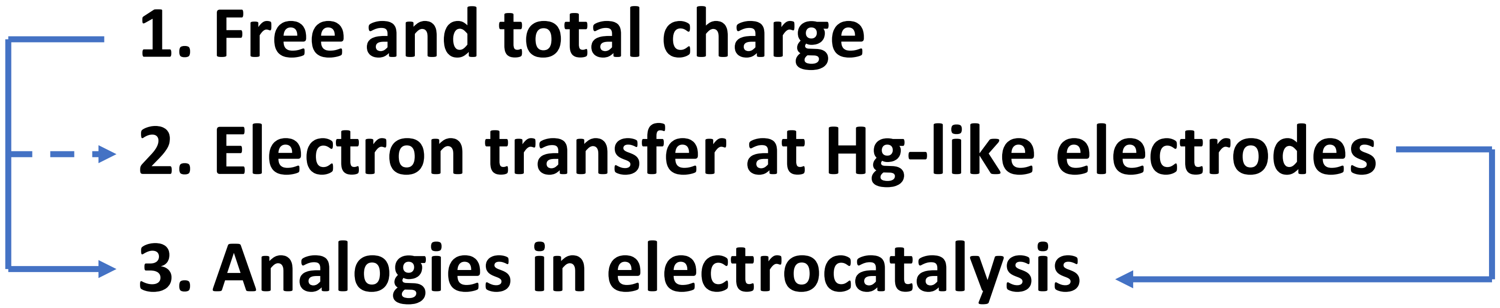
Charged interface and its effects on heterogeneous electron transfer: experimental information creating challenges and verification tools for theory



1. **Free and total charge**
2. **Electron transfer at Hg-like electrodes**
3. **Analogies in electrocatalysis**

General strategy of theory-experiment interaction (electrode kinetics):

- to minimize the uncertainty of interfacial zone **in the absence of any reactants**, if possible,
- to imagine/hypothesize the **reactant location and surrounding** at molecular level,
- to understand **what factors** (*always more than one*) can affect reaction zone/rate,
- to arrange some series of experiments under conditions corresponding to **predominating roles of single factors**,
- to formulate **agreements/disagreements** with theoretical predictions, involving computational tools to estimate unknown parameters, if necessary.

Galina A. Tsirlina

CENN Nanocenter, Ljubljana, Slovenia

Galina.Tsirlina@nanocenter.si

1. Free and total charge

- **Thermodynamics of perfectly polarizable electrodes, experimental challenges**
- **Free charge vs. potential dependencies at various pH, the data for dispersed platinum group metals** <*for kinetics, we need these dependences, not only pzc!*>
- **Displacement and maximum entropy strategies, the uncertainty increasing with pH**
- **Available data on adsorption of ions on noble metals**
- **Still scarce knowledge for copper and nickel**

***Key issue*: free charge inversion**

Galina A. Tsirlina

CENN Nanocenter, Ljubljana, Slovenia

Galina.Tsirlina@nanocenter.si

Thermodynamics of perfectly polarizable electrode is a field **pioneered by A.N. Frumkin.** Naturally grown from electrocapillarity research, it was extended in 1960-70s with participation of **O.A. Petrii** and **B.B. Damaskin**. Later contributions of **M. Weaver, J.M. Feliu + Alicante school, J. Lipkowski, A. Wieckowski**, **R.R. Adzic, N.M. Markovic**, **G. Horanyi** are extremely important for the area.

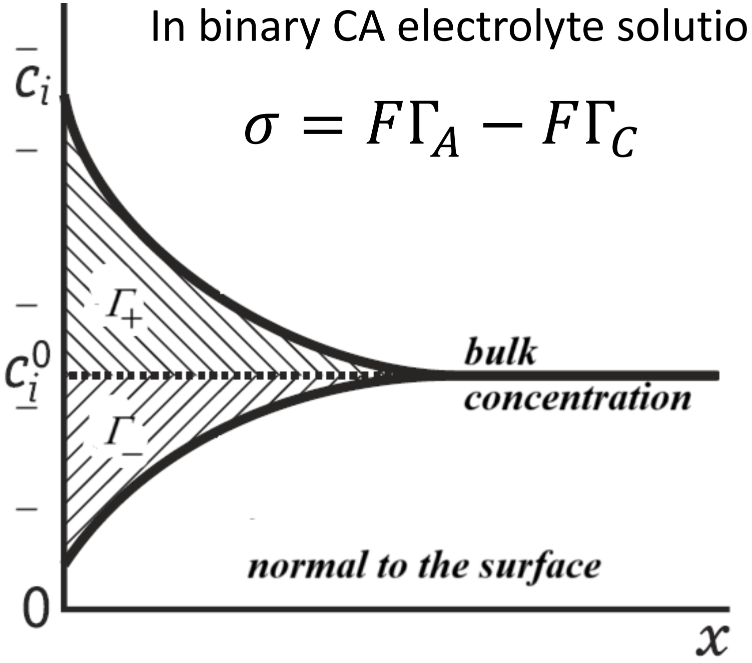
Ideally polarizable electrode (no adsorption with charge transfer): relationships between charge σ, Gibbs adsorptions Γ, surface tension γ, and electrode potential E (μ is chemical potential)

To create a new surface unit at constant system composition, one needs to add (1) charge and (2) *i*-th components.

S. Trasatti, E. Lust, in Modern Asp. Electrochem. 33 (**1999**) 1 – 216 <***916 Refs***>; E. Lust, in Bard's Enc. Electrochemistry (**2002**) 188-224; in Enc. Interfac. Electrochem (**2018**) 316-344

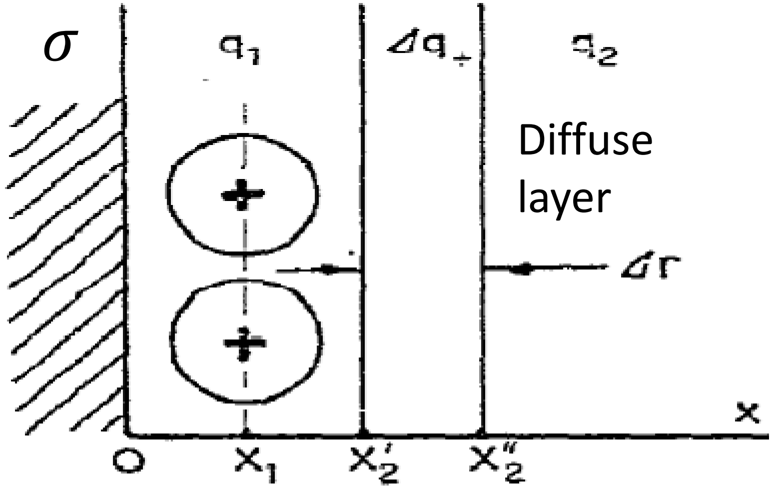
$$d\gamma = -\sigma dE - F\sum_i \Gamma_i d\mu_i$$

No problems with precise measurements of charge and Gibbs adsorptions of ions. This allowed to develop 'double layer' models addressing *both electrostatic and specific* adsorption. **To provide an example:**



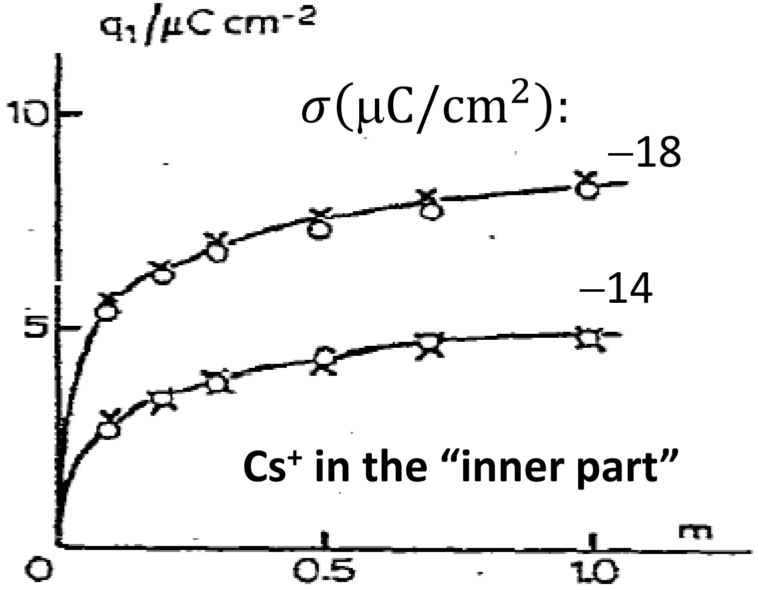
In binary CA electrolyte solution,

$$\sigma = F\Gamma_A - F\Gamma_C$$



Diffuse layer

mc CsCl + (1-m)c LiCl



$\sigma(\mu C/cm^2)$:

−18

−14

Cs^+ in the "inner part"

B.B. Damaskin, J. Electroanal. Chem. 65 (**1975**) 799-814

Discreteness-of-charge treatment of specific adsorption mostly worked for anions.

Free charge σ, total charge Q, and Gibbs adsorptions Γ relationships for H adsorbing metals

(γ is surface tension, E is electrode potential, μ is chemical potential, and A is surface concentration)

To create a new surface unit at constant system composition, one can

(1) add Γ_{H^+} of H^+ and Γ_H of H, in this case *no electricity* is required, **OR**

(2) to add $(\Gamma_{H^+} + \Gamma_H)$ of **only one** of these components, and also electricity. E.g., **if we add only H^+**, we should add $-F\Gamma_H = Q$ ***total*** charge.

$H^+ + e \leftrightarrow H$

salt CA (j = C or A)

$\mu_C, \mu_A, \mu_H = \text{const:}$

$$d\gamma = -\Gamma_H d\mu_H - \Gamma_{H^+} d\mu_{H^+} - \sum_i \Gamma_i d\mu_i$$

$$dE = {d\mu_{H^+}}/{F} - {d\mu_H}/{F}$$

$$-\left(\frac{\partial \gamma}{\partial E}\right)_{\mu_H, \mu_j} = F\Gamma_{H^+} = \sigma + FA_{H^+}$$

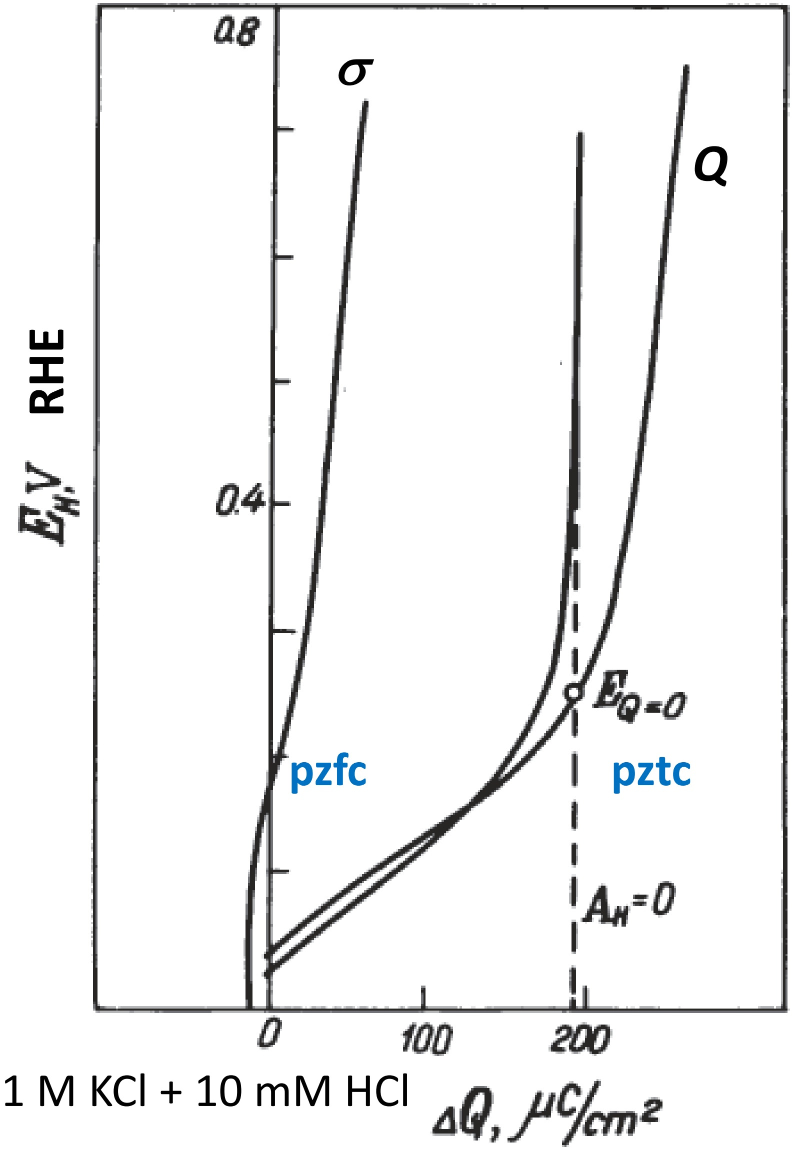
If [CA]>>[H^+], and A_{H^+} ~ 0, the value of Γ_{H^+} represents free charge. $\sigma = F\Gamma_A - F\Gamma_C$

Beyond-thermodynamic assumptions: no specific adsorption of H^+, no charge transfer from C^+ and A^-.

Isoelectric shifts of potential:

$$\left(\frac{\partial E}{\partial \mu_{H^+}}\right)_{Q,\mu_j} = -\left(\frac{\partial \Gamma_{H^+}}{\partial E}\right)_{\mu_{H^+},\mu_j} \left(\frac{\partial E}{\partial Q}\right)_{\mu_{H^+},\mu_j}$$

The slope of charging curves at fixed solution composition



1 M KCl + 10 mM HCl

A.N. Frumkin, O.A. Petrii, B.B. Damaskin, Compr. Treatise Electrochem. 1 (**1980**) 221-289

Experimental protocols of 1960-1970s:

0. Measure galvanostatic **equilibrium** charging curve Q, E.
1. Measure free charge by means of **solution analysis** for at least one potential.
2. Measure **isoelectric shifts** of potential: $\left(\dfrac{\partial E}{\partial \mu_{H^+}}\right)_{Q,\mu_j}$
3. Calculate the derivative $\left(\dfrac{\partial \Gamma_{H^+}}{\partial E}\right)_{\mu_{H^+},\mu_j}$
4. Integrate, using the value from point 1 as integration constant, to obtain σ, E.
5. Subtract, to determine pztc.

Initial protocol of 1930s:

A. Šlygin, A. Frumkin, W. Medwedowsky, Acta Physicochim. URSS 4 (**1936**) 911-928

0. Charging curve.
1. Solution analysis for various potentials.
2. Subtract, to determine pztc.

The most important early works

Collection of original Frumkin's articles: http://www.elch.chem.msu.ru/wp3/index.php/en/history-2/a-n-frumkin/collection_frumkin/

Notion of pzc and thermodynamic equations: A. Frumkin, A. Gorodetzkaja, *Z. phys. Chem.* 136 (**1928**) 451-472 <**Tl(Hg)!**>

The most complete early version of thermodynamic equations for Pt: A. Frumkin, A. Šlygin, Acta Physicochim. URSS 5 (**1936**) 819-840

Original data, partly republished later: A. Šlygin, A. Frumkin, W. Medwedowsky, Acta Physicochim. URSS 4 (**1936**) 911-928

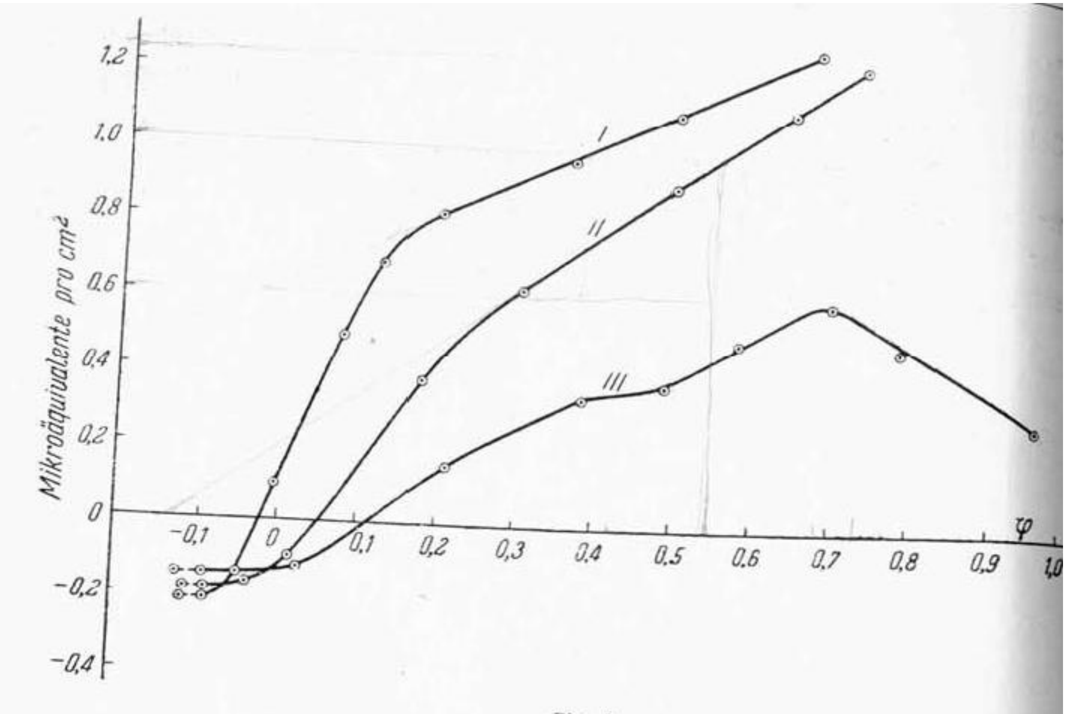


Fig. 2.
Adsorption an einer Platinelektrode in angesäuerten Salzlösungen.
I—norm. NaBr+0,01 HBr; II—norm. NaCl+0,01 norm. HCl; III—norm. Na_2SO_4+0,01 norm. H_2SO_4.

A.N. Frumkin, O.A. Petrii, B.B. Damaskin, Compr. Treatise Electrochem. 1 (**1980**) 221-289

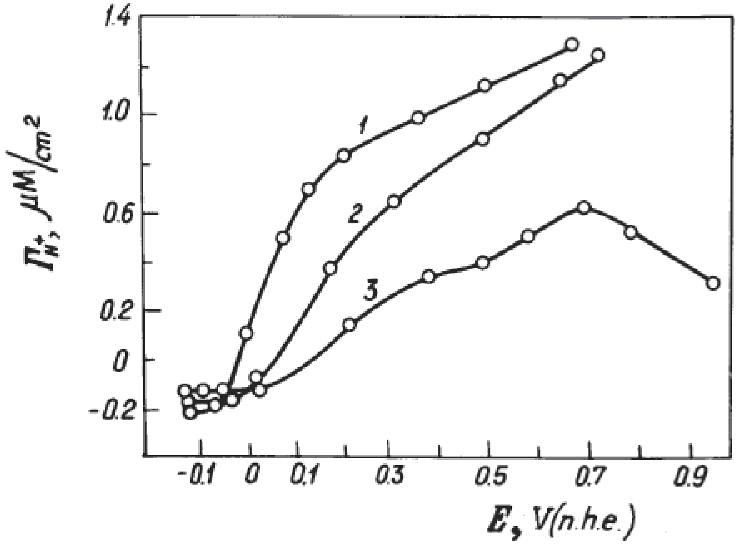


Figure 4. Dependence of Γ_{H^+} on potential on a Pt/Pt electrode in acidified solutions of salts. Initial composition of solutions: 1, 1 *M* NaBr + 0.01 *M* HBr; 2, 1 *M* NaCl + 0.01 *M* HCl; 3, 0.5 *M* Na_2SO_4 + 0.005 *M* H_2SO_4.[25]

Direct determination of free charge and/or Gibbs adsorption

~ 10^{15} atoms/cm^2

~ 10^{-9} mole/cm^2 in the monolayer

Consider 10 mL of solution:
its concentration can increase by **0.1 μM if monolayer is completely desorbed** from 1 cm^2;
by already **1 mM** for desorption from 1 m^2.

Smaller volumes (few mL) and/or higher areas (few m^2) are required to quantify adsorption using titration, conductivity, etc.

Porous electrodes (roughness factors 100…1000): PGM; Cu, Au?

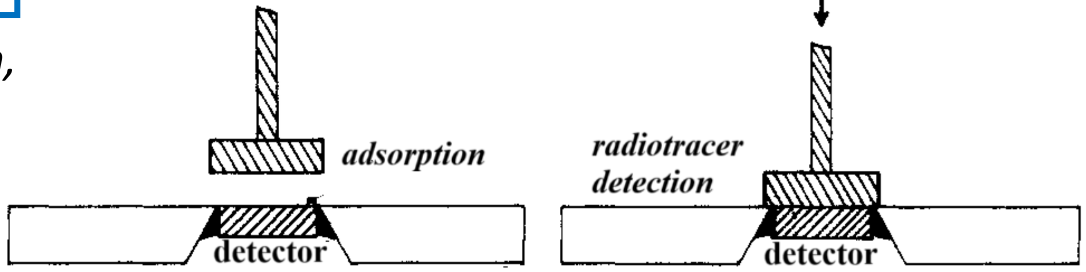
Titration-based and other "thermodynamic" techniques requiring high surface area. Mostly Frumkin school.

Low acid or alkali concentration, as compared to salt concentration; beyond-thermodynamic assumptions

$$\sigma = F\Gamma_A - F\Gamma_C$$

Smooth electrodes, incl. single crystals

E.K. Krauskopf, K. Chan, **A. Wieckowski**, J. Phys. Chem. 91 (**1987**) 2327-2332



Radiotracer techniques (higher sensitivity). **Horanyi; Sobkowski… Zelenay; Balashova-Kazarinov**

Not too high concentrations, a limited availability of suitable isotopes, no possibility to measure negative adsorption.

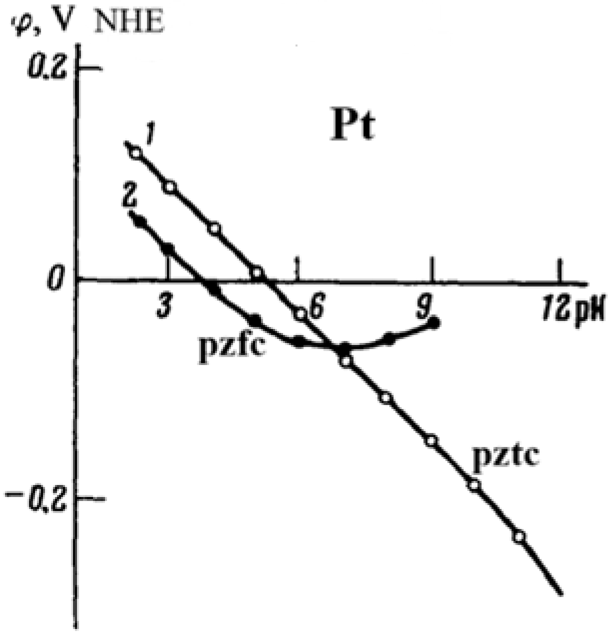
Slow equilibration *is a problem of both approaches, it is typical for oxygen adsorption regions.*

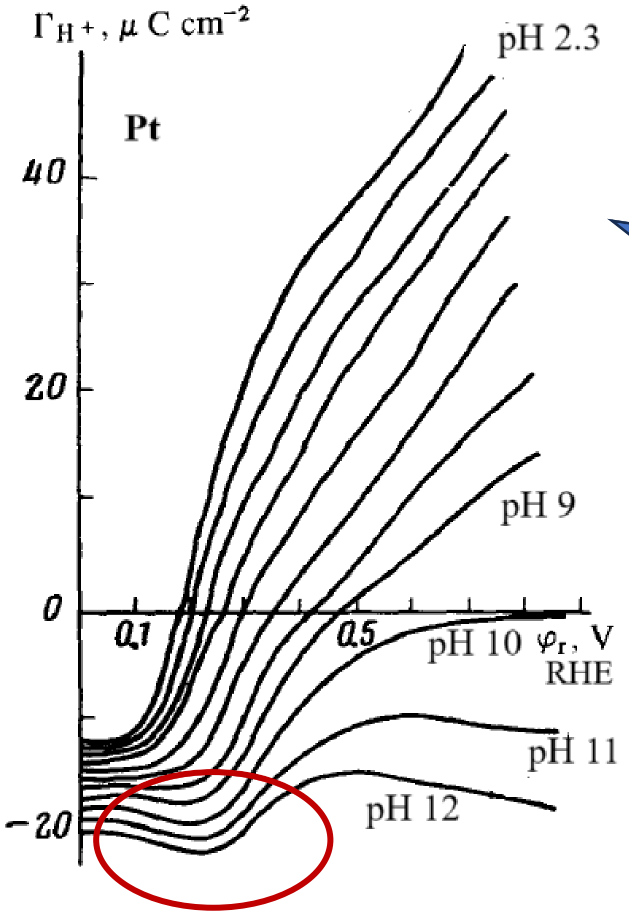
pH dependence of the free electrode charge: no pzfc (σ=0) in alkaline solutions

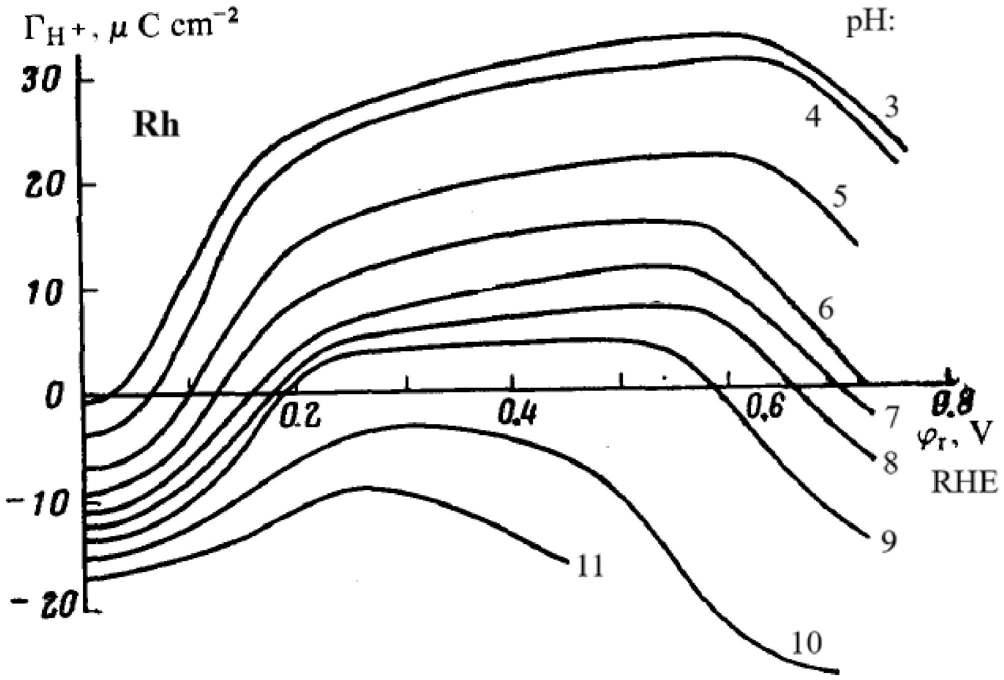
0.1 M KCl

Partial charge transfer from chloride, violation of one assumption.

Note in respect to ORR: ~ - 20 μC cm^{-2} at ~0.85 V RHE in alkaline solution? Does chloride affect the value?



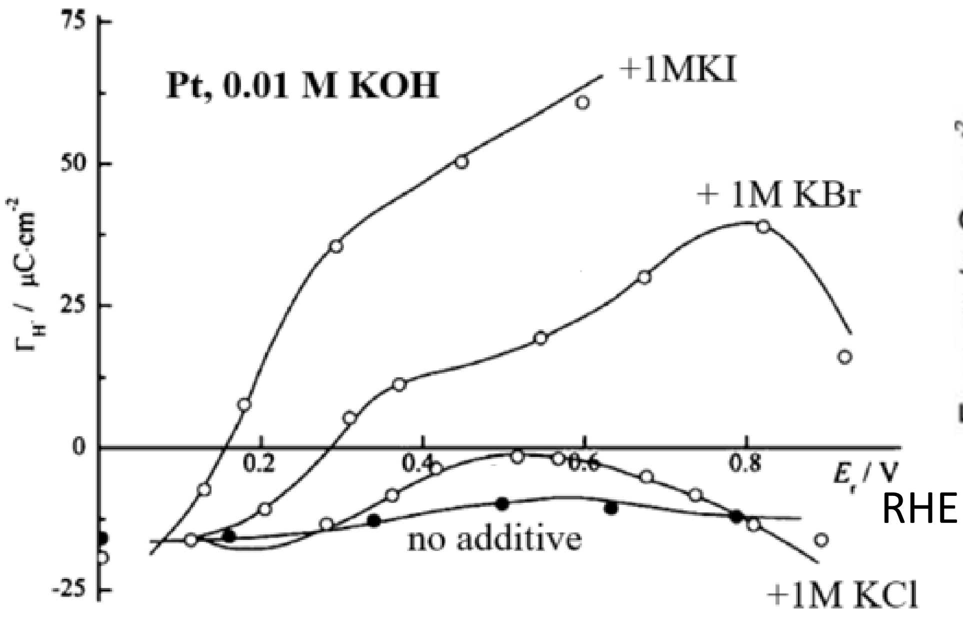




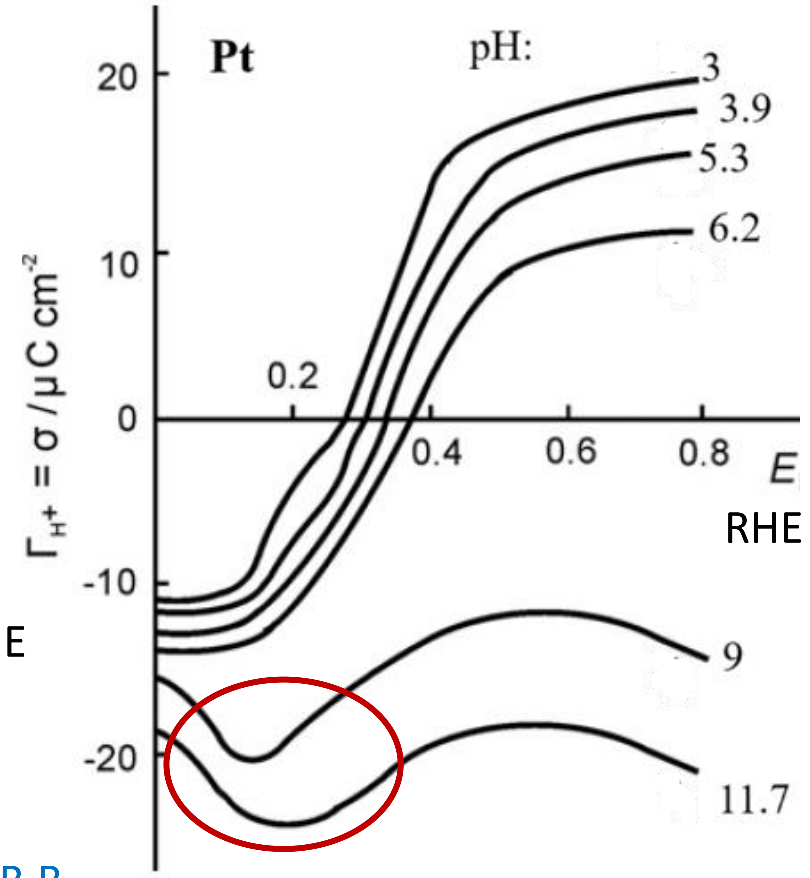
Available in English: A.N. Frumkin, O.A. Petrii, B.B. Damaskin, Compr. Treatise Electrochem. 1 (**1980**) 221-289; O.A. Petrii, Rus. Chem. Rev. 44 (**1975**) 973-981; G.A. Tsirlina, in Modern Asp. Electrochem. 51 (**2011**) 107-158

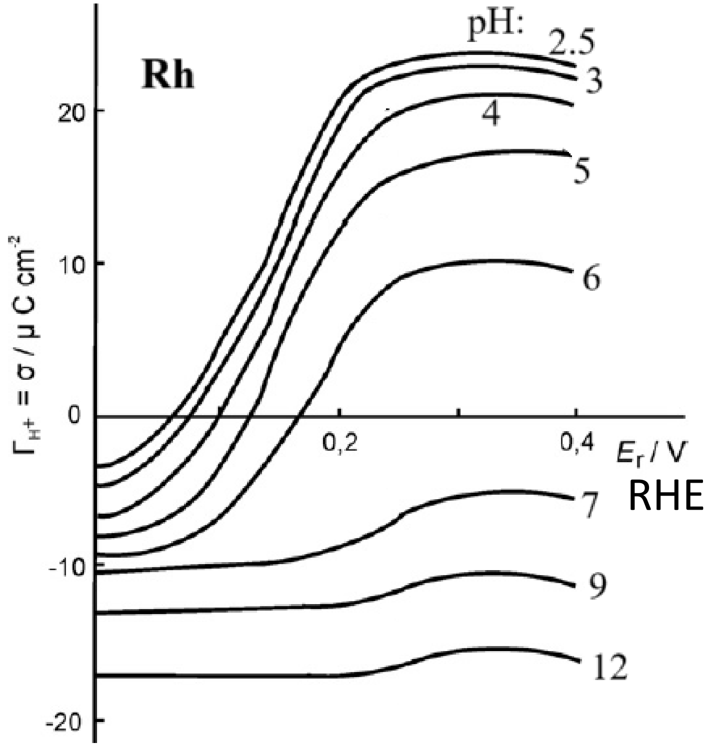
Free electrode charge: **no pzfc** **at high pH, free charge plateau and sometimes maximum at low pH** (*sulfate solutions are better matched to assumptions*)

Note in respect to ORR: ~ – 20 μC cm^{-2} at ~0.8 V RHE in alkaline, and + 20 μC cm^{-2} in acidic solutions.



0.05 M Na_2SO_4

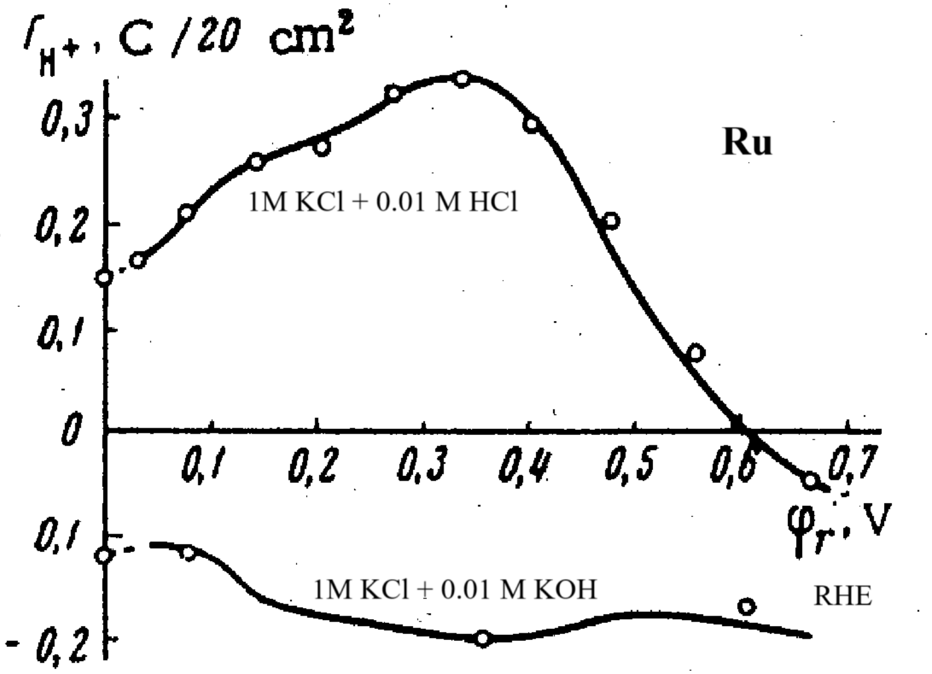


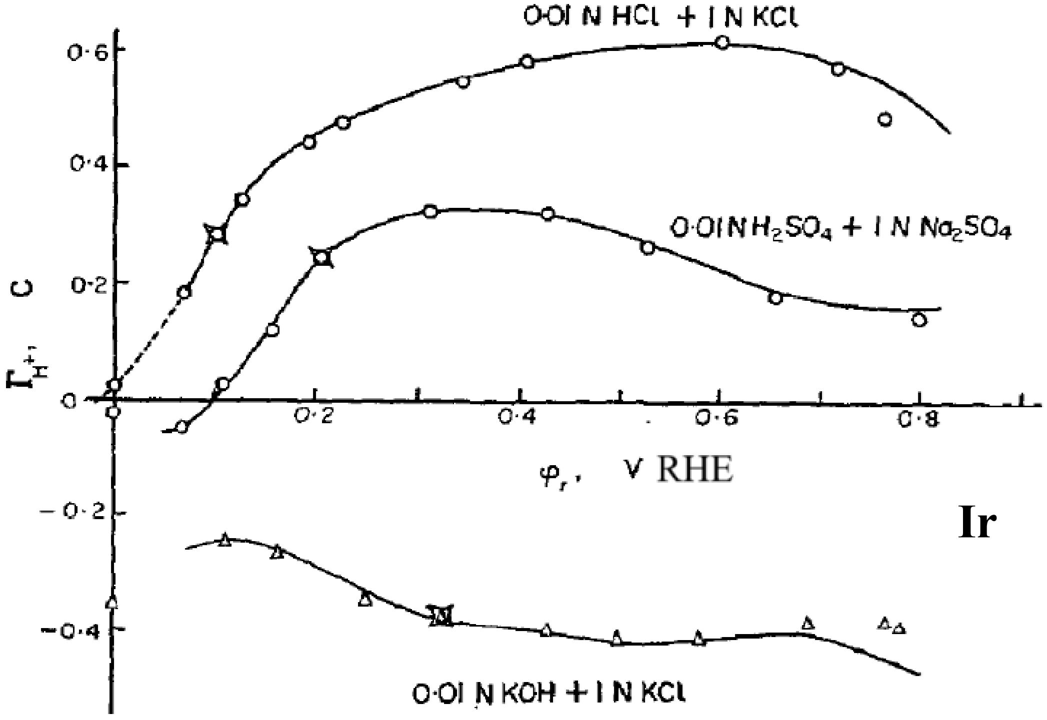


Available in English: A.N. Frumkin, O.A. Petrii, B.B. Damaskin, Compr. Treatise Electrochem. 1 (**1980**) 221-289; B.B. Damaskin, O.A. Petrii, J. Solid State Electrochem. 15 (**2011**) 1317–1334

Strongly delayed publication: O.A. Petrii, T.Ya. Safonova, J. Electroanal. Chem. 688 (**2013**) 336–348

Free electrode charge of Ru and Ir (no data on the real surface area)





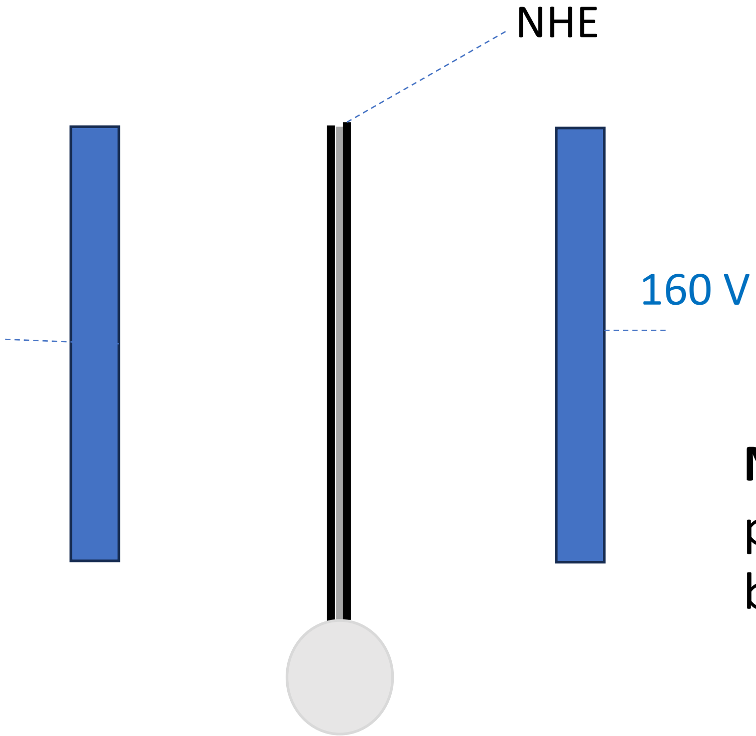
Pt-Ru in acid behaves similar to Pt, not to Ru

A.N. Frumkin, O.A. Petry, Electrochim. Acta 15 (**1970**) 391-403

A. Frumkin, O. Petry, A. Kossaya, V. Entina, V. Topolev, J. Electroanal. Chem. 16 (**1968**) 175-191;
V.S. Entina, O.A. Petrii, Sov. Electrochem. 4 (**1968**) 457-461

Inversion of the sign of free charge in alkaline solutions is a general phenomenon. Will it always happen in acidic solutions at higher potentials?

Inverse pzfc was confirmed by electrokinetic data (deviation of Pt wire in electric field, observed using optical microscope)

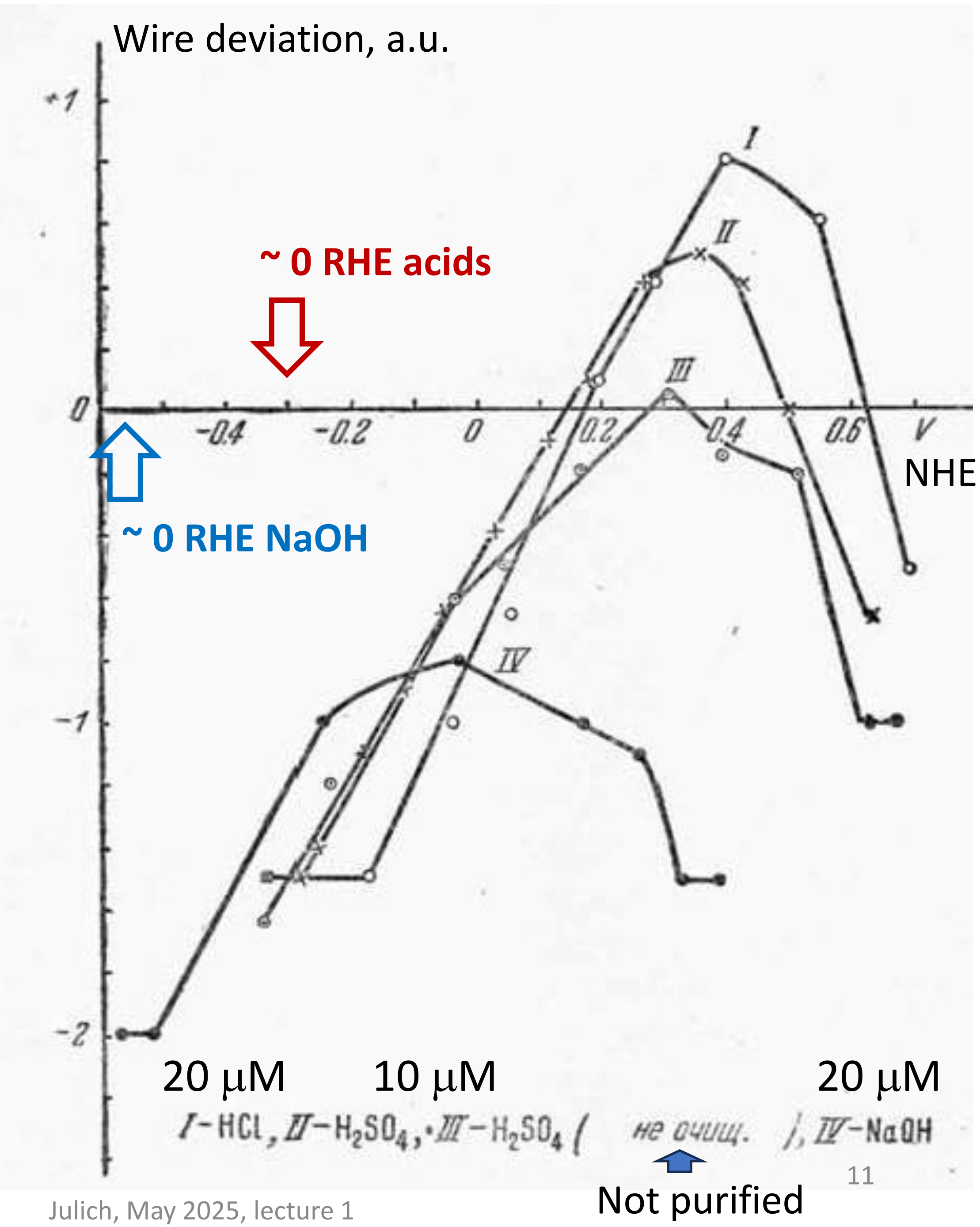


No Pt polarization: potential is shifted by bubbling H_2 or N_2+O_2

Initial wire diameter 20 μm, ca. 50 μm after platinization.

Limitation: solution should be highly diluted.

N.A. Balashova, A.N. Frumkin, Doklady AN SSSR 20 (**1938**) 449-452

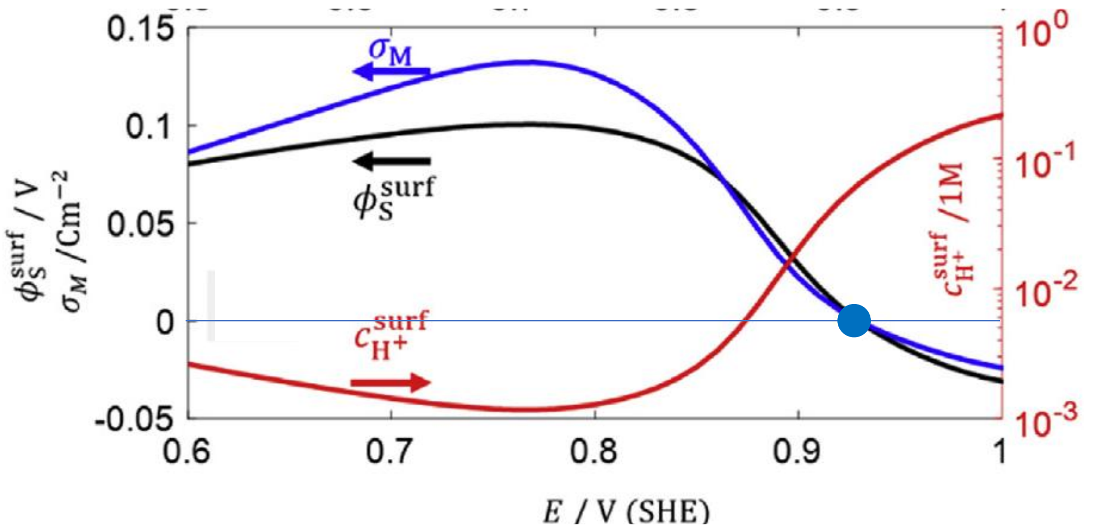


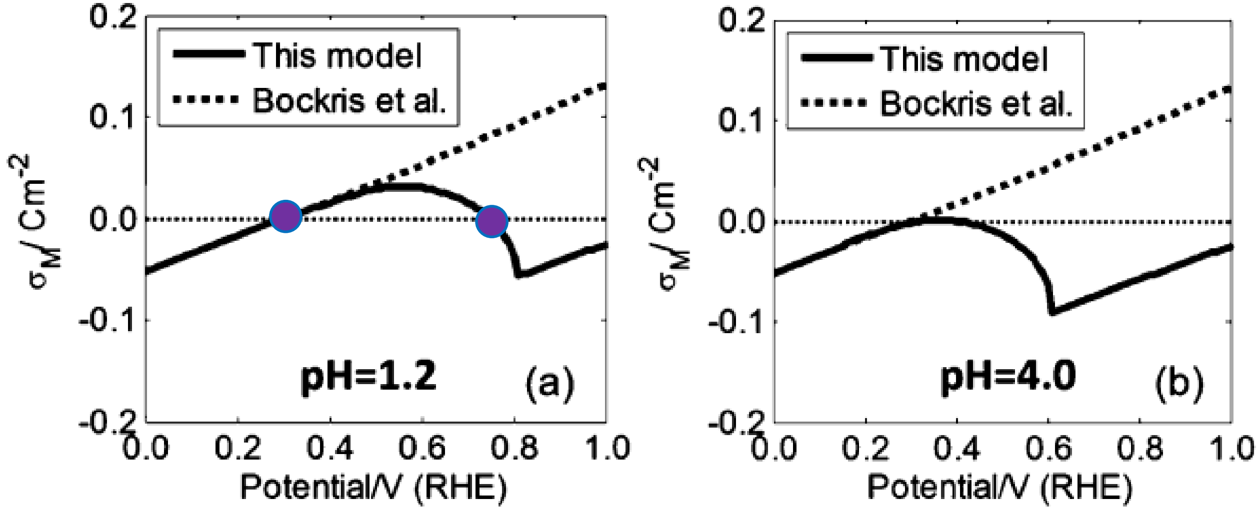
Comparison with recent modeling

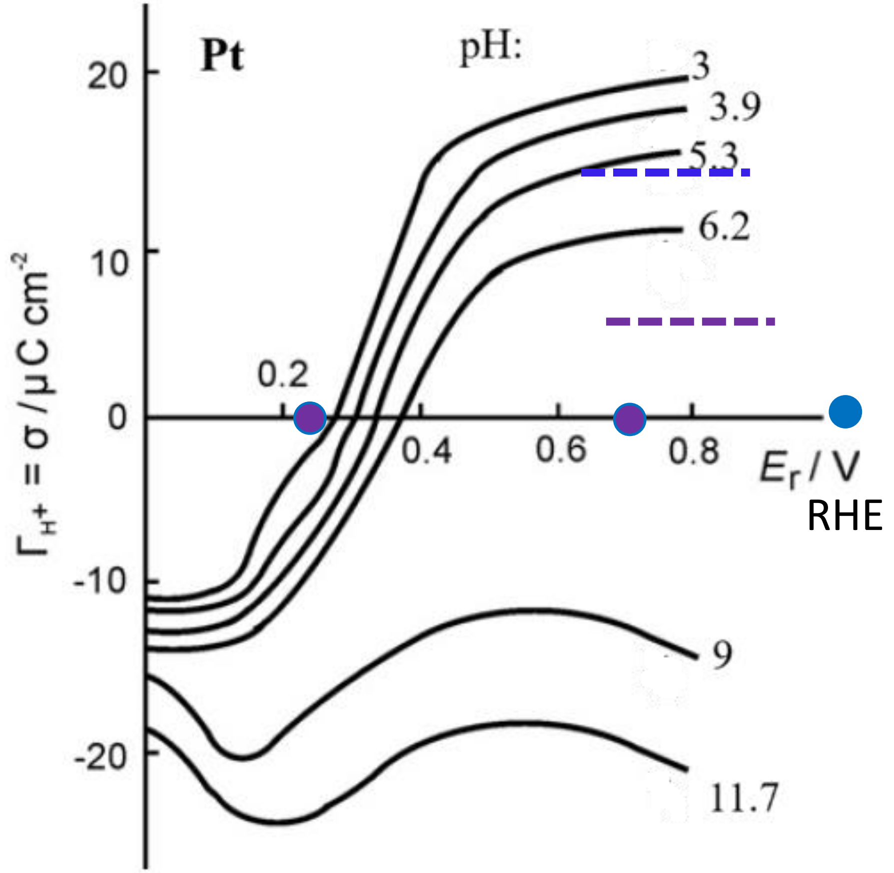
pH 1.2, Pt(111), parametrization is based on ORR kinetic data, XPS, and DFT

J. Huang, J. Zhang, M.H. Eikerling, PCCP 148 (**2018**) 044704

R. Martínez-Hincapié, V. Climent, J.M. Feliu, Electrochim. Acta 307 (**2019**) 553-563:
signatures of inverted pzfc starting from pH 5







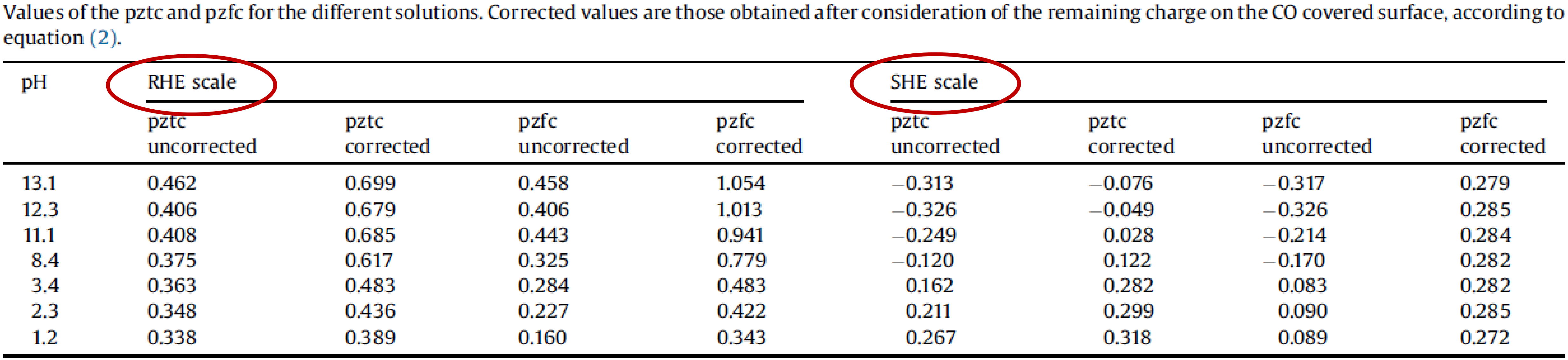
Parametrization agreed with some experimental data (incl. XPS) and DFT

J. Huang, A. Malek, J. Zhang, M.H. Eikerling, J. Phys. Chem. C 120 (**2016**) 13587–13595, corr. 121 (**2017**) 26140

SHE

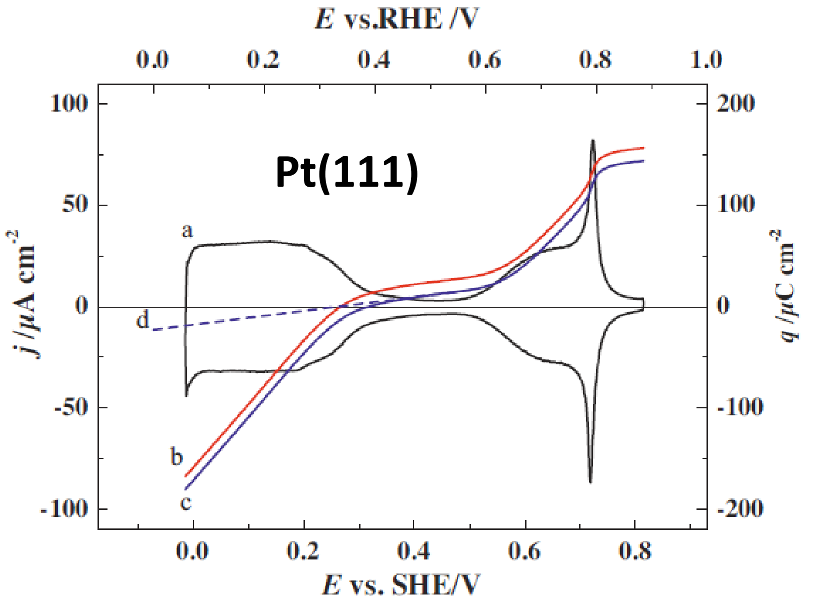
Alicante approach: pztc first, then pzfc

R. Rizo, E. Sitta, E. Herrero, V. Climent, J.M. Feliu, Electrochim. Acta 162 (**2015**) 138-145

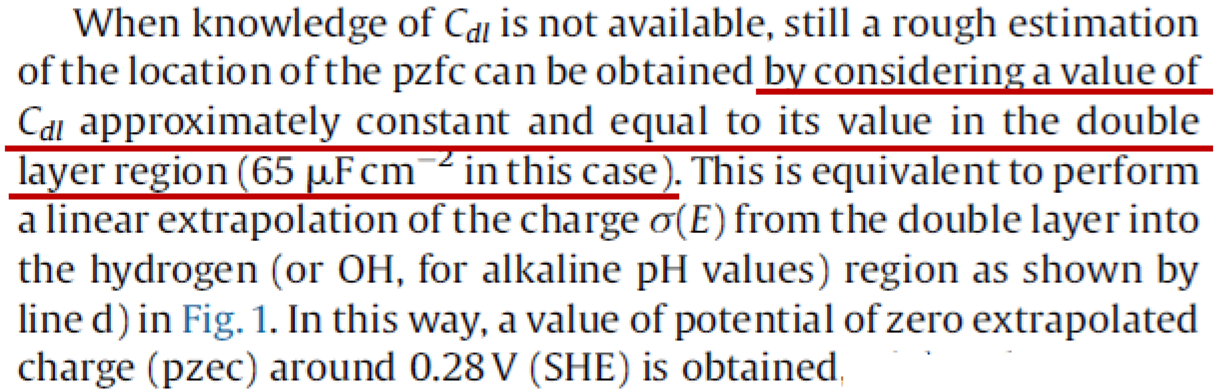


Values of the pztc and pzfc for the different solutions. Corrected values are those obtained after consideration of the remaining charge on the CO covered surface, according to equation (2).

pH	RHE scale				SHE scale			
	pztc uncorrected	pztc corrected	pzfc uncorrected	pzfc corrected	pztc uncorrected	pztc corrected	pzfc uncorrected	pzfc corrected
13.1	0.462	0.699	0.458	1.054	−0.313	−0.076	−0.317	0.279
12.3	0.406	0.679	0.406	1.013	−0.326	−0.049	−0.326	0.285
11.1	0.408	0.685	0.443	0.941	−0.249	0.028	−0.214	0.284
8.4	0.375	0.617	0.325	0.779	−0.120	0.122	−0.170	0.282
3.4	0.363	0.483	0.284	0.483	0.162	0.282	0.083	0.282
2.3	0.348	0.436	0.227	0.422	0.211	0.299	0.090	0.285
1.2	0.338	0.389	0.160	0.343	0.267	0.318	0.089	0.272

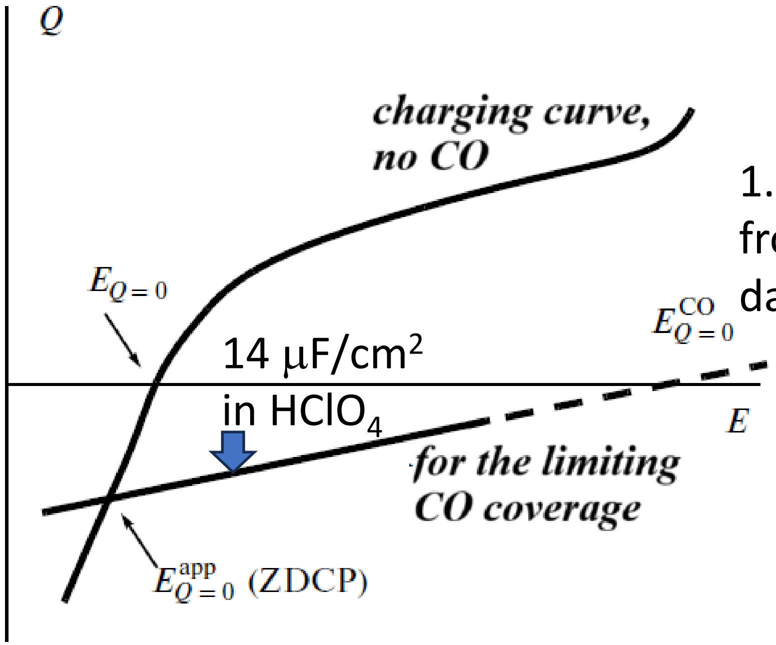


This is not the real zero free charge, but “zero extrapolated charge (pzec)“! **Correction is 200 – 600 mV, increases with pH**.



When knowledge of C_{dl} is not available, still a rough estimation of the location of the pzfc can be obtained by considering a value of C_{dl} approximately constant and equal to its value in the double layer region (65 μF cm^{-2} in this case). This is equivalent to perform a linear extrapolation of the charge $\sigma(E)$ from the double layer into the hydrogen (or OH, for alkaline pH values) region as shown by line d) in Fig. 1. In this way, a value of potential of zero extrapolated charge (pzec) around 0.28 V (SHE) is obtained.

Total charge from CO displacement



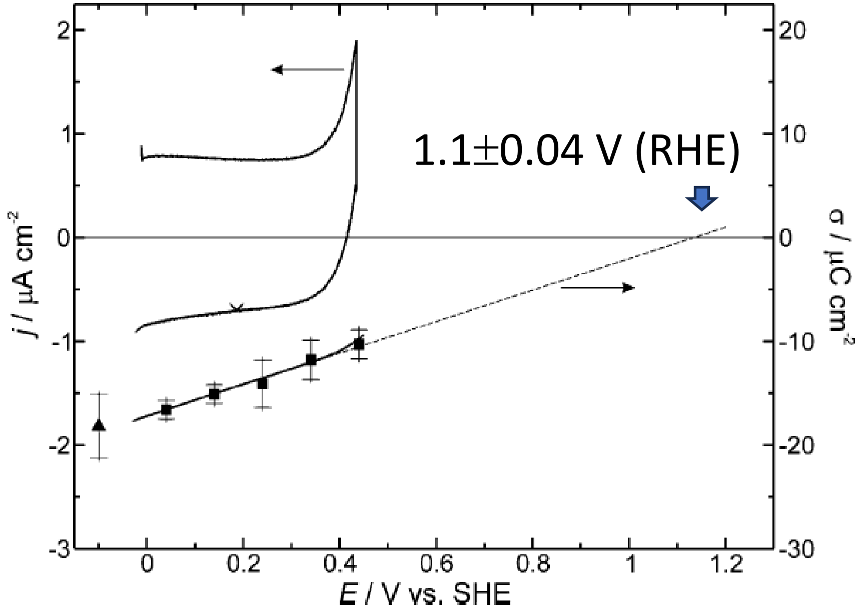
14 μF/cm^2
in HClO$_4$

zero displaced charge
potential

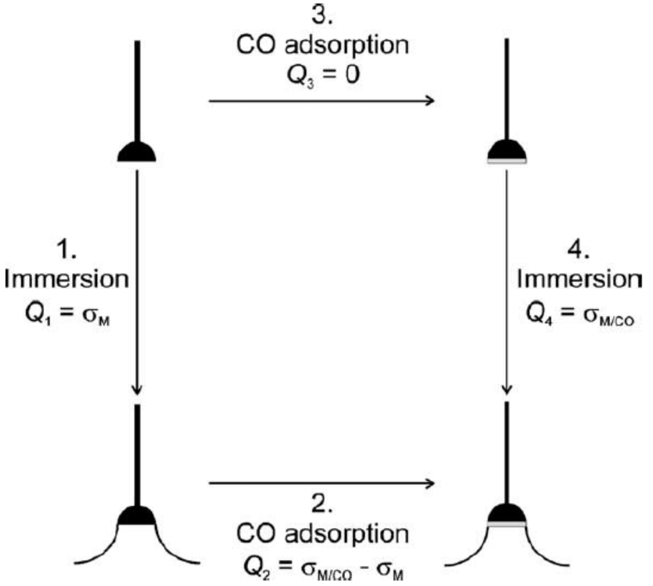
1.0±0.2 V (RHE),
from „non-situ“
data

Requirements

1. **The value of pztc must be below CO oxidation onset.**
2. **The capacitance of CO covered electrode should be much lower than the total capacitance in pztc region.**



1.1±0.04 V (RHE)



Alicante-Clavilier work started in ~1992,
with further participation of Wieckowski.

A. Cuesta, Surface Sci. 572 (**2004**) 11-22:
Correction for pztc increases with pH (**0.05 V at pH 1, 0.09 V at pH 3**)

Clarification of important details resulted from „non-situ“ experiments: M.J. Weaver, Langmuir 14 (**1998**) 3932-3936

See also the comments in: O.A. Petrii, Rus. J. Electrochem. 49 (**2013**) 401-422

Potentials of zero charge from probe reactions

G.A. Attard , A. Ahmadi, J. Electroanal. Chem. 389 (**1995**) 175-190:

N_2O reduction current maximums correspond to the local **pztc**.

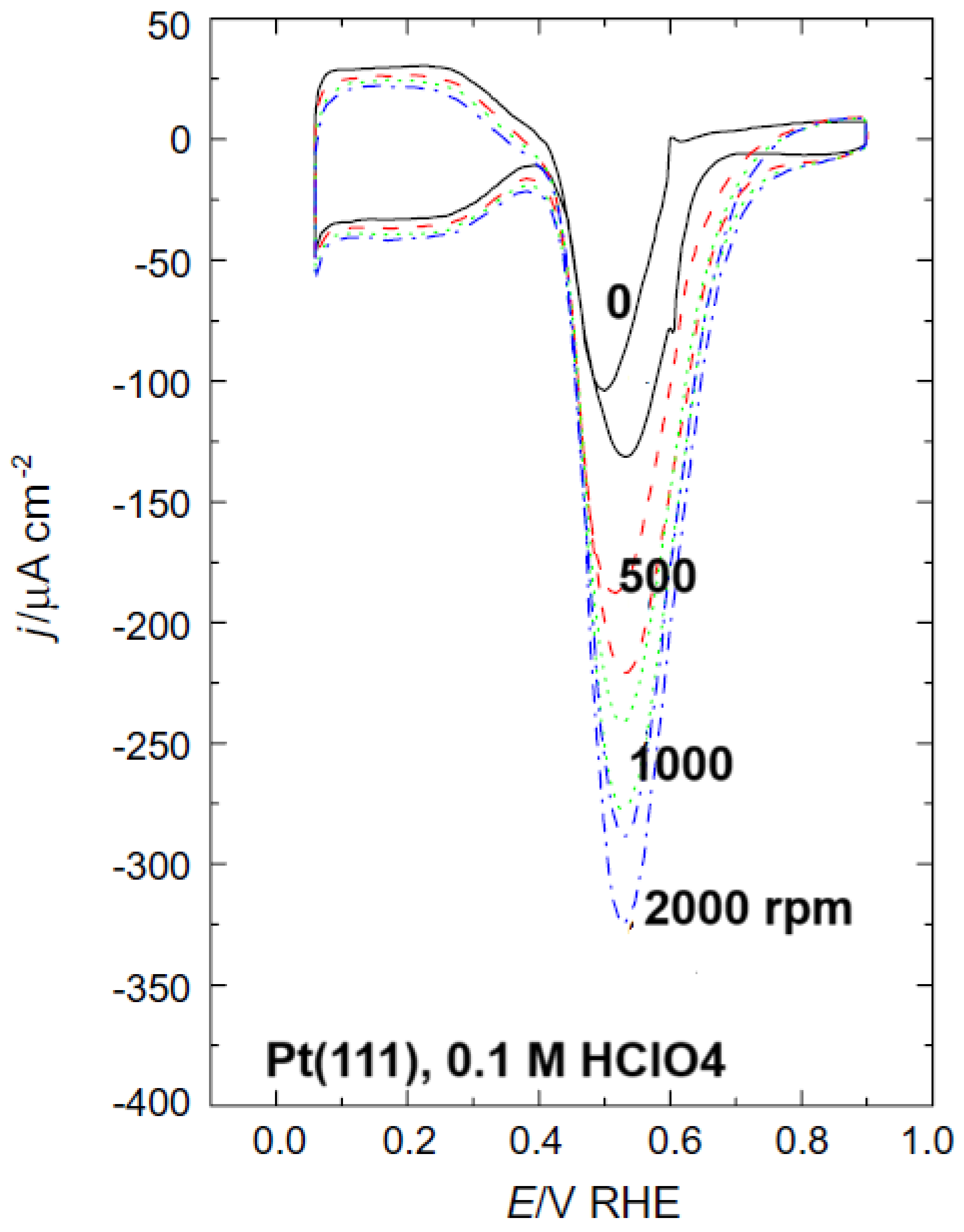
V. Climent, M. Dolores Macia, E. Herrero, J.M. Feliu, O.A. Petrii, J. Electroanal. Chem. 612 (**2008**) 269-276:

$S_2O_8^{2-}$ reduction onset is close to the local(?) **pztc**.

⬇ **?**

R. Martínez-Hincapié, V. Climent, J.M. Feliu, Electrochem. Commun. 88 (**2018**) 43-46; Electrochim. Acta 307 (**2019**) 553-563; J. Electroanal. Chem. 847 (**2019**) 113226 (*for pH 1 – 5*):

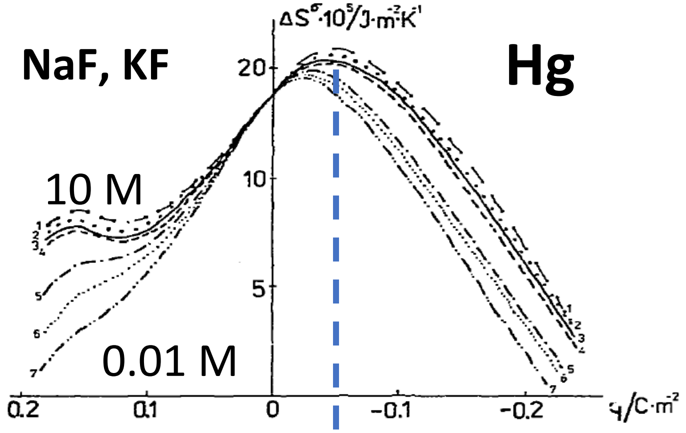
$S_2O_8^{2-}$ reduction onset correspond to the local **pzfc**.

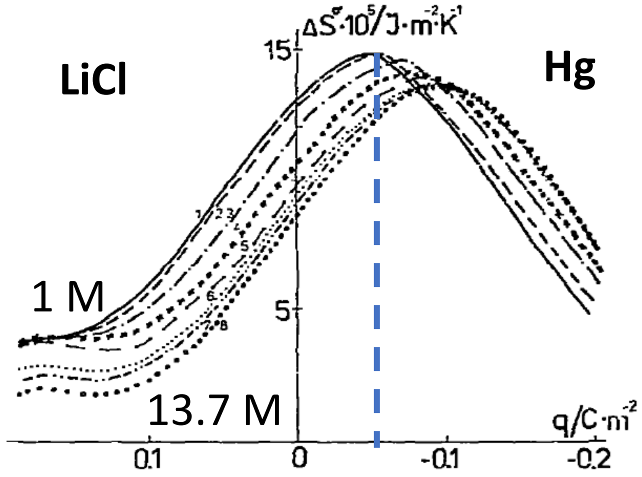


Note: peroxodisulfate behavior on Pt was not systematically tested for electrostatic effects, which will be discussed tomorrow.

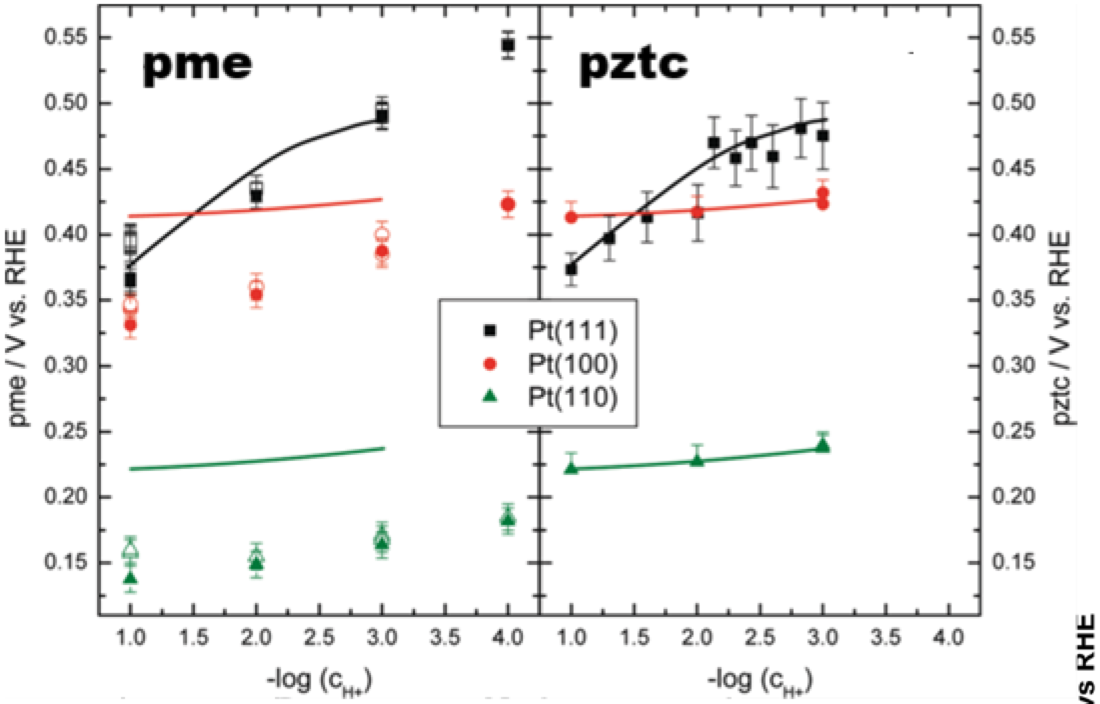
Potential of maximum entropy (pme) < pzfc < pztc?

V. Climent, B.A. Coles, R.G. Compton, J. Phys. Chem. B 106 (**2002**) 5988-5996; V. Climent, B.A. Coles, R.G. Compton, J.M. Feliu, J. Electroanal. Chem. 561 (**2004**) 157-165…..





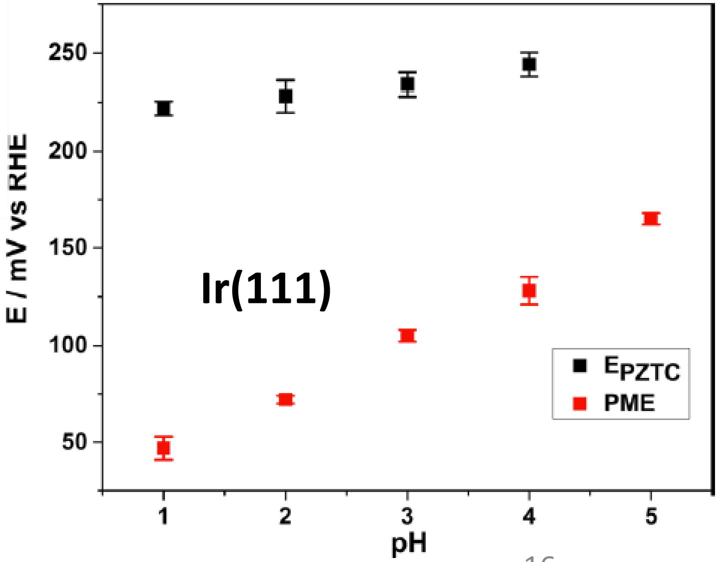
V.A. Benderskii, G.I. Velichko, J. Electroanal. Chem. 140 (**1982**) 1-22; V.A. Benderskii, G.I. Velichko, I.V. Kreitus, J. Electroanal. Chem. 181 (**1984**) 1-20



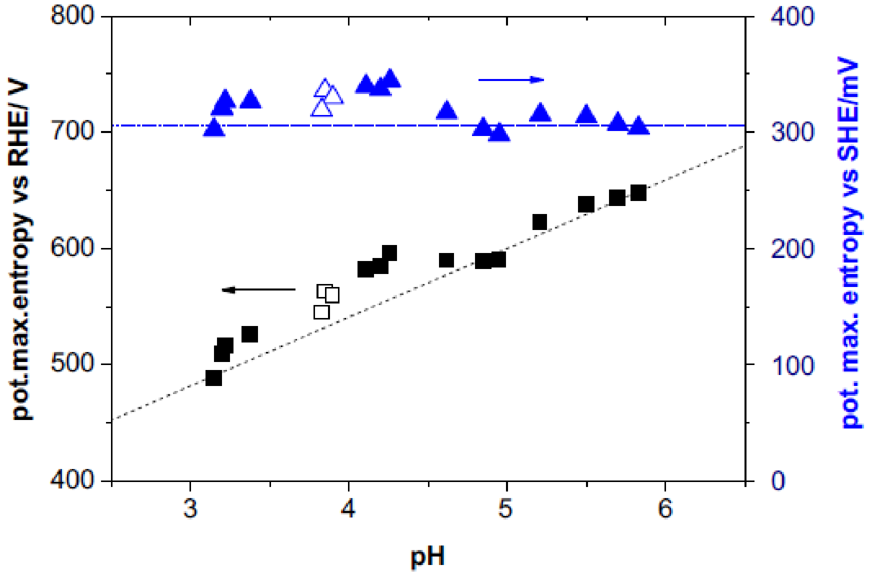
(0.1-x)M $KClO_4$ + x M $HClO_4$

N. Garcia-Araez, V. Climent, J. Feliu, J. Phys. Chem. 113 (**2009**) 9290-9304

A. Ganassin$_1$, P. Sebastián, V. Climent, W. Schuhmann, A.S. Bandarenka, J. Feliu, Sci. Rep. 7 (**2017**) 1246

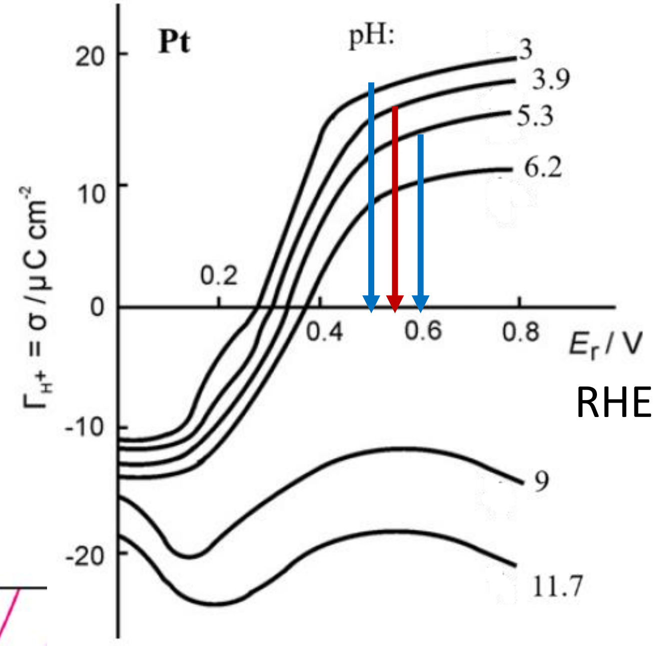


Disagreement of pzc estimates for Pt(111), perchlorate, and dispersed Pt-poly, sulfate, is significant



P. Sebastián, R. Martínez-Hincapié, V. Climent, J.M. Feliu, Electrochim. Acta 228 (**2017**) 667-676

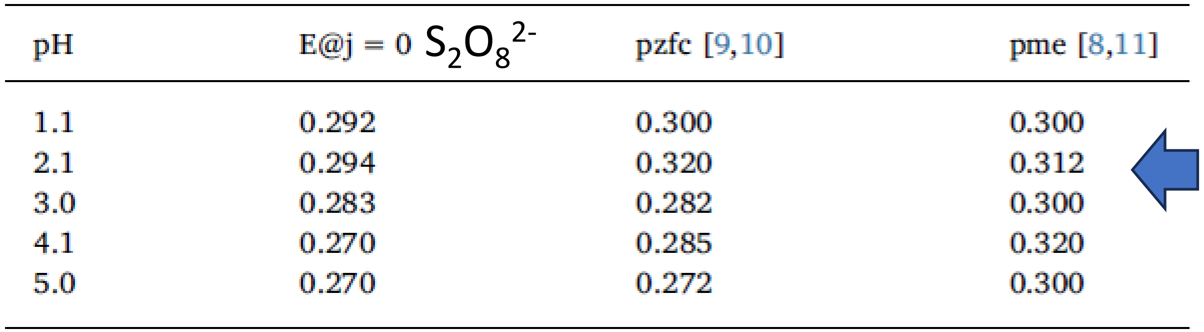
R. Martínez-Hincapié, V. Climent, J.M. Feliu, Curr. Opin. Electrochem. 14 (**2019**) 16-22: **this is the second (inverse) pzfc - ?**



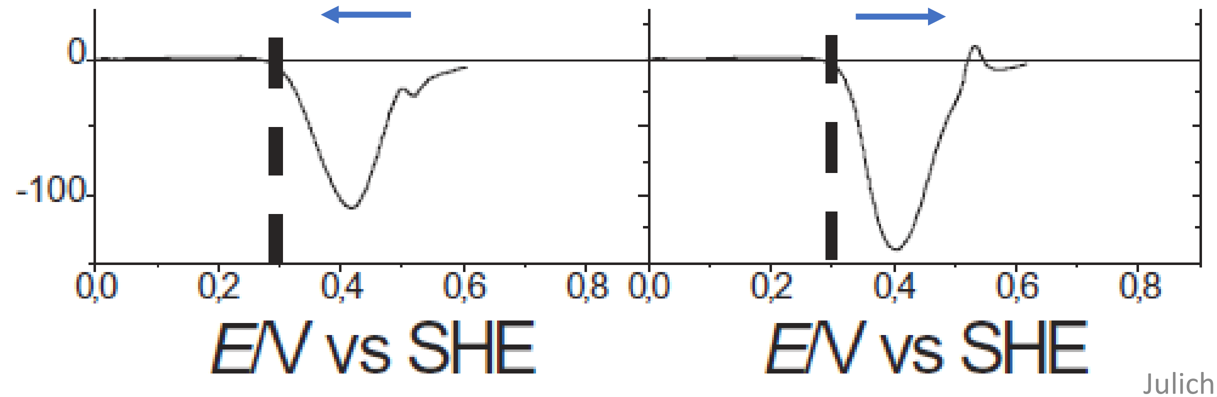
RHE

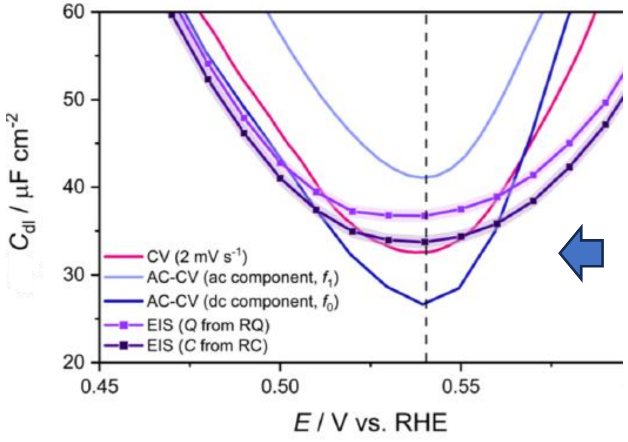
R. Martínez-Hincapié, V. Climent, J.M. Feliu, Electrochem. Commun. 88 (**2018**) 43-46

Values of E@j = 0, pzfc and pme (V vs SHE) as a function of pH.



pH	E@j = 0 $S_2O_8^{2-}$	pzfc [9,10]	pme [8,11]
1.1	0.292	0.300	0.300
2.1	0.294	0.320	0.312
3.0	0.283	0.282	0.300
4.1	0.270	0.285	0.320
5.0	0.270	0.272	0.300

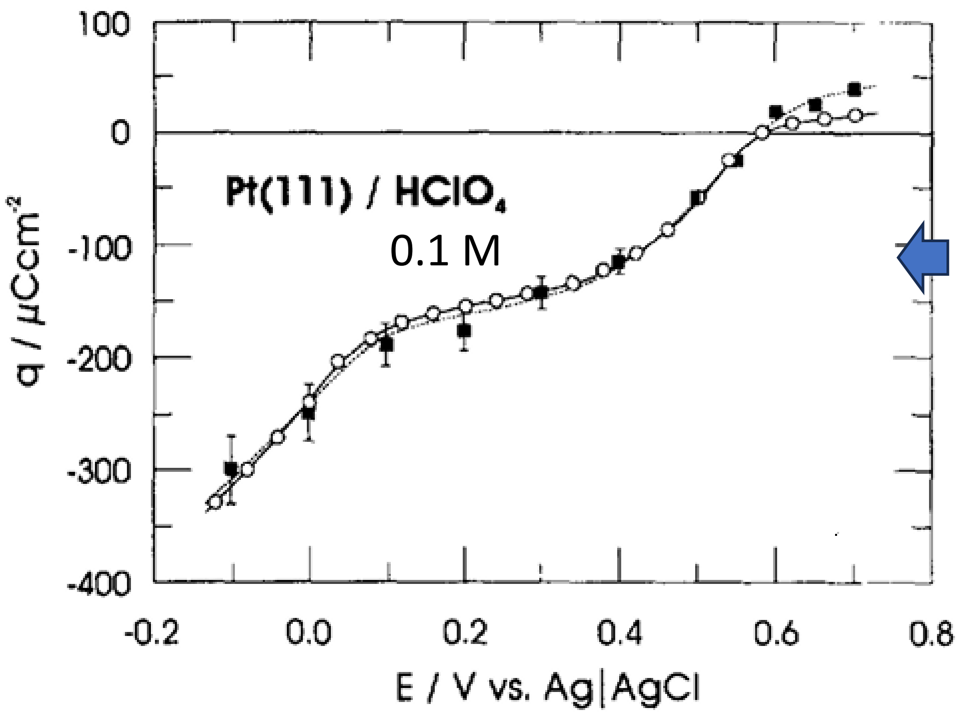




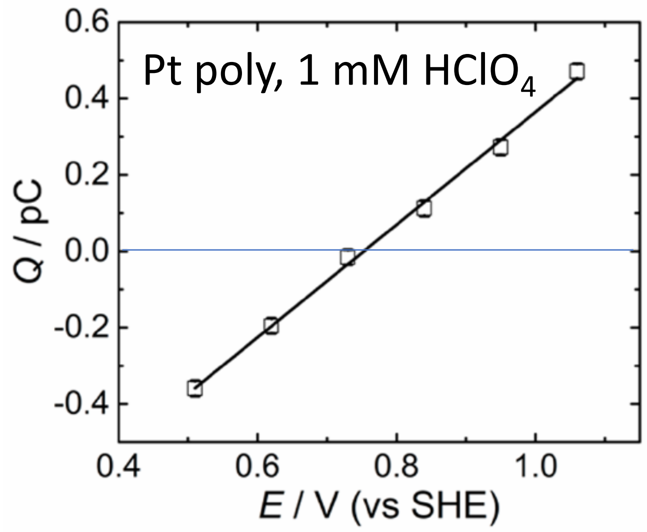
N.L. Fröhlich, J.J.J. Eggebeen , M.T.M. Koper, Electrochim. Acta 494 (**2024**) 144456

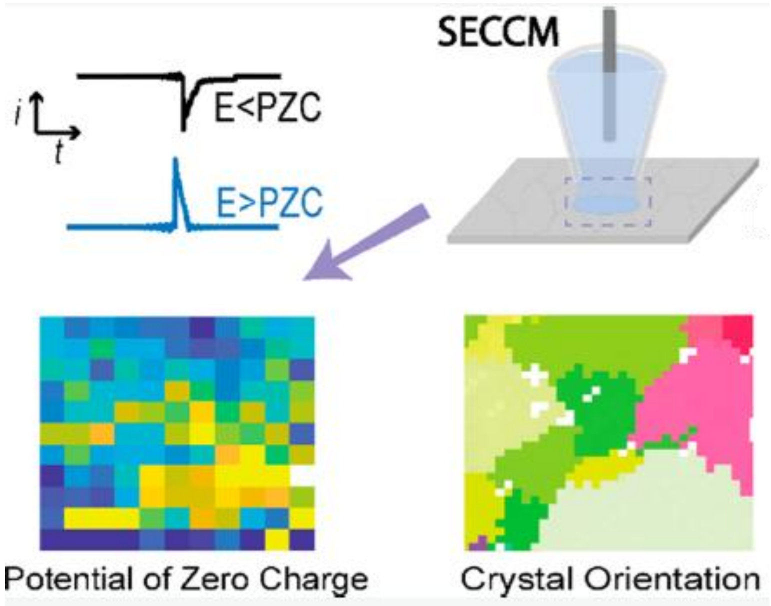
Capacitance differs from 65 µF/cm^2 used to obtain pzfc.

Be careful with pzc values from immersion-like techniques!

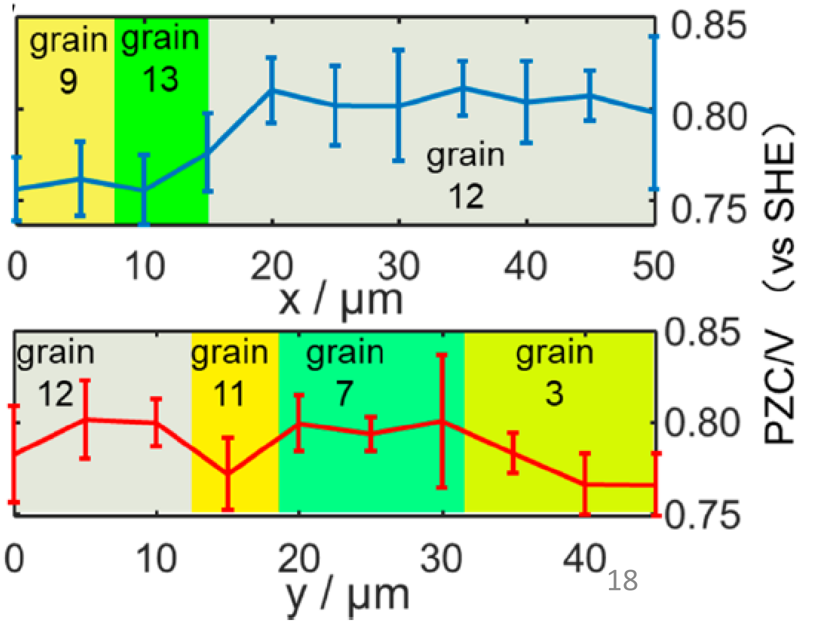


U.W. Hamm, D. Kramer, R.S. Zhai, D.M. Kolb, J. Electroanal. Chem. 414 (**1996**) 85-89





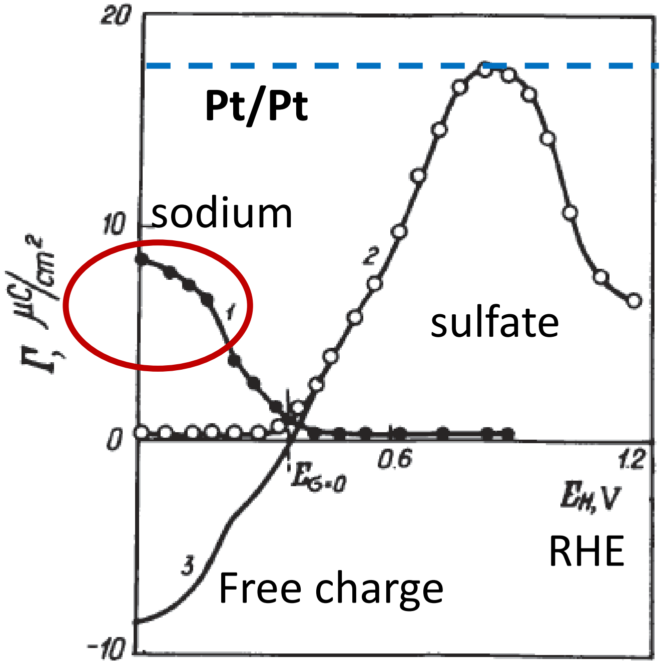
Y. Wang, E. Gordon, H. Ren, Anal. Chem. 92 (**2020**) 2859–2865



Immersion after UHV treatment (Kolb) and local SECMM result in **surely too high pzc values** ~0.8 V SHE for Pt in $HClO_4$.
This is known for other versions of 'direct' techniques, results most probably from residual O_2 in solution and/or oxygen dissociatively adsorbed from vapor in the course of transfer.

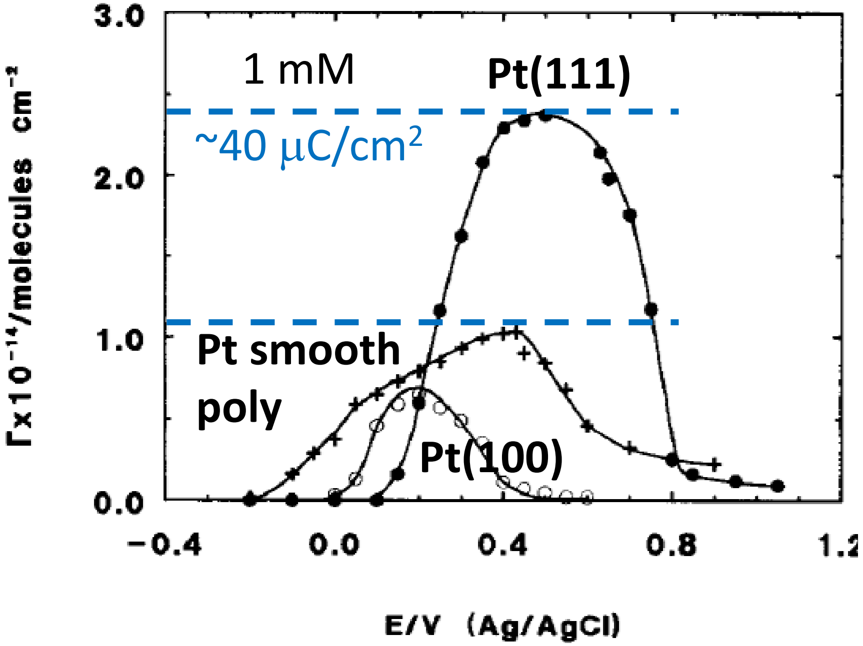
Direct radiotracer data on ionic adsorption, various platinum electrodes

0.5 mM H_2SO_4 + 1.5 mM Na_2SO_4

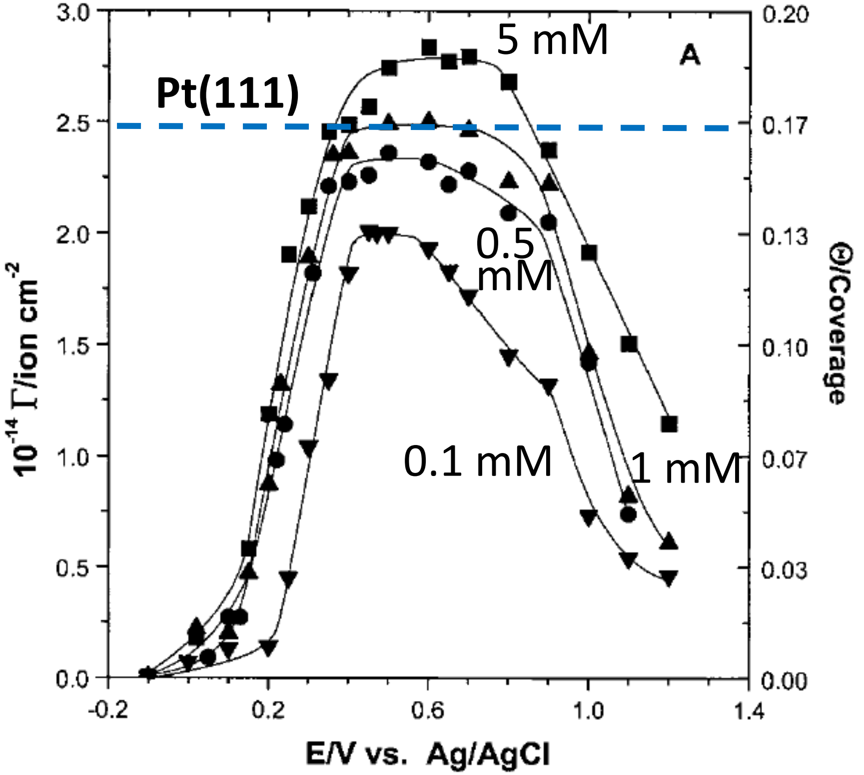


A.N. Frumkin, O.A. Petrii, B.B. Damaskin, Compr. Treatise Electrochem. 1 (**1980**) 221-289

0.1 M $HClO_4$ + H_2SO_4



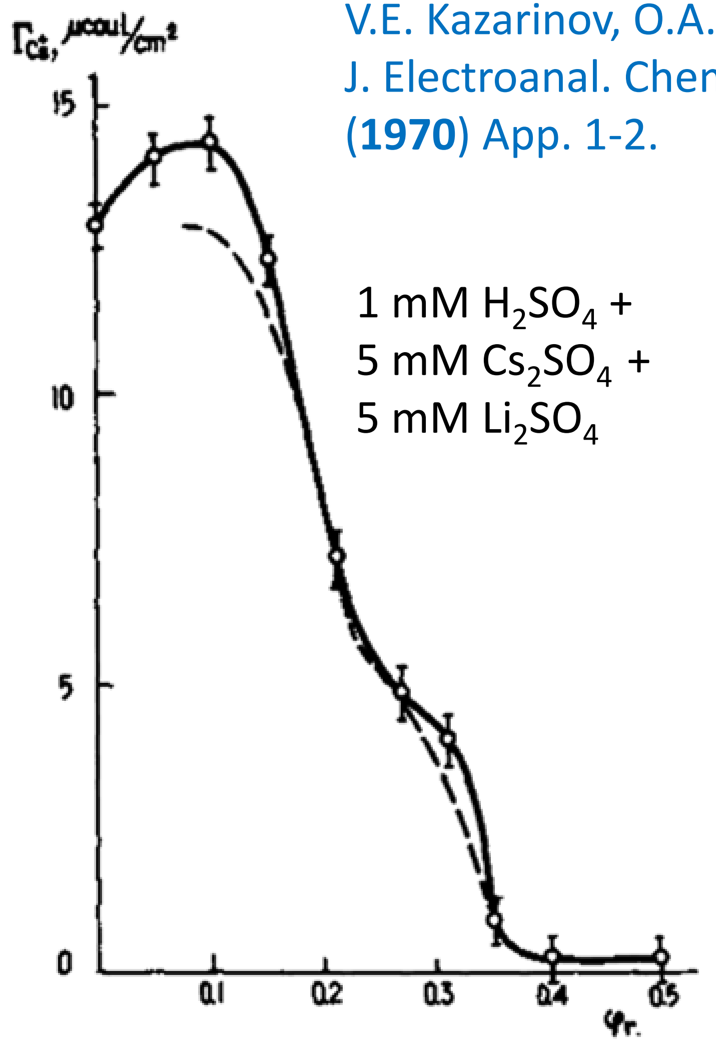
Y.-E. Sung, A. Thomas, M. Gamboa-Aldeco, K. Franaszczuk, A. Wieckowski, J. Electroanal. Chem. 378 (**1994**) 131-142



A. Kolics, A. Wieckowski, J. Phys. Chem. B 105 (**2001**) 2588-2595

No inversion of free charge in acidic solutions was observed directly, but anion adsorption decrease is its signature. **What happens with cations?**

Cations in the “normal” region, can be suppressed by H_{ad}

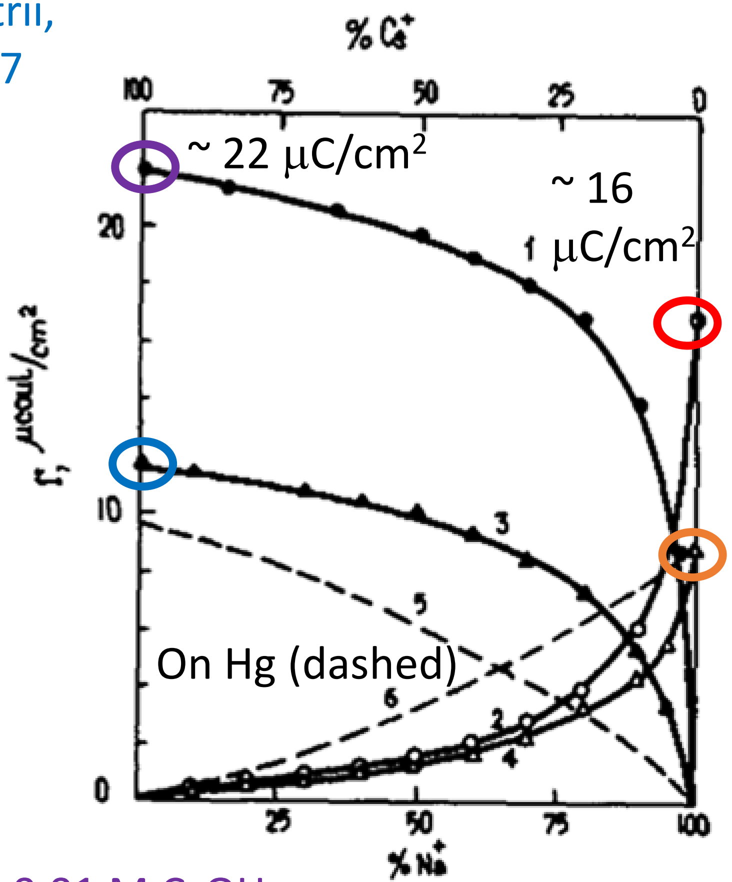


V, RHE

V.E. Kazarinov, O.A. Petrii, J. Electroanal. Chem. 27 (**1970**) App. 1-2.

1 mM H_2SO_4 +
5 mM Cs_2SO_4 +
5 mM Li_2SO_4

At 0 RHE:



~ 22 μC/cm²

~ 16 μC/cm²

On Hg (dashed)

0.01 M CsOH

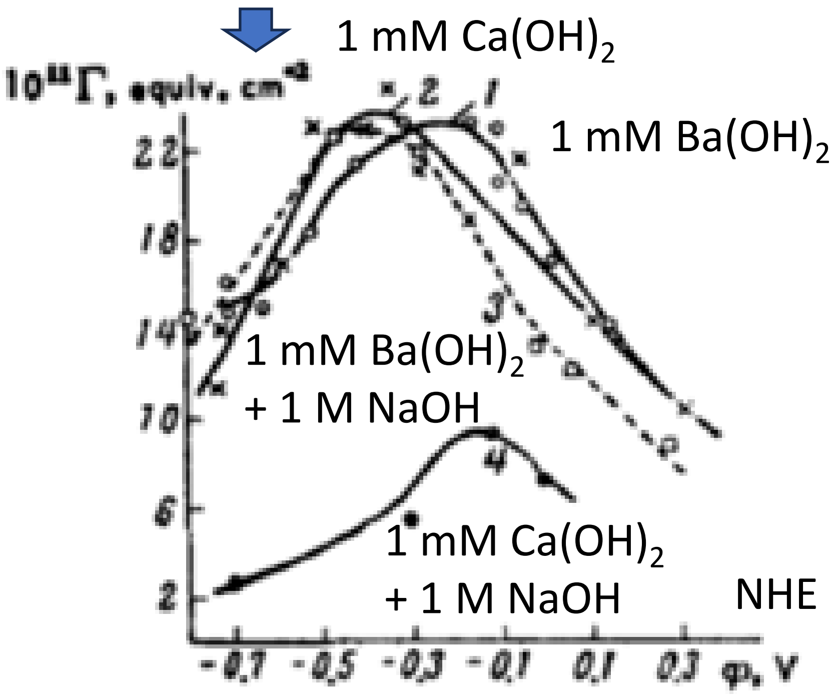
0.01 M Cs_2SO_4

0.01 M NaOH

0.01 M Na_2SO_4

(in 1 mM H_2SO_4)

H upd region



1 mM $Ca(OH)_2$

1 mM $Ba(OH)_2$

1 mM $Ba(OH)_2$
+ 1 M NaOH

1 mM $Ca(OH)_2$
+ 1 M NaOH

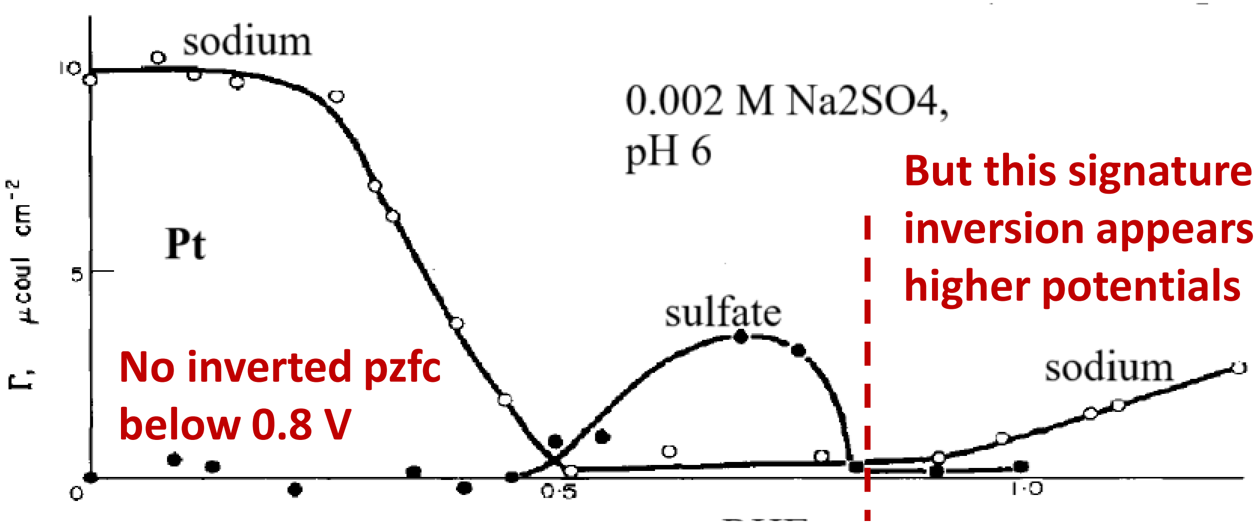
NHE

N.A.Balashova, V.E.Kazarinov, Russ. Chem. Rev. 34 (**1965**) 730-736

Cation adsorption in the “normal” region is the same or stronger than on Hg at the same free charges. Cs/Na difference is more pronounced.

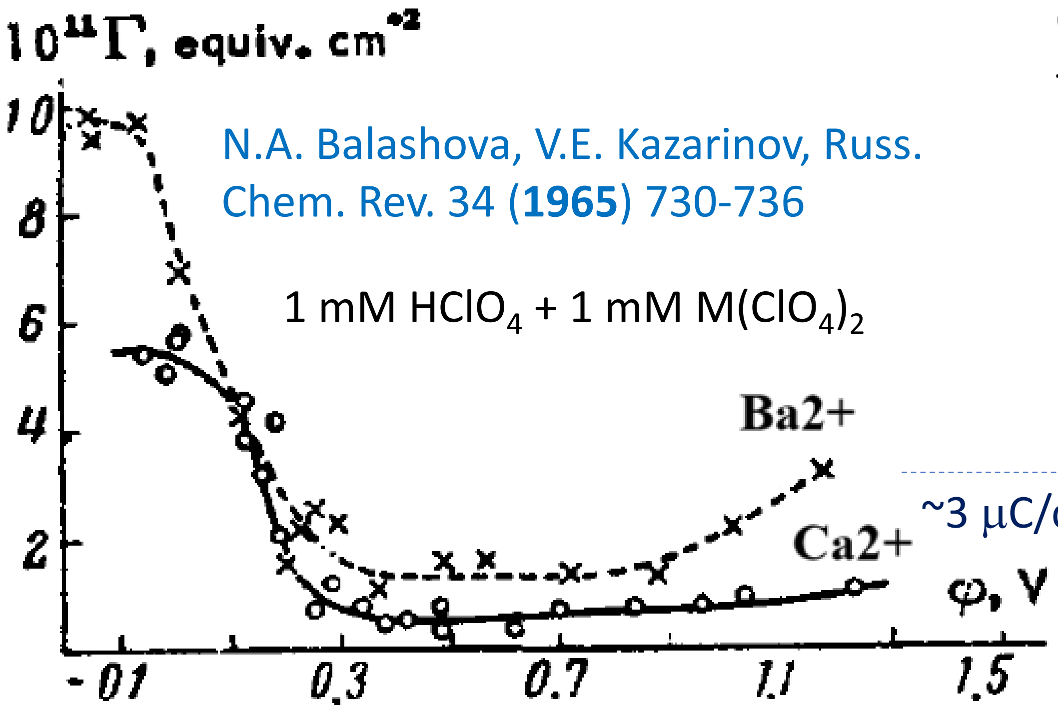
O(OH)-induced adsorption of cations in “inverted” region?

A.N. Frumkin, O.A. Petrii, Electrochim. Acta 20 (**1975**) 347-359



No inverted pzfc below 0.8 V

But this signature of inversion appears at higher potentials



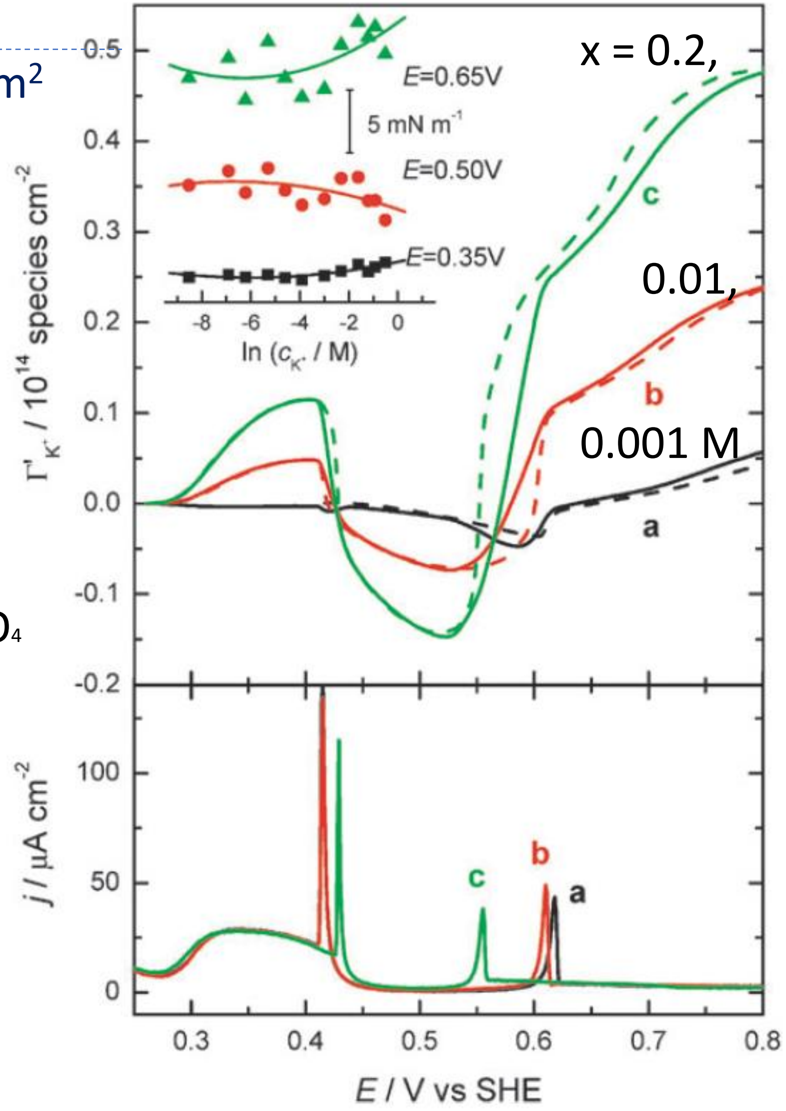
N.A. Balashova, V.E. Kazarinov, Russ. Chem. Rev. 34 (**1965**) 730-736

1 mM $HClO_4$ + 1 mM $M(ClO_4)_2$

~3 μC/cm²

(0.4 – x) M Na_2SO_4 + x M K_2SO_4 + 0.1 M H_2SO_4

~8 μC/cm²



x = 0.2,

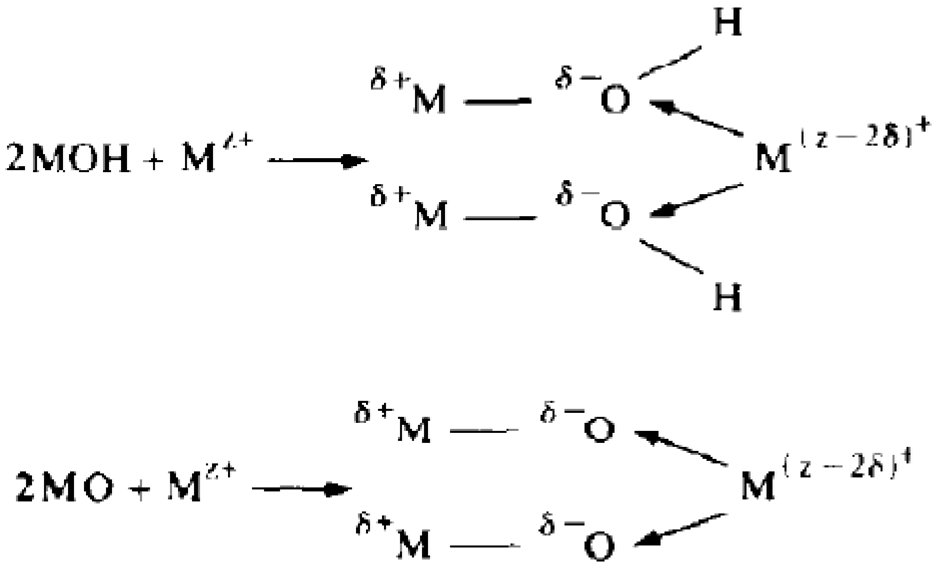
0.01,

0.001 M

N. Garcia-Araez, V. Climent, P. Rodriguez, J.M. Feliu, PCCP 12 (**2010**) 12146-12152

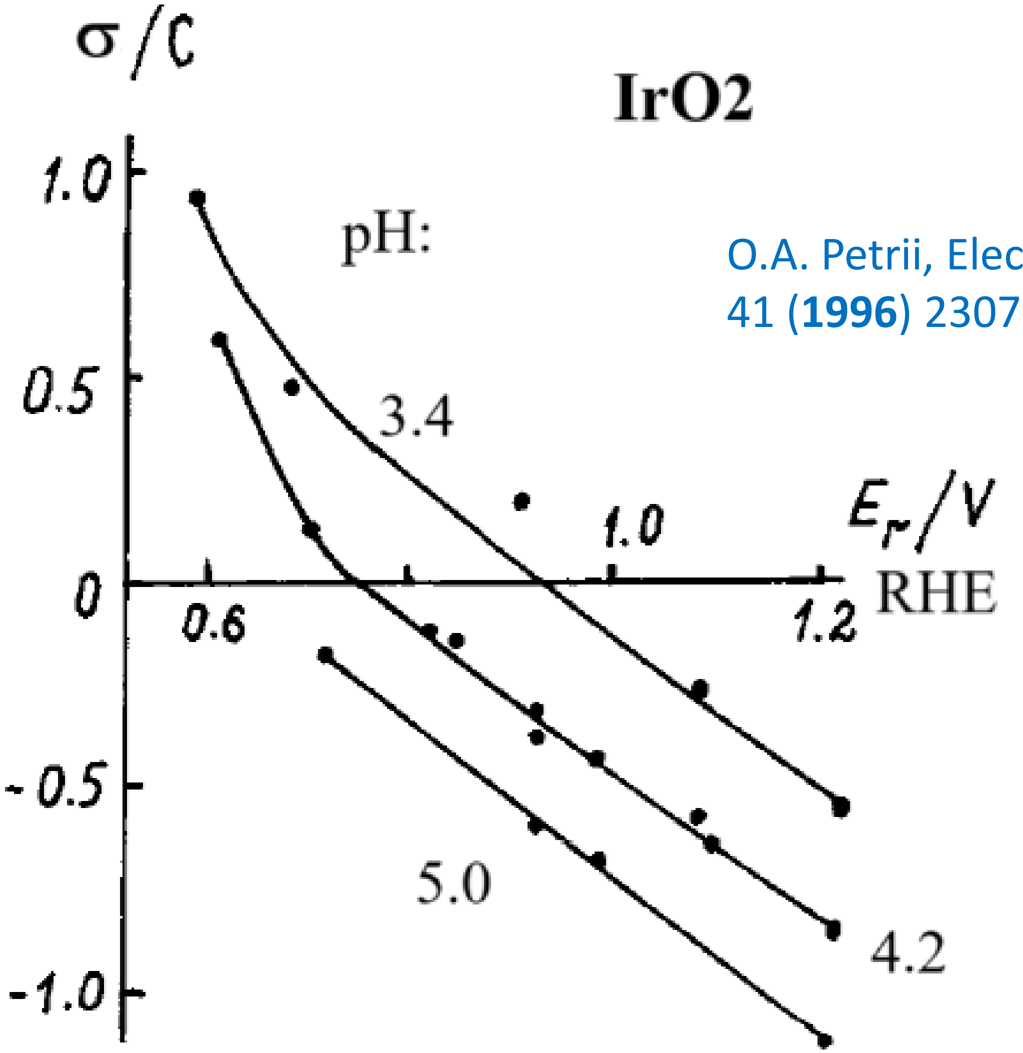
Cations in “inverted” region

Electroreflection signal decreases in presence of cations in acid, starting from ~1 V RHE for Au, and even at lower potentials for Pt.



R.R. Adzic, N.M. Markovic, J. Electroanal. Chem. 102 (**1979**) 263-279; Electrochim. Acta 30 (**1985**) 1473-1479

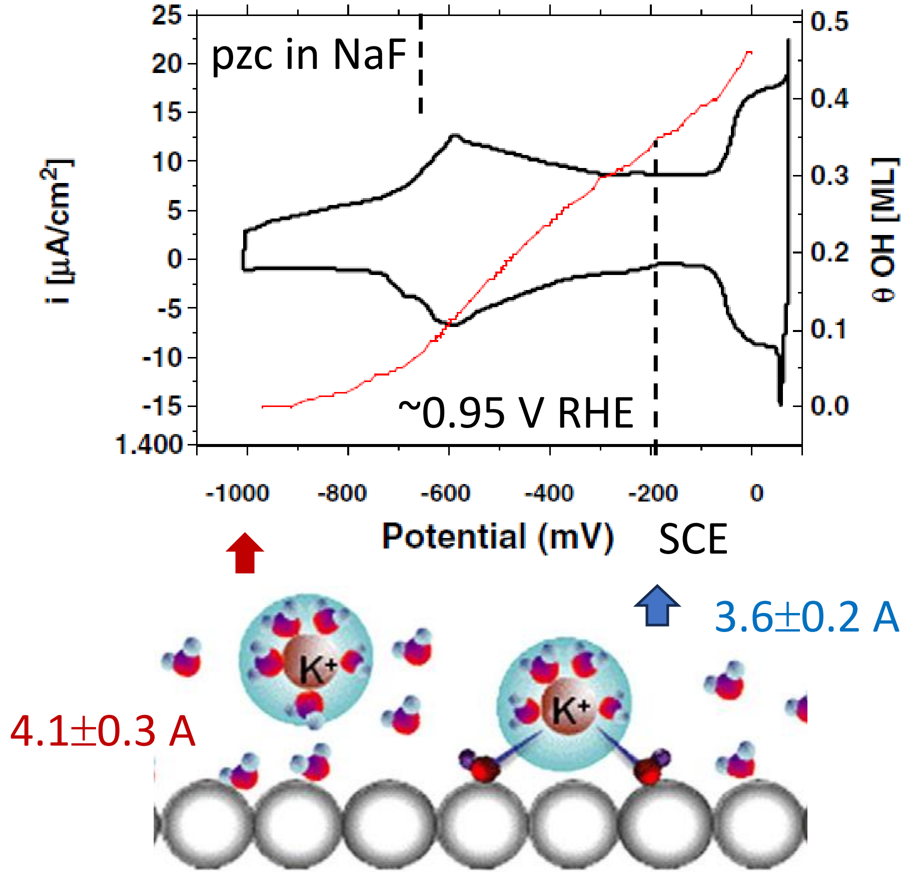
Inverted pzfc is known for oxide as well

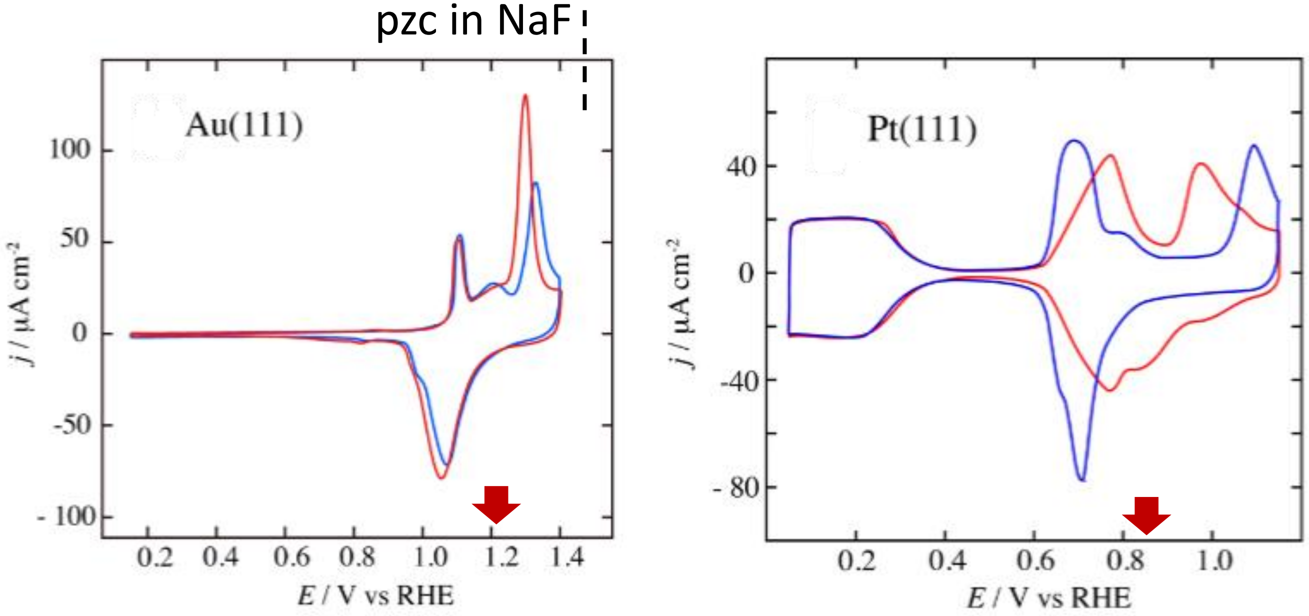


O.A. Petrii, Electrochim. Acta 41 (**1996**) 2307-2312

Cations in the “normal” and “inverted” region, silver, X-ray scattering; problem with gold is surface reconstruction

Ag(111), 0.1 M KOH

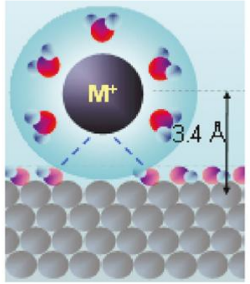




0.1 M CsOH and LiOH

M. Nakamura, Y. Nakajima, K. Kato, O. Sakata, N. Hoshi, J. Phys. Chem. C 119 (**2015**) 23586–2359; *see also*: Y. Gründer, G.S. Harlow$_1$, E. Cocklin, J. Fogg, J.W. Beane, C.A. Lucas, Surface Sci. 680 (**2019**) 113-118

C.A. Lucas, P. Thompson, Y. Gründer, N.M. Markovic. Electrochem. Commun. 13 (**2011**) 1205-1208; *slow cations rearrangement*: Y. Grunder, E.M.Cocklin, P. Thompson, C. A. Lucas, Electrochem. Sci. Adv. 5 (**2025**) e2400009.

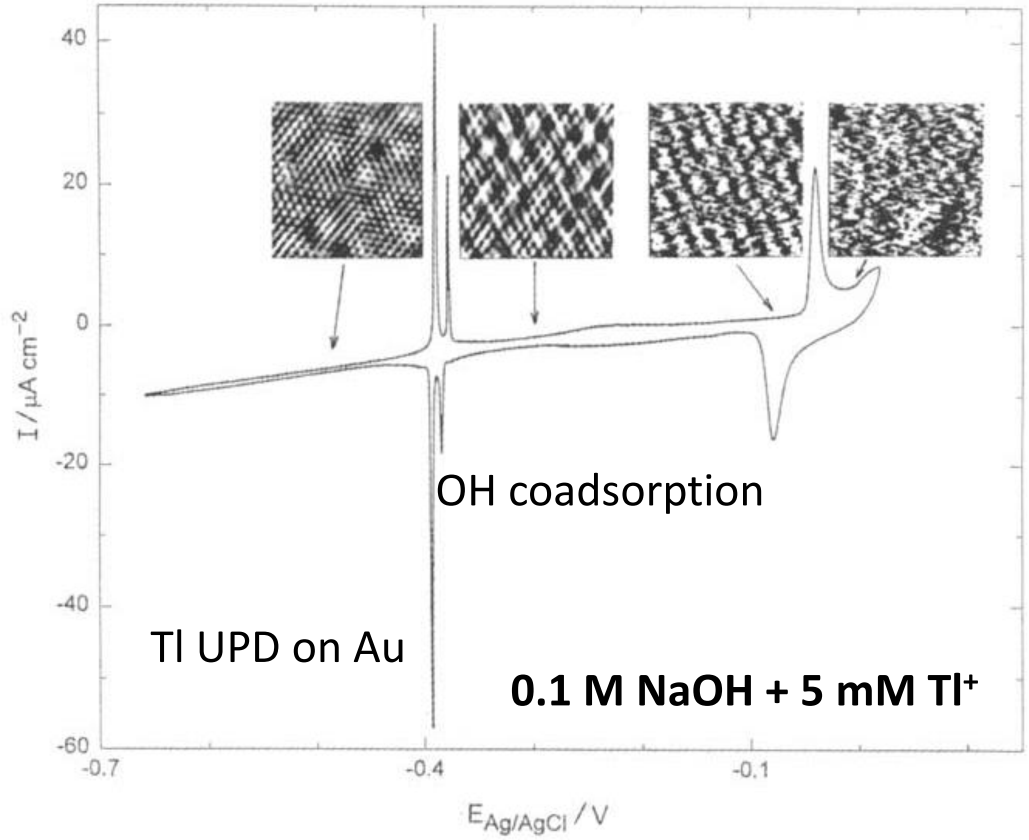


Ba^{2+}on Pt(111)/KOH: 3.48±0.05 A at 0.85 V RHE

D. Strmcnik, ..., N.M. Markovic, Phys. Chem. Lett. 2 (**2011**) 22733-2736

Some cations can form a sort of 2D oxide in “inverted” region,

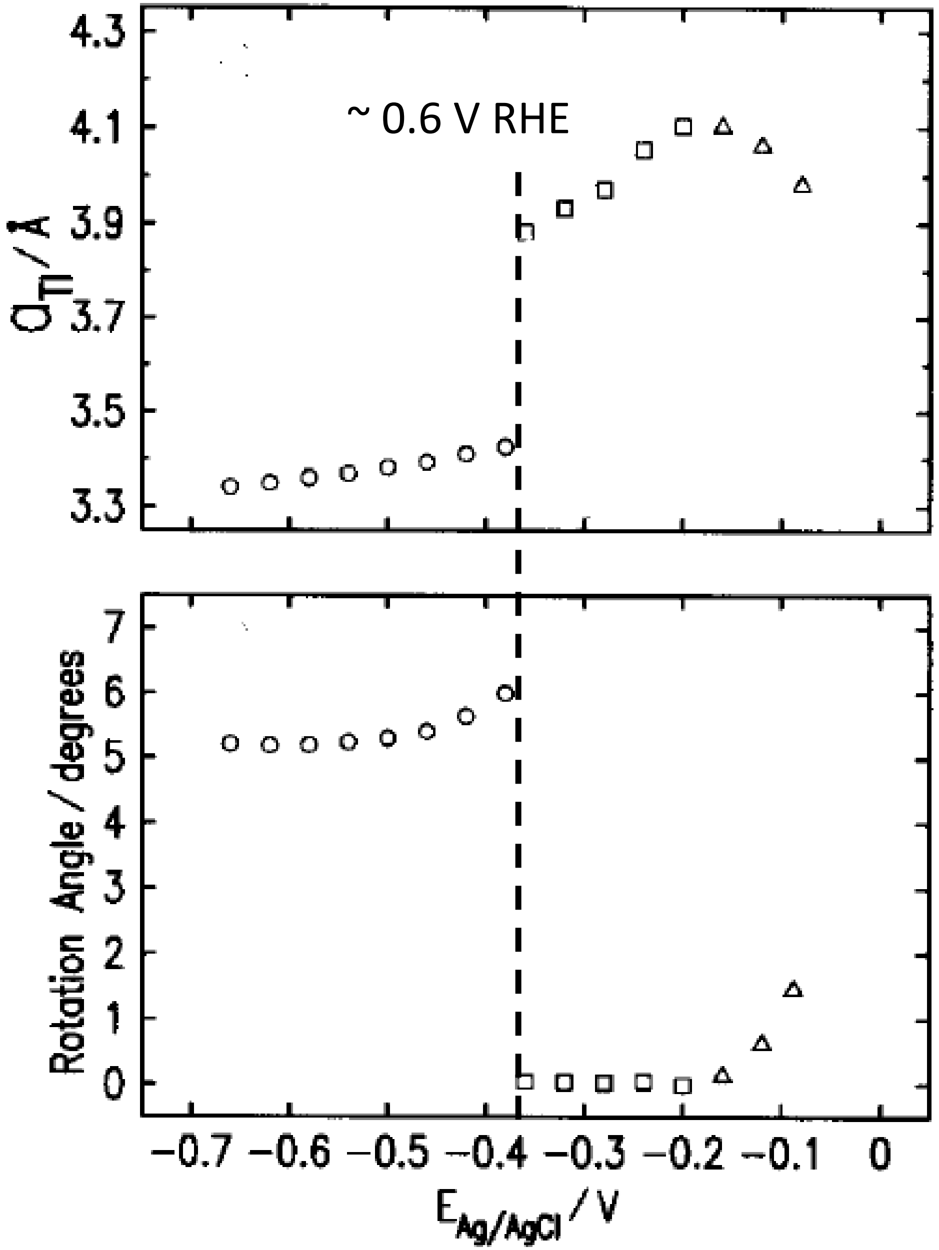
OH⁻ adsorption affects the specific cations adsorption already at low OH coverage



OH coadsorption

Tl UPD on Au

0.1 M NaOH + 5 mM Tl⁺

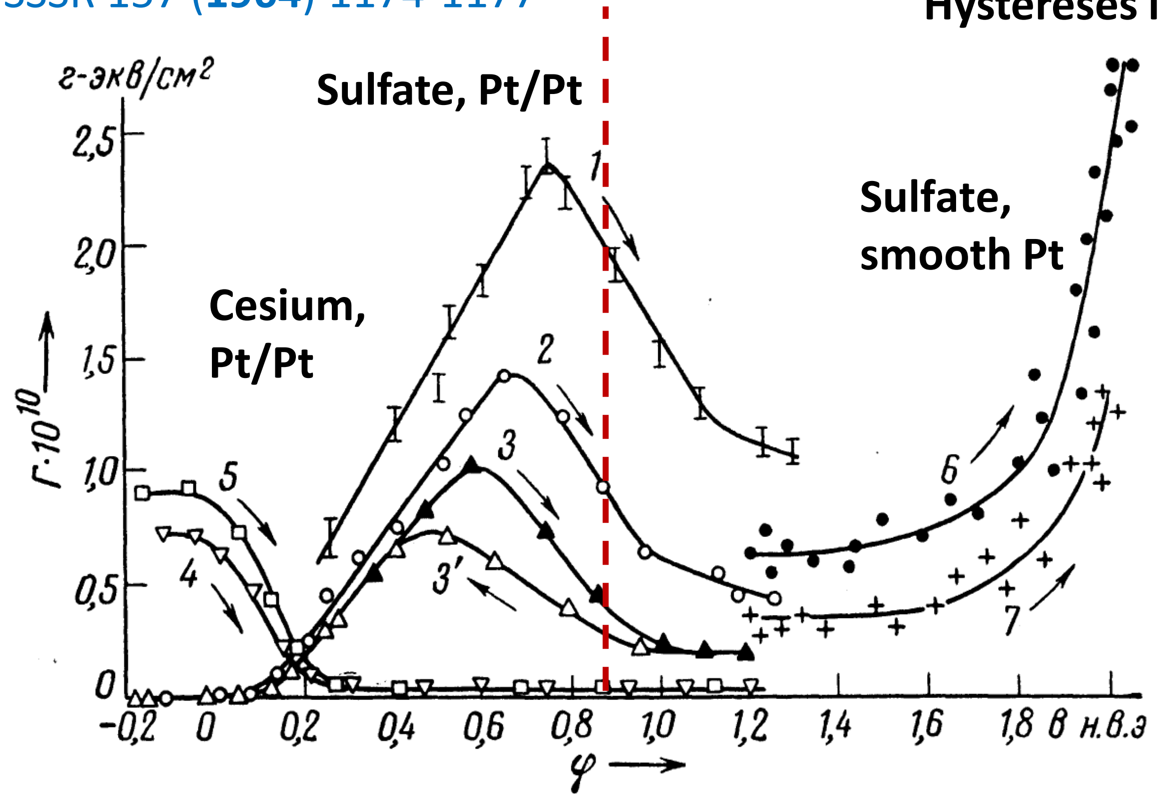


~ 0.6 V RHE

W. Polewska, J.X. Wang, B.M. Ocko, R.R . Adzic,
J. Electroanal. Chem. 376 (**1994**) 41-47

Ionic adsorption at high potentials can be hardly addressed precisely

V.E. Kazarinov, N.A. Balashova, Doklady AN SSSR 157 (**1964**) 1174-1177



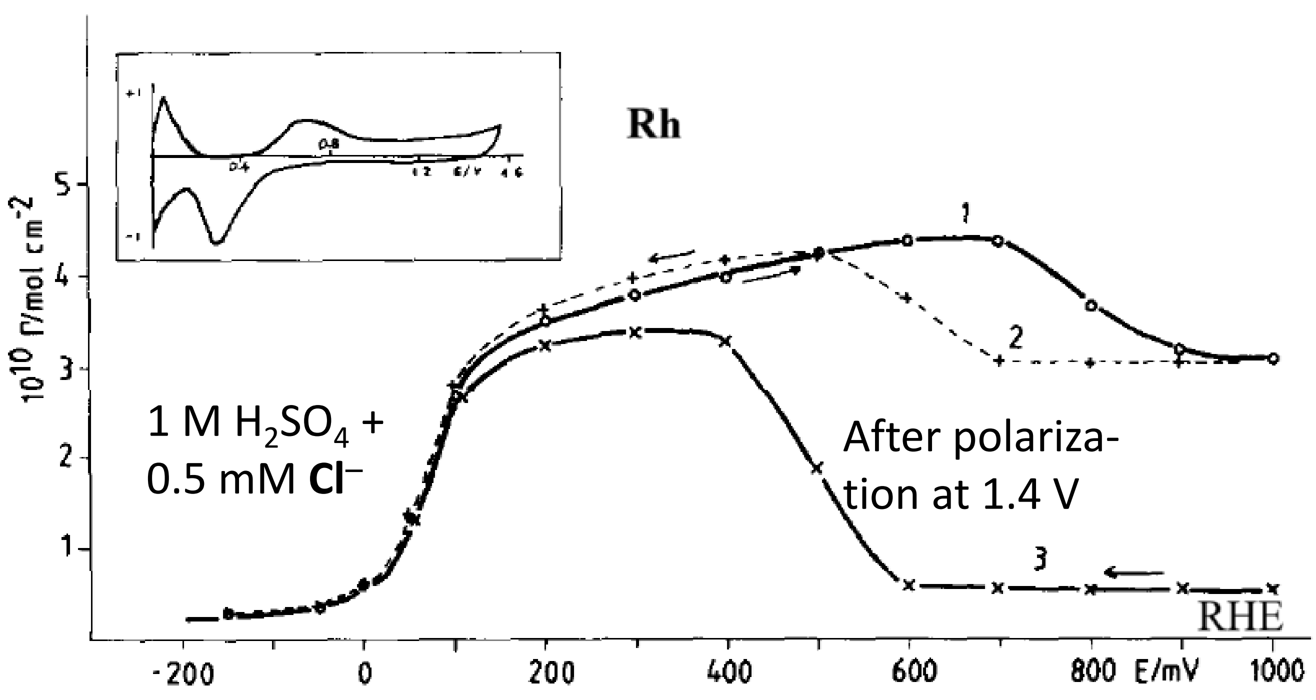
Sulfate, Pt/Pt

Cesium, Pt/Pt

Sulfate, smooth Pt

Hystereses in the oxygen region

G. Horanyi, E.M. Rizmayer, J. Electroanal. Chem. 198 (**1986**) 379-391



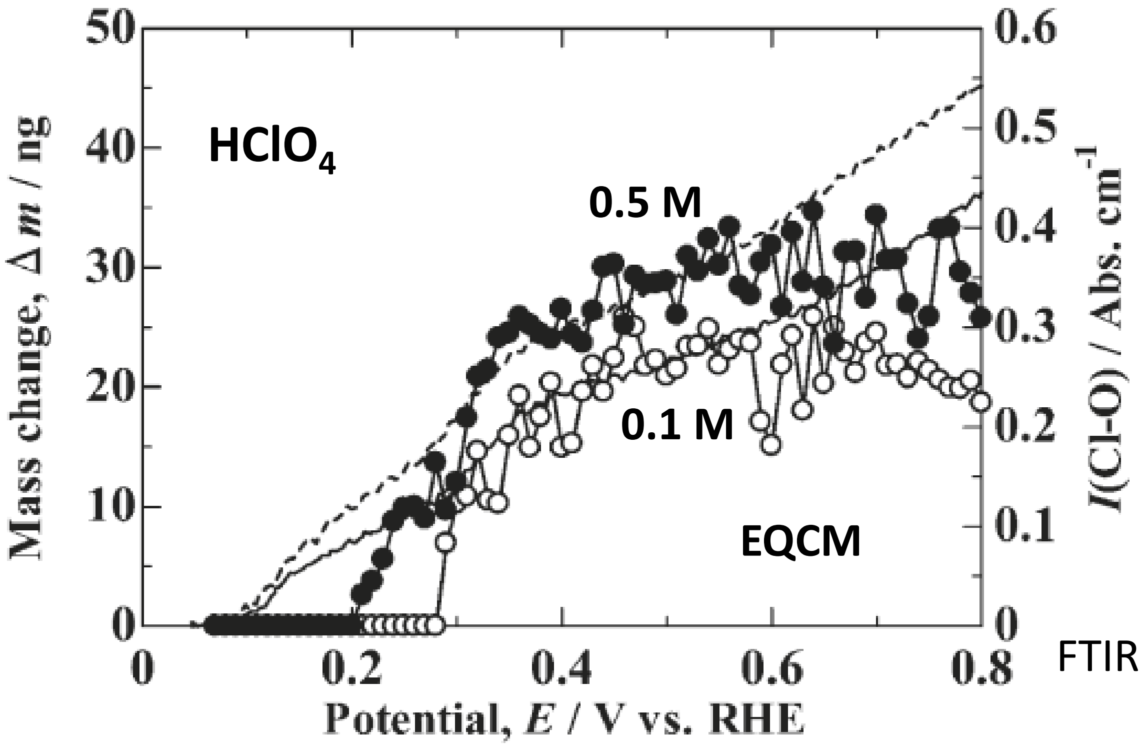
$1\ M\ H_2SO_4$ + 0.5 mM $\mathbf{Cl^-}$

After polarization at 1.4 V

0.05 M H_2SO_4: curves 1, 6
0.005 M H_2SO_4: curve 2, 7
0.005 M H_2SO_4 + 0.01 M Cs_2SO_4: curves 2, 4
0.001 M H_2SO_4 + 0.018 M Cs_2SO_4: curve 5
0.0005 M H_2SO_4: curves 3, 3’

Considering **steady-state** OER data, we should consider oxide, not metal. There is no reliable information even for PGM, as stabilization is typically long enough.

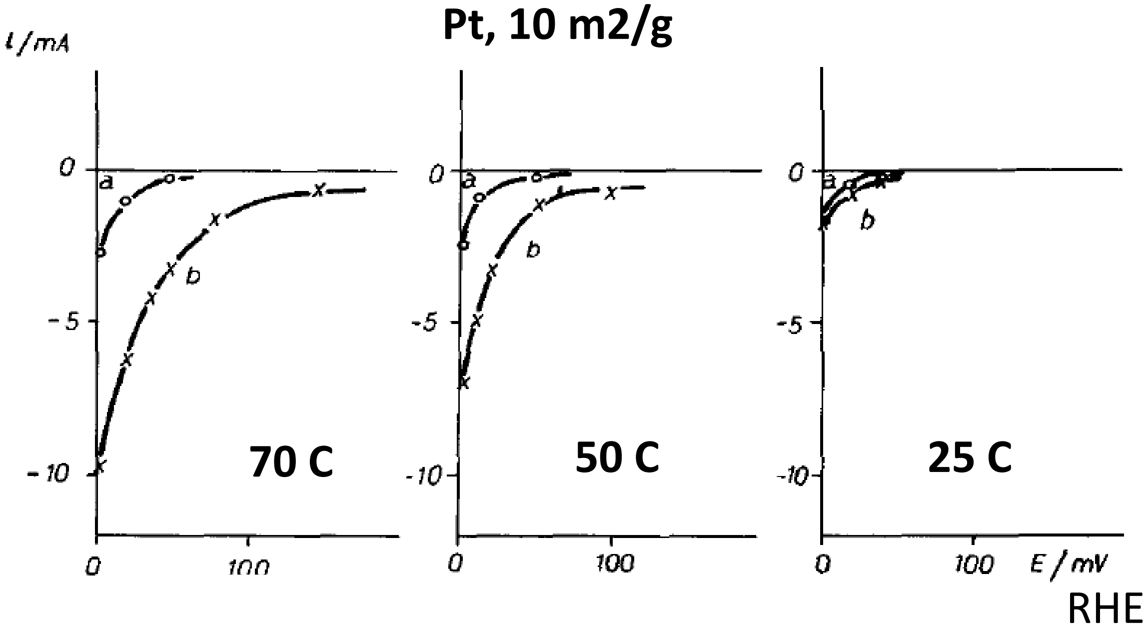
No old data for perchlorate adsorption on Pt, but the trend is the same as for sulphate



J. Omura, H. Yano, M. Watanabe, H. Uchida, Langmuir 27 (**2011**) 6464-6470

Be cautious with perchlorate at low RHE potentials!!

Pt, 10 m2/g



1 M H_2SO_4 (upper curves) and 1 M H_2SO_4 + $HClO_4$
The curves are steady-state!!

G. Horanyi, G. Vertes, J. Electroanal. Chem. 64 (**1975**) 252-254

Where we are with understanding total and free charge for the most studied metals?

“Thermodynamic” values require high surface area electrodes and cannot be obtained for slow equilibration (oxygen region)

Development for single crystals (limited to pH 1 – 5):

CO displacement provides **the estimates of the total charge**, the accuracy decreases with pH.

Free charge estimates are even less accurate.

Potentials of maximum entropy are somewhat close to pzfc.

More information on pzc than on charge vs. potential dependencies in wide potential intervals.

Very important for structural vs electronic effects, including surface crystallography and particle size. This can be done in acidic solutions exclusively.

Radiotracer technique can work for **free charge** on smooth electrodes, equilibration time is still a problem

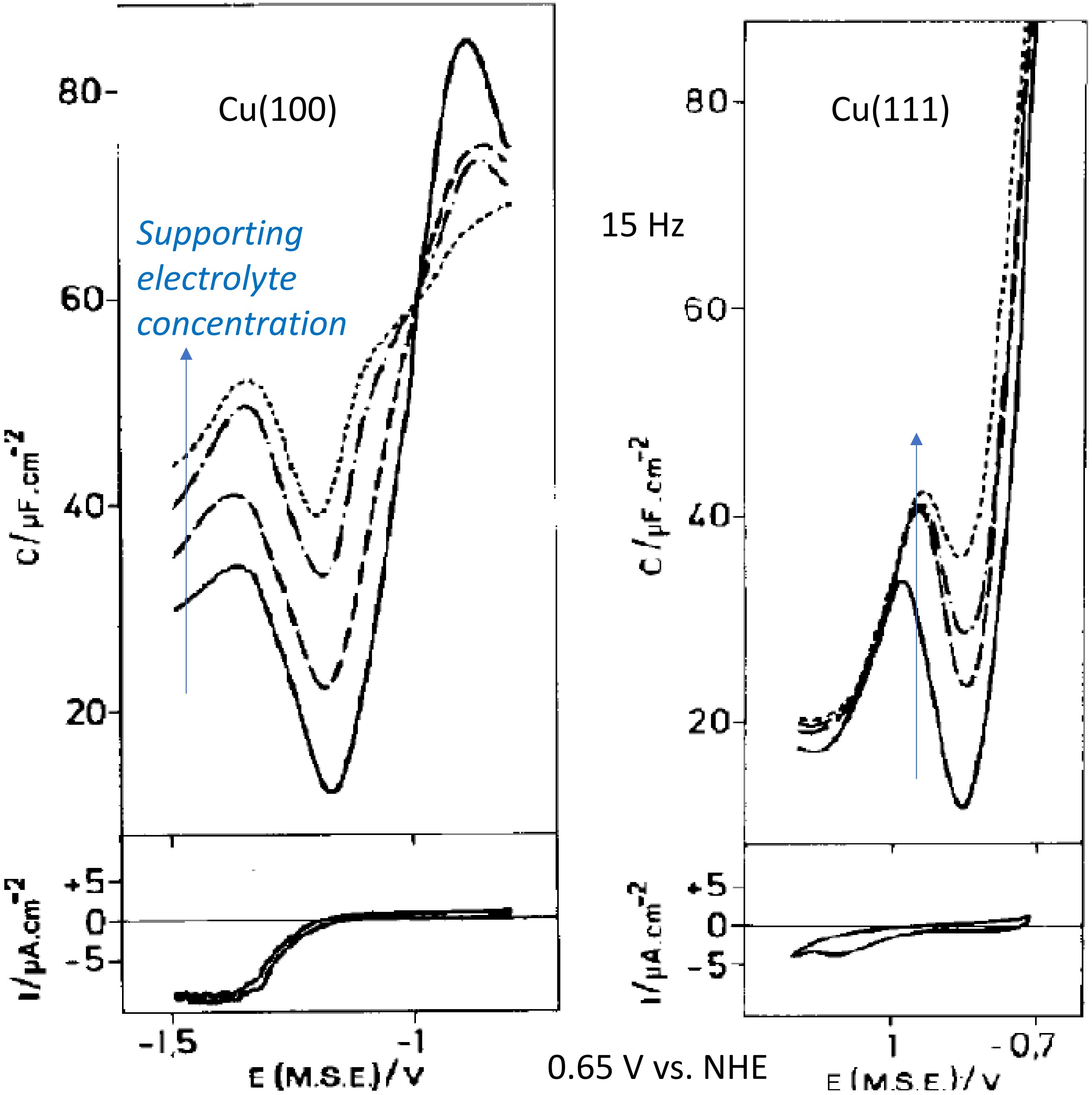
*To characterize reaction zone of electrocatalytic processes, **especially for alkaline solutions**, it is better to use available data for dispersed polycrystalline metals <better than nothing>.*

*The most important **qualitative** trends are*
- *inversion of free charge,*
- *absence of pzfc in alkaline medium (free charge is negative at all potentials within stability window),*
- *H-induced suppression of cations adsorption*

*The **quantities of ionic adsorptions** can be also used, at least for estimates.*

See O.A. Petrii, Russ. J. Electrochem. 49 (**2013**) 401-422 *for other important comments*

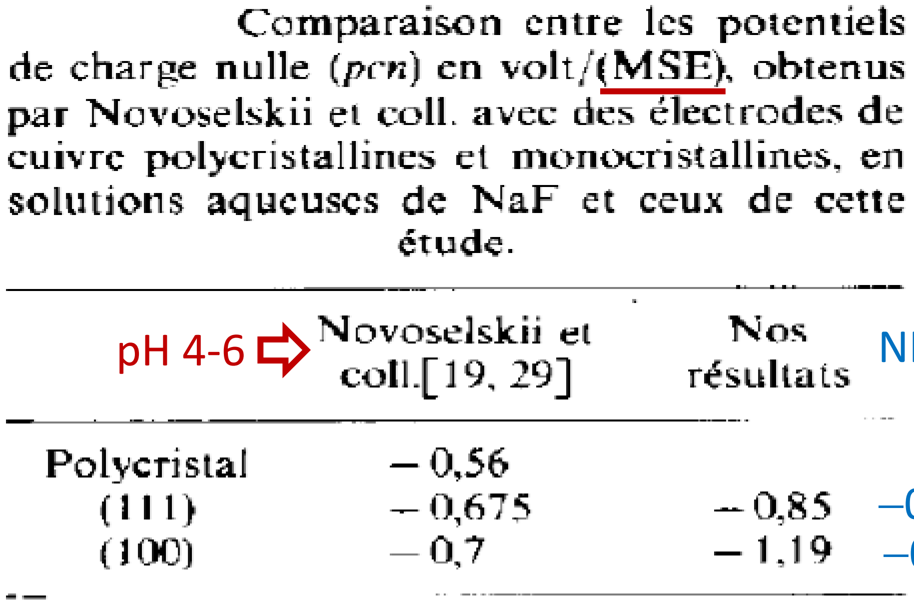
Copper in acid is ideally polarizable?



15 Hz

0.65 V vs. NHE

1, 5, 20, 40 mM $KClO_4$, **pH 4**



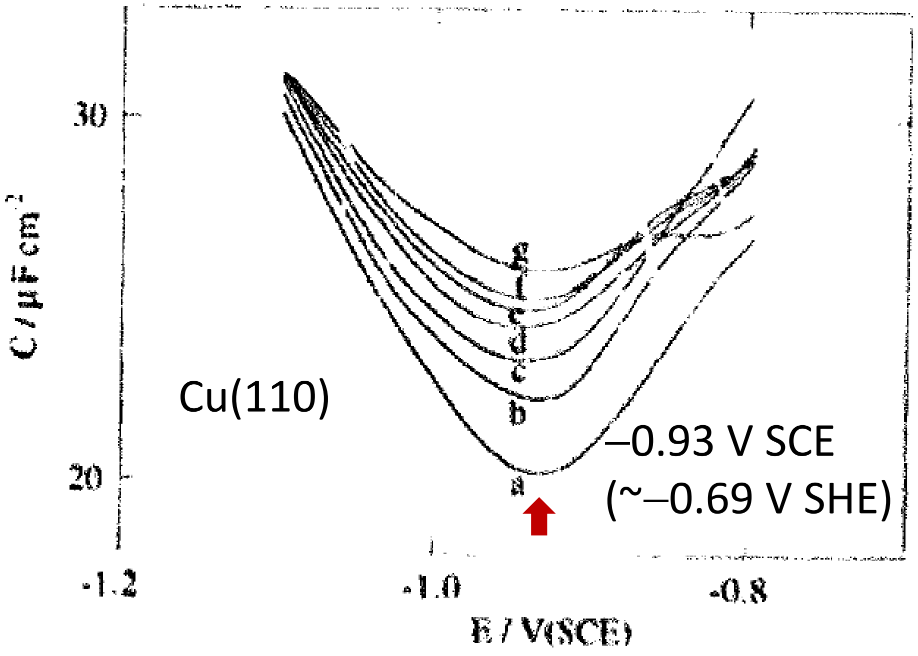
Comparaison entre les potentiels de charge nulle (*pcn*) en volt/(MSE), obtenus par Novoselskii et coll. avec des électrodes de cuivre polycristallines et monocristallines, en solutions aqueuses de NaF et ceux de cette étude.

pH 4-6 ⇨

	Novoselskii et coll.[19, 29]	Nos résultats	NHE:
Polycristal	– 0,56		
(111)	– 0,675	– 0,85	–0.20
(100)	– 0,7	– 1,19	–0.54

J. Lecoeur, J. P. Bellier, Electrochim. Acta 30 (1985) 1027-1033

If copper in acid is ideally polarizable in a limited potential interval, pzc should be pH-independent

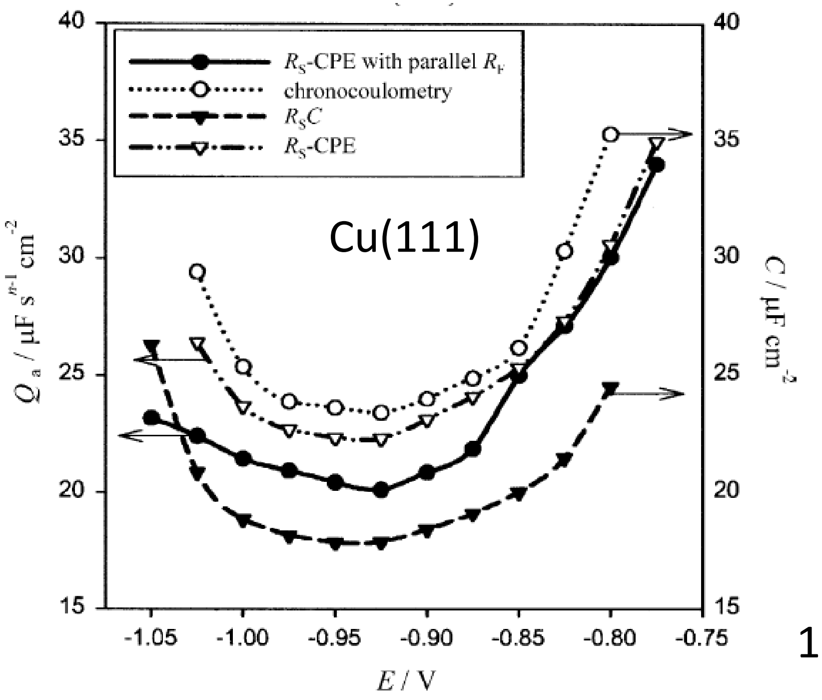


Cu(110)

–0.93 V SCE
(~–0.69 V SHE)

$0.1\ mM\ HClO_4 + (5 – 18)\ mM\ KClO_4$

M.L. Foresti, G. Pezzatini, M. Lnnocenti, J. Electroanal. Chem. 434 (**1997**) 191-200



Cu(111)

$10\ mM\ NaClO_4$

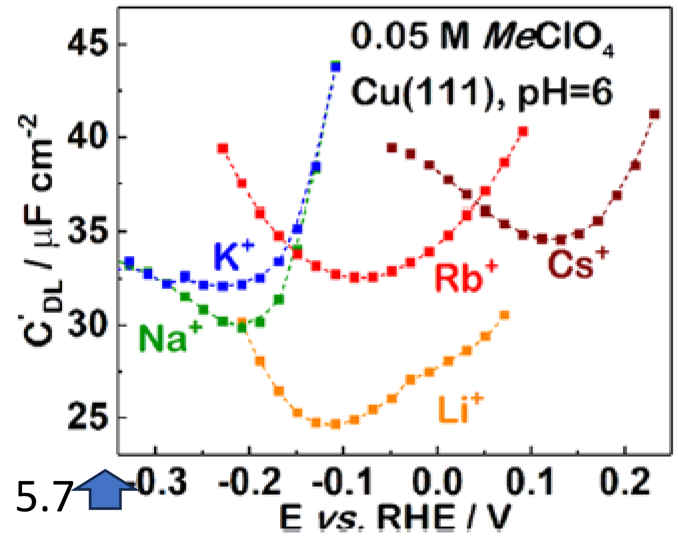
A.Łukomska, J.Sobkowski, J. Electroanal. Chem. 564 (**2004**) 95-102

The dependence of pzc of Cu electrodes on pH of solution

Electrode	Potential of zero charge (V) vs SHE[a]				
	pH				
	5.7	4.2	4	3.7	3.2
Cu (1 1 1)	−0.70	−0.68	−0.20	−0.65	−0.55
Cu (1 0 0)	−0.73	−0.72	−0.54	−0.71	−0.62
Cu (1 1 0)	−0.75	−0.73		−0.72	−0.66
Cu (poly)	−0.73	−0.72		−0.70	−0.64

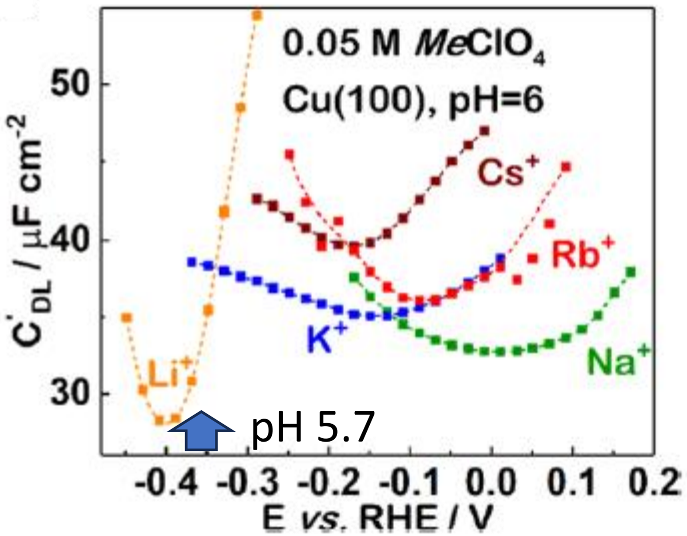
40 - 60 mV/pH

Copper can be hardly considered as ideally polarizable in neutral media

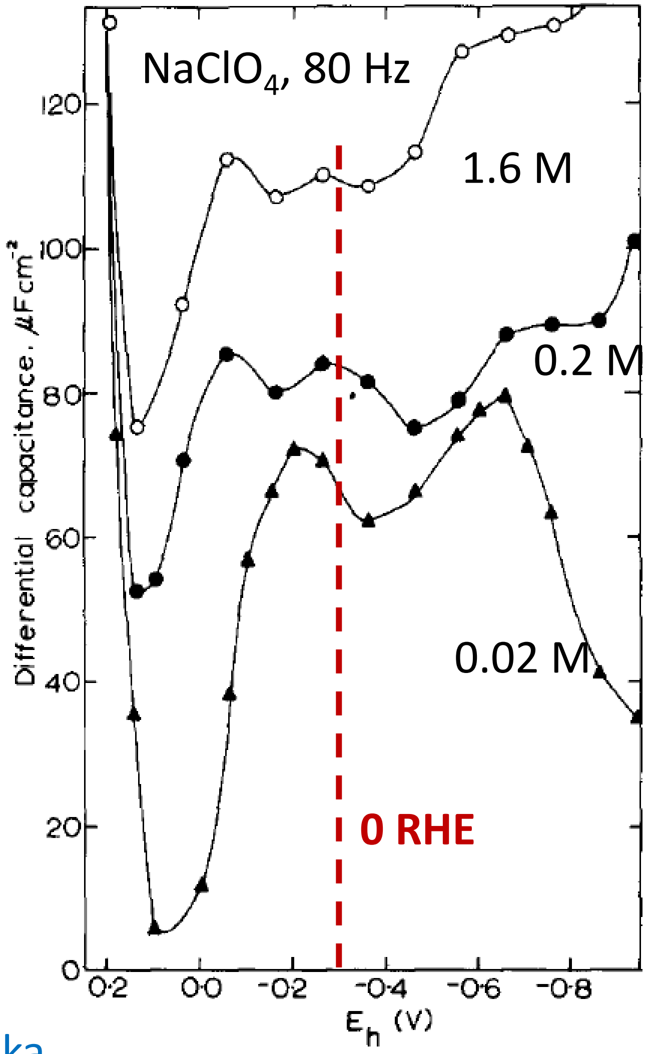


pH 5.7

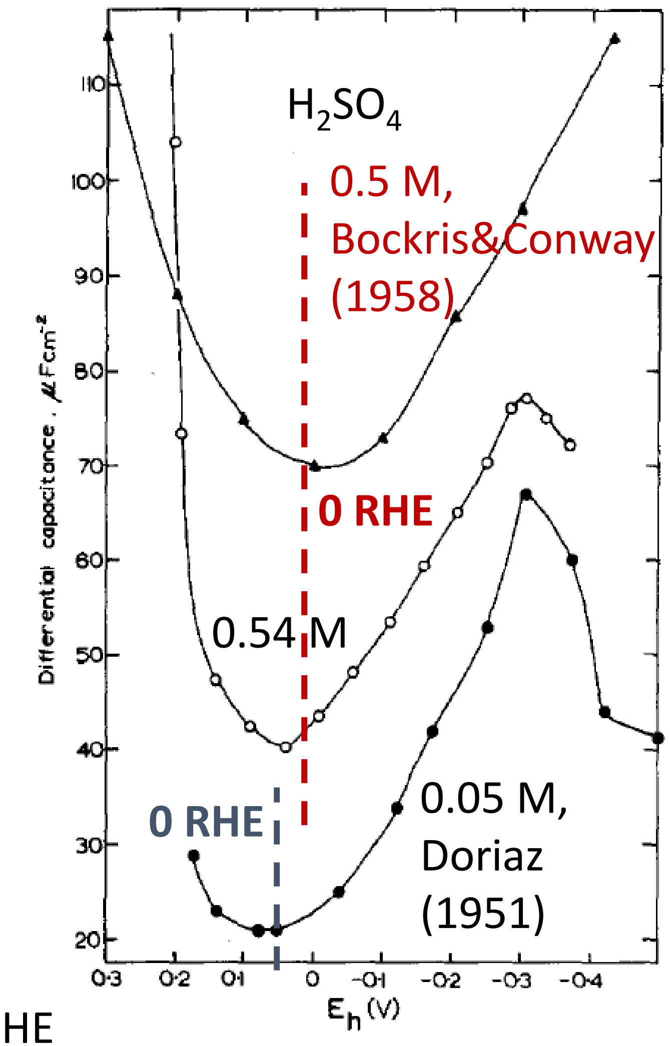
1 Hz - 30 kHz, CPE (exponent above 0.95)



S. Xue….A.S. Bandarenka, J. Phys. Chem. C 124 (**2020**)12442-12447

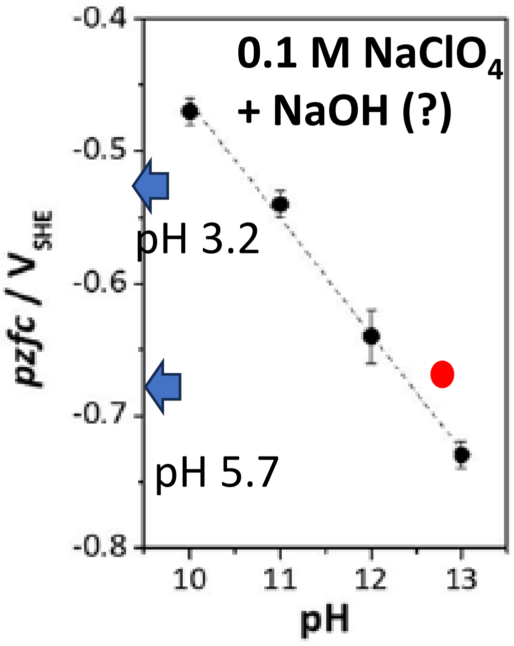


NHE

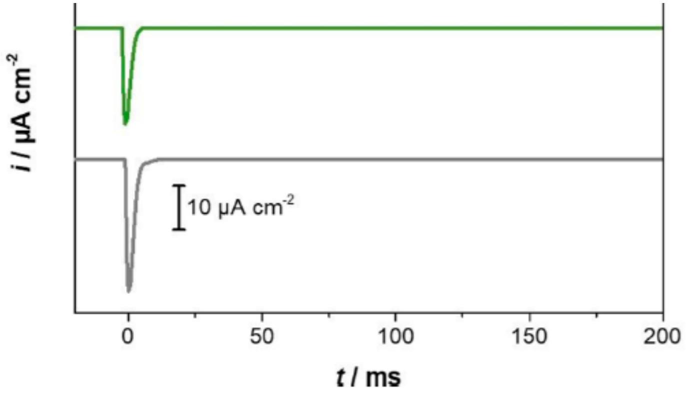


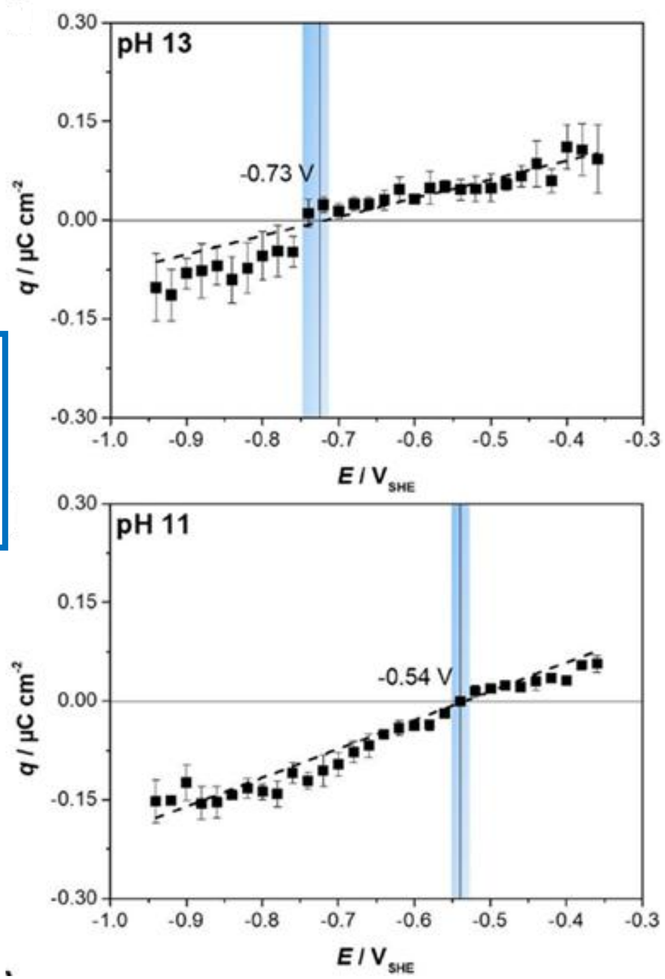
D. Armstrong, N.A. Hampson, R.J. Latham, J. Electroanal. Chem. 23 (**1969**) 361-367; much higher capacitance in alkaline solutions: N.A. Hampson, R.J. Latham, J.B. Lee, K.I. Macdonald, J. Electroanal. Chem. 31 (**1971**) 57-62

Copper, laser jump technique

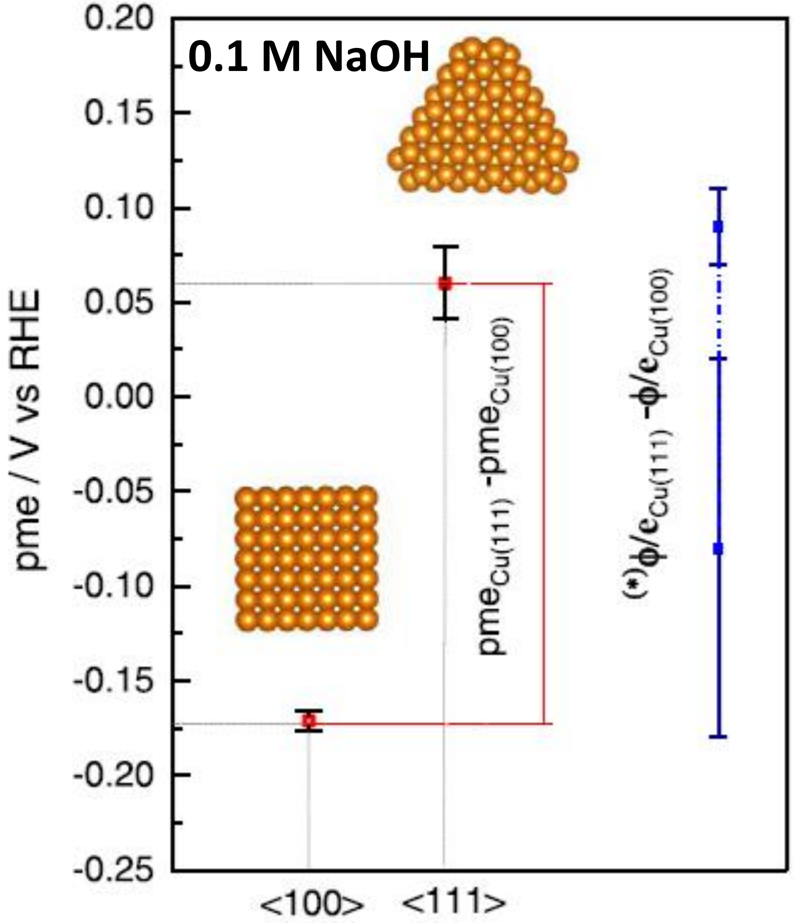


~90 mV/pH instead of 40 - 60





Cu(111), 0.5 M NaClO$_4$ + NaOH (?)

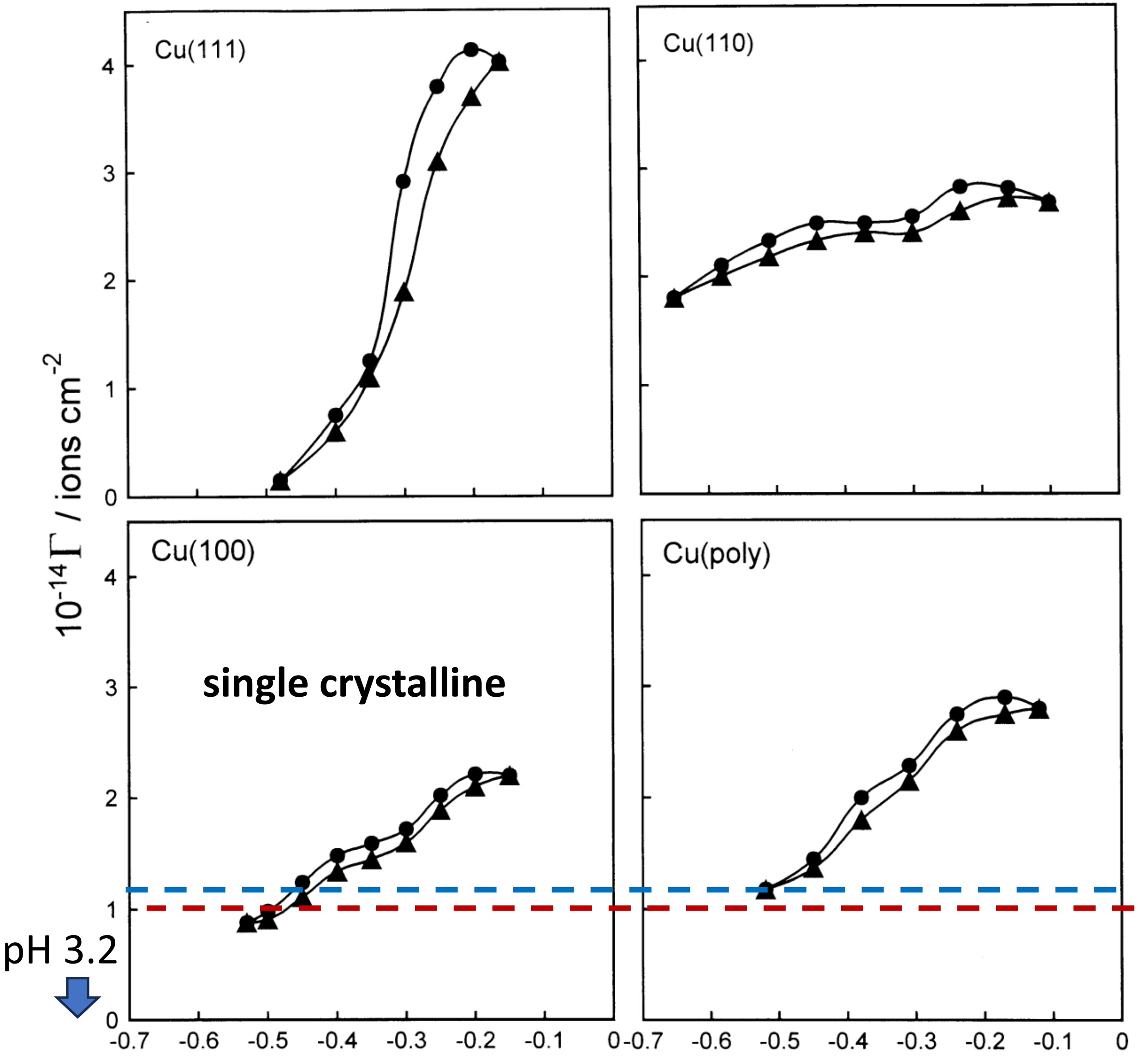


A. Auer, X. Ding, A.S. Bandarenka, J. Kunze-Liebhäuser, J. Phys. Chem. C 125 (**2021**) 5020-5028

Are the times of the order of ms allow to exclude contribution from OH adsorption?

P. Sebastián-Pascual, F.J. Sarabia, V. Climent, J.M. Feliu, M. Escudero-Escribano, J. Phys. Chem. C 124 (**2020**) 23253-23259

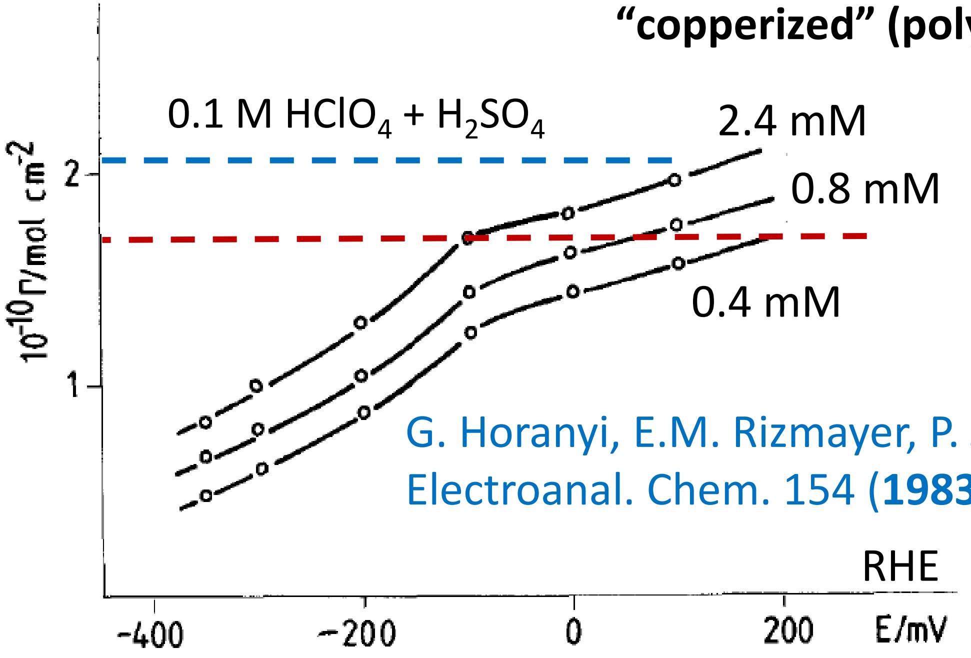
Radiotracer data on sulfate adsorption on Cu



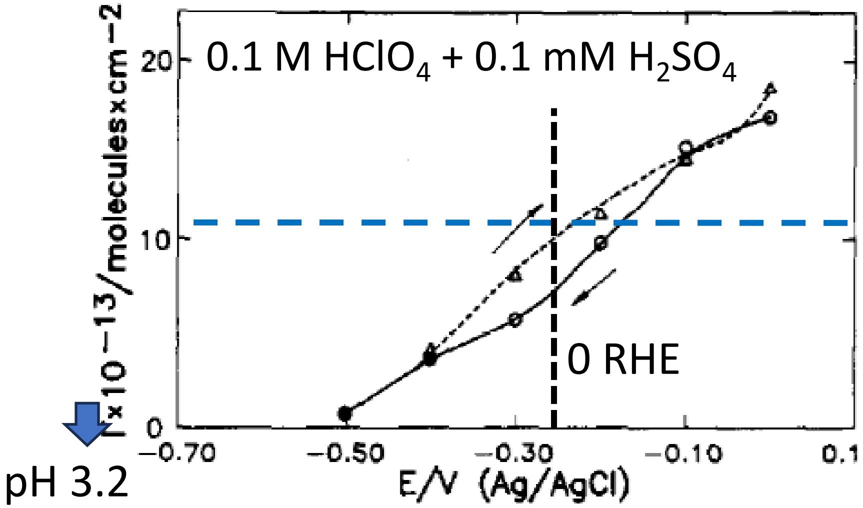
0.1 M $HClO_4$ + 0.5 mM H_2SO_4 E / V AgCl/Ag

S. Smolinski, J. Sobkowski, J. Electroanal. Chem. 463 (**1999**) 1-8

"copperized" (poly, porous)



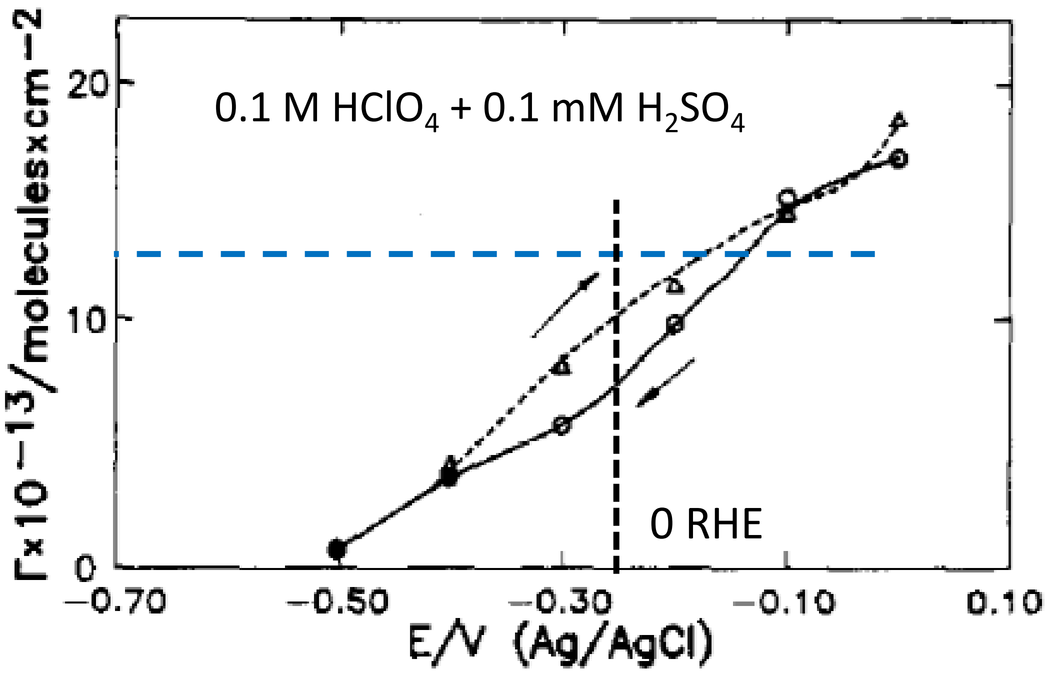
G. Horanyi, E.M. Rizmayer, P. Joo, J. Electroanal. Chem. 154 (**1983**) 281-286

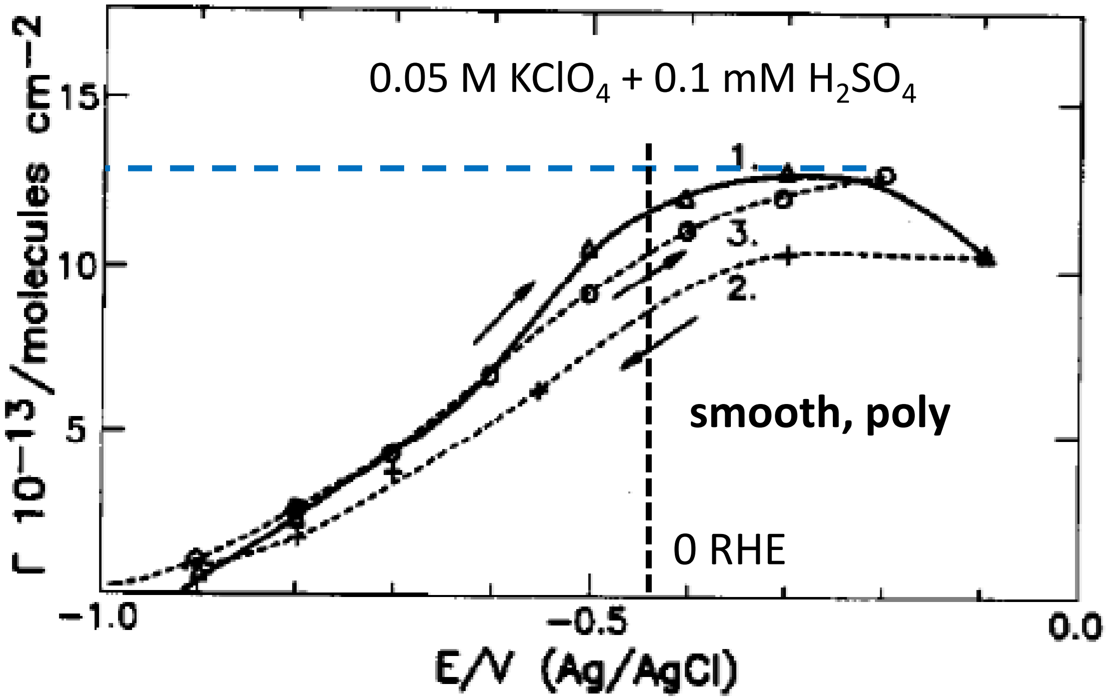


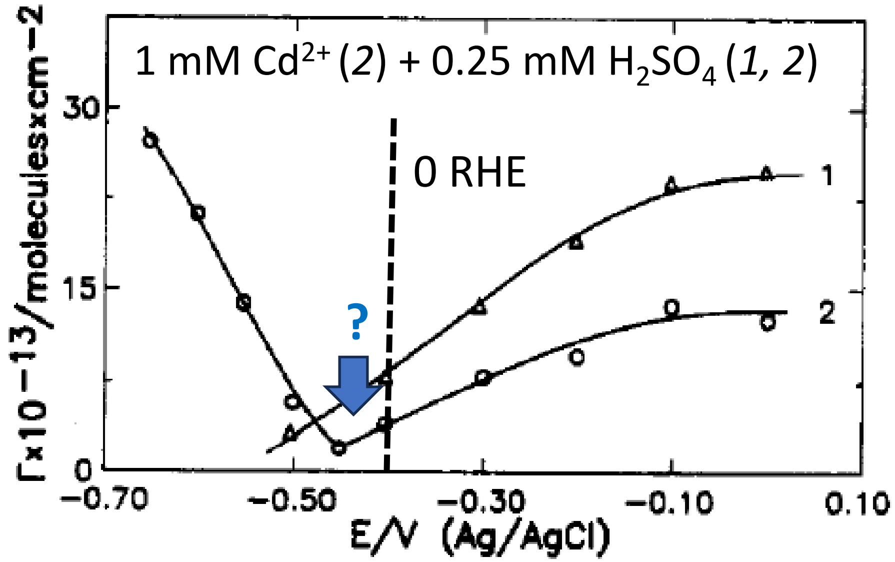
Poly, smooth

L. M. Rice-Jackson, G. Horanyi, A. Wieckowski, Electrochim. Acta 36 (**1991**) 753-757

Copper, sulphate adsorption at pH ~1 and ~4



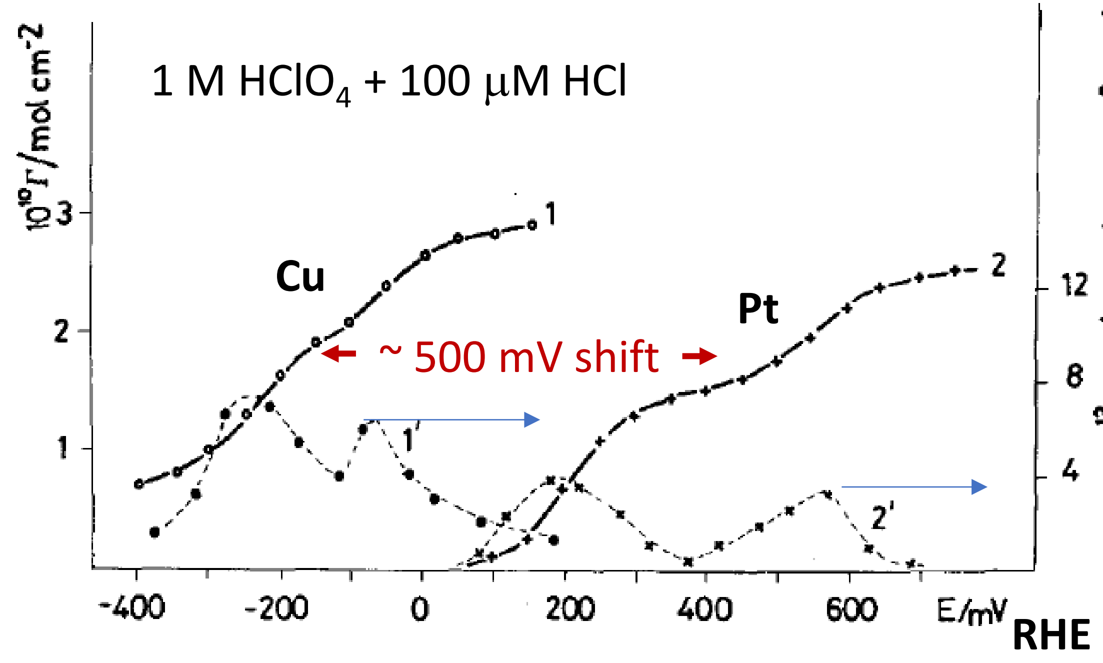


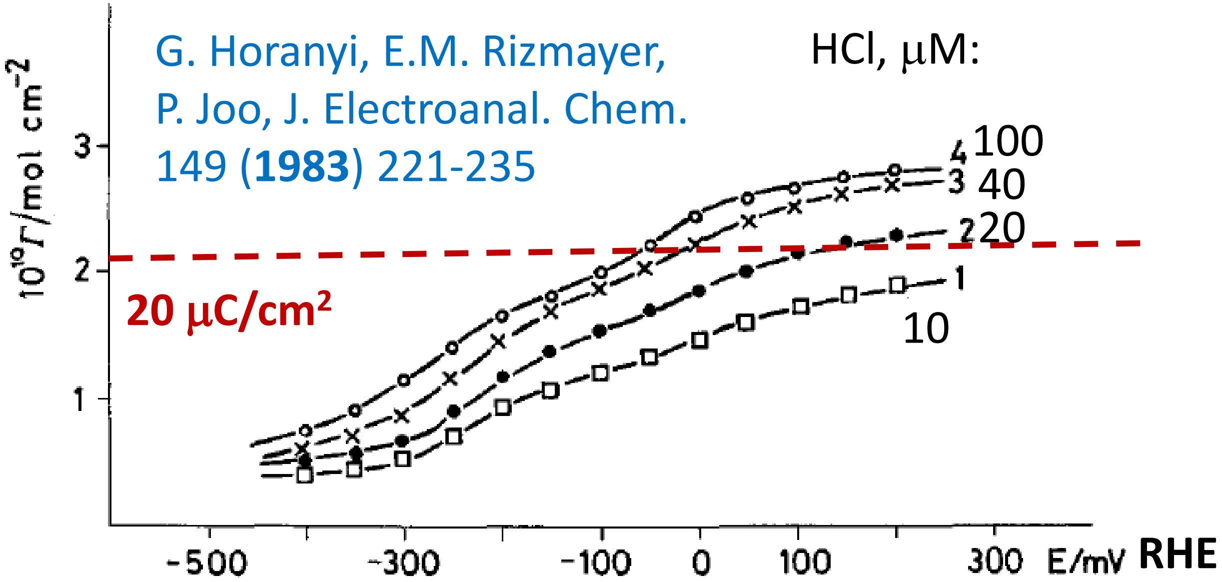


L. M. Rice-Jackson, G. Horanyi, A. Wieckowski, Electrochim. Acta 36 (**1991**) 753-757

Looks like pzfc in acid is below RHE zero, and pH-induced shift seems to be stronger than known for Pt. Induced adsorption of sulfate?

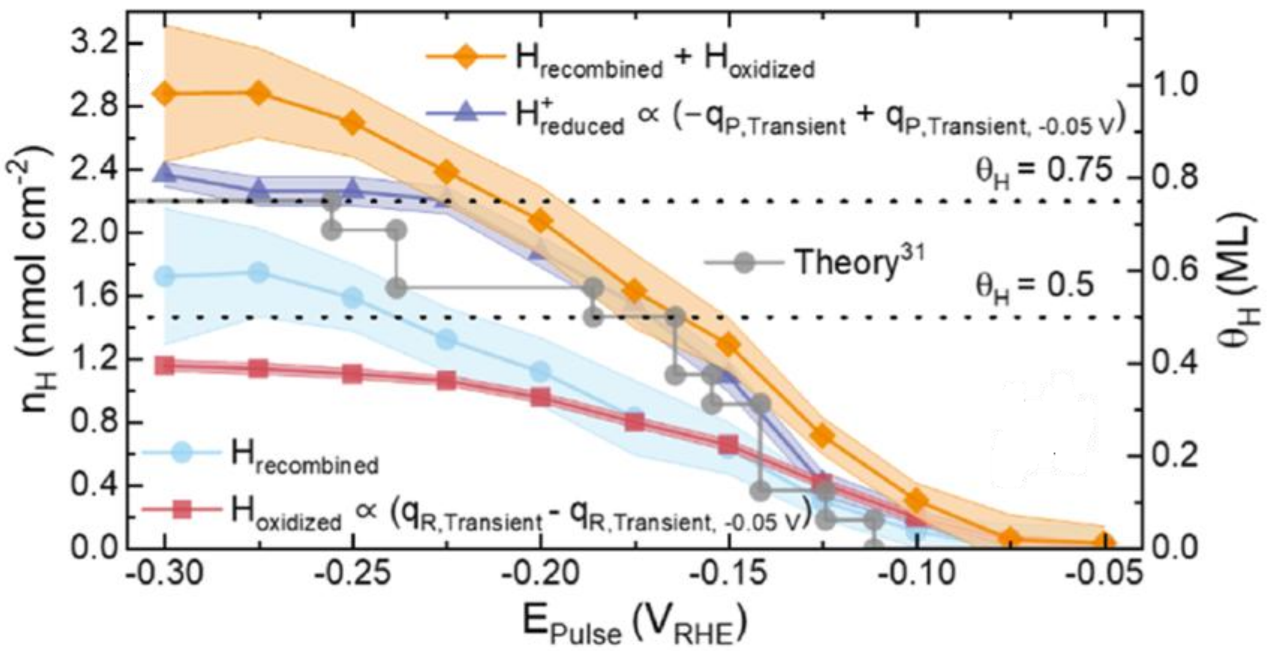
“Copperized” electrodes with roughness factor up to 80, radiotracer technique (left) and recent estimates of H coverage (right)





G. Horanyi, E.M. Rizmayer, P. Joo, J. Electroanal. Chem. 149 (**1983**) 221-235

Cu(111), 0.1 M HClO$_4$

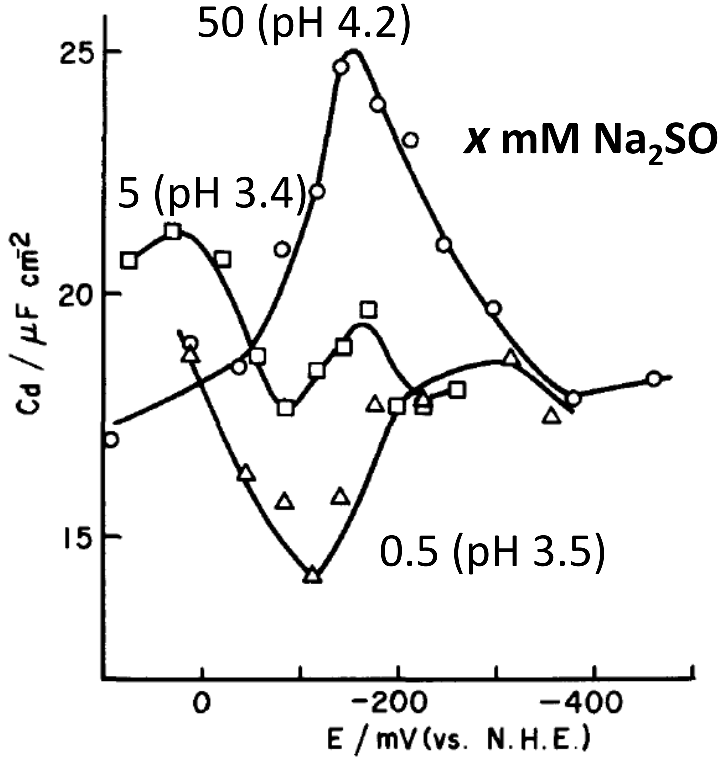


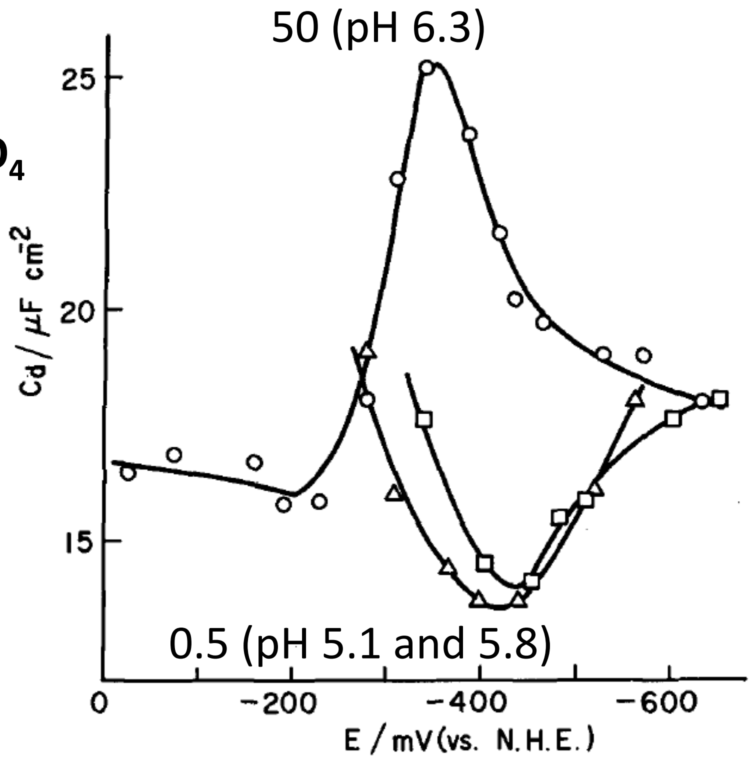
Estimates from in situ mass-spectrometry are not qualitative, but confirm essential H surface coverage in the vicinity of the supposed pzfc.

D. Raciti, T.P. Moffat, J. Amer. Chem. Soc. 147 (**2025**) 4038-4051, *they name this H hydride*

Capacitance data for Ni…. …and direct radiotracer pzfc data (rather inaccessible publication)

T. Ohmori, J. Electroanal. Chem. 157 (**1983**) 159-164



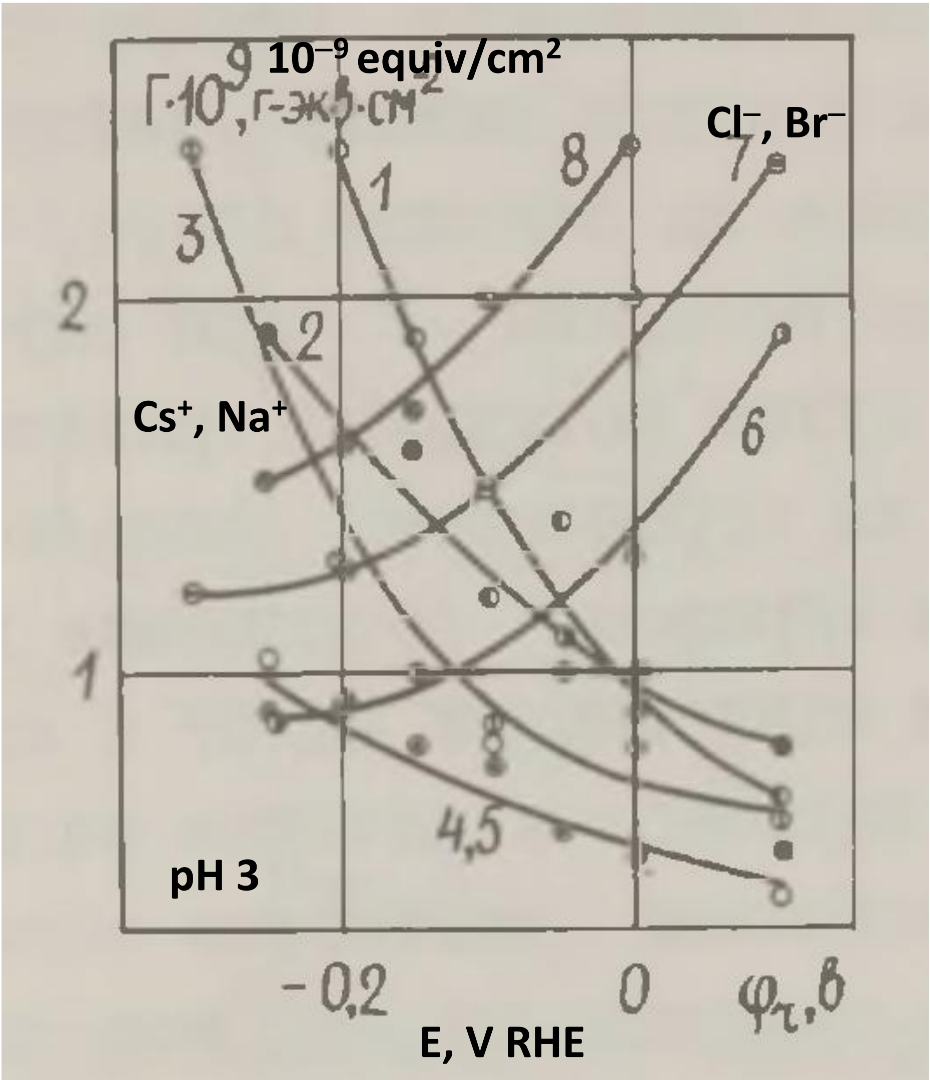


~ 0.1 V RHE **~ – 0.1 V RHE**

no recognizable trend, it is better to compare in NHE scale:

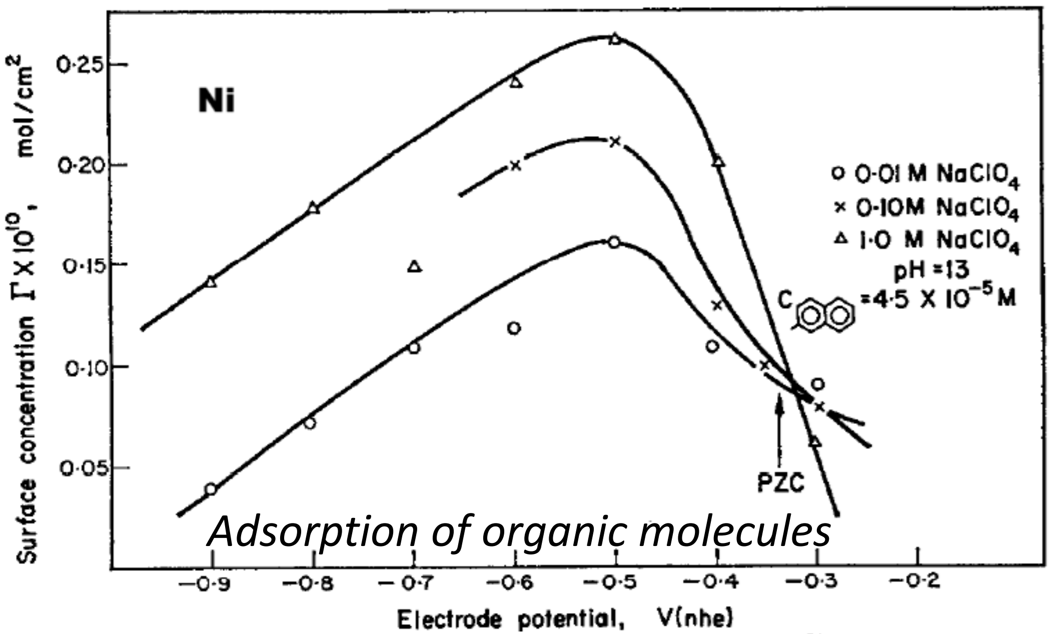
G. Nagy, D. Roy, Chem. Phys. Lett. 214 (1993) 197-202; Surface Sci. 320 (**1994**) 7-16

~ – 0.4 V NHE in 50 mM $NaClO_4$, supported by anions adsorption data from SHG



N.A. Balashova et al., in "Double layer and adsorption on solid electrodes" IV, Tartu (**1975**) 24-32

Less direct pz(f?)c estimates for Ni

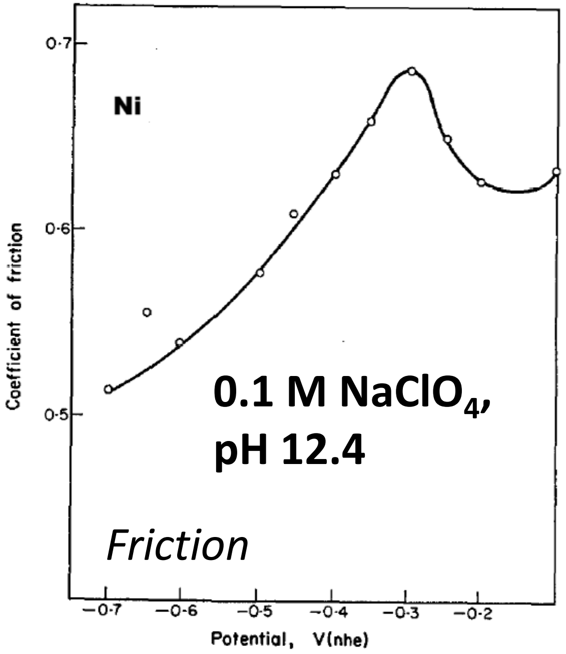


Adsorption of organic molecules

J.O'M. Bockris, S.D. Argade, E. Gileadi, Electrochim. Acta 14 (**1969**) 1259-1283

~ + 0.4 V RHE in alkaline medium

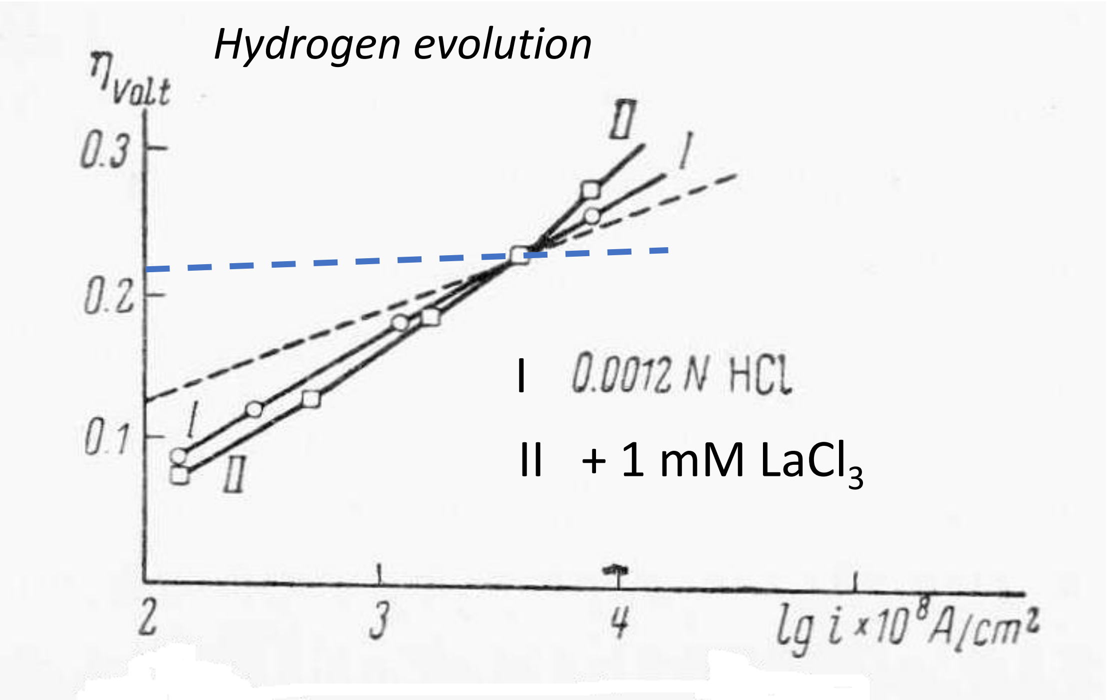
Can be considered as a sort of electrocapillary curve?



0.1 M $NaClO_4$, pH 12.4

Friction

~ – 0.2 V RHE in acidic medium



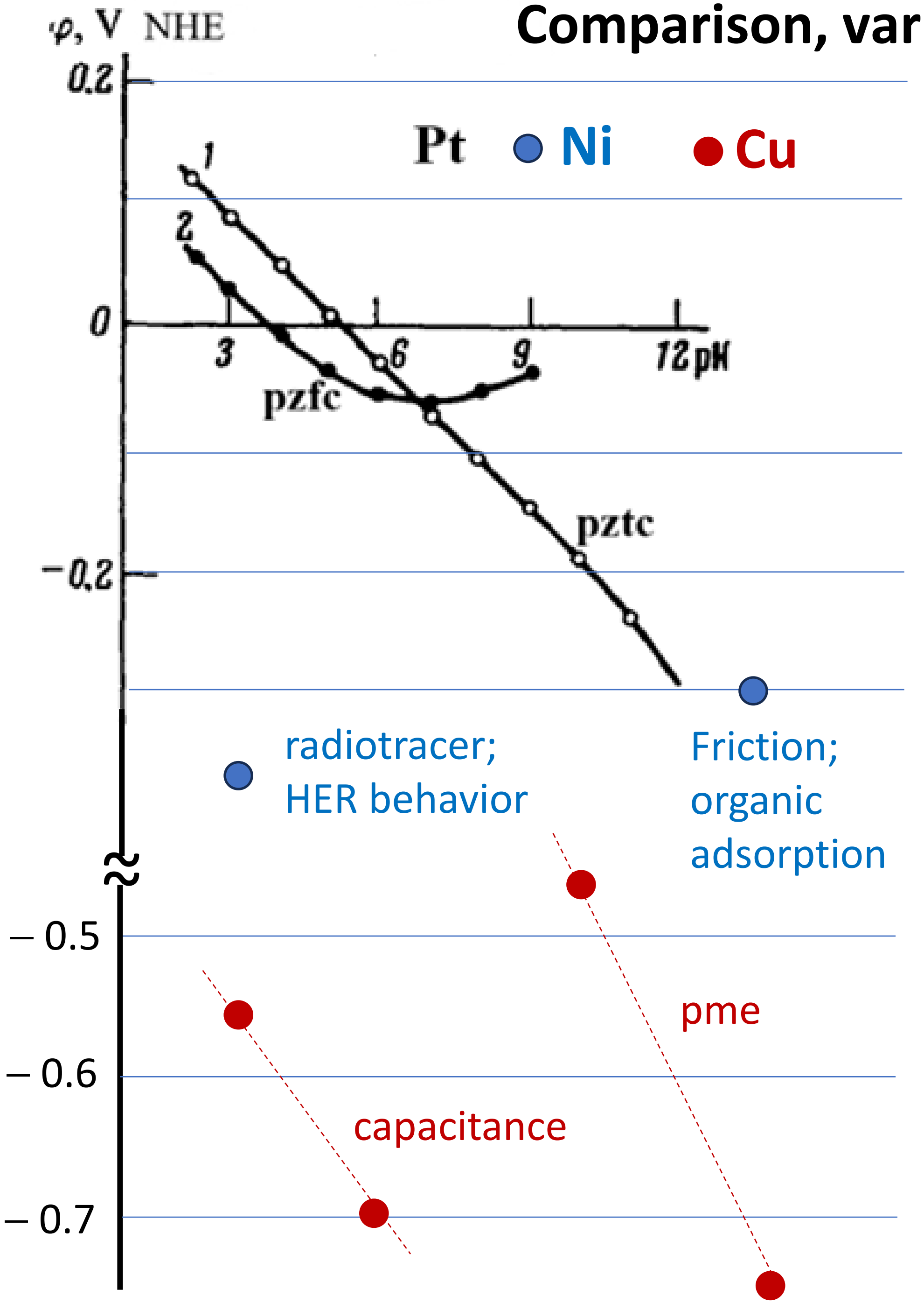
Hydrogen evolution

I 0.0012 N HCl

II + 1 mM $LaCl_3$

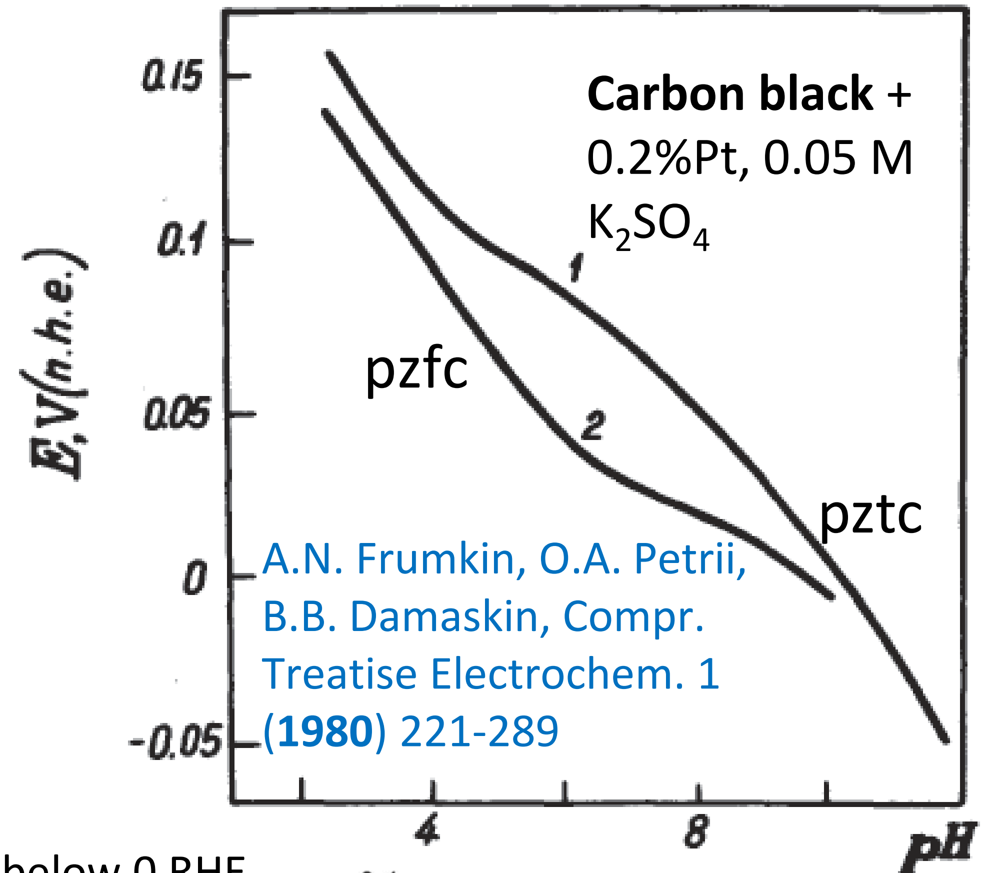
P. Lukowzew, S. Lewina, A. Frumkin, Acta Physicochim. URSS 11 (**1939**) 21-44

Comparison, various materials



radiotracer; HER behavior

Friction; organic adsorption

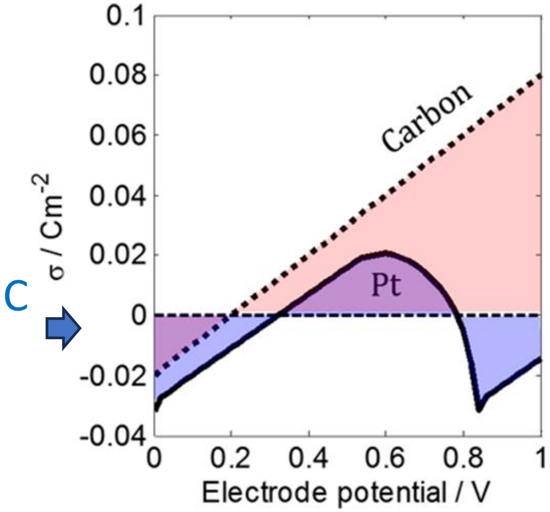


Carbon black + 0.2%Pt, 0.05 M K_2SO_4

A.N. Frumkin, O.A. Petrii, B.B. Damaskin, Compr. Treatise Electrochem. 1 (**1980**) 221-289

For Cu, slightly below 0 RHE at pH 6.8 (CO_2 reduction)

J. Huang, J. Zhang, M. H. Eikerling, J. Phys. Chem. C 121 (**2017**) 4806-4815



Preliminary summary (to continue with electrocatalysis, lecture 3)

Hg-like metals, survive in **acidic and neutral media**;
pzc=pzfc: in the interval –0.17 (Sb) - –0.9 (Zn) V SHE;
'double layer' data are available for potentials between
HER onset and anodic oxidation onset.

Au, Ag, (Cu), iron group metals:
pzc=pzfc in a limited interval,
especially at high pH

Oxides, pzfc is pH-dependent

Platinum group metals, pzfc is
pH-dependent; pzfc inversion

Surface reconstruction

Surface and even bulk
reconstruction

Hg-like metals
as well

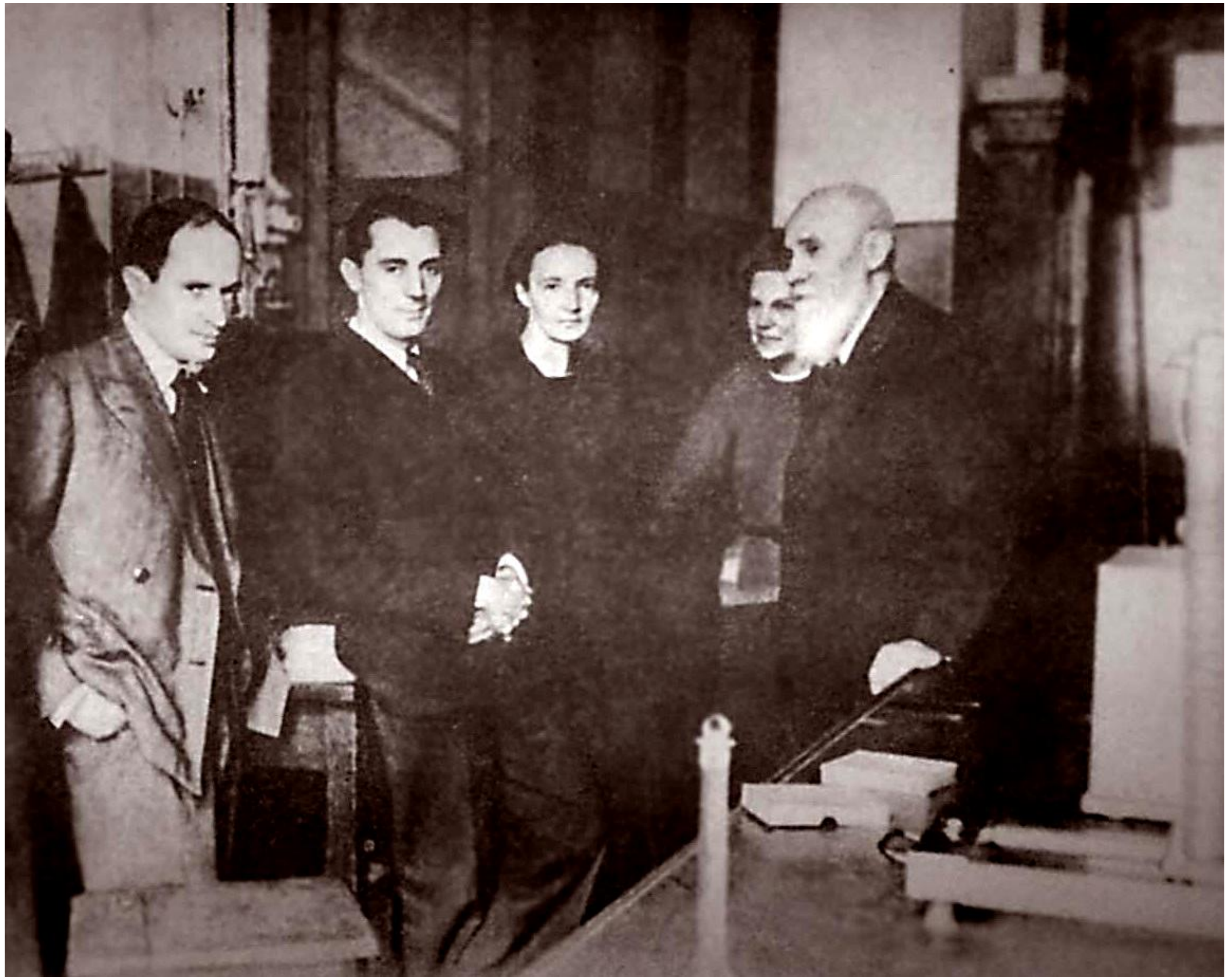
Platinum group metals
and sometimes Au

Platinum group metals,
Au, Ag

- **Uncertainty of interfacial zone is minimal for reactions occurring in water stability window; for CO_2RR and OER the uncertainty exists for any catalyst, but we should try to guess on the basis of available trends.**

1935

1975



Alexander N. Frumkin (1895-1976)

with F. and I. Jolio-Curie, N.A. and A.N. Bakh

Boris B. Damaskin
(1932-2019)

Oleg A. Petrii
(1937-2021)