Thermodynamics of the perfectly polarizable electrodes: complicating and less known issues

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- Experimental origin of free and total charge values
- Inversion of free charge and negative equilibrium “double layer” capacitance
- Effects of foreign adsorbates (in respect to reaction zones in electrocatalysis)
- Beyond platinum group metals: copper

Basic reading: *Frumkin, Petrii, Damaskin,* Compr. Treatise Electrochem. 1980; the articles of *Alicante school*, incl. their 1998-2000 articles with *M.J. Weaver* (let us also ask *Victor Climent* to advise).

The most important quantities and relationships

Free charge σ

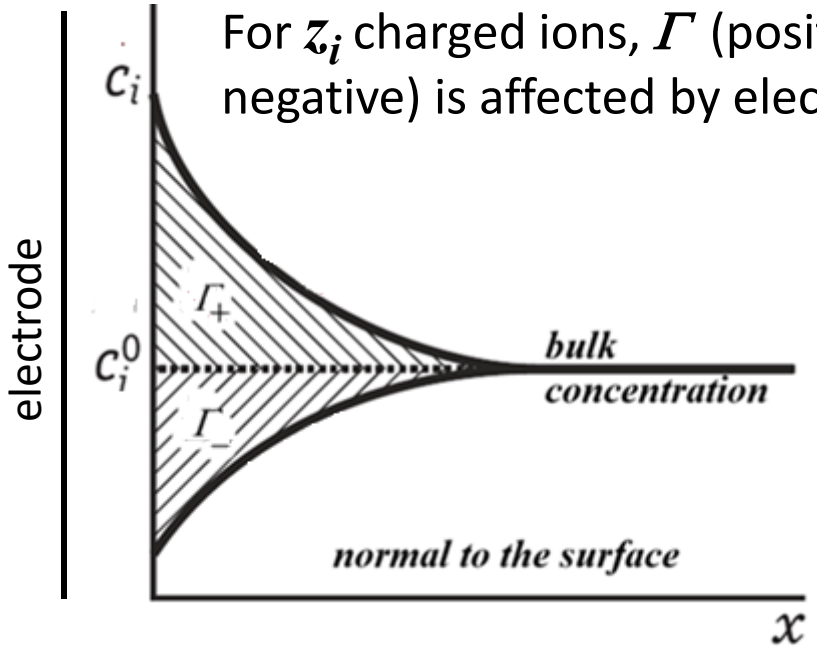
Surface excess Γ <Gibbs adsorption>

Total charge Q

Work of surface formation γ

$$\sigma = -F\sum_i (z_i\Gamma_i)$$

For z_i charged ions, Γ (positive or negative) is affected by electrostatics



From voltammetry or galvanostatic experiments: ΔQ

For ideally polarizable electrodes: $\sigma = Q$, one only needs to determine a single value, potential of zero charge.

For perfectly polarizable electrodes (**coadsorption of ions and atoms**), separation of σ is required. Potentials of zero total charge (pztc) and zero free charge (pzfc) are different.

In both cases, it is also possible to operate with Gibbs Equation:

$$d\gamma = -\sum_j \Gamma_j d\mu_j$$ (μ is chemical potential)

Typical perfectly polarizable electrode: coadsorption of ions and H_{ad} atoms

$\mathbf{H^+ + e = H_{ad}}$ **(or** $\mathbf{H_2O + e = H_{ad} + OH^-}$**)** , well known for platinum group metals

Consider solution of acid HA supported by **excess of CA salt**.

H_{ad}, H^+, C^+, and A^- participate in equilibrium:

$$d\gamma = -\Gamma_H d\mu_H - \Gamma_{H^+} d\mu_{H^+} - \sum_j \Gamma_j d\mu_j \qquad \text{Gibbs Eq.}$$

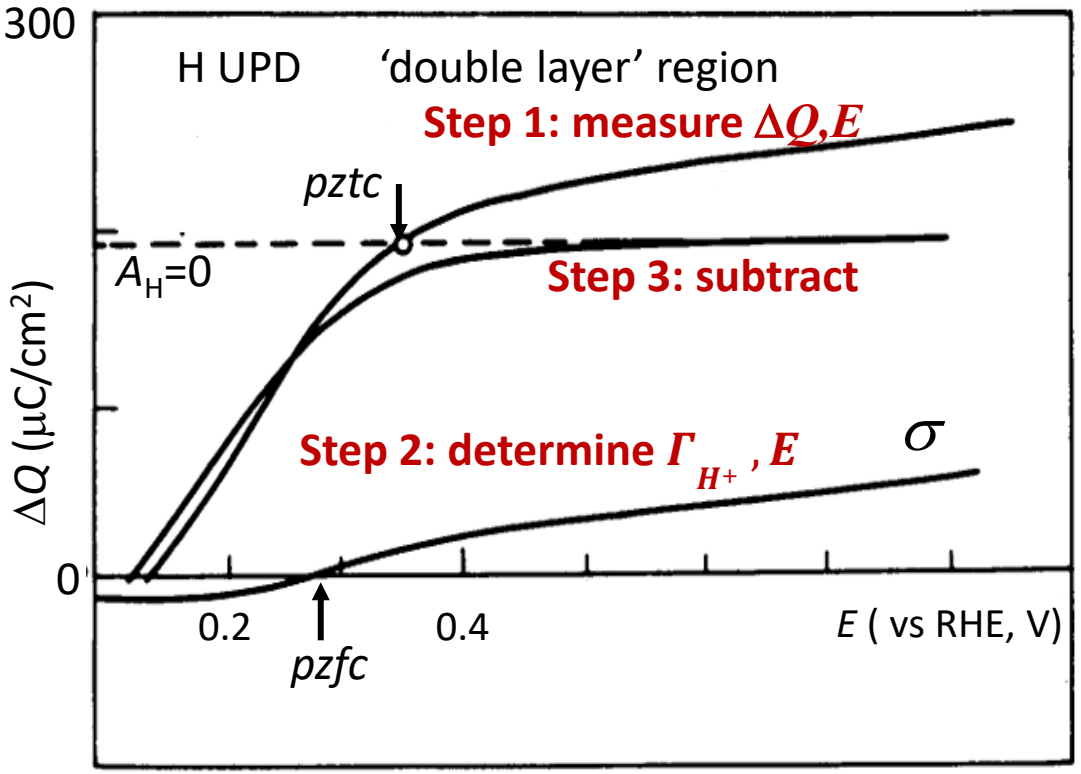
$$dE = {}^{d\mu_{H^+}}\!/_{F} - {}^{d\mu_H}\!/_{F} \qquad \text{Nernst Eq.}$$

To create a new surface unit, add $(\Gamma_{H^+} + \Gamma_H)$ amount of H^+, and electric charge $-F\Gamma_H$ to transform a portion of H^+ into adatoms:

$$F\Gamma_H = Q = \sigma - FA_H \qquad (\boldsymbol{A} \text{ is surface concentration})$$

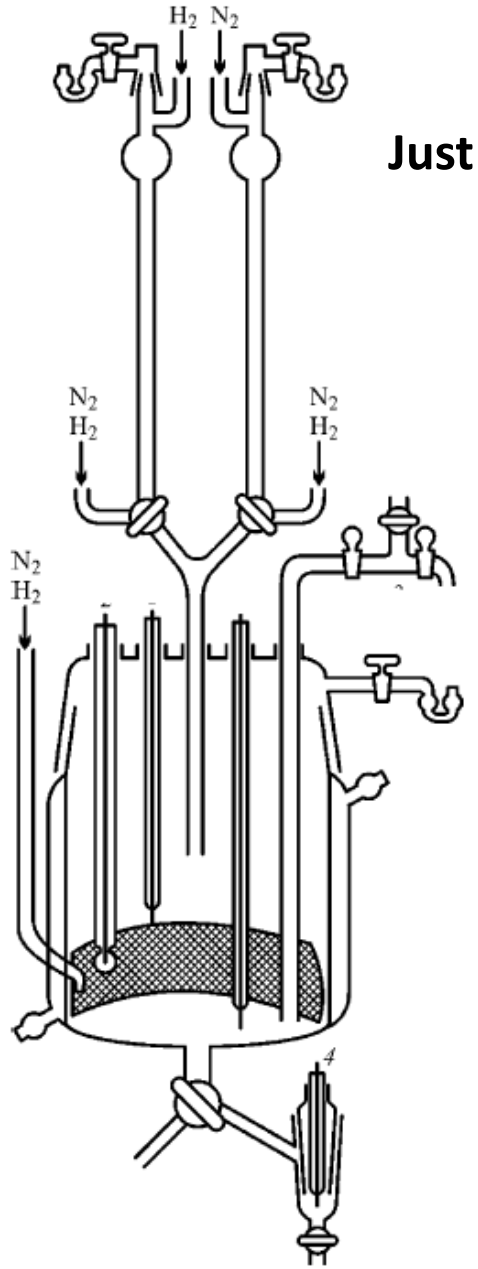
Assume μ_j (μ_C, and μ_A), $\mu_H = \text{const}$ (RHE scale)

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



Frumkin, Šlygin, Acta Physicochim. URSS 1936

This concentration in the "double layer" is negligible **if [C⁺] >> [H⁺] and if there is no specific adsorption of H⁺.**



How is it possible to determine Γ_{H^+}?

Just by titration if the real surface of electrodeposited metal ≥ 1 m².

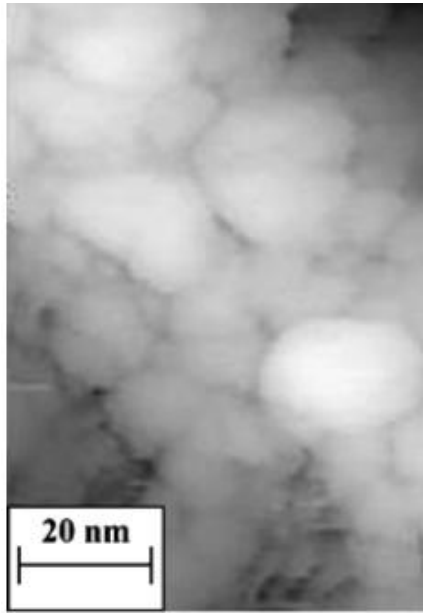
Surface: 10^{-9} mol/cm^2·10^4 cm^2 = **10^{-5}** mol

Solution bulk: 10^{-2} mol/dm^3·10^{-2} dm^3 = **10^{-4}** mol

Usual analytical techniques can be applied to determine surface excess for the electrodes with high roughness.
< **Radiotracer technique** can be sensitive enough even for smooth electrodes, but for a limited number of ions. >

Additional trick: isoelectric conditions

If Q is determined for any solution, one can replace this solution with another one, to measure E, and to recalculate Q, E curve from ΔQ, E curve.

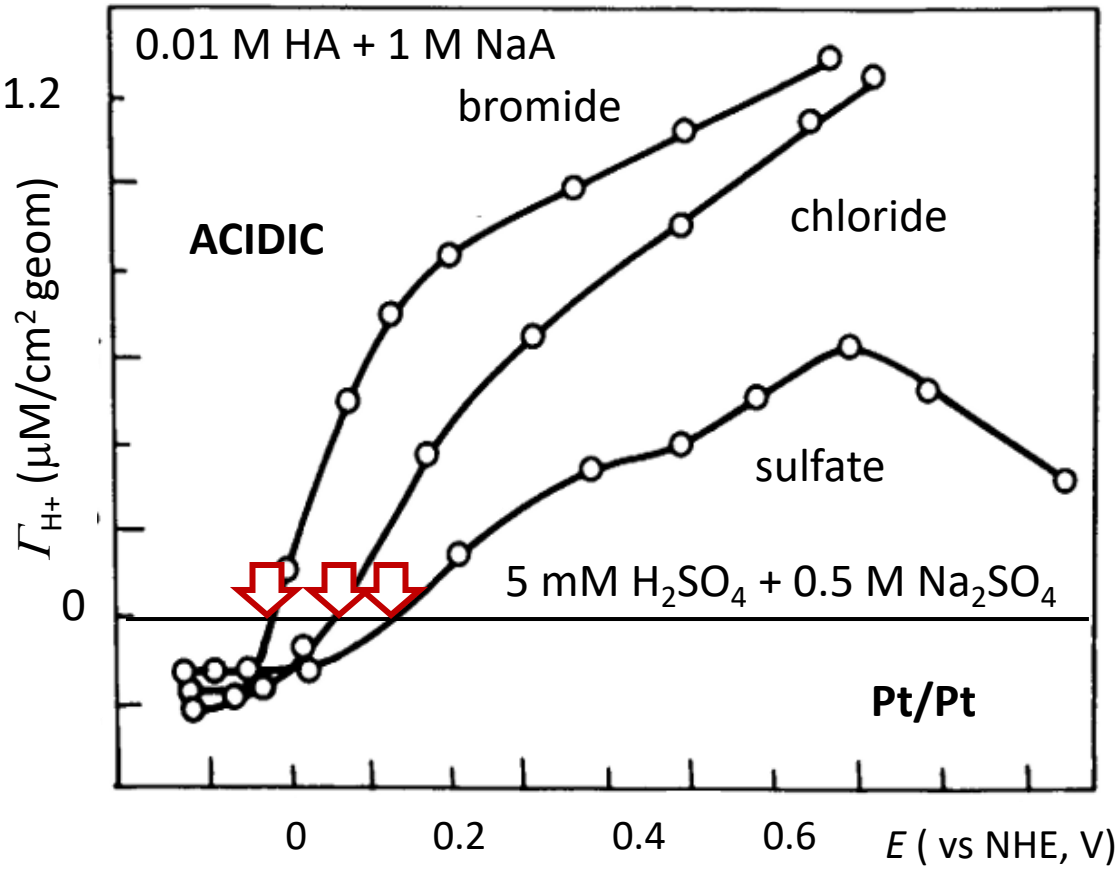


Platinized platinum (**Pt/Pt**):
mean particle size of ca. 10 nm;
thickness 1-2 μm.

Roughness factor ~ 1000

The most important qualitative effects

pzfc

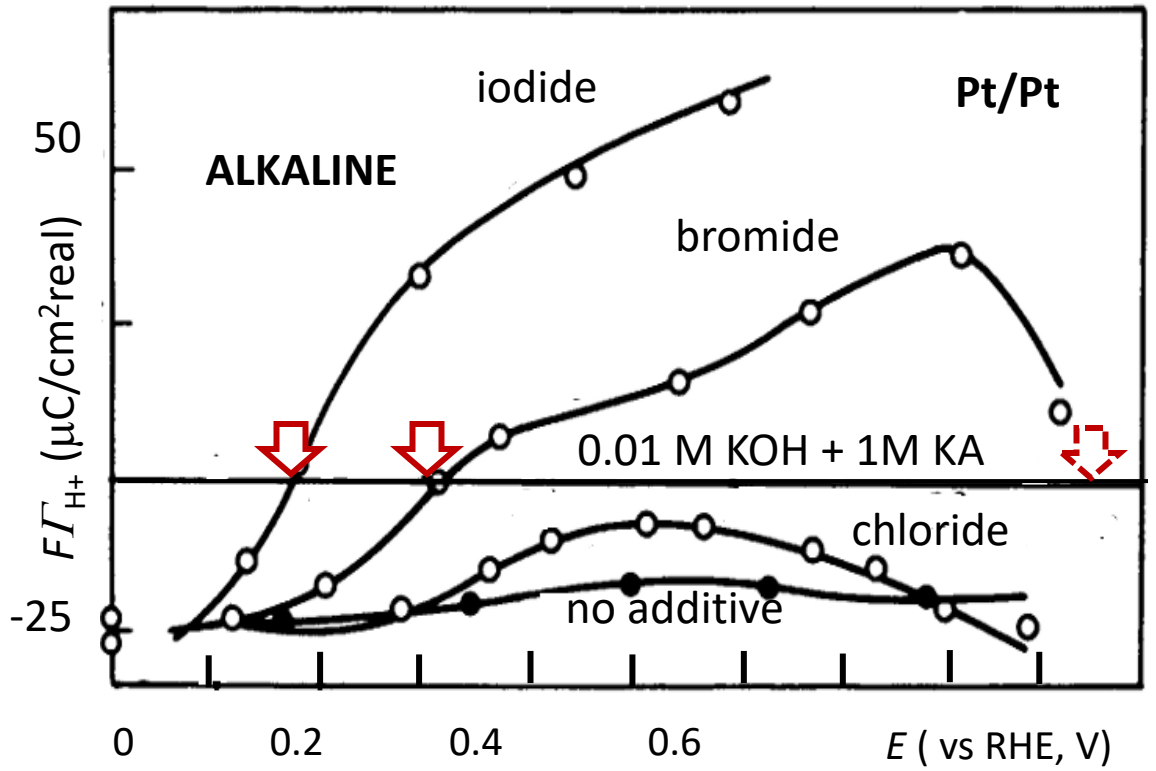


Šlygin, Frumkin, Medwedowsky, Acta Physicochim. URSS 1936
<real surface area remained unknown in 1930s>

Strong **deviations** of Γ_{H^+}, E curves (σ, E) from **linearity**,

and even their **nonmonotonic** behavior (charge inversion);

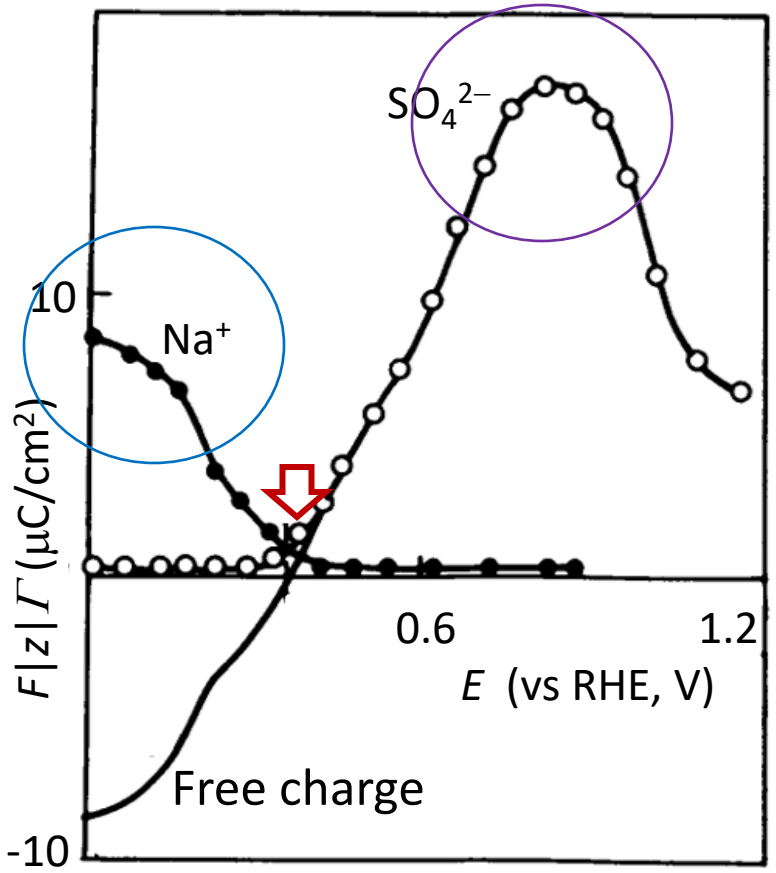
pzfc can be absent, or two pzfc can exist.



Petrii, Frumkin, Kotlov, J Inst Catal Hokkaido U 1968

Charge inversion is solidly confirmed by direct measurements of ionic adsorption: radiotracer techniques

1.5 mM Na_2SO_4 + 0.5 mM H_2SO_4



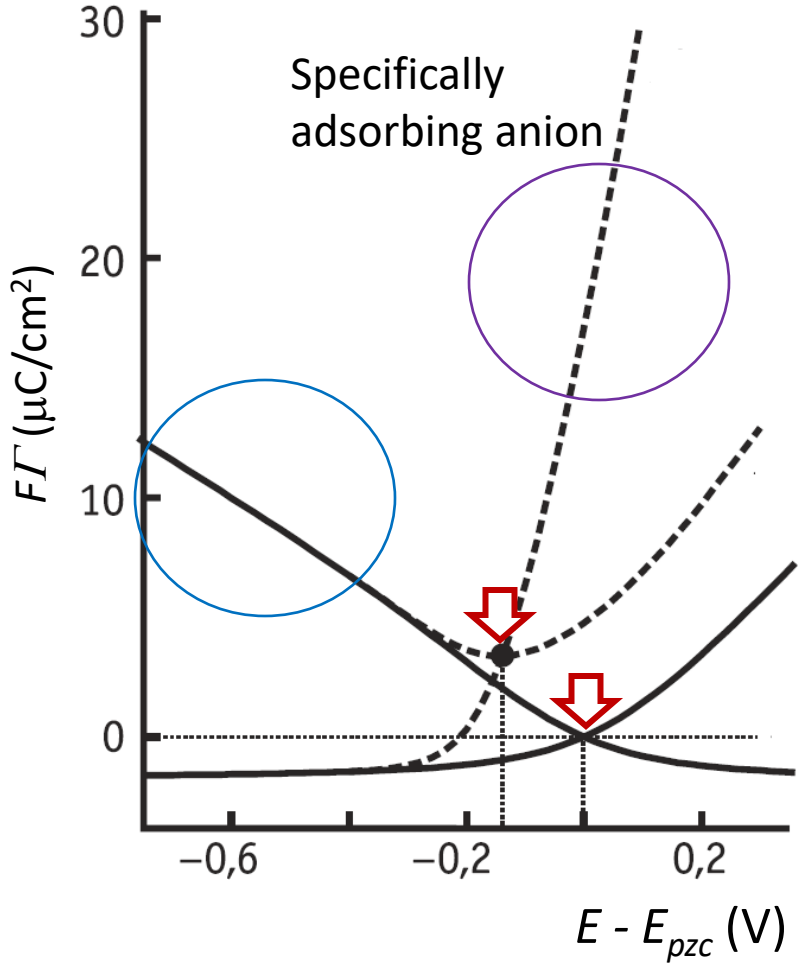
$$\sigma = -F\sum_i (z_i\Gamma_i)$$

Strong **deviations** of Γ_i, E curves from **linearity**,

Γ_i, E **nonmonotonic** behavior: adsorption is suppressed by adatoms:

- by H_{ad} for cations,
- by O_{ad} (or OH_{ad}) for anions.

Schematic dependence for ideally polarizable electrode

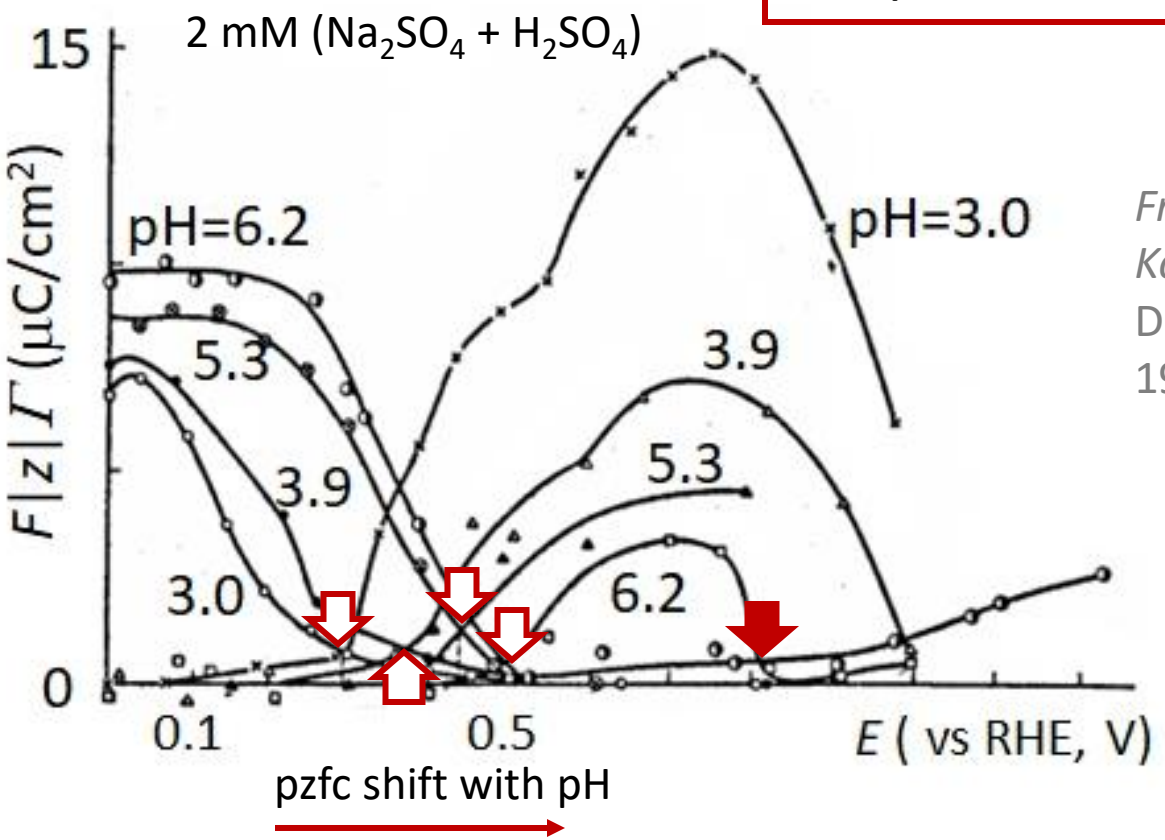


Kazarinov, Balashova, from various article of 1964-1966, as presented in Frumkin Chapter 1980

Charge inversion is strongly pH-dependent

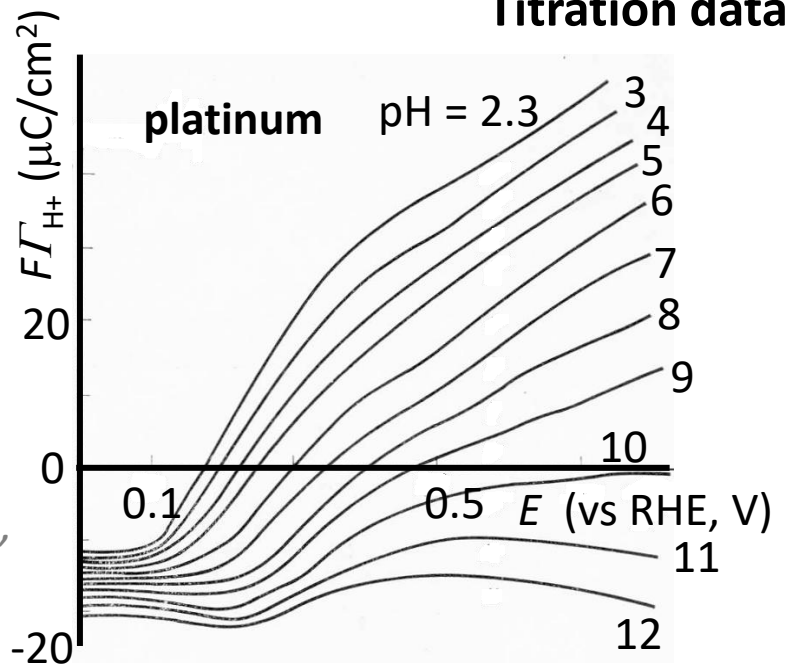
Radiotracer data

No pzfc in alkaline media.



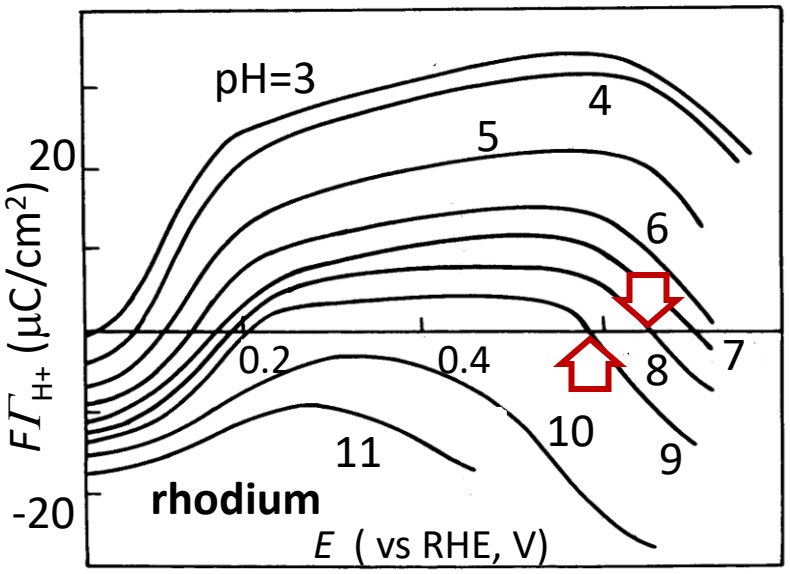
Kolotyrkina, Petrii, Kazarinov, Sov. Electrochem. 1974

Titration data



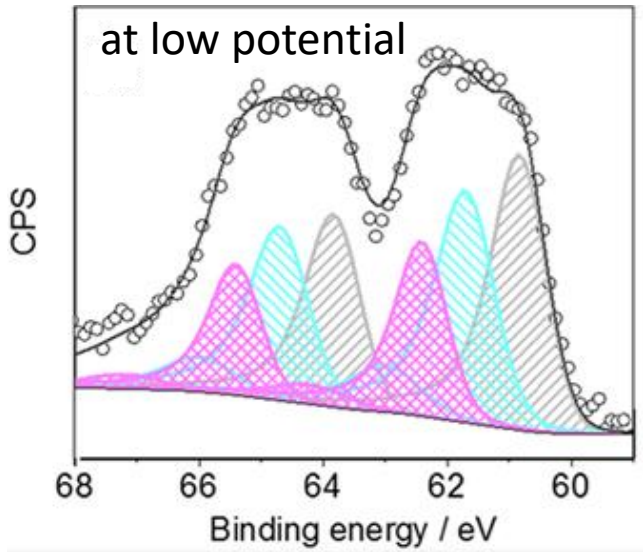
Frumkin, Petrii, Kolotyrkina-Safonova, Doklady Phys. Chem. 1975

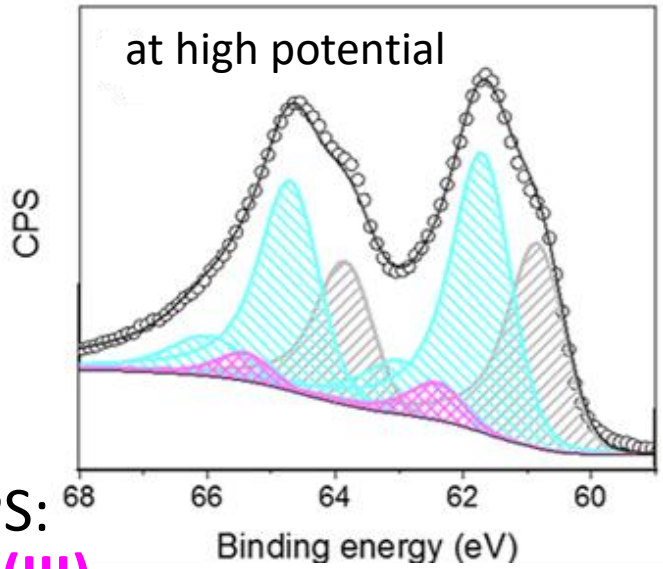
0.1 M KCl, various pH



Notoya, Petrii, Doklady Phys. Chem. 1976

Free charge behavior for IrO_x oxide is qualitatively the same as for metals in O_{ad} region



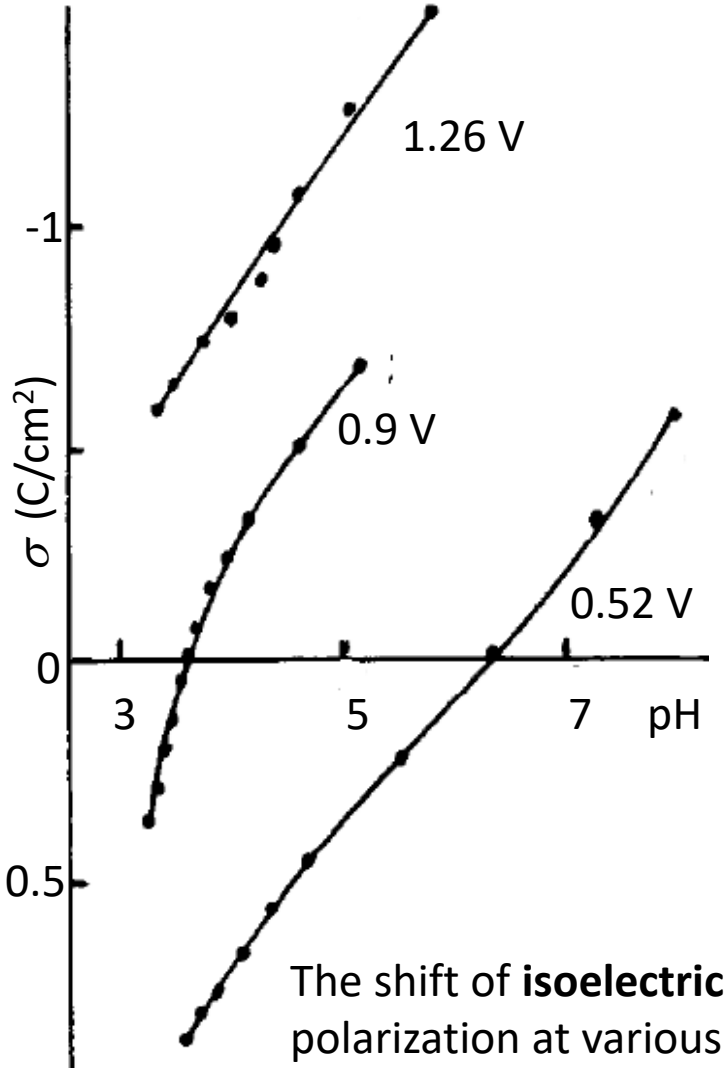


XPS:

Ir(III)

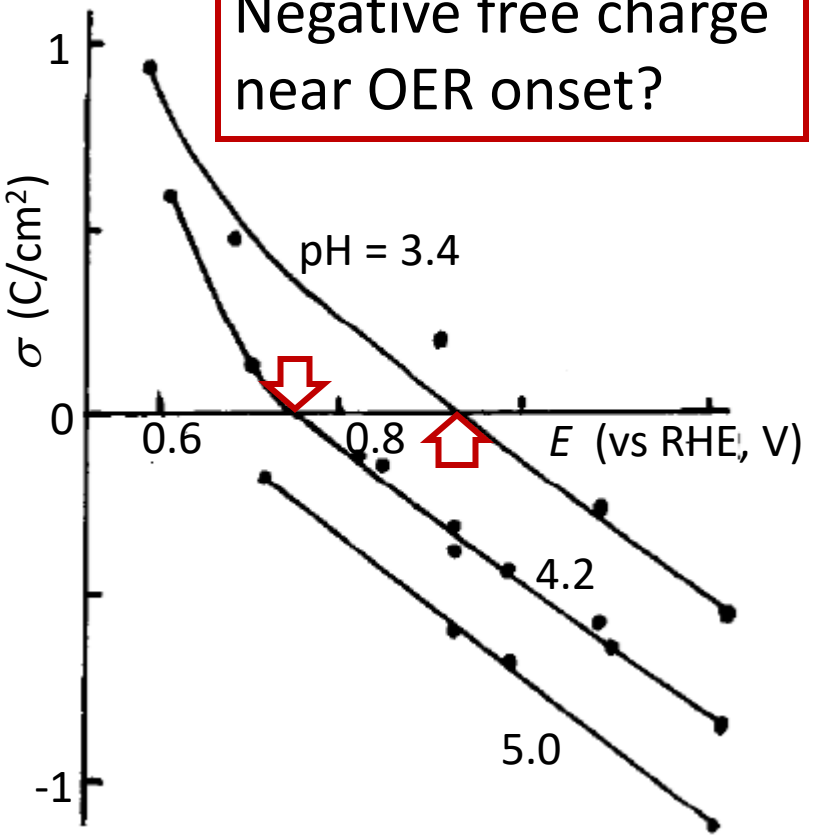
Ir(VI)

Saveleva…..Savinova, Phys. Chem. Lett. 2018



The shift of **isoelectric point** after polarization at various potentials

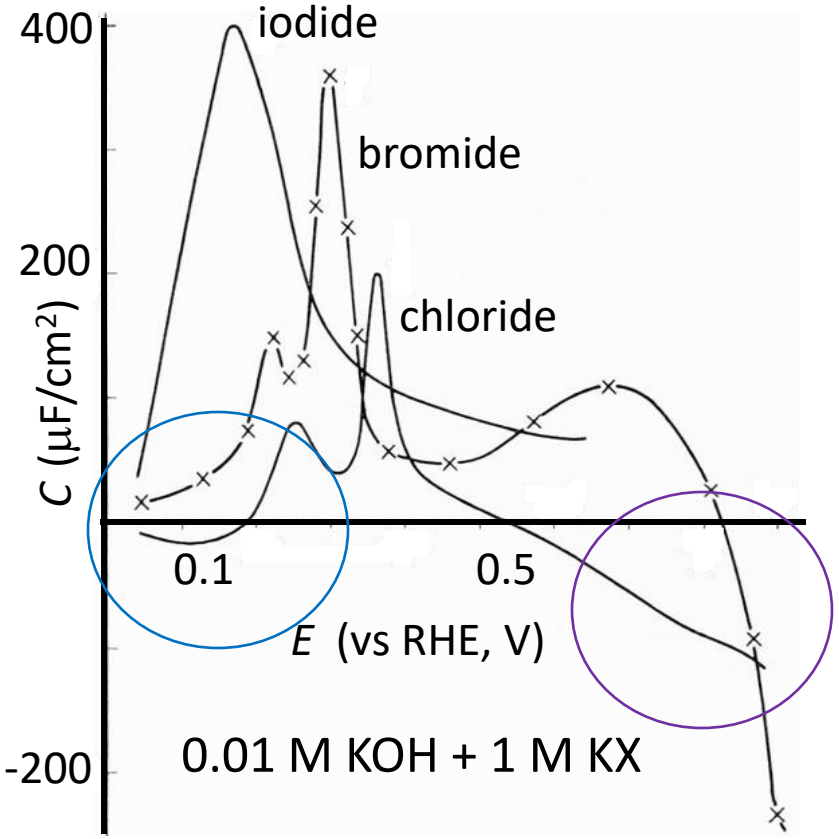
Negative free charge near OER onset?



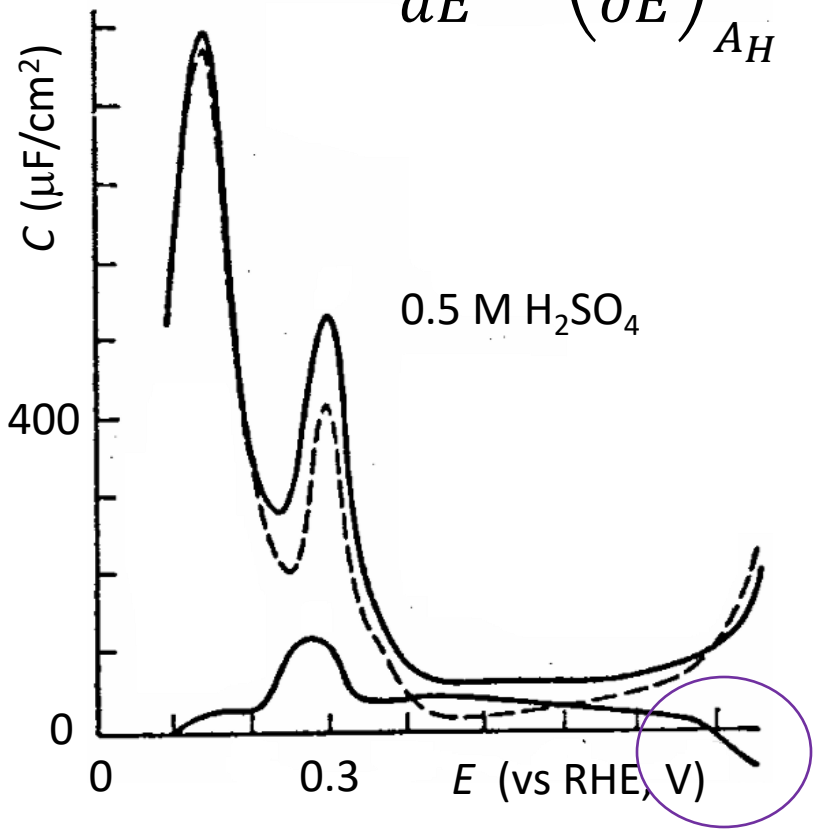
Petrii, Vītiņš, Elektrokhimiya 1991 <and Petrii's review in Electrochim. Acta 1996>

Charge inversion results in negative equilibrium capacity of the ionic "double layer"

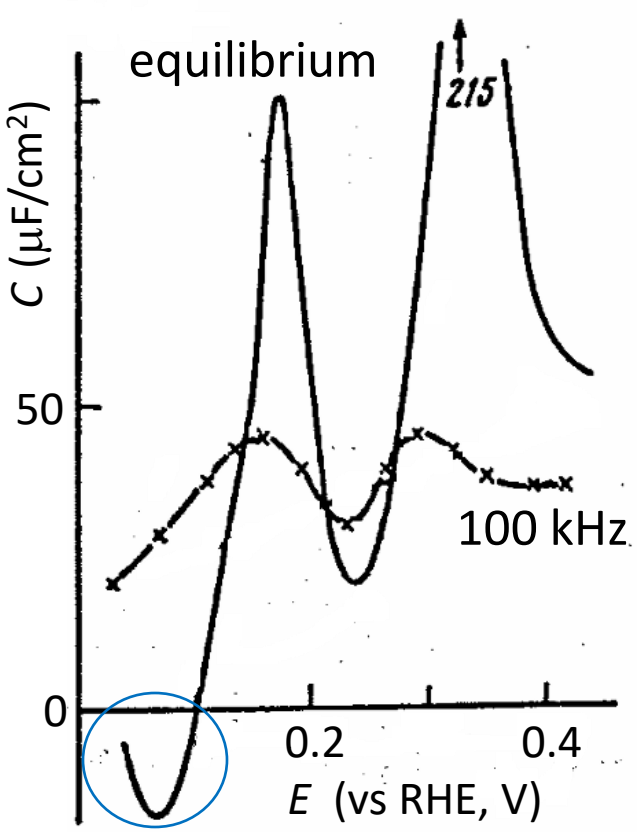
$$C = \frac{d\sigma}{dE} = \left(\frac{\partial\sigma}{\partial E}\right)_{A_H} + \left(\frac{\partial\sigma}{\partial A_H}\right)_E \cdot \frac{dA_H}{dE}$$



Petrii, Frumkin, Kotlov,
J Inst Catal Hokkaido U 1968



Petrii, Sveshnikova,
Sov. Electrochem. 1976

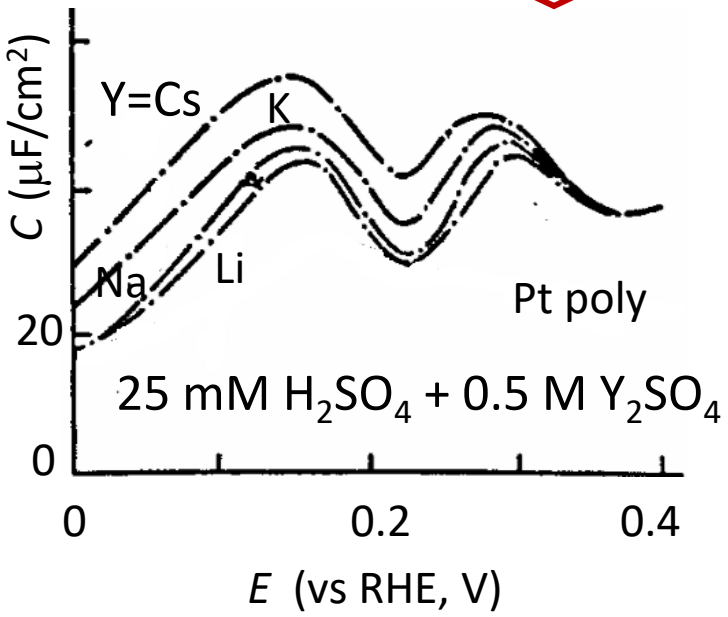


5 mM H_2SO_4 + 0.5 M Na_2SO_4

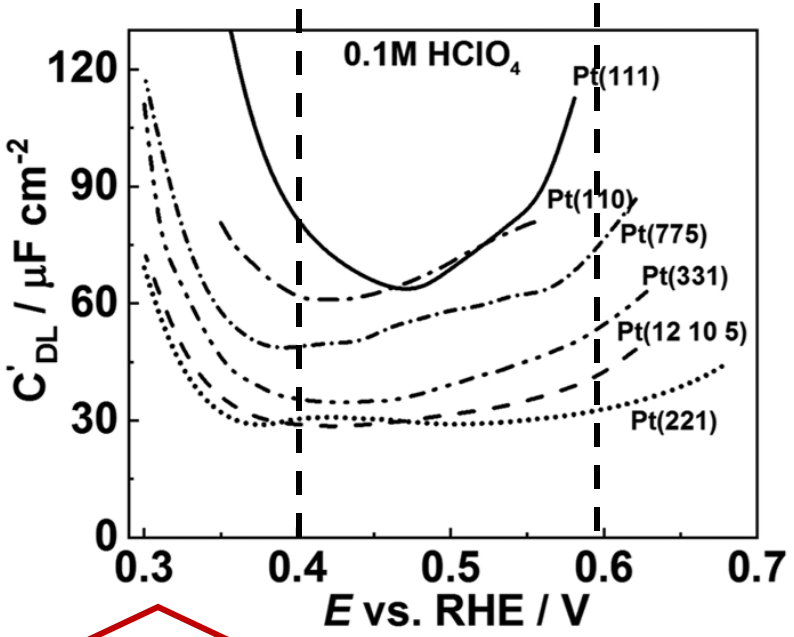
Petrii, Safonov, Shchigorev,
Sov. Electrochem. 1973

Voltammetry, impedance, etc. cannot address equilibrium ionic “double layer” in presence of adatoms

E.g., this example of “cations series” **does not mean** that the same happens with cations in presence of H_{ad}.



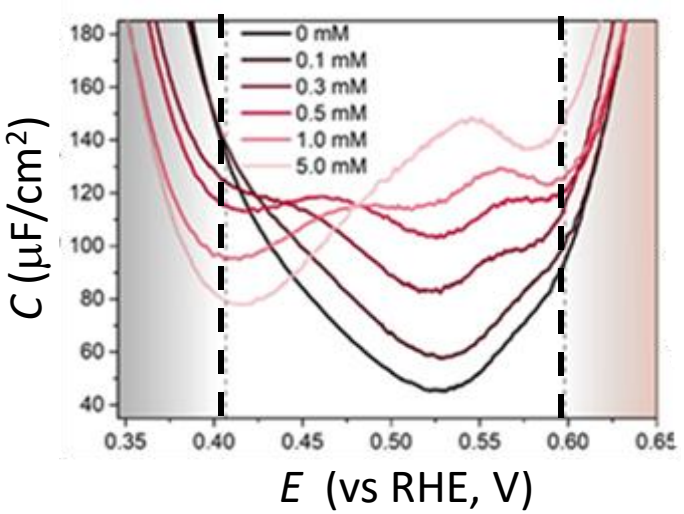
Petrii, Safonov, Shchigorev, Sov. Electrochem. 1973



Xue….Bandarenka, JACS 2024

This example requires at least some test for concentration dependence.

0.1 mM $HClO_4$ +… Pt(111)

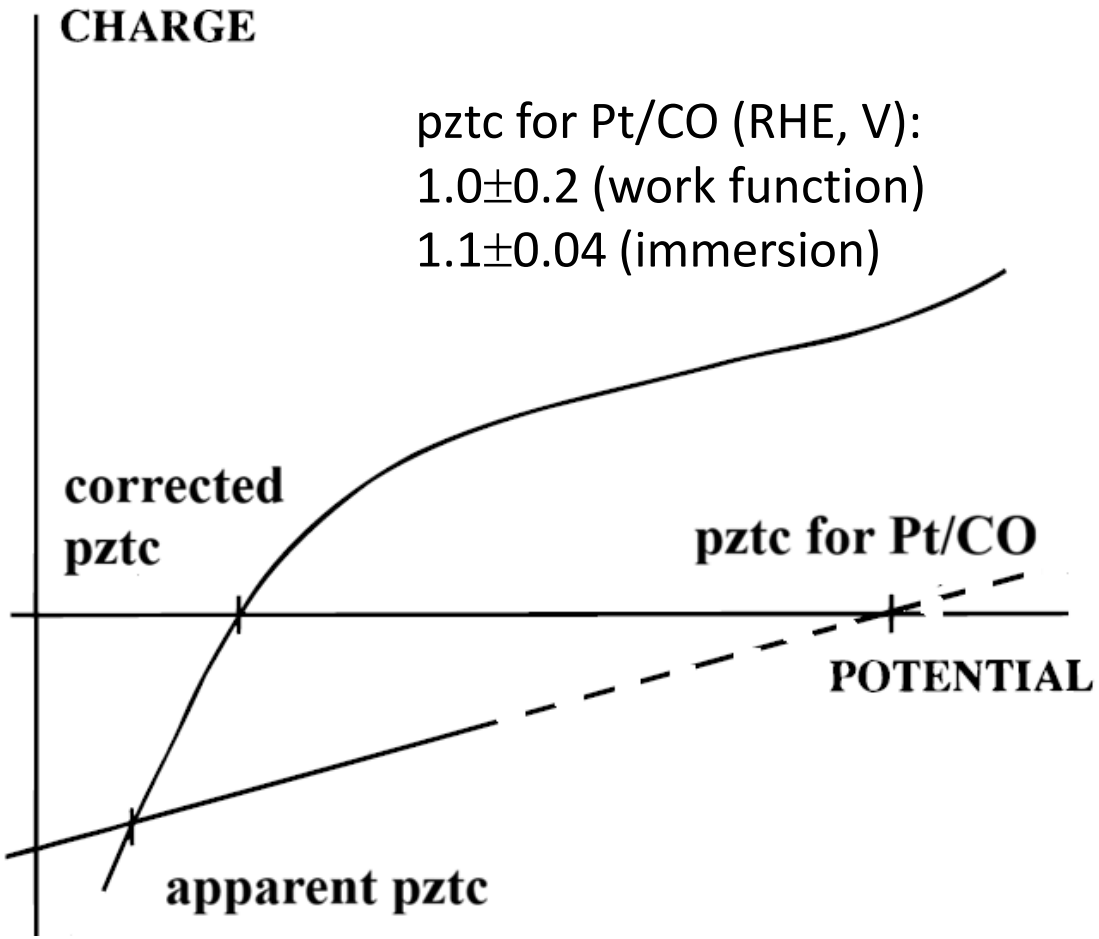


Ojha….Koper, Angew. Chem. Int. Ed. 2020

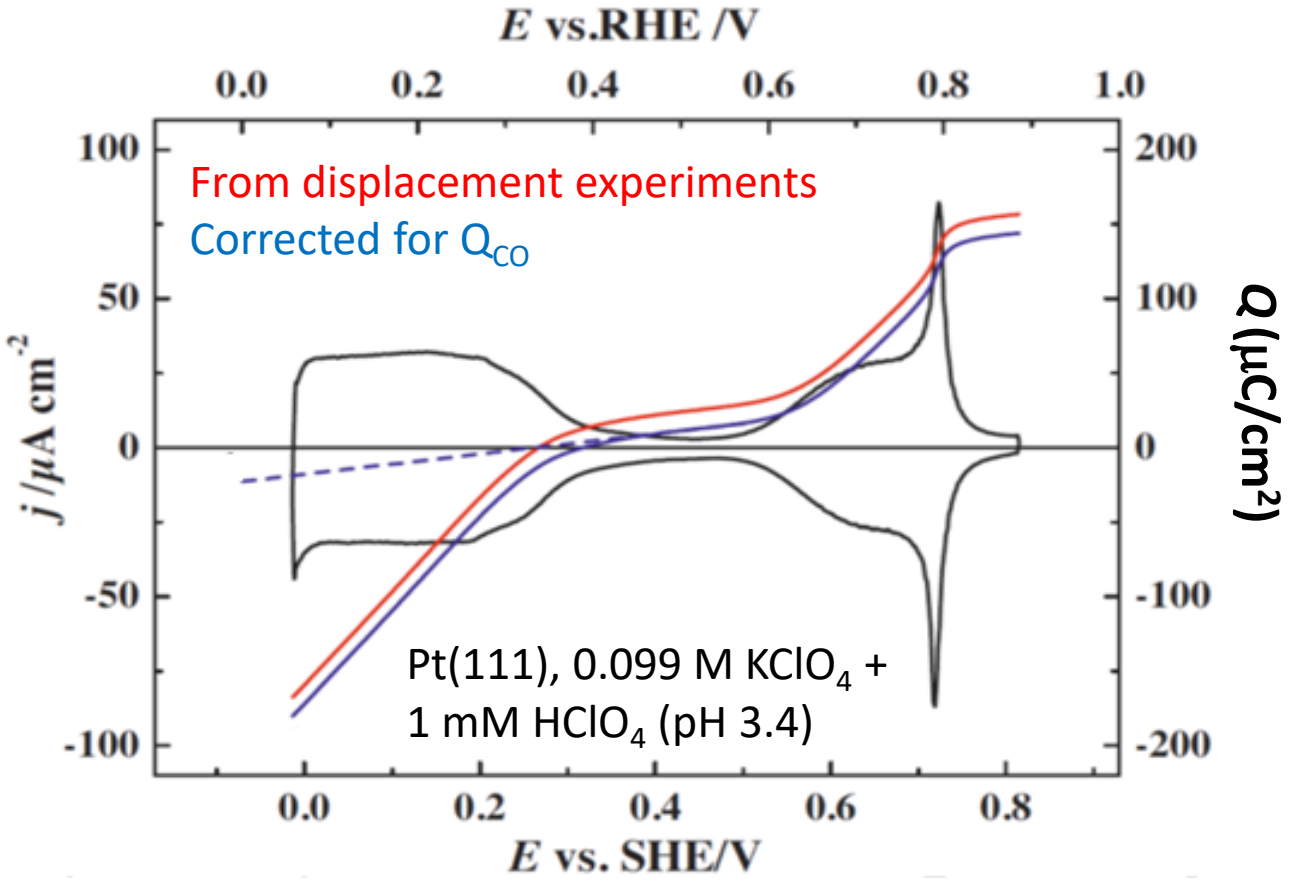
This example is ok for a narrow potential region, in $HClO_4$ exclusively.

Be very careful with interpretation of capacitance obtained from impedance. Note that its minimum for ideally polarizable electrodes typically is not shifted by cations!

CO displacement approach: correction is unavoidable; serious limitations for σ



Weaver, Langmuir 1998



- - - - - - - - - Assumed contribution of ionic "double layer"

Rizo, Sitta, Herrero, Climent, Feliu, Electrochim. Acta 2015

Two strategies to obtain thermodynamic quantities (both start from ΔQ measurements)

Research schemes:

σ, E; pzfc

⇩

$(\Delta Q - \sigma), E$

⇩ ⇩

$A_H = 0$ or isoelectric experiment

⇩

pztc; Q, E

Titration/radiotracer based strategy:

- **requires high real surface area**
- **limited to pH ~ 2……12, salt excess**
- **assumes one beyond thermodynamics assumption (no specific adsorption of H^+)**
- **OR avoids this assumption, but works for a limited number of available isotopes**

More accurate σ and ionic adsorptions, **but** for solutions of a limited "electrocatalytic interest" and electrodes of a limited "surface science interest".

CO displacement based strategy:

- **allows smooth surfaces, incl. single crystalline**
- **allows acids and bases without salt additive**
- **requires correction for metal/CO_{ad} contribution Q_{CO} [less known pztc]**
- **requires rather uncertain extrapolation of the "double layer" region**

Uniquely important for surface science, **but** meets the problems with specific adsorption and very low accuracy of σ.

$Q_{displacement}$

⇩

Q_{CO} subtraction

⇩

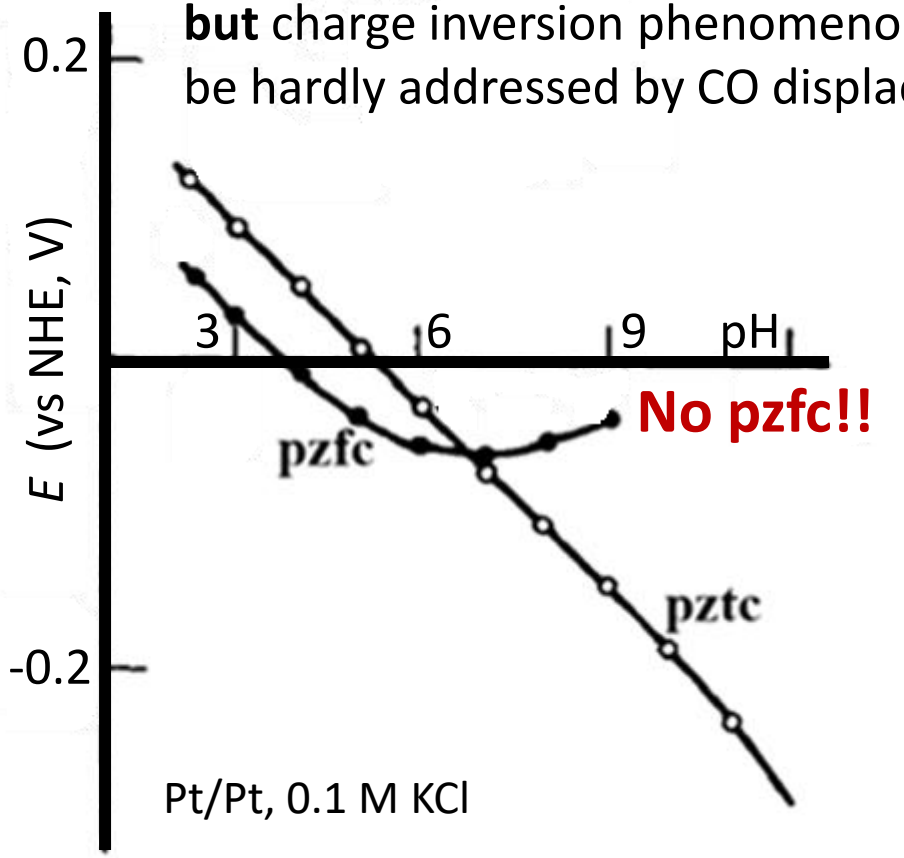
Q, E; pztc

⇩

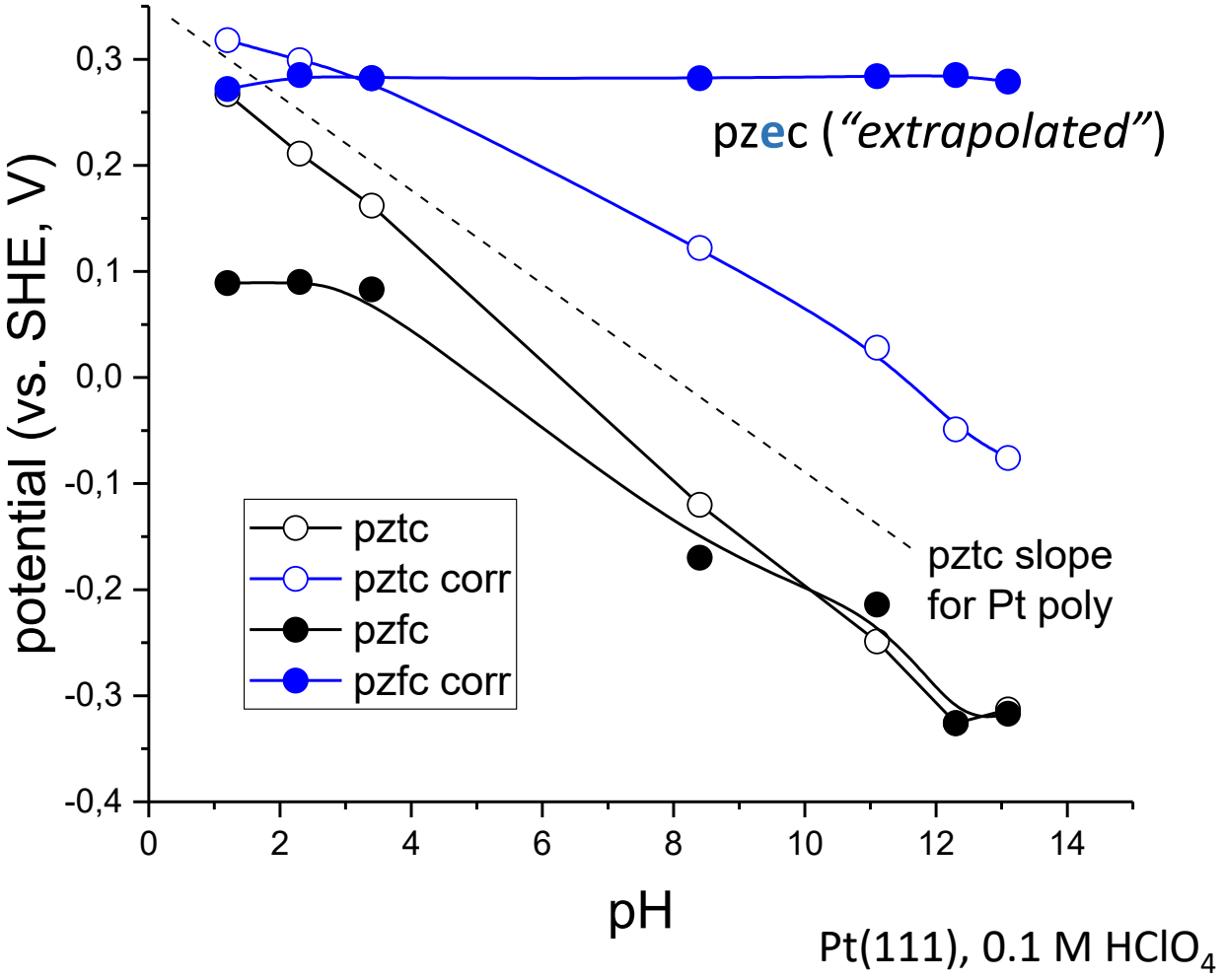
pzec instead of pzfc

pH dependencies of pzfc and pztc from the alternative strategies (only the trends can be compared!)

Not so bad in respect to total charge,
but charge inversion phenomenon can be hardly addressed by CO displacement.



Frumkin, Petrii, Kolotyrkina-Safonova,
Doklady Phys. Chem. 1975



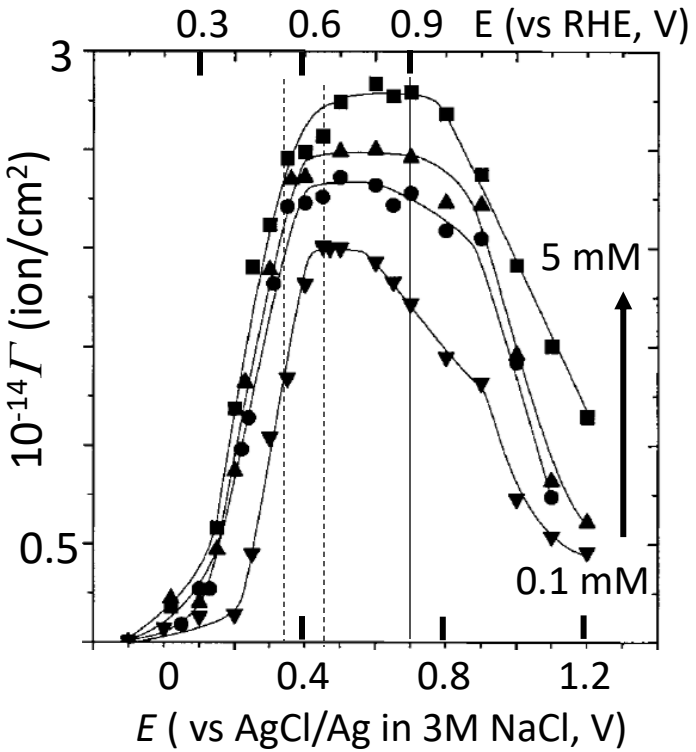
Plotted from the data tabulated in:
Rizo, Sitta, Herrero, Climent, Feliu, Electrochim. Acta 2015

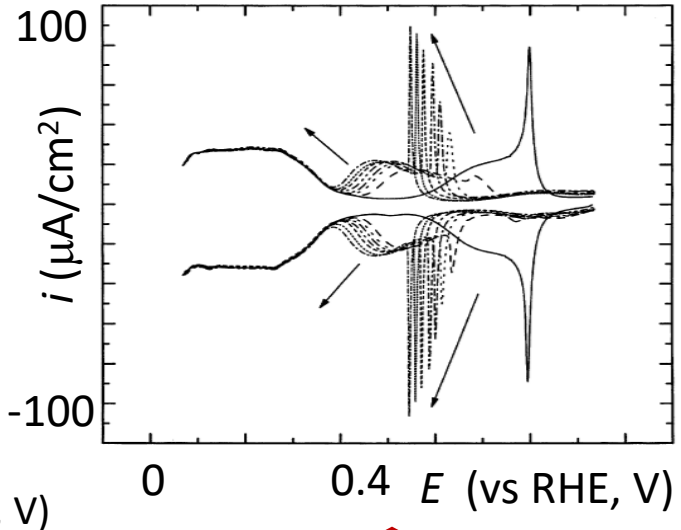
Ionic adsorption from the total charge data

Pt(111)

0.1 M $HClO_4$ + x mM H_2SO_4

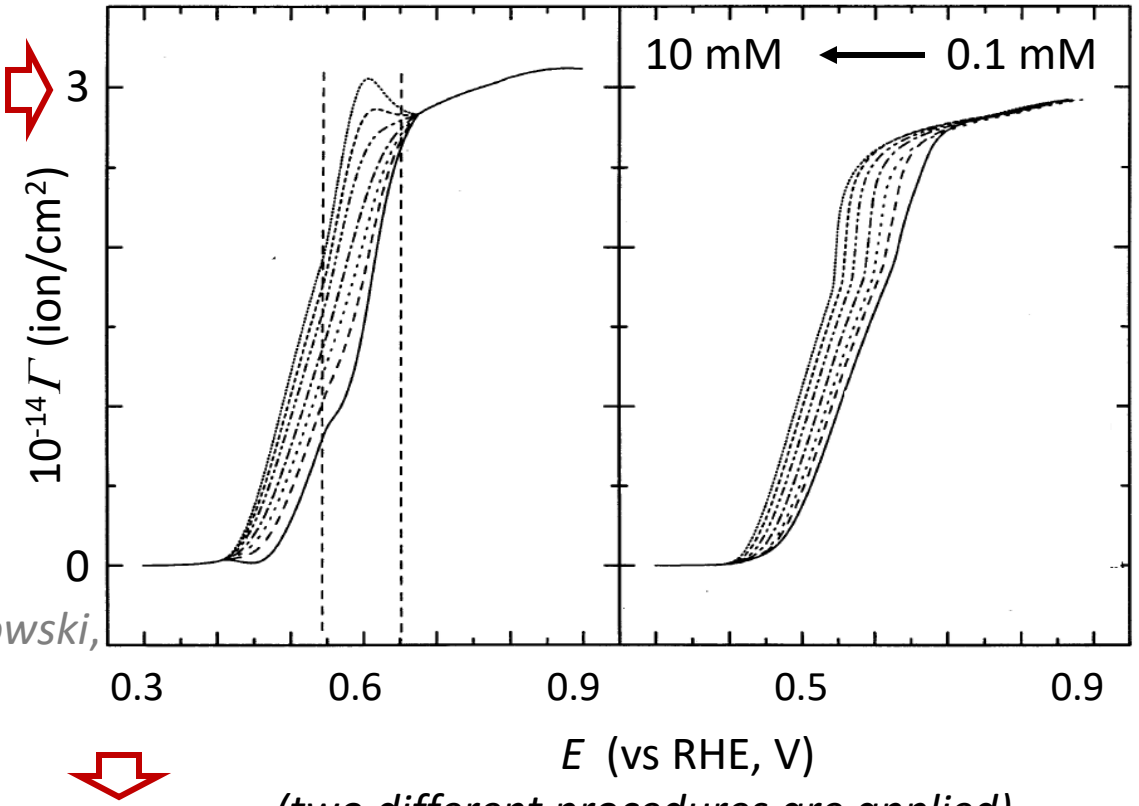
Kolics, Wieckowski,
J. Phys. Chem. B 2001





Herrero, Mostany, Feliu, Lipkowski,
J. Electroanal. Chem. 2002

Thermodynamic analysis



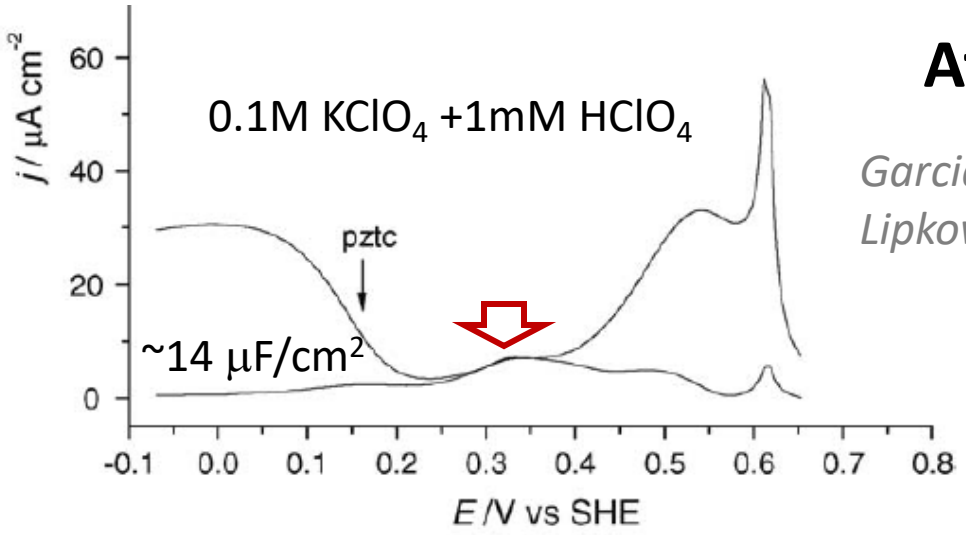
(two different procedures are applied)

Compare to radiotracer data

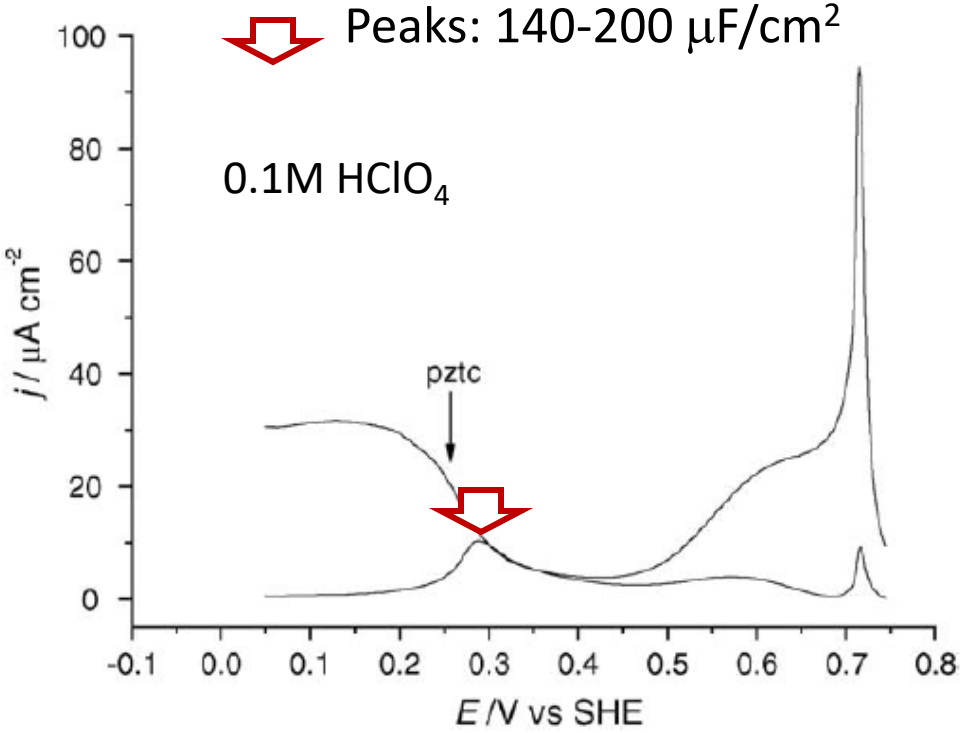
Again, very reasonable agreement in potential interval suitable for analysis, **but** looks like there is no chance for the region of charge inversion. *This region is important for kinetics of ORR and organic molecules oxidation.*

Attempt to refine “double layer” contribution:

Garcia-Araez, Climent, Herrero, Feliu, Lipkowski, Electrochim. Acta 2006

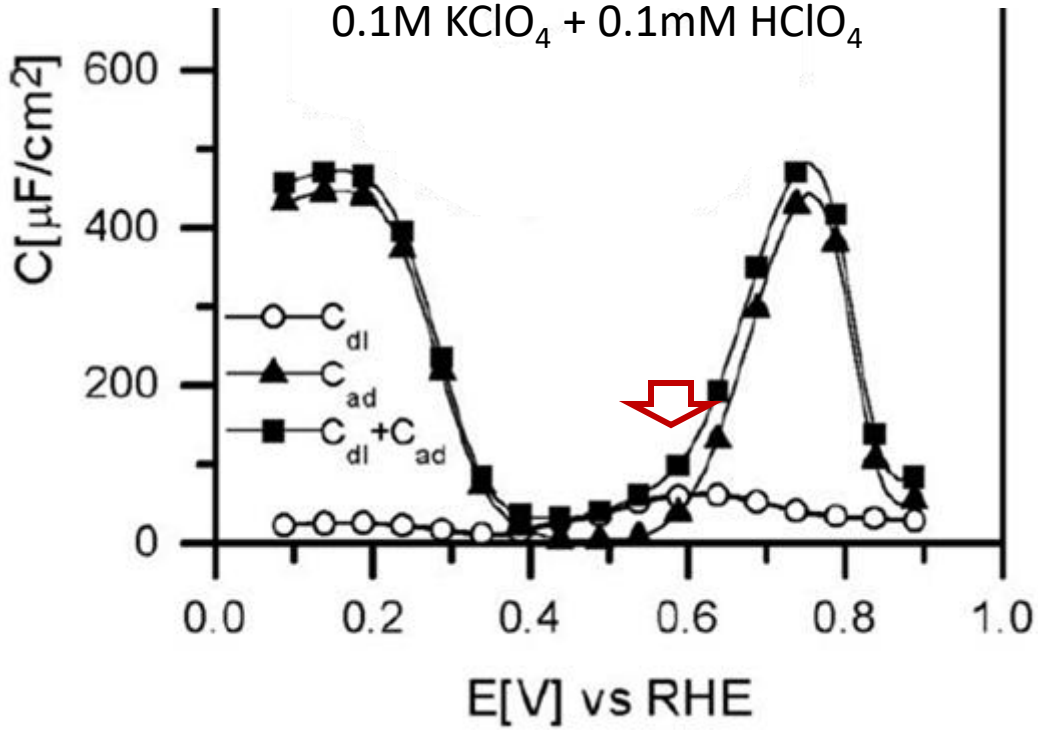


Peaks: 140-200 μF/cm²



Peaks are essentially higher than obtained from impedance, and pH-dependent.

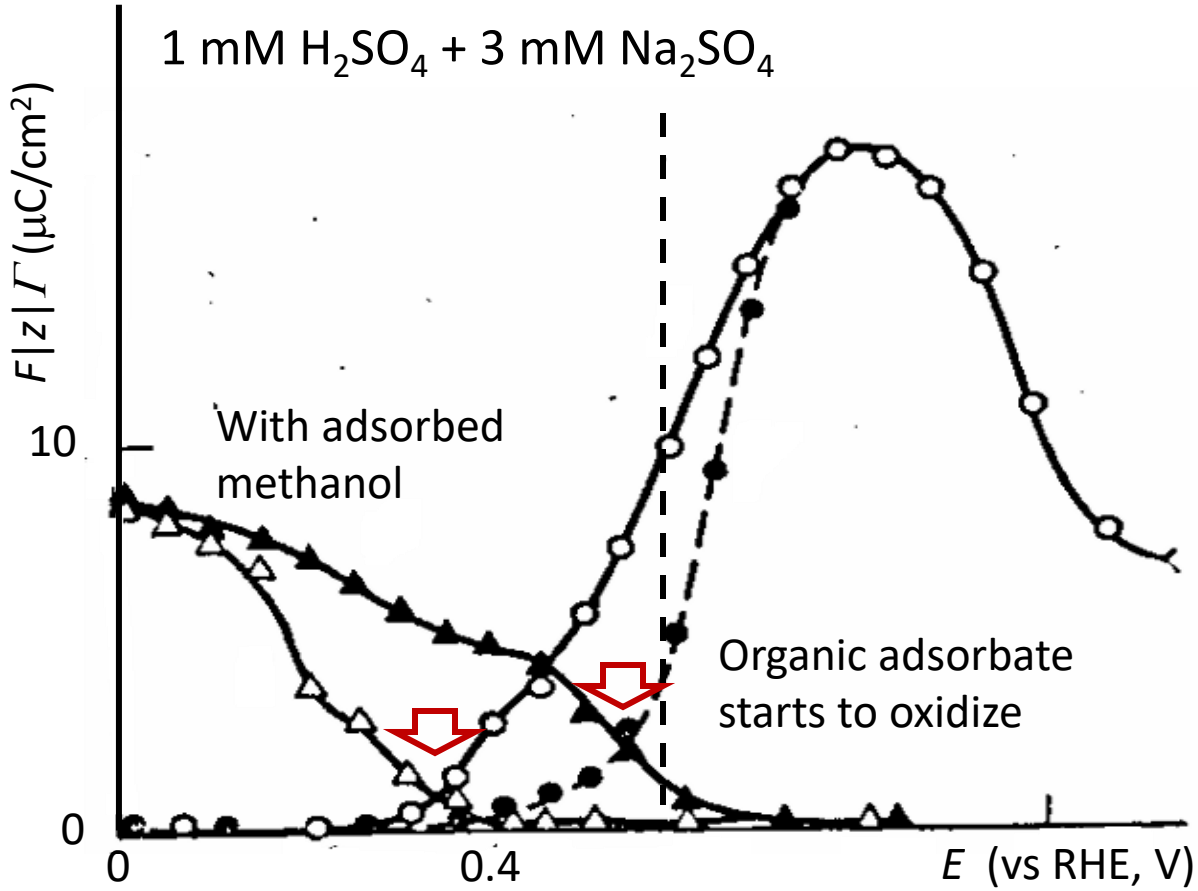
Pajkossy, Kolb, Electrochim. Acta 2001



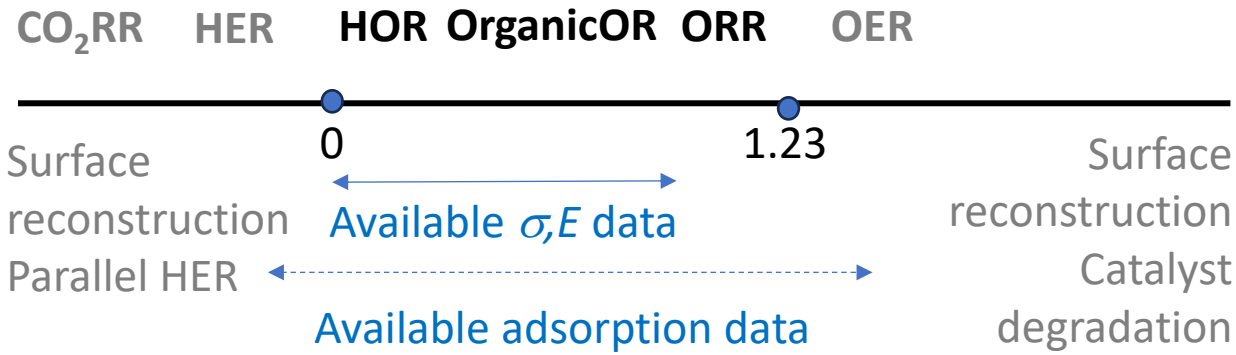
see Refs at https://elchi.eu/frumkin-school/

When thermodynamic information can be of interest for electrode kinetics?

Equilibrium interface, not obligatory the same as in supporting electrolyte.



Kazarinov, Frumkin, Tysyachnaya, Dokl. Phys. Chem. 1971



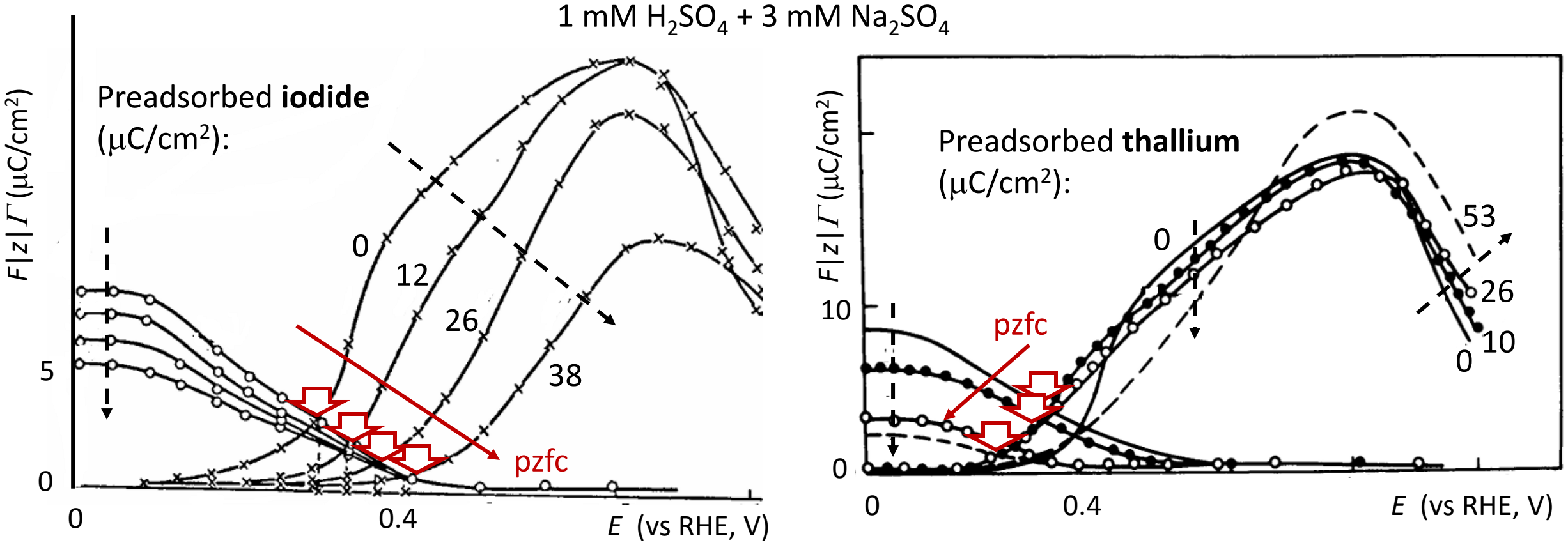
Notice when you start with **HOR on CO-poisoned Pt**: the amount of cations in reaction zone is much higher than one can judge from the data for supporting electrolyte.

Keep this also in mind when interpreting **IR spectra of organic adsorbates**: their state/bonding is affected by free charge.

Similar effects of foreign adatoms, sign of residual charge on adatom is important

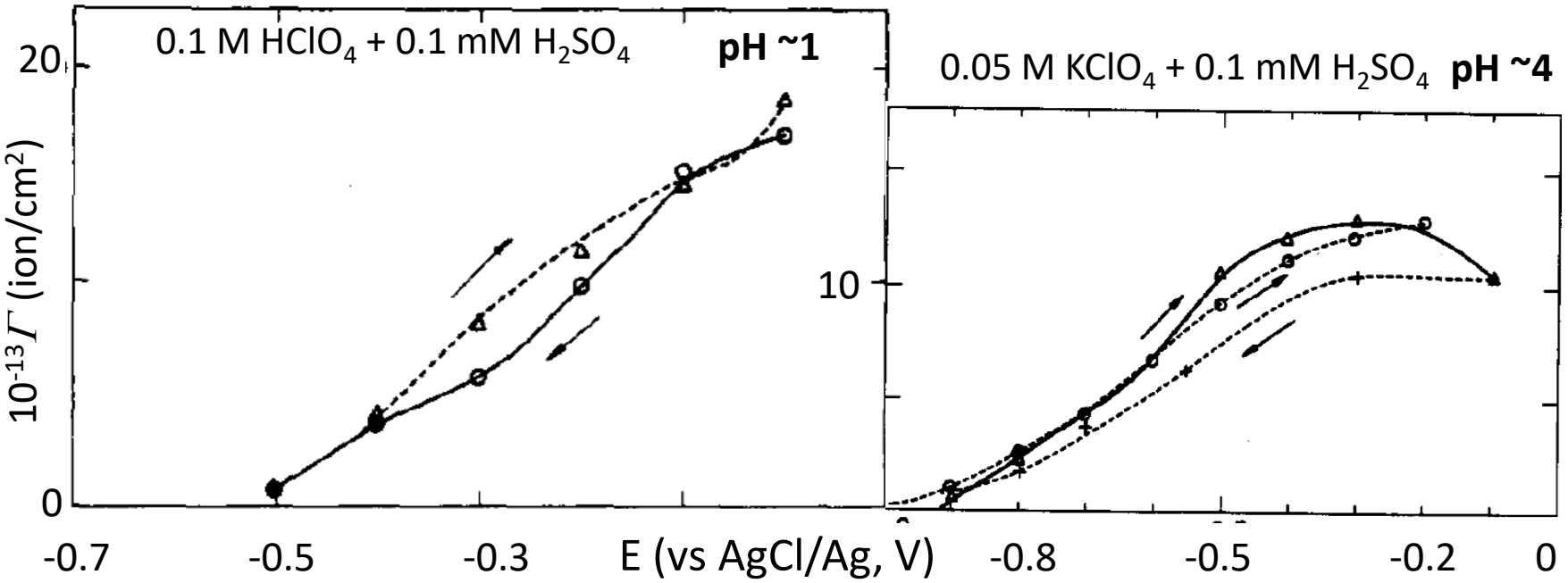
For electrocatalysis at modified electrodes, the data of this sort can be used directly.

In other cases, qualitative predictions are possible for various adsorbed intermediate species.



Frumkin, Malysheva, Petrii, Kazarinov, Sov. Electrohem. 1971

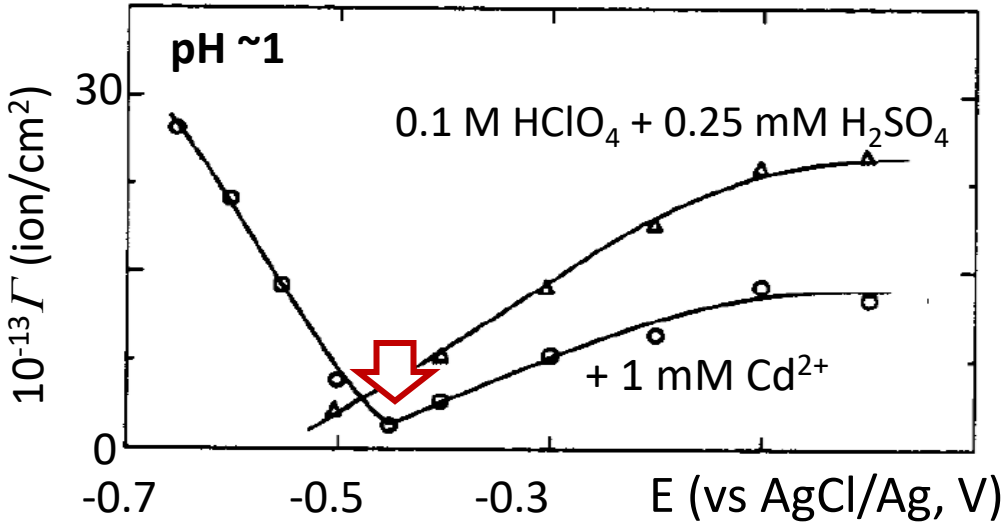
Copper is also perfectly, not ideally polarizable in a wide pH and potential intervals



Cu poly (smooth)

Nonmonotonic behavior is evident for sulphate.

Rice-Jackson, Horanyi, Wieckowski, Electrochim. Acta 1991

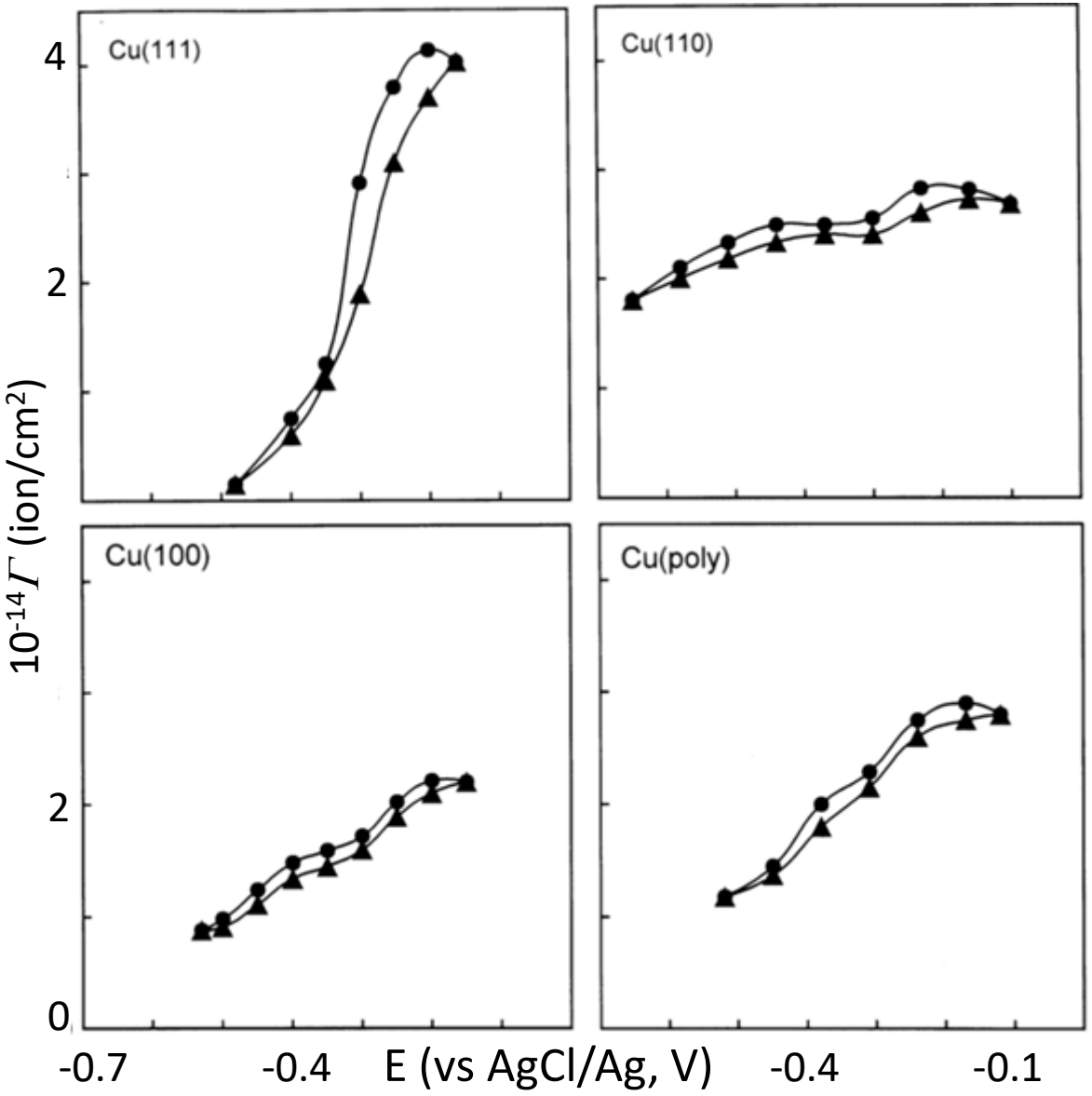


It is highly probable that pz(f)c **of Cu poly in acid** is located **far below RHE zero,** so there is no interplay with OH or O adsorption. However, the **interplay with H adsorption** is quite possible. *See mass-spectroscopic data on high H coverage on Cu(111) in 0.1 M $HClO_4$ just at these potentials:*

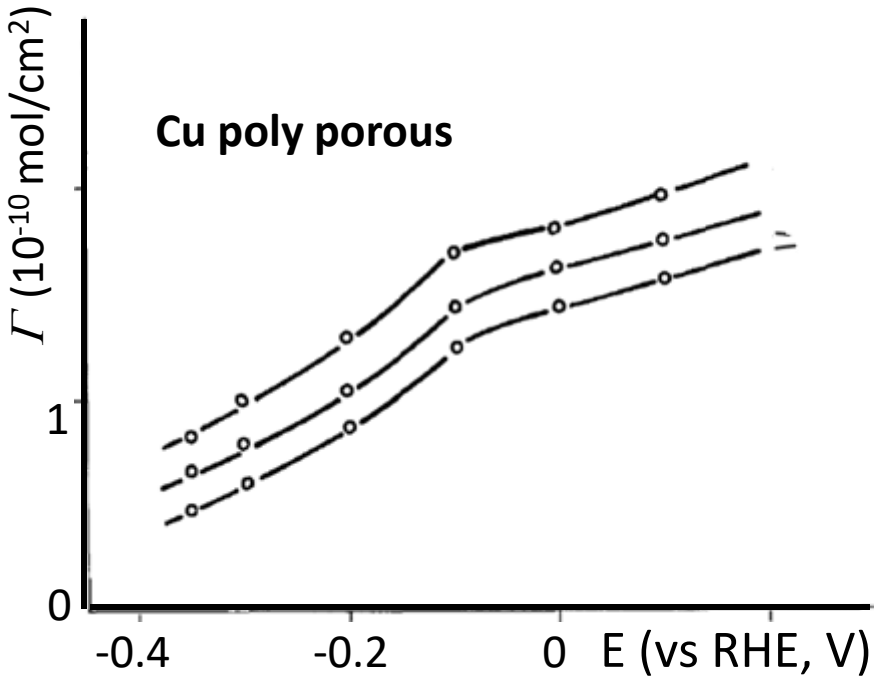
Raciti, Moffat, J. Amer. Chem. Soc. 2025

Copper: deviations from ideal polarizability appear already in acid, for both poly and single crystalline electrodes

0.1 M $HClO_4$ + 0.5 mM H_2SO_4



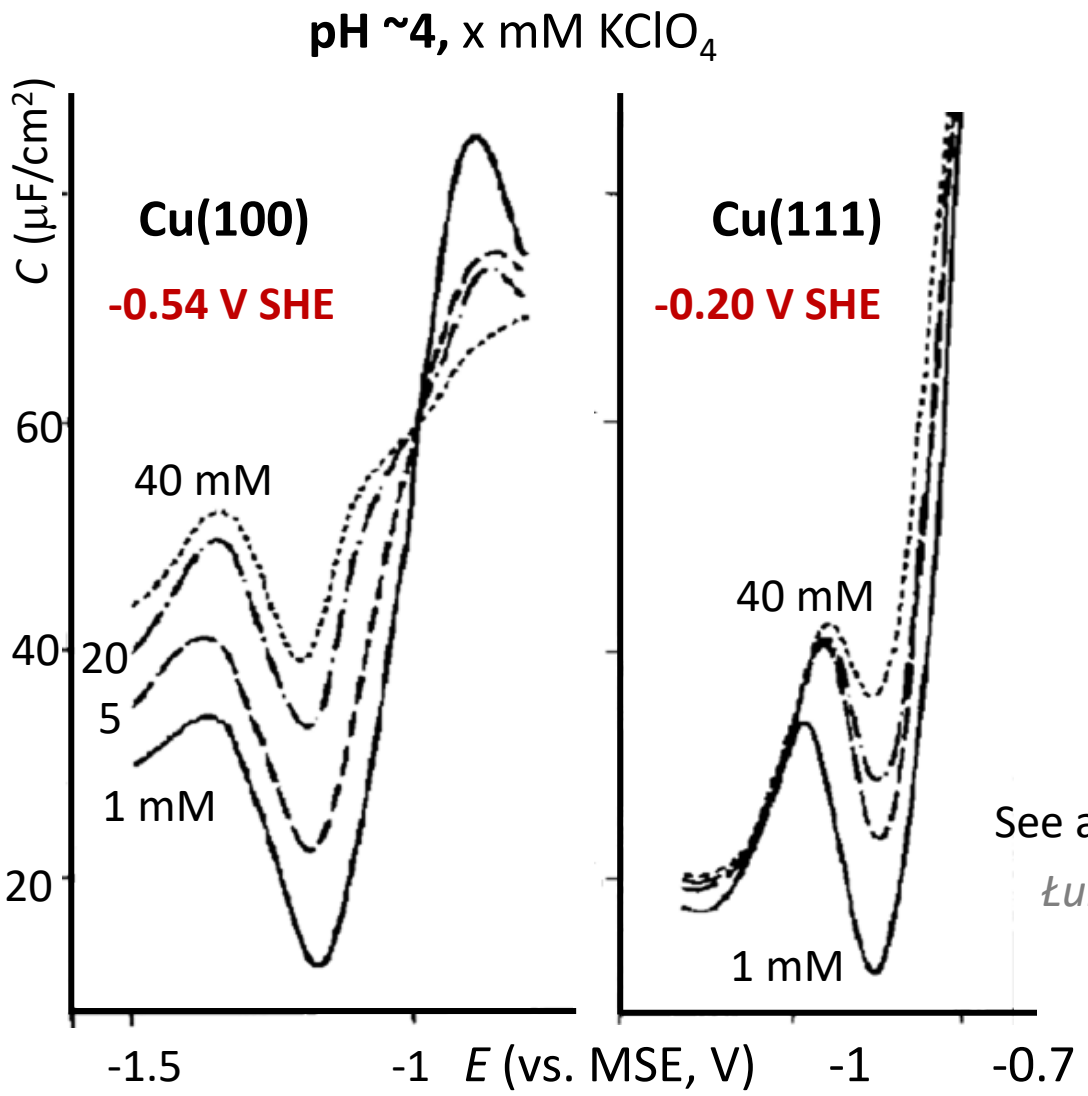
The start of sulfate adsorption at negative RHE potentials is also a general trend.



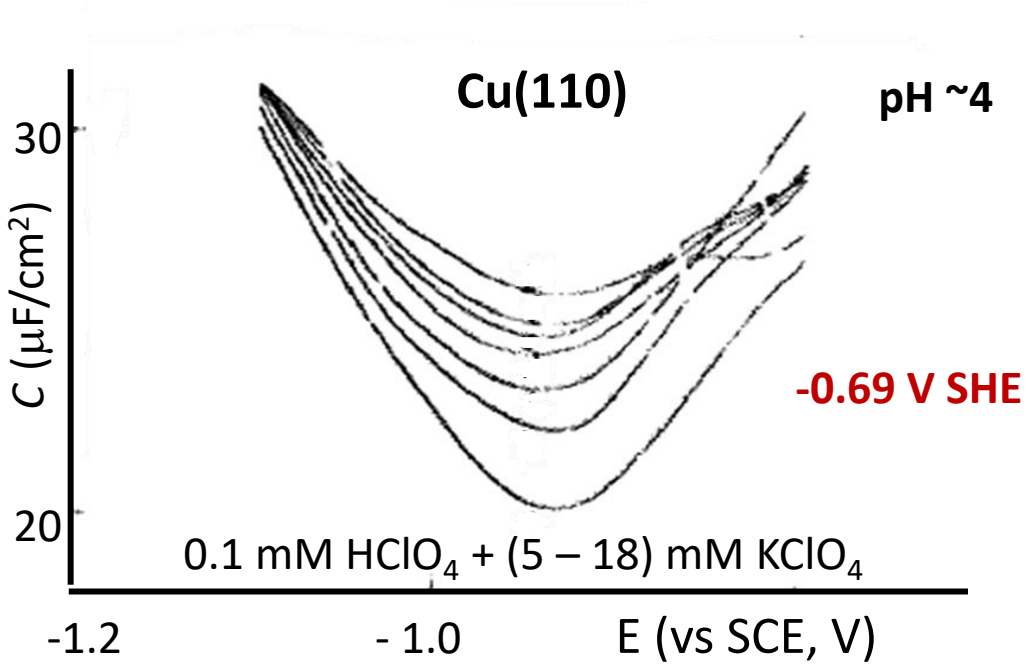
Smolinski, Sobkowski, J. Electroanal. Chem. 1999

Horanyi, Rizmayer, Joo, J. Electroanal. Chem. 1983

Copper: nice capacitance minimums do not mean that it is ideally polarizable; if yes, where is pzc?



Lecoeur, Bellier, Electrochim. Acta 1985



Foresti, Pezzatini, Innocenti, J. Electroanal. Chem. 1997

See also for Cu (hkl) and Cu poly **at pH 3.2-5.7**: **-0.75…..-0.55 V SHE**

Łukomska, Sobkowski, J. Electroanal. Chem. 2004

Be very careful with interpretation of capacitance. Note that for ideally polarizable electrodes pzc is pH-independent!

Concluding remarks on complicating and less known issues

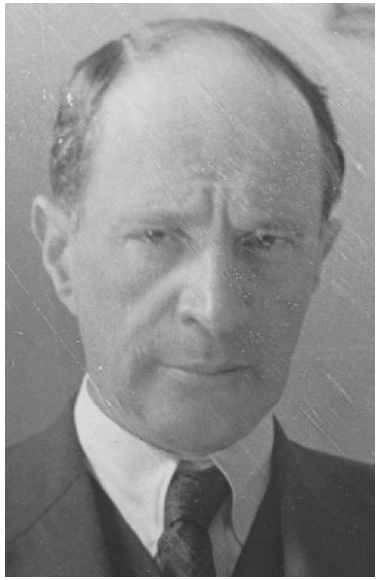
Two strategies (pzfc→pztc and pztc→pzfc) should not be opposed. Instead, their strongest results should be combined. *Desirable experimental efforts*:

- careful **CO displacement on Pt/Pt** for comparison with well-characterized electrodes;
- “reanimation” of radiotracer technique, new attempts for **cations**.

High frequency capacitance **cannot address the ionic “double layer”** formed in presence of adatoms. In particular, it is helpless in respect to charge inversion phenomenon crucial for understanding reaction zones in electrocatalysis.

For understanding electrode kinetics, we need not only pz(f, t)c, but quantitative **charge vs potential dependencies**. Equilibrium “double layer” for the surfaces with irreversibly adsorbed foreign species can imitate some reaction zones.

Copper in the “hydrogen region” should be considered as perfectly polarizable electrode. *Desirable*: application of classical thermodynamic strategy to **copper with high surface area**. <To nickel as well!>



Aleksandr N. Frumkin
(1895-1976)

Aleksandr I. Shlygin
(1905-1979)

Vol’f A. Medvedovskyi
(1904-1979)

Rein
Marvet

Zhanna
Malysheva

Yuriy
Kotlov

Valeriya
Entina (Dubasova)

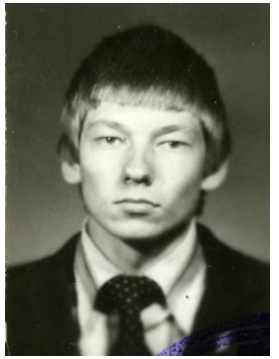
Igor
Shchigorev

Tat’yana
Kolotyrkina
(Safonova)

Oleg A. Petrii (1937-2021) and Boris B. Damaskin (1932-2019)

Dzhanet
Sveshnikova

Viktor Topolev



Aigars
Vītiņš

No longer with us

György Horányi (1934–2006)

Andrzej Więckowski (1945-2019)

Michael J. Weaver (1947-2002)

Let me hope that the next electrochemical generations manage to do something of comparable value.