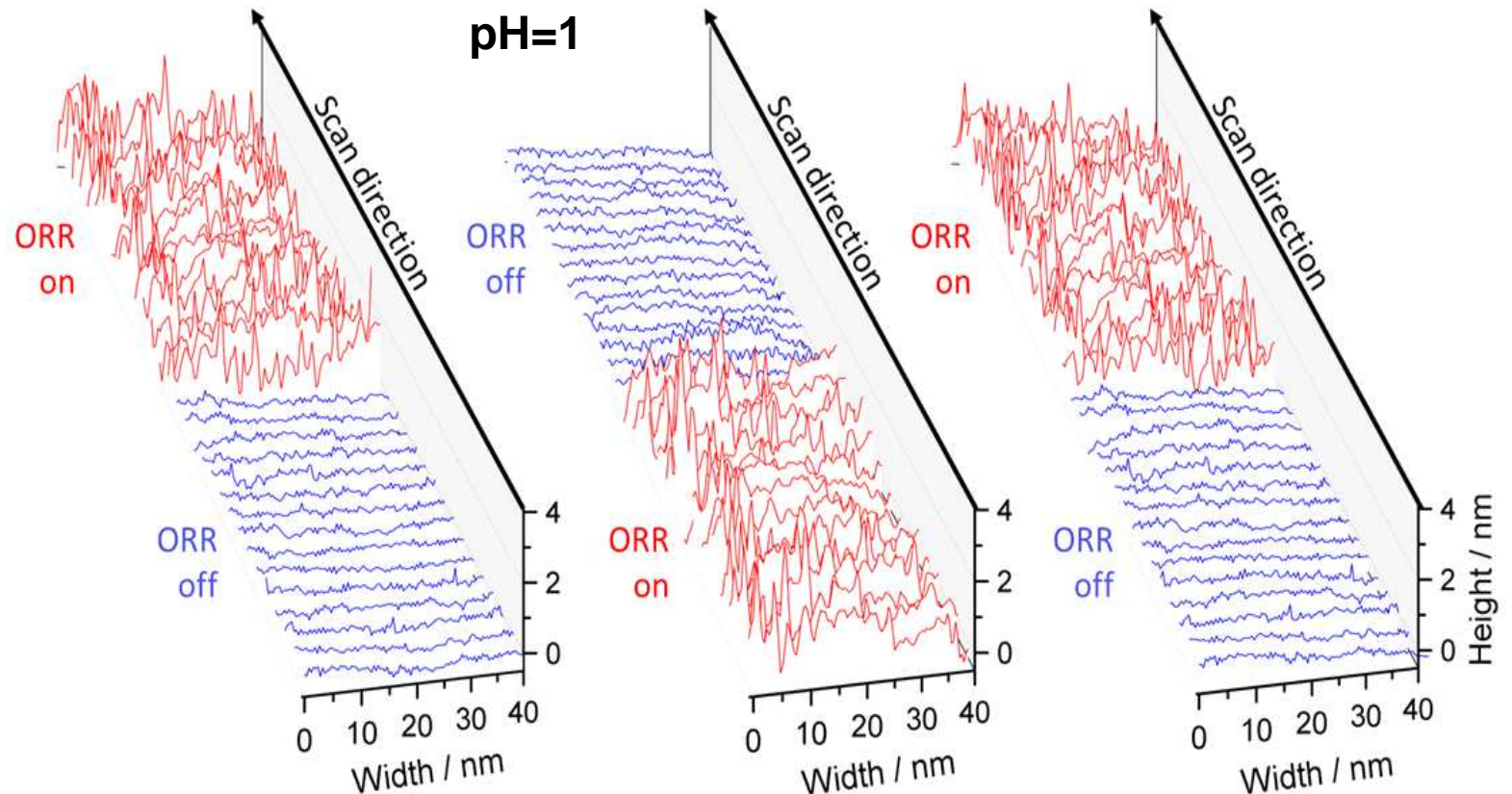

Heterogeneous Catalysis
How much do we know?

I. Chorkendorff, J. W. Niemantsverdriet, Concepts of Modern Catalysis and Kinetics

Identification of active sites using EC-STM?

J. Pfisterer, Y. Liang, O. Schneider, A.S. Bandarenka // **Nature** *549* (2017) 74
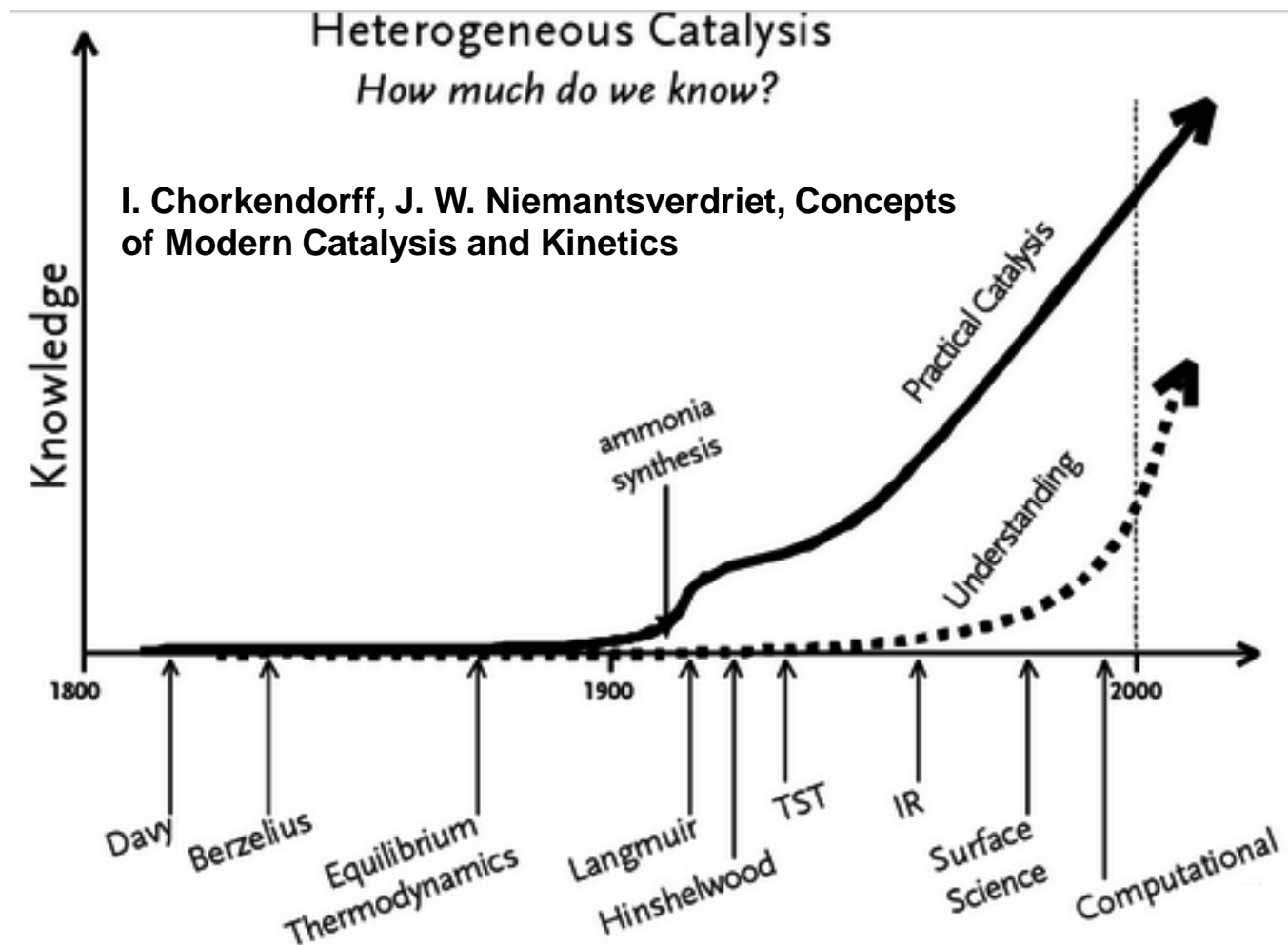
Identification of active sites using electrochemical STM?

Oxygen reduction reaction at a Pt(111) terrace

J. Pfisterer, Y. Liang, O. Schneider, A.S. Bandarenka // **Nature** *549* (2017) 74

Hydrogen evolution at a Pt(111) terrace

pH=1

J. Pfisterer, Y. Liang, O. Schneider, A.S. Bandarenka // **Nature** *549* (2017) 74
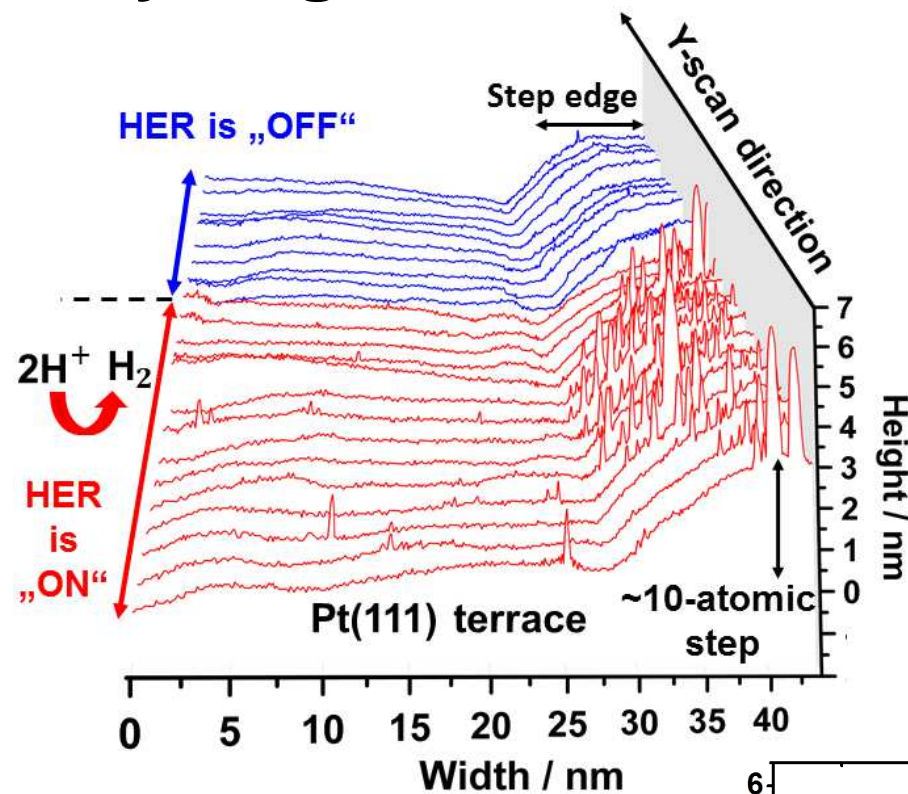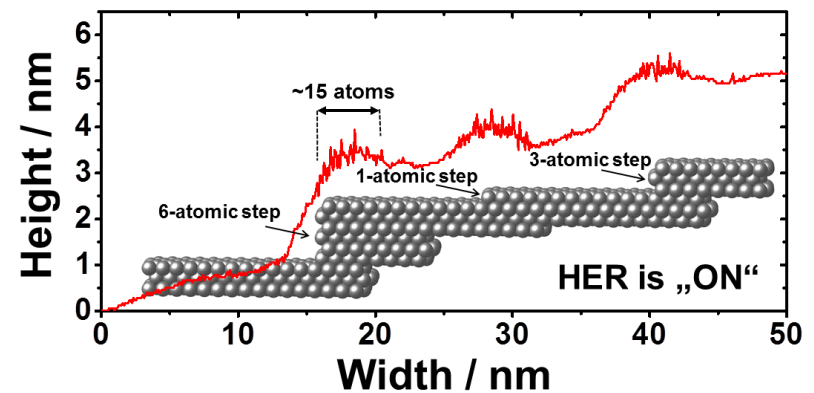
Oxygen reduction at a Pt(111)
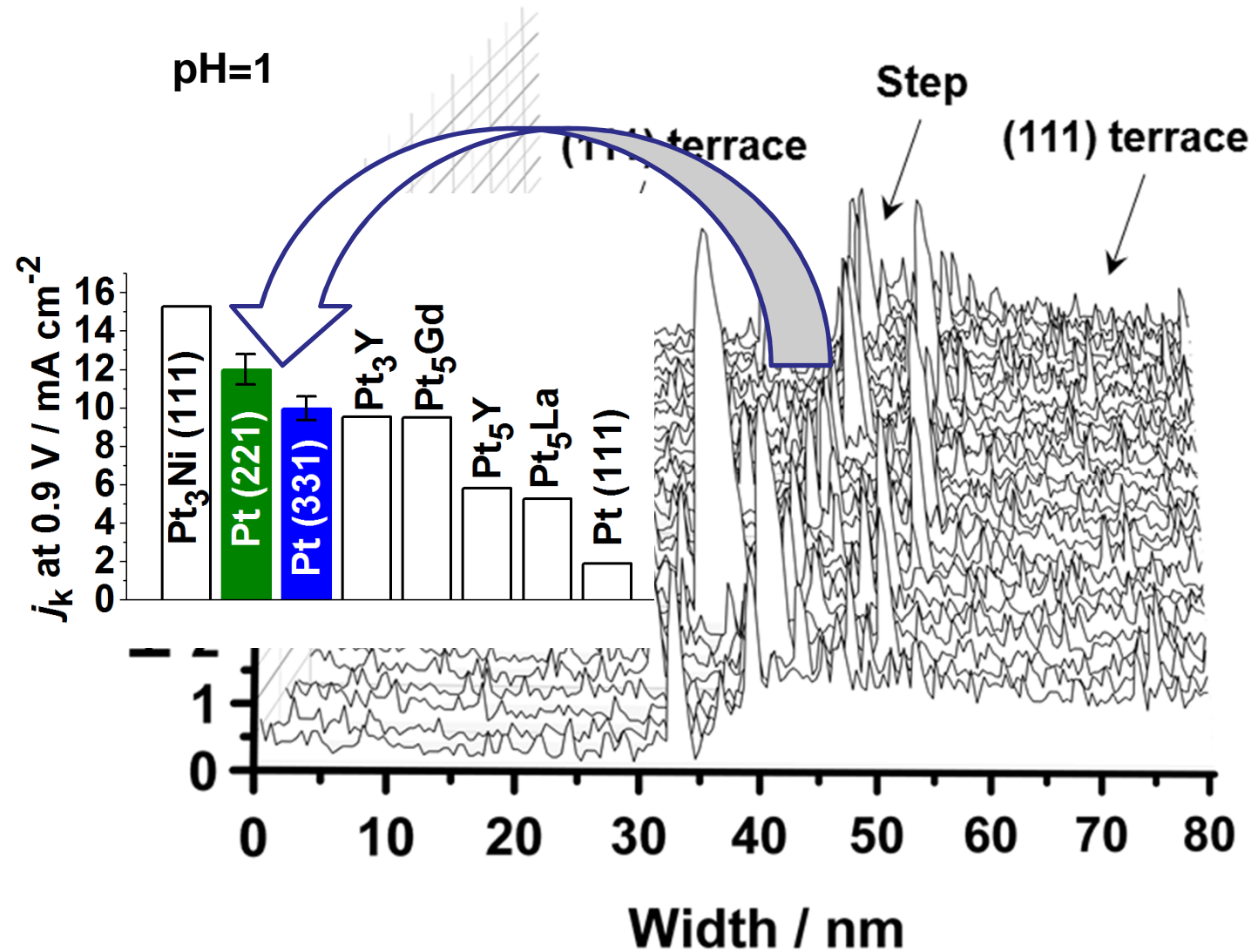
pH=1

J. Pfisterer, Y. Liang, O. Schneider, A.S. Bandarenka // **Nature** *549* (2017) 74

Hydrogen evolution at Au(111)/<u>Pd</u>(ML)

pH=1

J. Pfisterer, Y. Liang, O. Schneider, A.S. Bandarenka // **Nature** *549* (2017) 74

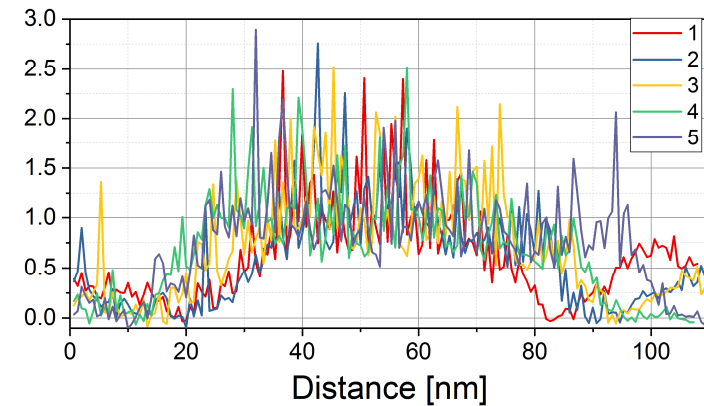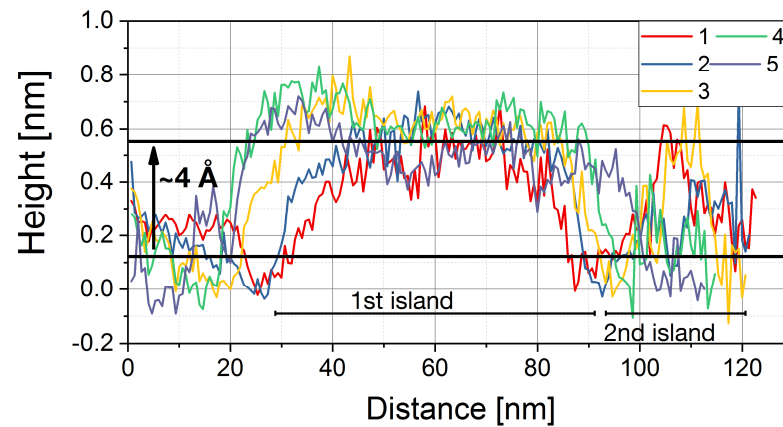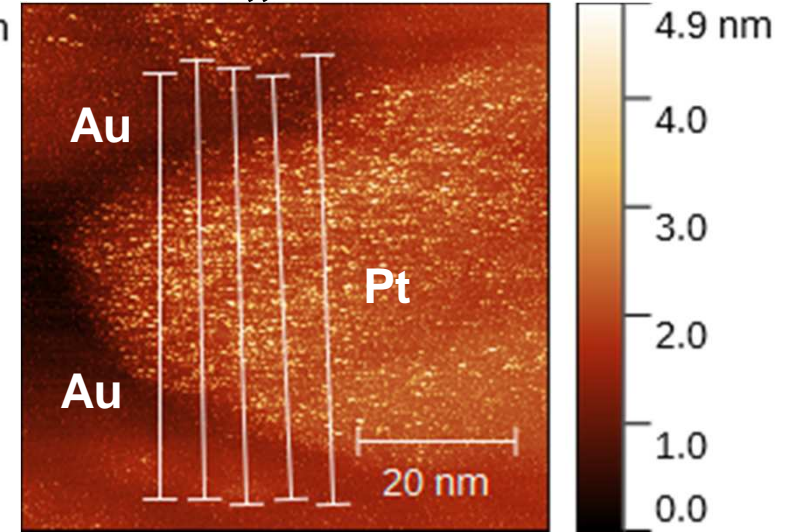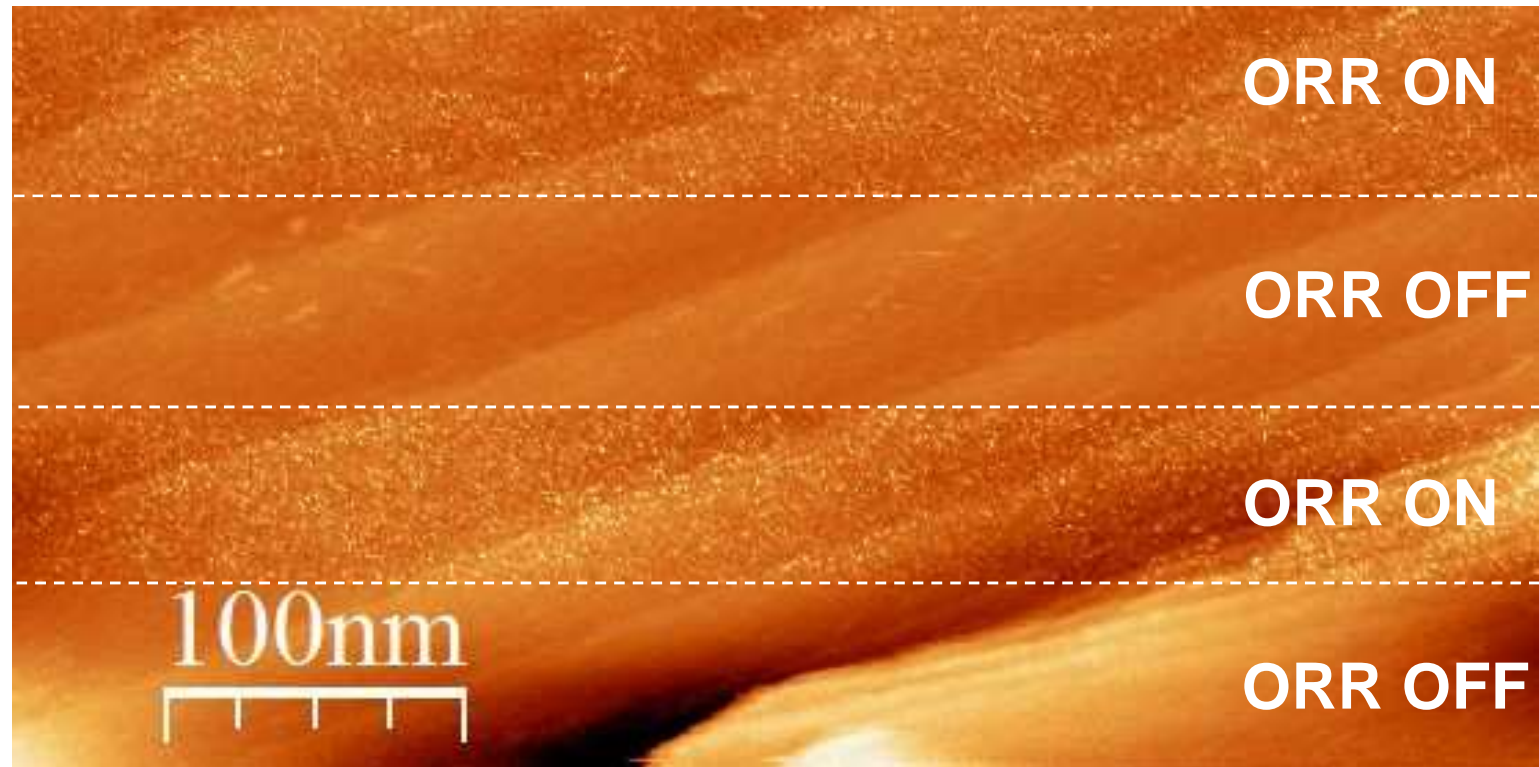# Hydrogen evolution at Au(111)/<u>Pt</u>(ML)

Y. Liang, C. Csoklich, A.S. Bandarenka // in preparation

Oxygen electroreduction at Pt(111) in 0.1M LiOH

Y. Liang, D. McLaughlin, A.S. Bandarenka // in preparation

Oxygen electroreduction at Pt(111) in 0.1M LiOH

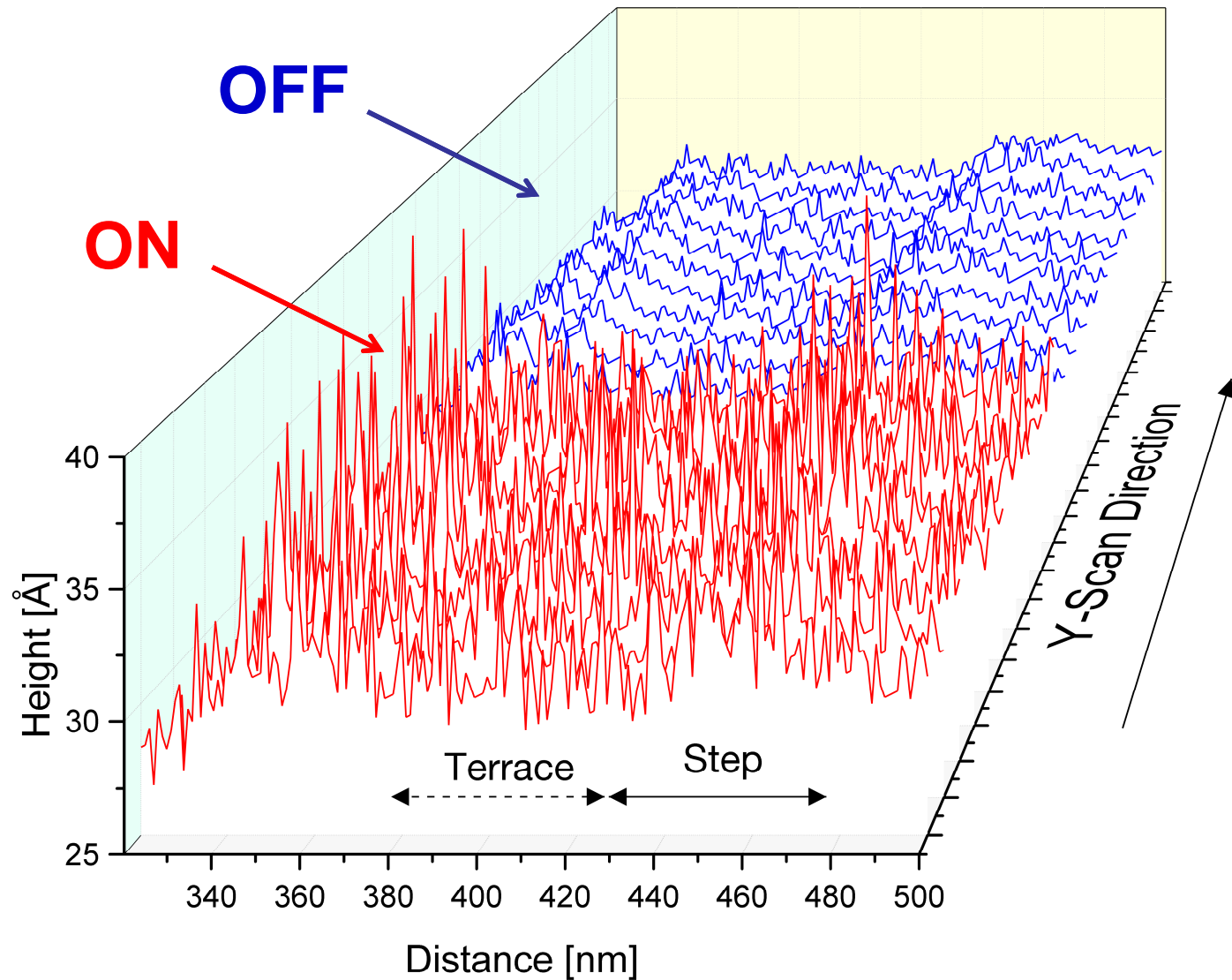Y. Liang, D. McLaughlin, A.S. Bandarenka // in preparation
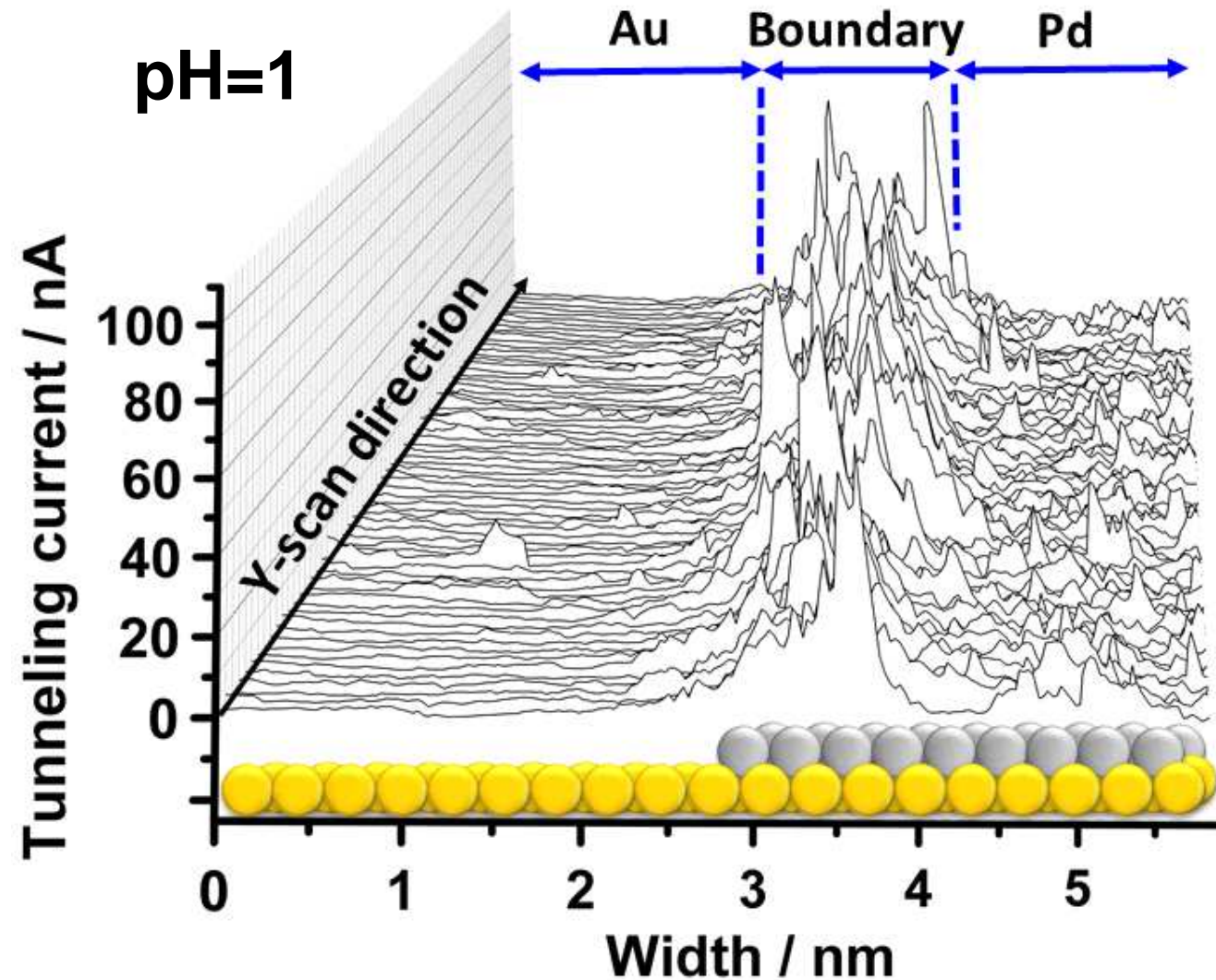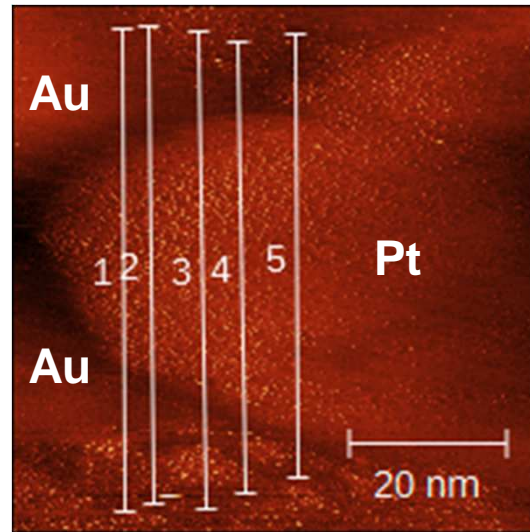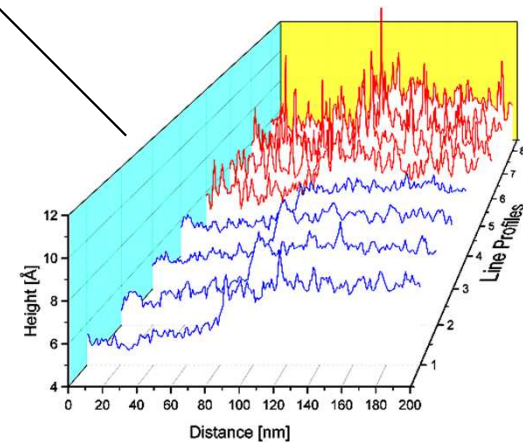
Oxygen electroreduction at Pt(111) in 0.1M LiOH
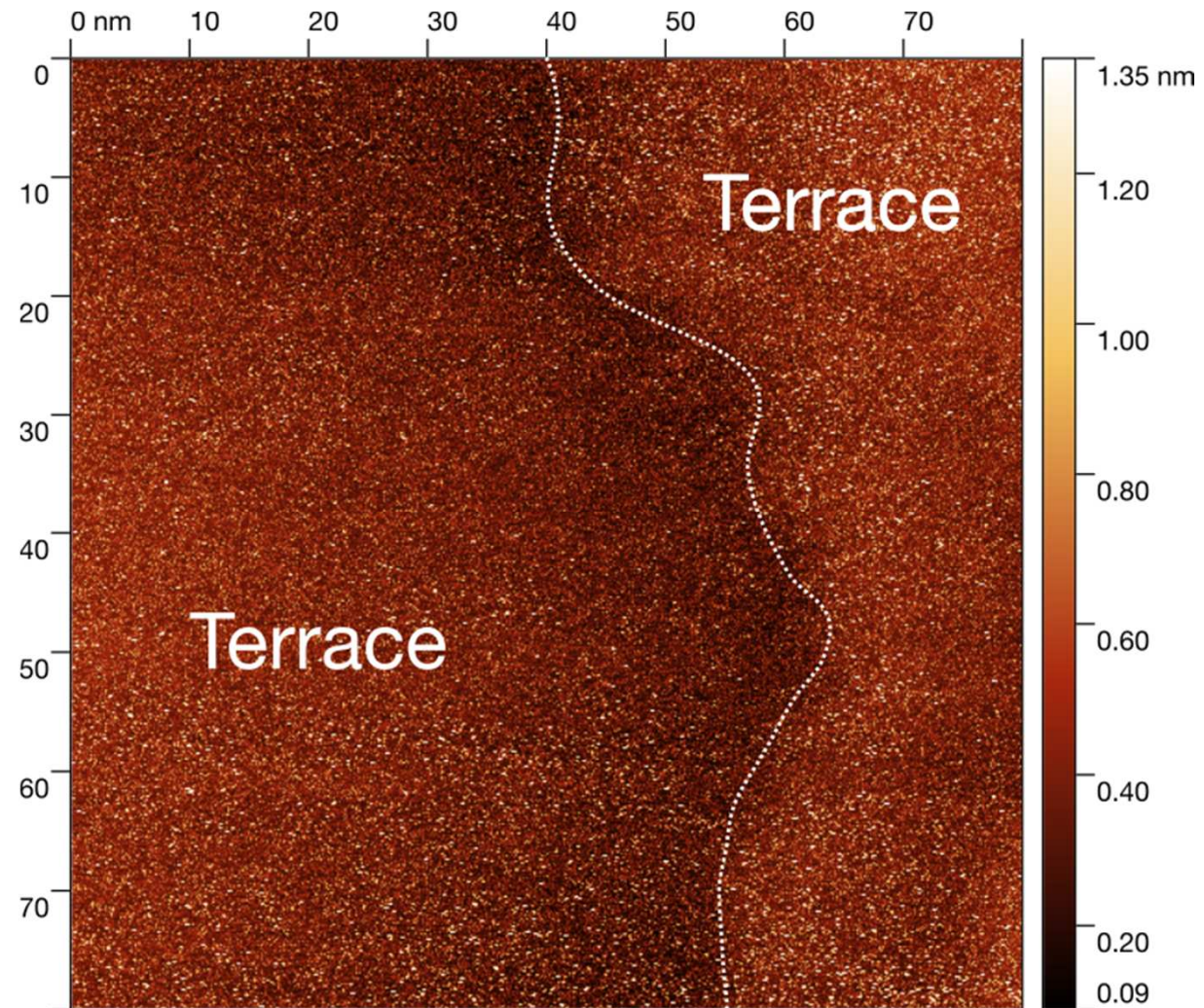
Oxygen electroreduction at Pt(111) in 0.1M KOH
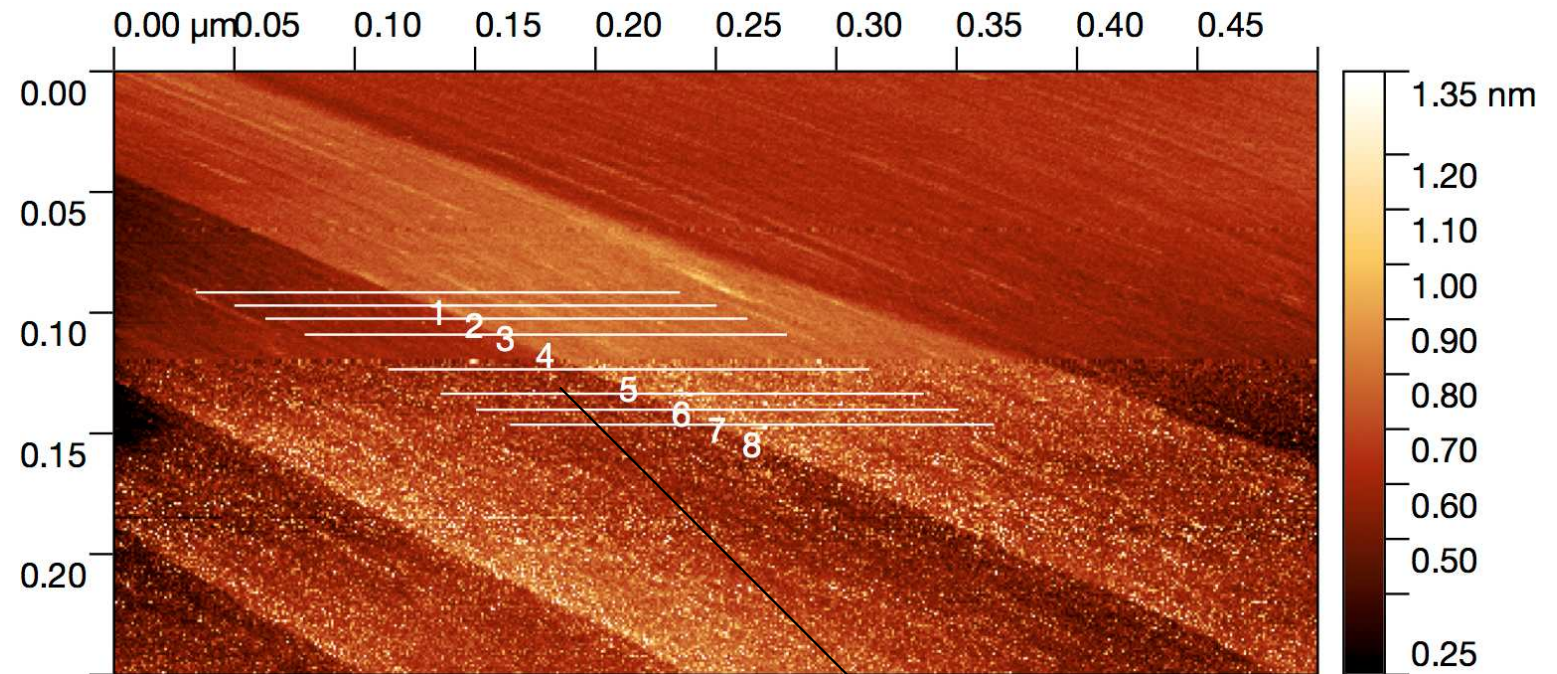
ORR ON

ORR OFF

ORR ON

16nm

Y. Liang, D. McLaughlin, A.S. Bandarenka // in preparation

Oxygen electroreduction at Pt(111) in 0.1M KOH

Y. Liang, D. McLaughlin, A.S. Bandarenka // in preparation
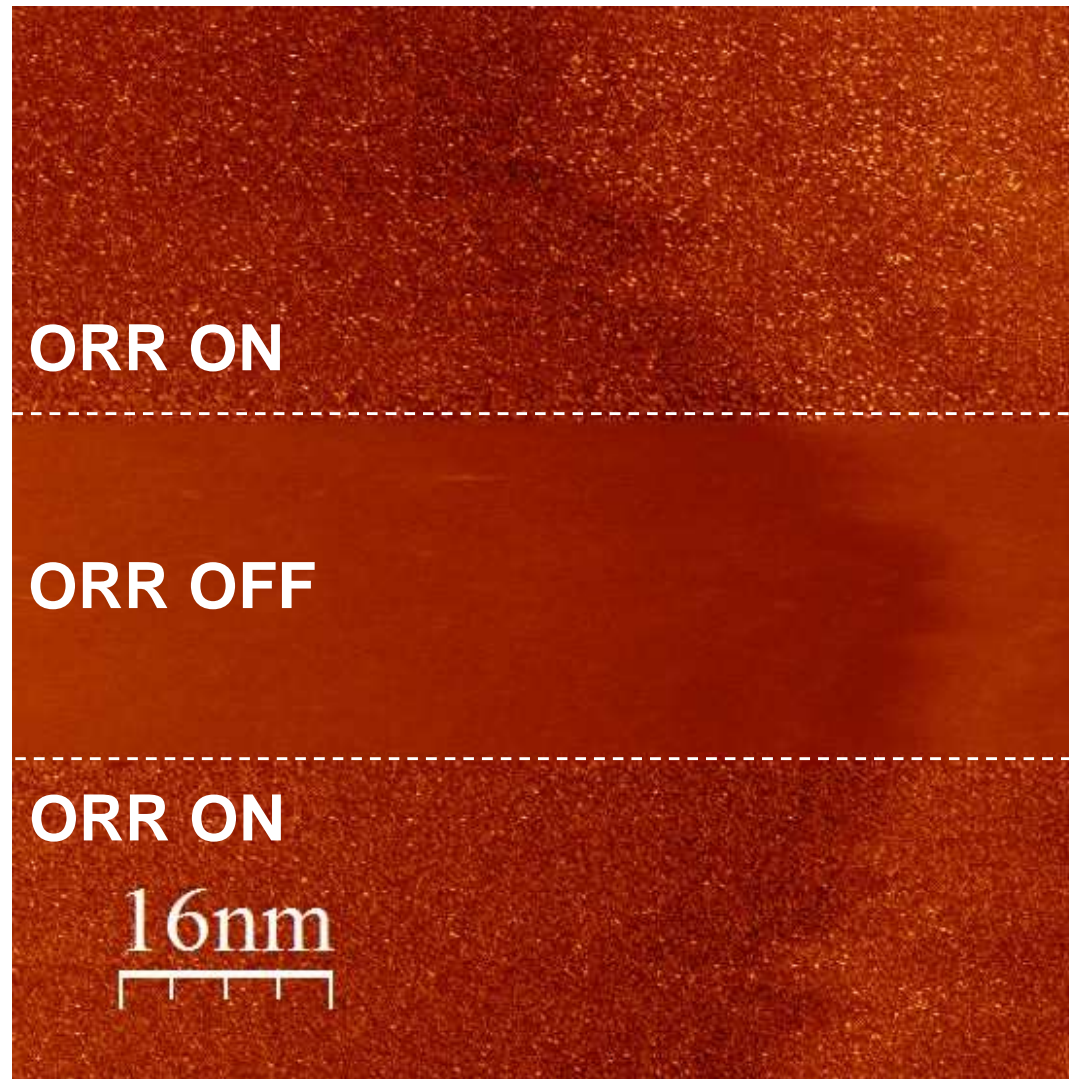
Oxygen electroreduction at Pt(111) in 0.1M CsOH
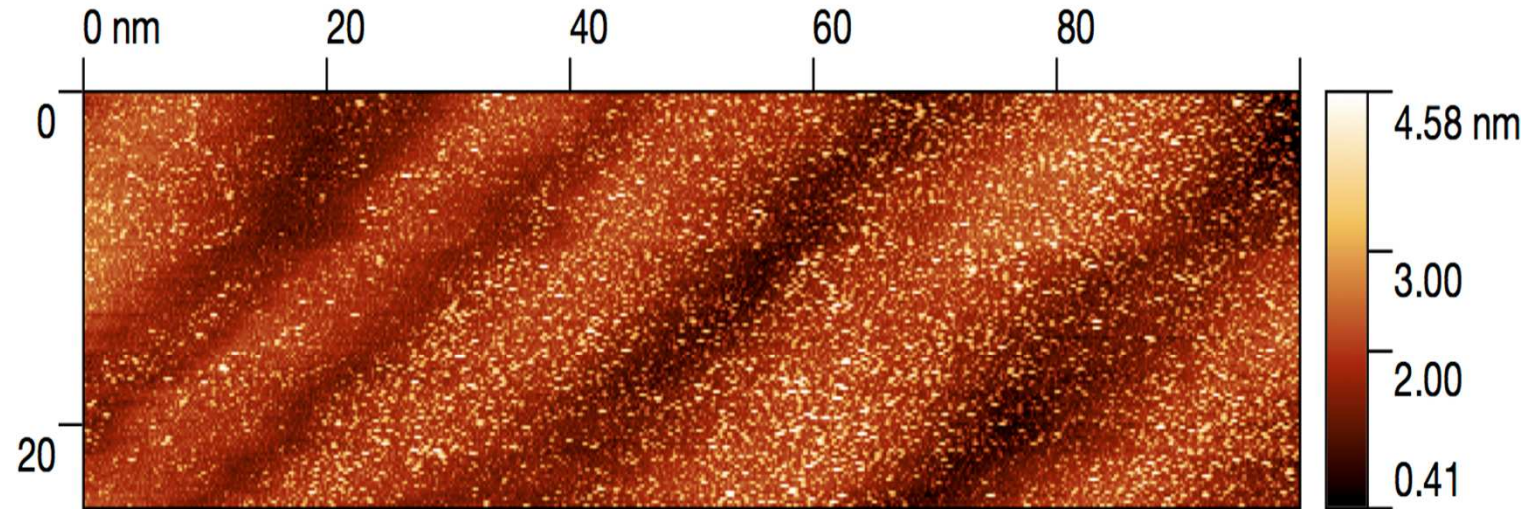
Compare with:
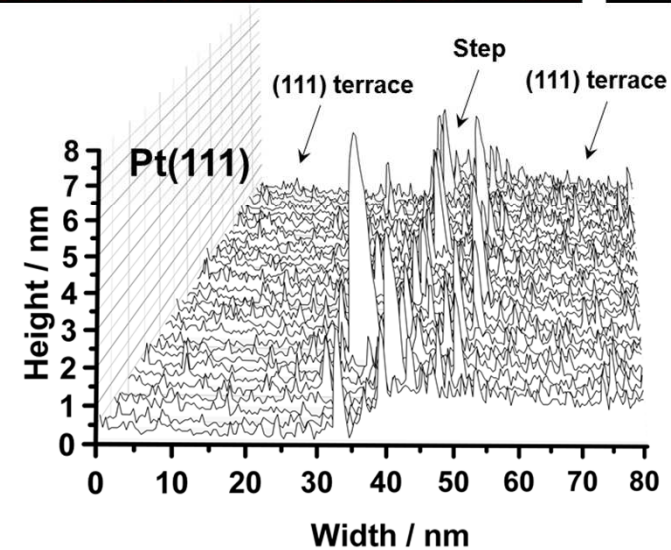
Forward *vs* inverse problems

We know the model   **We calculate the response**

Forward problem:

We measure the response

Inverse problem:

???

…

$y = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \ldots ???$
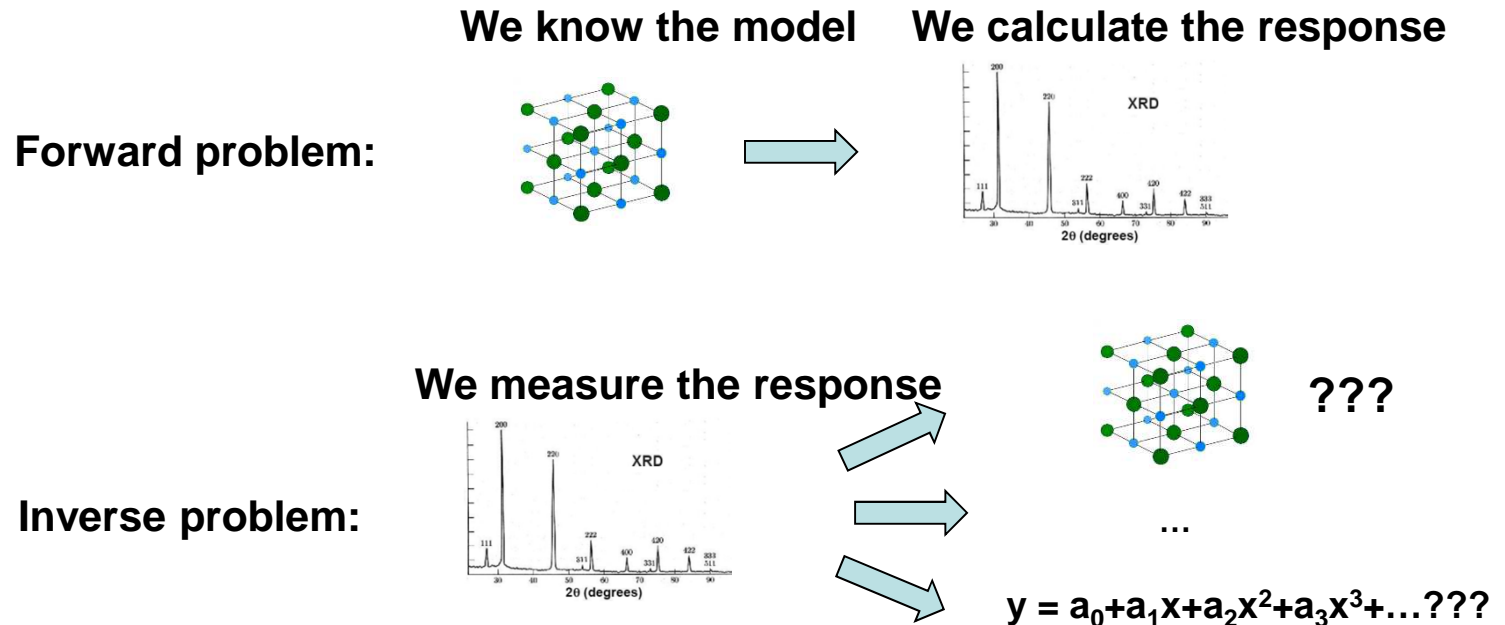
The inverse problem consists of using the actual result of some measurements to <u>infer the model</u> and <u>get the parameters</u> that characterize the system.

While the forward problem has (in deterministic physics) a unique solution, the inverse problem does not

<u>Learn more</u>*: Albert Tarantola*. Inverse problem theory and methods for model parameter estimation. Siam 2005, ISBN 0-89871-572-5

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Thank you for your attention!

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