A Wide Variety of Electrochemistry As Irresistible Attraction

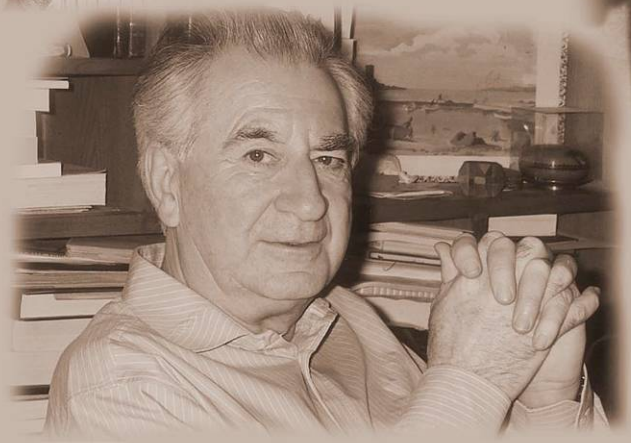
ou bien

Le charme discret de l'électrochimie dans sa diversité

Oleg A. Petrii

Award lecture

Nice, September 29, 2010



My Variety of Electrochemistry

Experimental verification of the charge transfer theories

Electrocatalysis

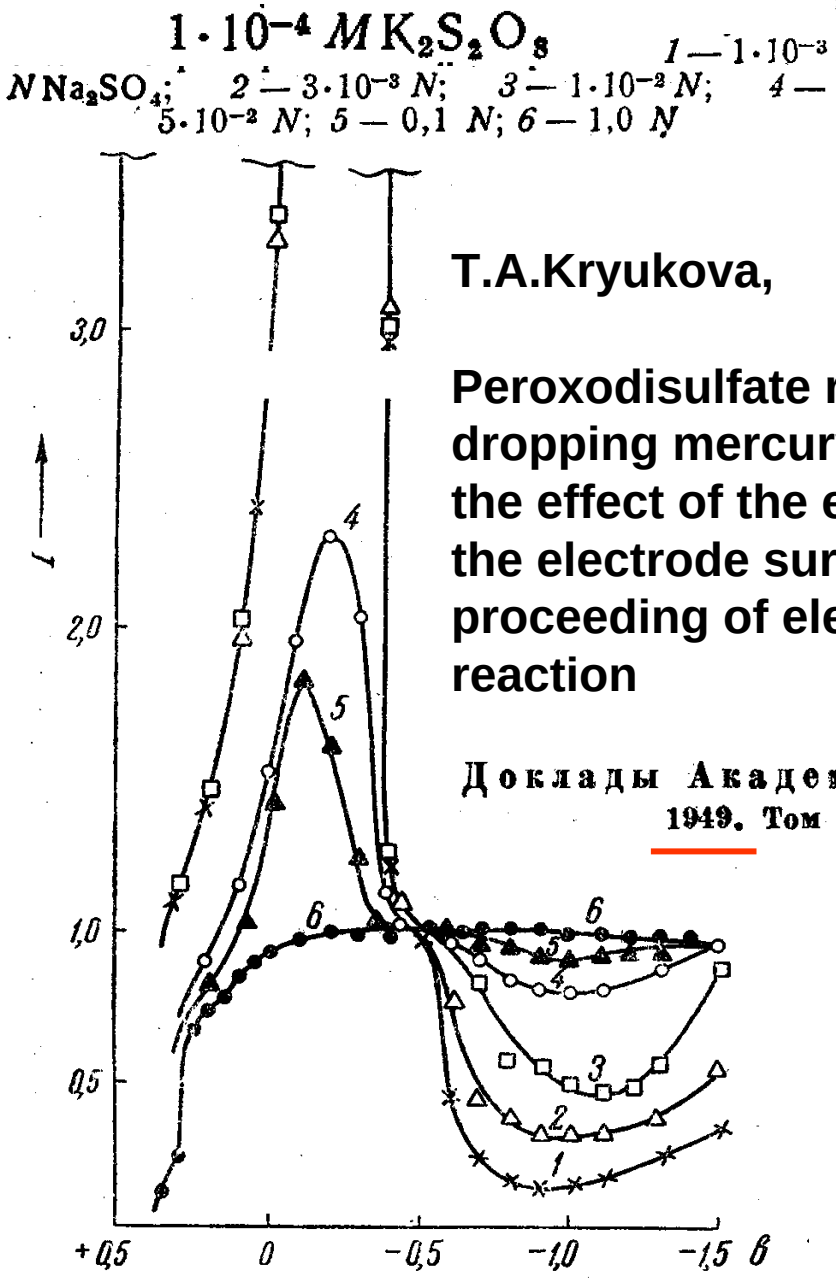
Surface thermodynamics of the perfectly polarizable electrode

Electrochemical material science

Т. А. КРЮКОВА

ВОССТАНОВЛЕНИЕ ПЕРСУЛЬФАТА НА РТУТНОМ КАПЕЛЬНОМ КАТОДЕ И ВЛИЯНИЕ ЭЛЕКТРИЧЕСКОГО ПОЛЯ ЗАРЯДОВ ПОВЕРХНОСТИ ЭЛЕКТРОДА НА ПРОТЕКАНИЕ ЭЛЕКТРОХИМИЧЕСКОЙ РЕАКЦИИ

(Представлено академиком А. Н. Фрумкиным 5 II 1949)



T.A.Kryukova,

Peroxodisulfate reduction at the dropping mercury electrode and the effect of the electric field of the electrode surface on the proceeding of electrochemical reaction

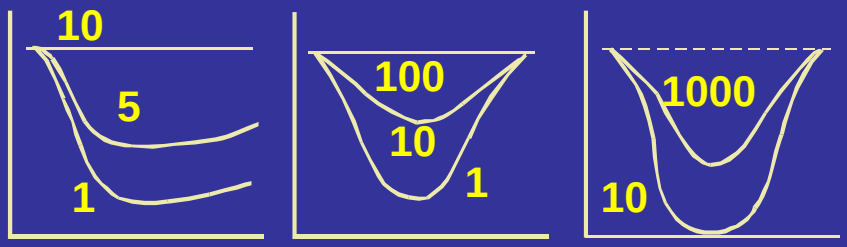
Доклады Академии Наук СССР
1949. Том LXV, № 4

Tatyana A. Kryukova

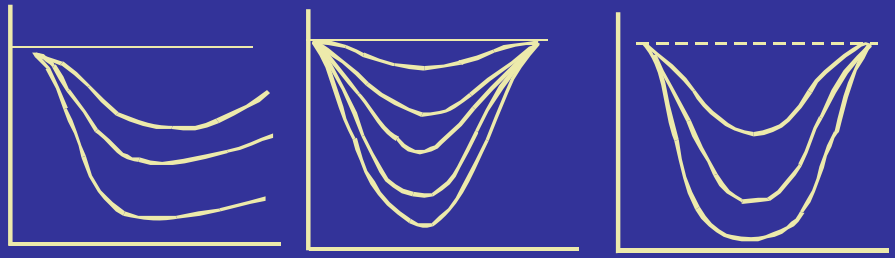
Nina V. Fedorovich

$[Fe(CN)_6]^{3-}$ $S_2O_8^{2-}$ $[PtCl_4]^{2-}$

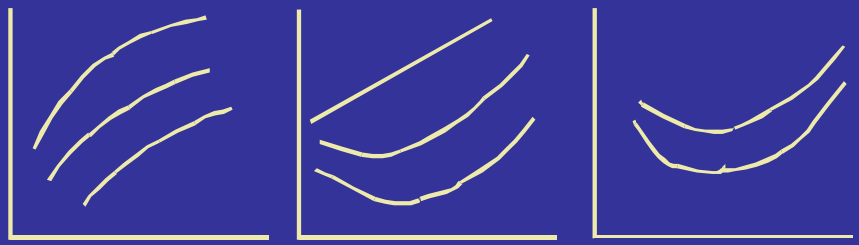
Various supporting electrolyte concentrations, mM

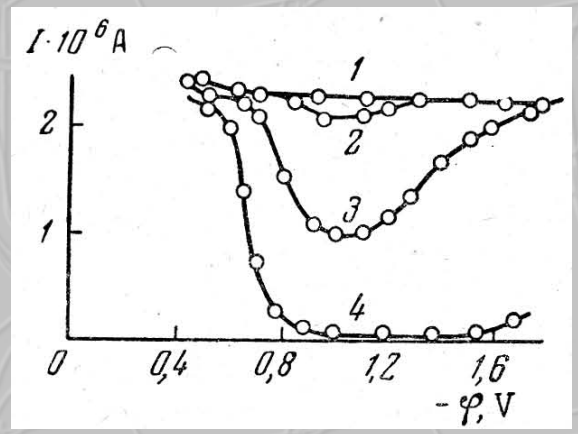


Typical effect of cation nature (decrease: Cs…Li)



and corresponding CTP





Galina M. Florianovich

$$i = k\,[\mathrm{A}] \exp \frac{\alpha F}{RT}\left(-\varphi + \frac{n+\alpha}{\alpha}\psi_1\right)$$

Академик А. Н. ФРУМКИН и Г. М. ФЛОРИАНОВИЧ

ЭЛЕКТРОВОССТАНОВЛЕНИЕ АНИОНОВ

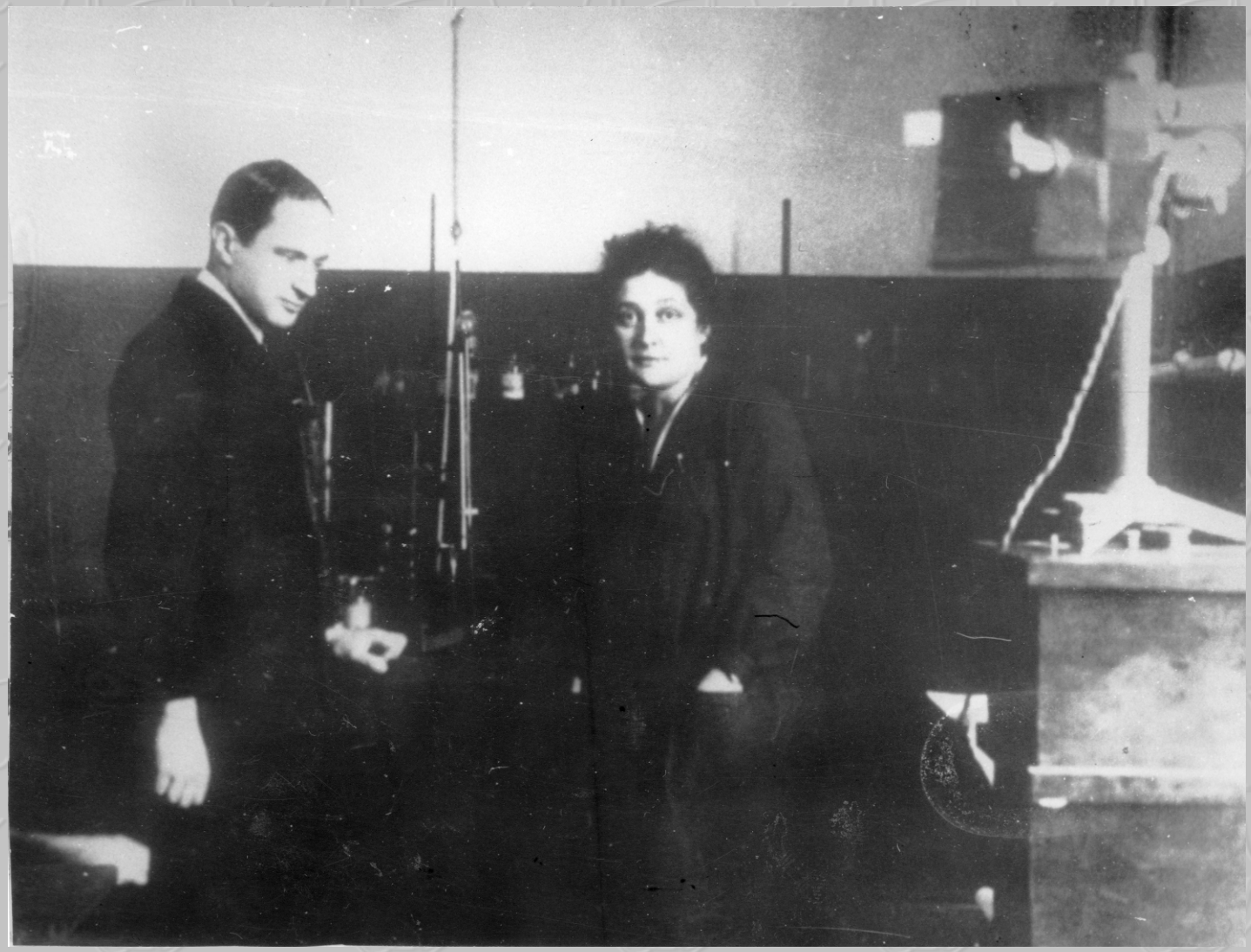
Доклады Академии Наук СССР
1951. Том LXXX, № 6

О МЕХАНИЗМЕ ЭЛЕКТРОВОССТАНОВЛЕНИЯ АНИОНОВ НА РТУТНОМ ЭЛЕКТРОДЕ

Г. М. Флорианович и А. Н. Фрумкин

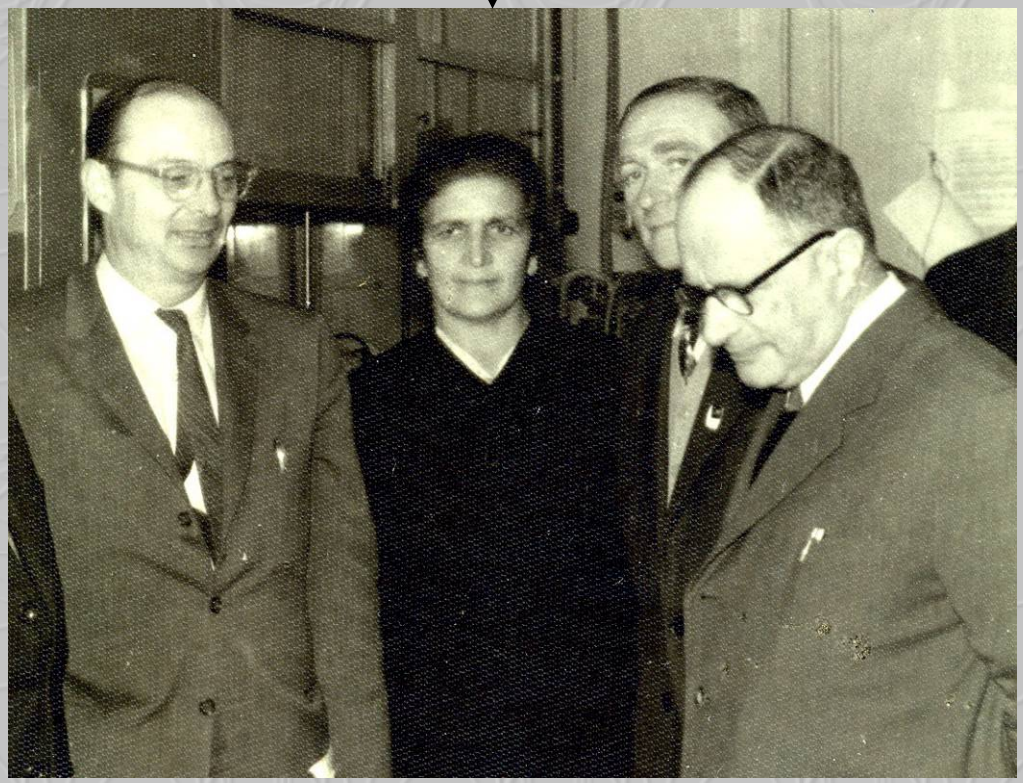
1955 ЖУРНАЛ ФИЗИЧЕСКОЙ ХИМИИ

A.N.Frumkin and A.D.Obrucheva



R. Kh. Burshtein

M. I. Temkin

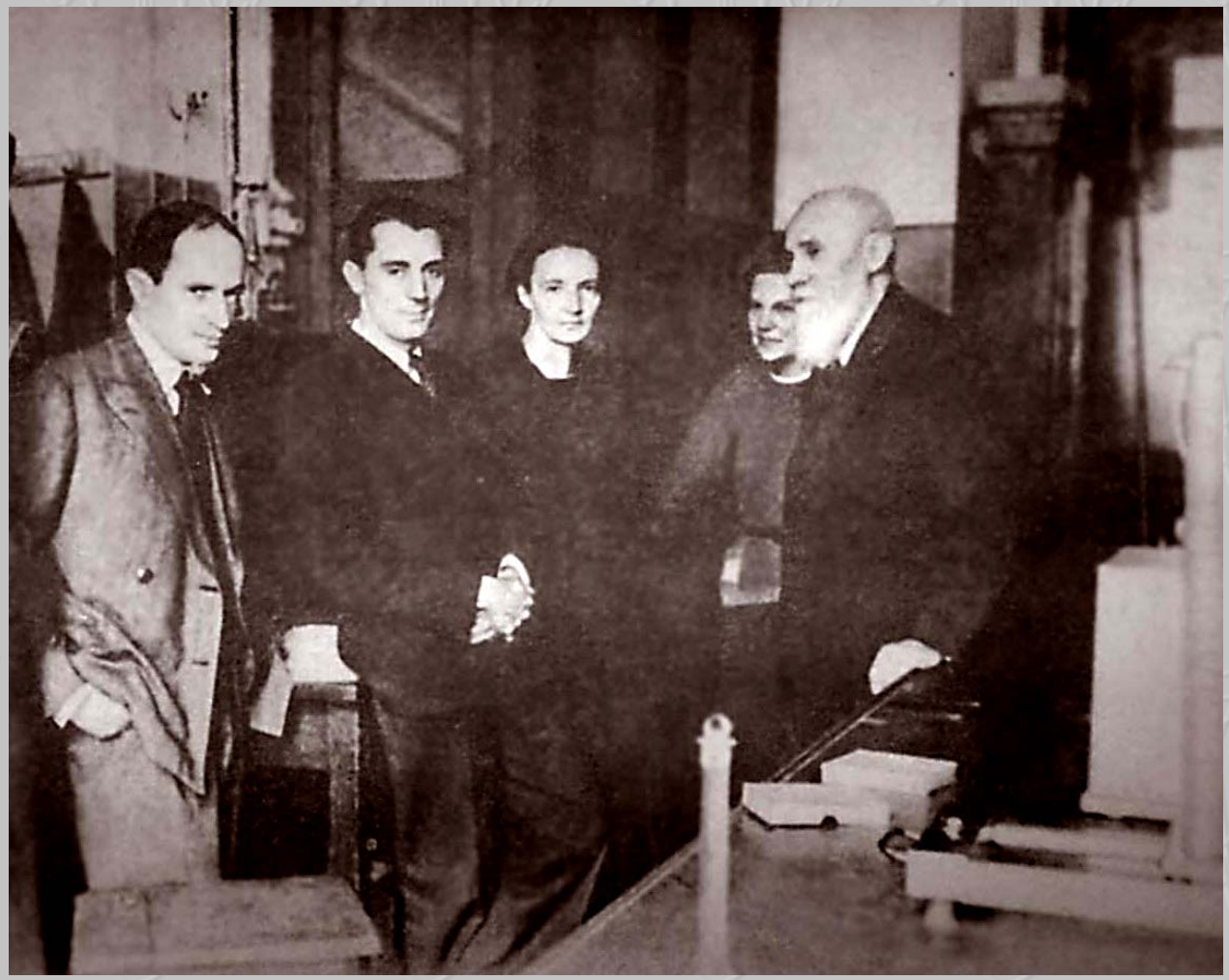


Grahame's visit to Moscow, 1956

A.N.Bakh

N.A.Bakh

Frederic and Iren Jolio-Curie



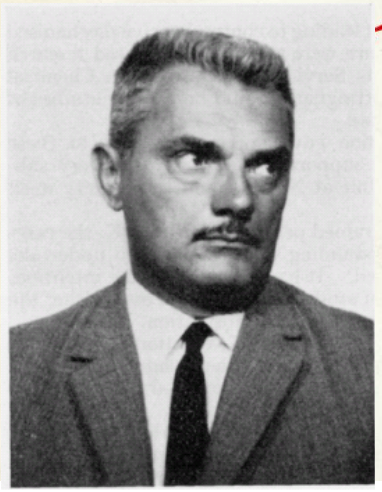
Karpov Institute (Moscow), 1935

Université Libre de Bruxelles

Faculté des Sciences

Chimie Analytique

Cinétique d'approche et réactions d'électrodes irréversibles



Prof. Gierst

Lucien GIERST

Thèse présentée à la Faculté des Sciences

de l'Université libre de Bruxelles

pour l'obtention du grade d'agrégé

de l'enseignement supérieur

COMMISSION D'EXAMEN

Les professeurs:

L. de Brouckère, Président
P. Goldfinger, Secrétaire
C. Decroly
R. Defay
I. Prigogine, Membres

I thank Prof. Cl.Bues-Hermann for her kind help.

Electrochimica Acta. 1963. Vol. 8. pp. 177 to 192.

ON THE DETERMINATION OF THE VALUE OF THE CHARGE OF THE REACTING PARTICLE AND OF THE CONSTANT α FROM THE DEPENDENCE OF THE RATE OF ELECTRO-REDUCTION ON THE POTENTIAL AND CONCENTRATION OF THE SOLUTION*

A. N. FRUMKIN, O. A. PETRY and N. V. NIKOLAEVA–FEDOROVICH

$$\left(\frac{\partial \ln i}{\partial \ln c}\right)_{\varphi-(RT/n_2F)\ln c,\ Cr} = -\frac{n_1}{n_2}$$

← Reactant charge

← Supporting ion charge

↑ *Corresponds to constant electrode charge, if it is high enough*

First published in: A.N.Frumkin, O.A.Petrii, Doklady AN SSSR, 1962, v.147, p.418.

Next step: O.A.Petrii, B.B.Damaskin, Elektrokhimiya, 1974, v.10, p.756.

Later (for ion pairing complications):
G.A.Tsirlina, O.A.Petrii, Russ. J.Electrochem., 2003, v.39, p. 323-327
and Refs therein

Corrected Tafel Plots: logI - ψ' *vs*. E –ψ'

hexacyanoferrate

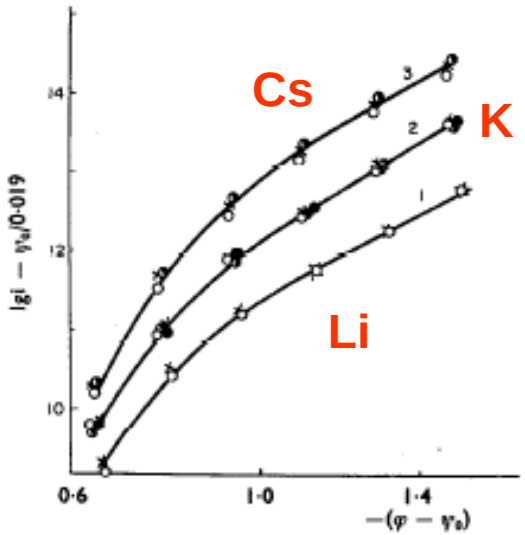


FIG. 4. Corrected Tafel plots of $Fe(CN)_6^{3-}$ reduction in solutions: (1) 10^{-3} N $Li_3Fe(CN)_6$ in the presence of LiCl in concentrations 10^{-2} N (× × × ×), 3×10^{-4} N (○ ○ ○ ○); (2) 10^{-3} N $K_3Fe(CN)_6$ in the presence of KCl in concentrations 0 (○ ○ ○ ○), 5×10^{-4} N (× × × ×), 10^{-3} N (◑ ◑ ◑ ◑), $1{\cdot}5 \times 10^{-3}$ N (● ● ● ●) (3) 10^{-3} N $Cs_3Fe(CN)_6$ in the presence of CsCl in concentrations 0 (○ ○ ○ ○), 3×10^{-4} N (× × × ×), 5×10^{-4} N (◑ ◑ ◑ ◑).

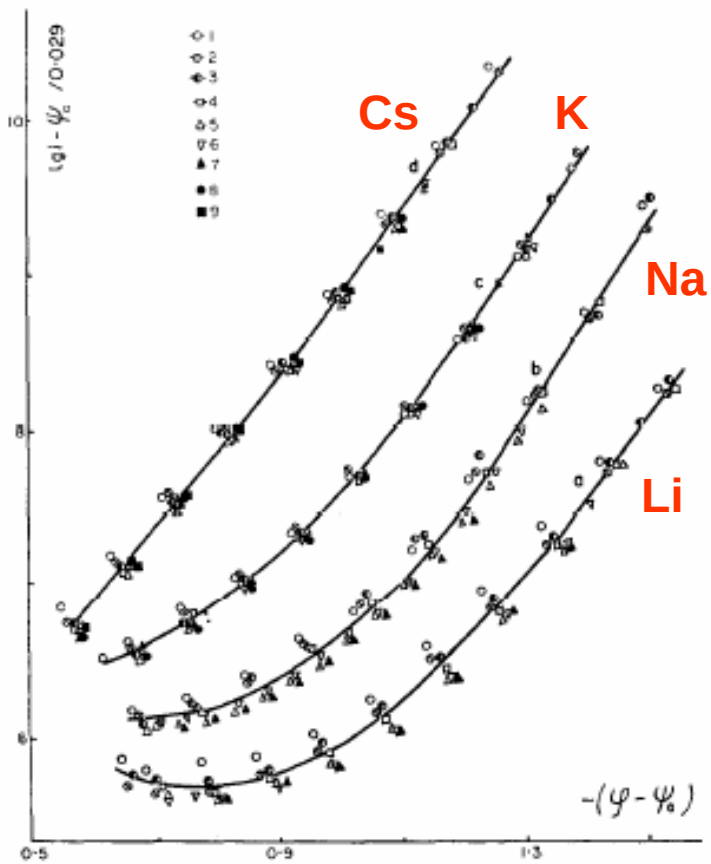


FIG. 3. Corrected Tafel plots of $S_2O_8^{2-}$ electro-reduction in solutions:
(a) 10^{-3} N $Na_2S_2O_8$: in the presence of LiCl + NaCl ([Li^+]:[Na^+] = 10:1) in concentrations 10^{-2} N (1); $1{\cdot}5 \times 10^{-2}$ N (2); 2×10^{-2} N (3); 3×10^{-2} N (4); 4×10^{-2} N (5); 5×10^{-2} N (6); 7×10^{-2} N (7).
(b) 10^{-3} N $Na_2S_2O_8$ in the presence of NaF in concentrations 3×10^{-2} N (1); 5×10^{-2} N (2); 7×10^{-2} N (3); 10^{-1} N (4); $1{\cdot}5 \times 10^{-1}$ N (5); 2×10^{-1} N (6); 3×10^{-1} N (7).
(c) 10^{-3} N $K_2S_2O_8$ in the presence of KCl in concentrations 2×10^{-2} N (1); 3×10^{-2} N (2); 4×10^{-2} N (3); 5×10^{-2} N (4); 6×10^{-2} N (5); 7×10^{-2} N (6); 8×10^{-2} N (7); 10^{-1} N (8).
(d) 10^{-3} N $Cs_2S_2O_8$ in the presence of CsCl in concentrations 0 (1); 5×10^{-4} N (2); 10^{-3} N (3); $1{\cdot}5 \times 10^{-3}$ N (4); 2×10^{-3} N (5); $2{\cdot}5 \times 10^{-3}$ N (6); 3×10^{-3} N (7); 4×10^{-3} N (8); 5×10^{-3} N (9).

peroxodisulfate

Original idea:

KAMEO ASADA,[1a] PAUL DELAHAY AND A. K. SUNDARAM

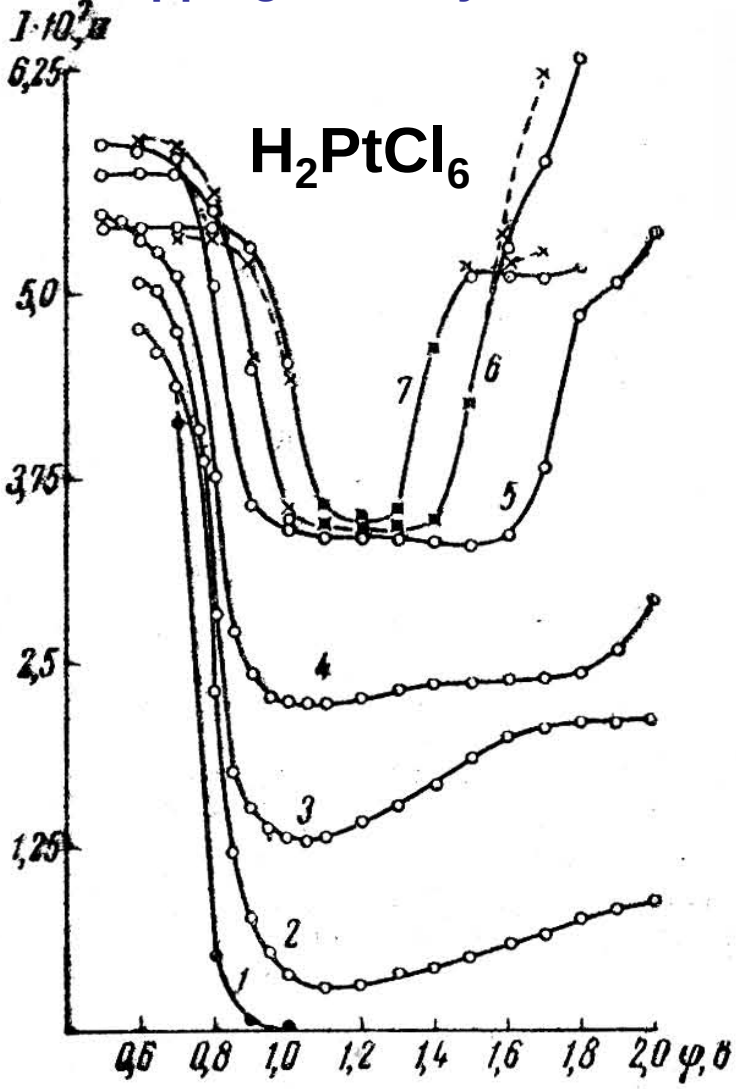
JACS, 1961, v.83, 3396-4000

Cations effect is still a challenge

О МЕХАНИЗМЕ ЭЛЕКТРОХИМИЧЕСКОГО ВОССТАНОВЛЕНИЯ ГАЛОИДНЫХ КОМПЛЕКСОВ ПЛАТИНЫ НА РТУТНОМ КАПЕЛЬНОМ ЭЛЕКТРОДЕ

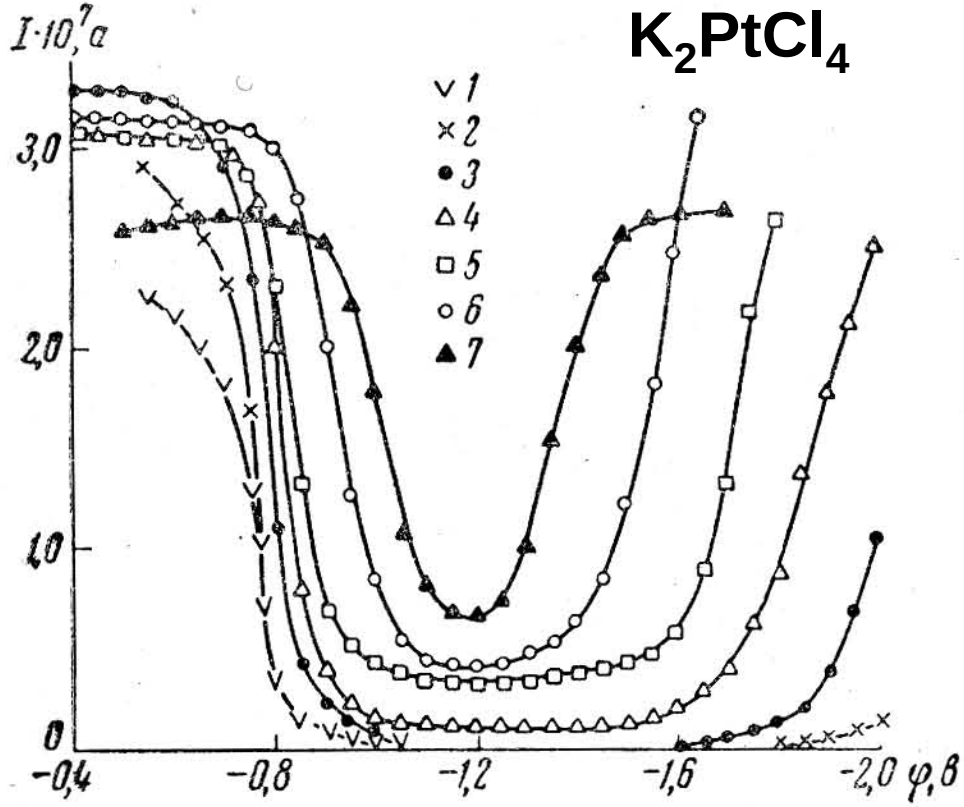
Н. В. Николаева-Федорович и О. А. Петрий

On the mechanism of electrochemical reduction of platinum halogenide complexes at the dropping mercury electrode, Zh. Fiz. Khimii, 1961, v.35, 1270-1277.

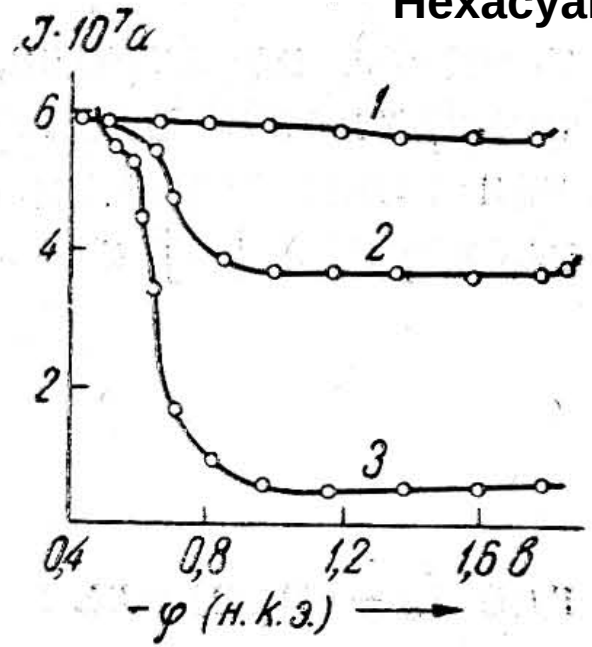


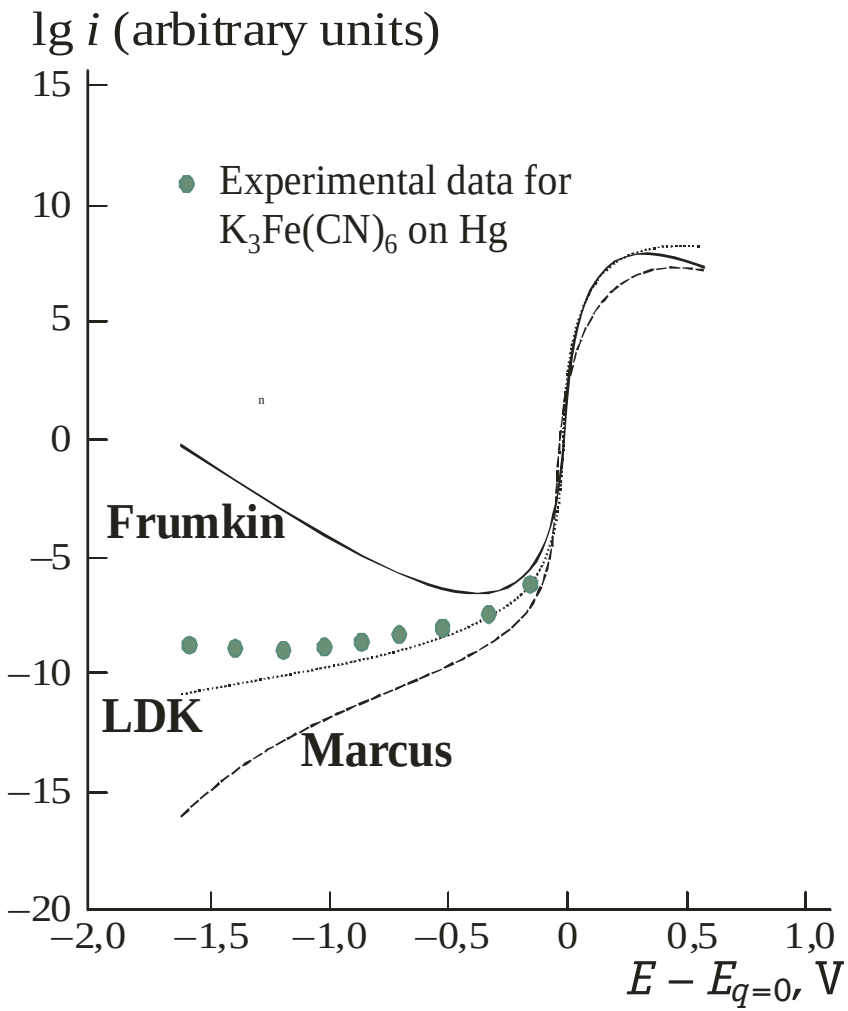
$$[PtCl_6]^{2-} + 2\bar{e} \rightarrow [PtCl_4]^{2-} + 2Cl^-,$$

$$[PtCl_4]^{2-} + 2\bar{e} \rightarrow Pt + 4Cl^-.$$



Hexacyanoferrate reduction – activationless process





Frumkin:

$$\ln j + \frac{n_i F \psi'}{RT} = \ln(k_s[C]) - \frac{\alpha(\varphi - \psi')F}{RT}$$

Levich-Dogonadze-Kuznetsov (LDK):

$$j = F[C]\left(\frac{\omega_{ef}}{2\pi}\right)\int_{-\infty}^{+\infty} d\varepsilon \int_{z_{min}}^{\infty} dz\,\rho(\varepsilon) f_{FD}(\varepsilon)\kappa_e(z)\exp\{-\Delta E_a(\varepsilon,z)/kT\}$$

$$\Delta E_a(\varepsilon,z) = W_i + (\Delta F_{if} + E_{tot} - \varepsilon)^2 / 4E_{tot}$$

J. Heyrowsky and A.N. Frumkin in Prague, 1964

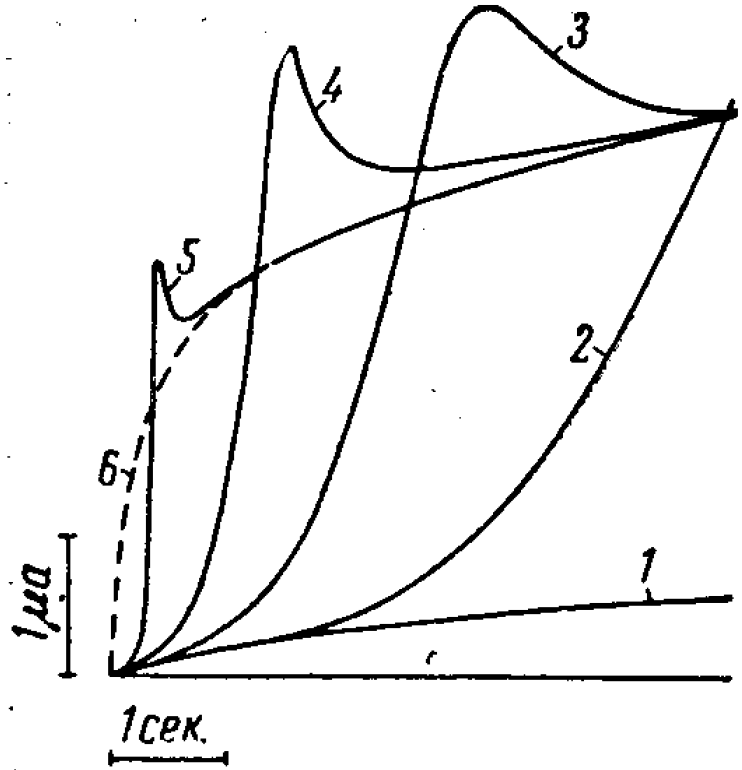
Доклады Академии наук СССР
1961. Том 136, № 5

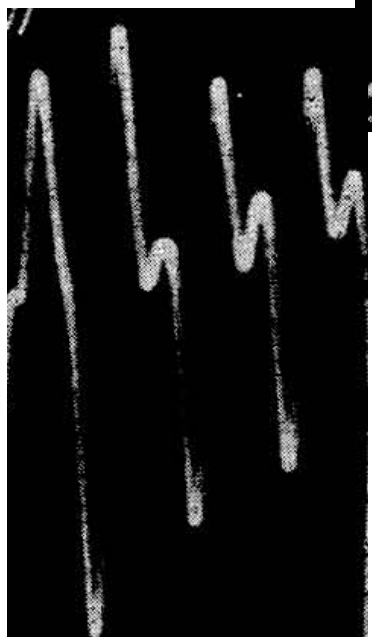
Академик А. Н. ФРУМКИН, О. А. ПЕТРИЙ и Н. В. НИКОЛАЕВА-ФЕДОРОВИЧ

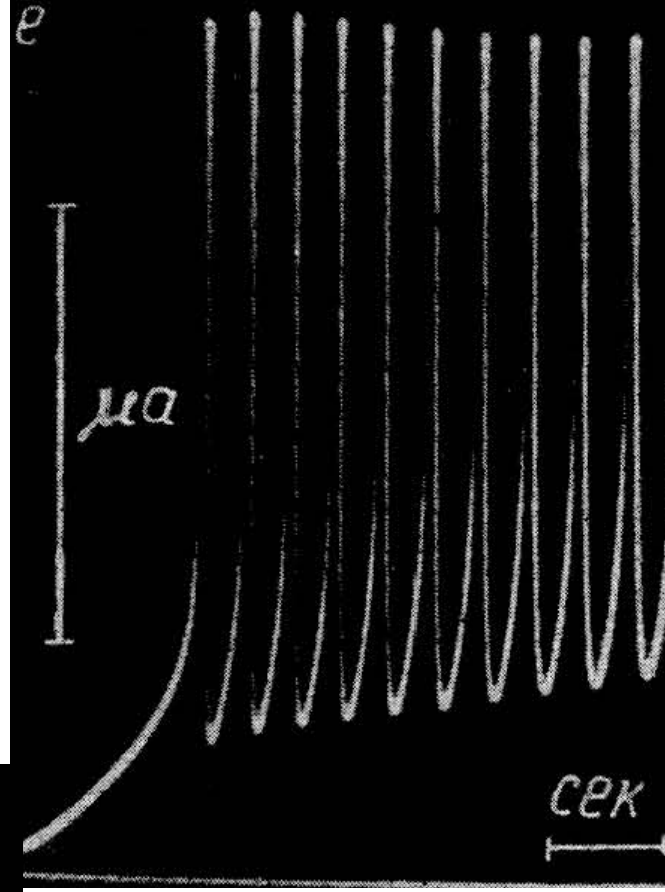
КРИВЫЕ ТОК—ВРЕМЯ ПРИ ВОССТАНОВЛЕНИИ АНИОНОВ НА КАПЕЛЬНОМ ЭЛЕКТРОДЕ

Current-time curves of anions reduction on the dropping electrode

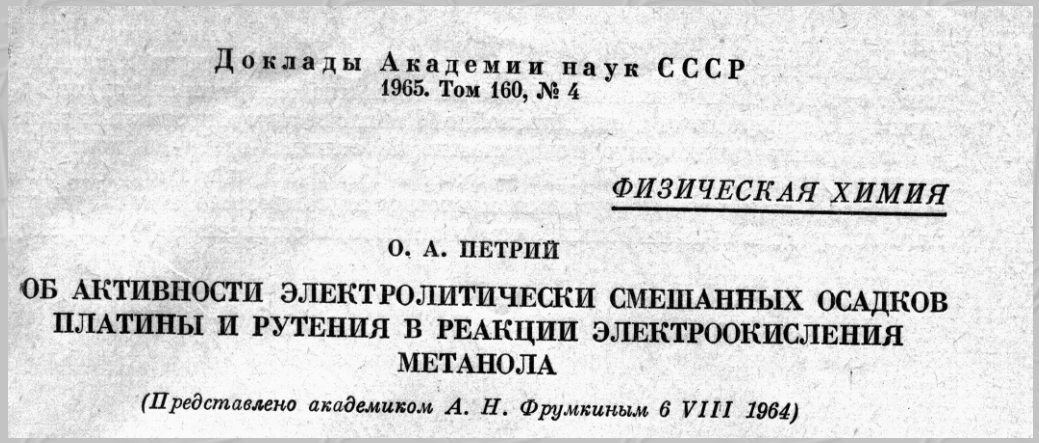
Peroxodisulphate reduction affected by tetrabutyl ammonium cation







Various types of oscillations observed for cation-affected reduction of anions



Доклады Академии наук СССР
1965. Том 160, № 4

ФИЗИЧЕСКАЯ ХИМИЯ

О. А. ПЕТРИЙ

ОБ АКТИВНОСТИ ЭЛЕКТРОЛИТИЧЕСКИ СМЕШАННЫХ ОСАДКОВ ПЛАТИНЫ И РУТЕНИЯ В РЕАКЦИИ ЭЛЕКТРООКИСЛЕНИЯ МЕТАНОЛА

(Представлено академиком А. Н. Фрумкиным 6 VIII 1964)

O.A.Petrii,
Doklady AN SSSR,
160(1965)871-874

On the activity of electrolytic mixed platinum-ruthenium deposits in methanol electrooxidation reaction

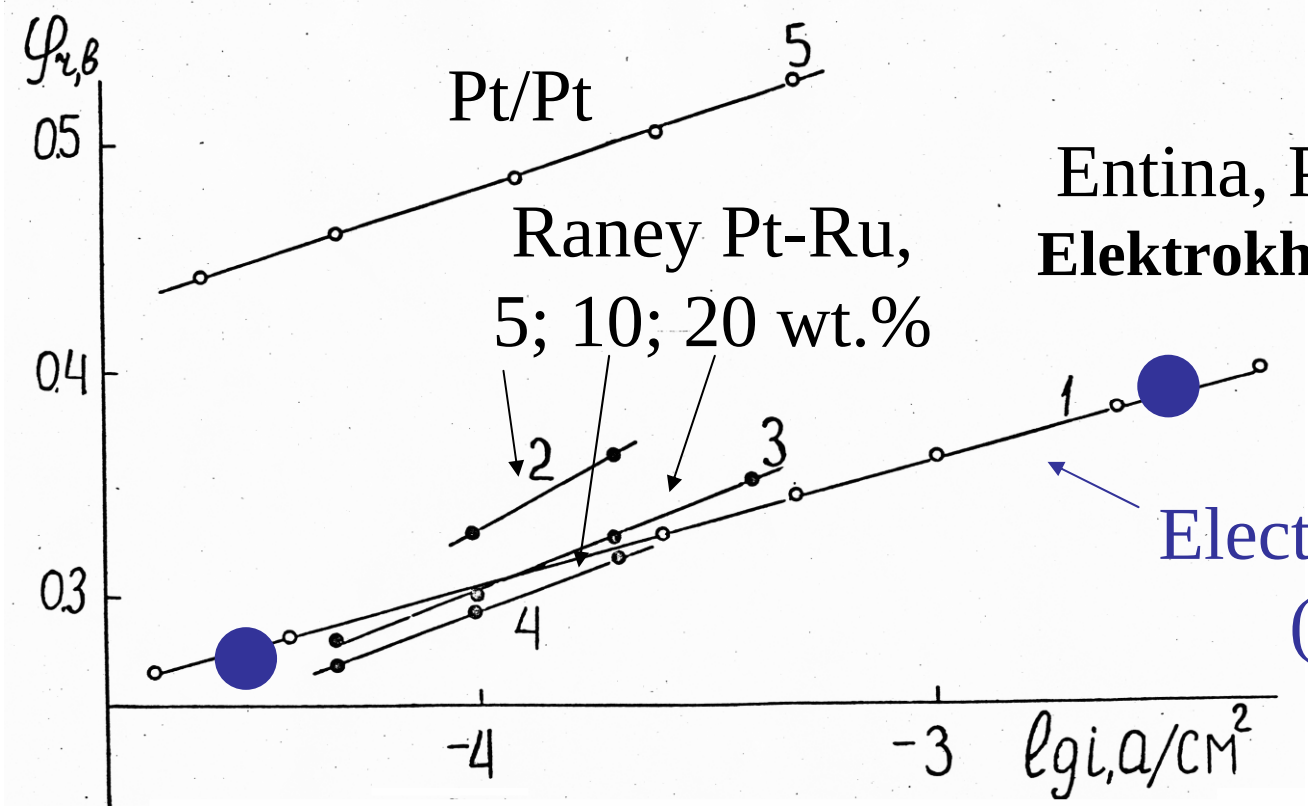
Recommended by Academician A.N.Frumkin, August 6, 1964

$H_2PtCl_6 + K_2Ru(NO)Cl_5$, 5-10-23-30-100 wt.% Ru;
Pt foil support

Further studies:
1964-1970, with participation of V.Entina

O.A.Petrii, V.E.Kazarinov, Elektrokhimiya 1(1965)1389

^{106}Ru radiotracer technique: $K_2{}^{106}Ru(NO)Cl_5$, galvanostatic



Entina, Petrii, Zhitnev,
Elektrokhimiya 3(1967)344

Electrodeposited Pt-Ru
(10 wt.% Ru)

Steady-state data for sol-gel Pt-Ru catalyst, **from J.Y.Kim, Z.G.Yang, C.-C.Chang, Y.I.Valdez, S.R.Narayanan, P.N.Kumta, J.Electrochem. Soc. 150(2003)A1421**

J Solid State Electrochem (2008) 12:609–642

Pt–Ru electrocatalysts for fuel cells: a representative review

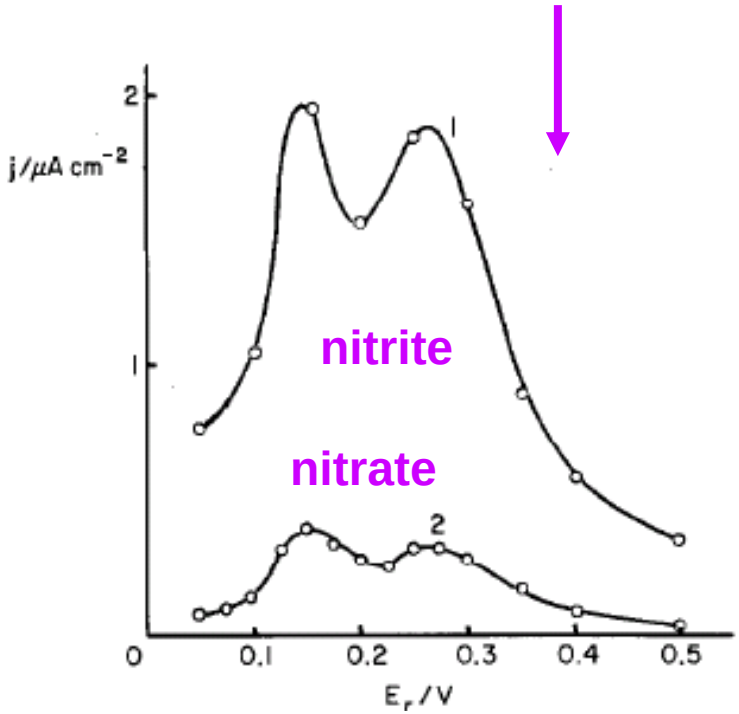
Oleg A. Petrii

Electrocatalytic reduction of inorganic anions on Pt metals

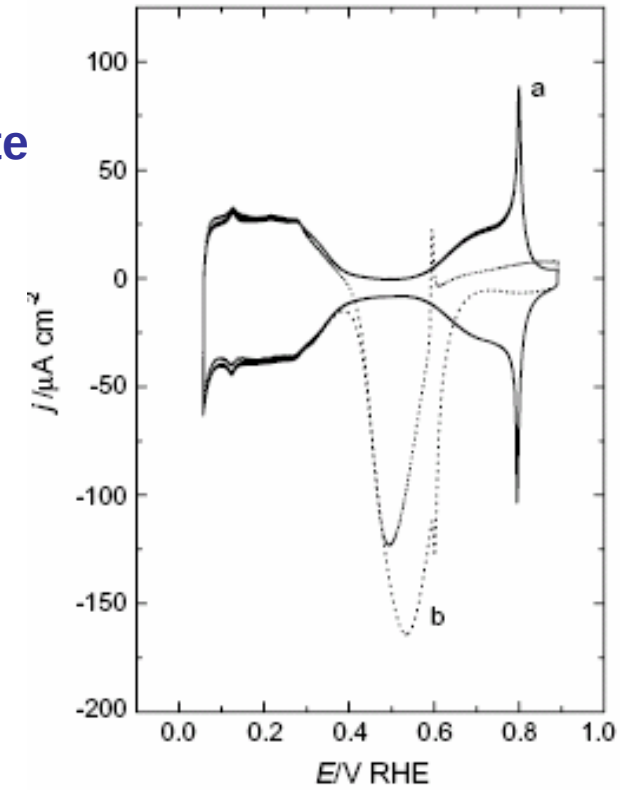
Electroreduction of nitrate and nitrite anions on platinum metals: a model process for elucidating the nature of the passivation by hydrogen adsorption *

J. Electroanal. Chem., 331 (1992) 897–912

Oleg A. Petrii and Tatiana Ya. Safonova



Peroxodisulfate on Pt(111)

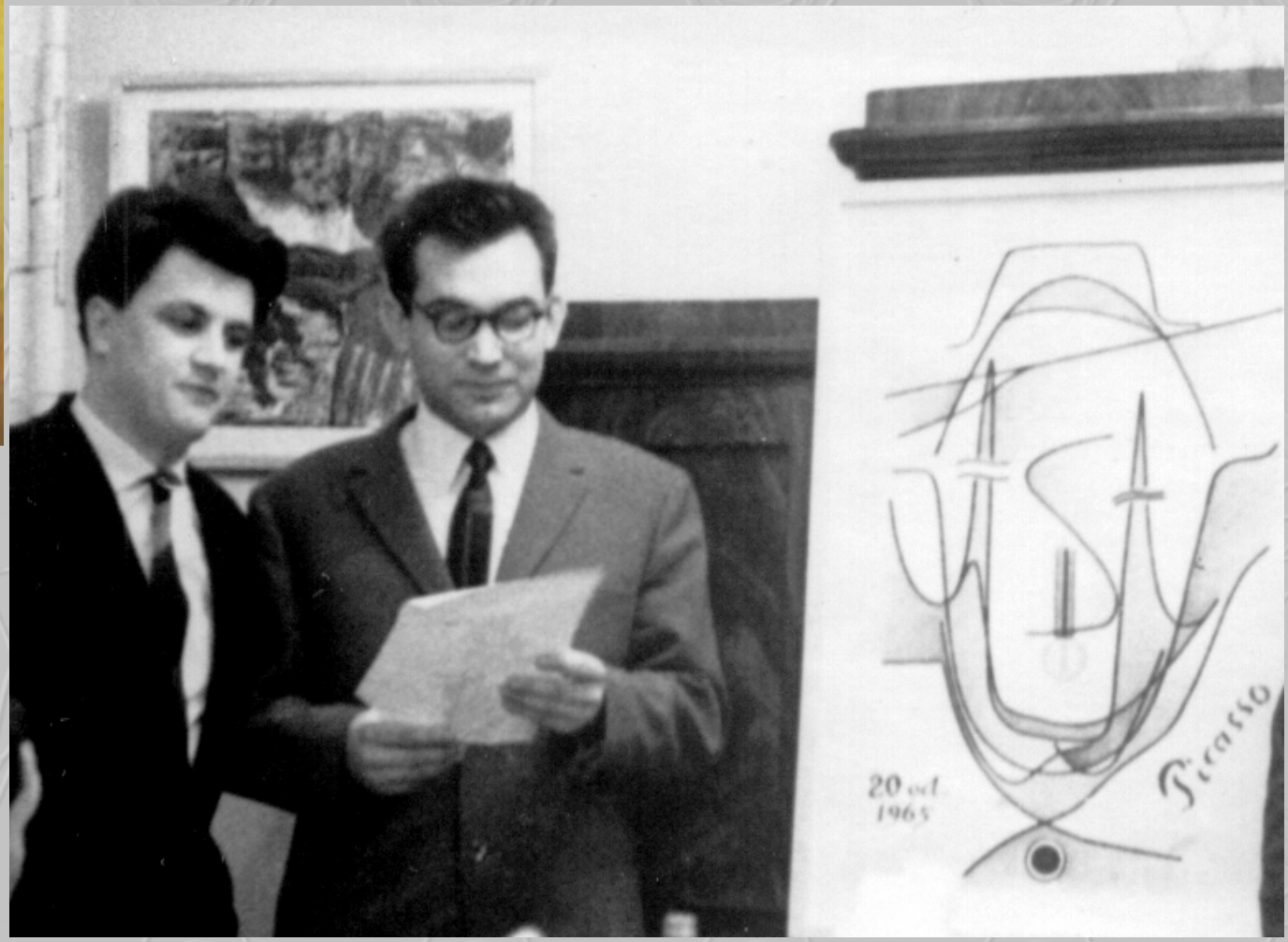


Journal of Electroanalytical Chemistry 612 (2008) 269–276

Peroxodisulphate reduction as a novel probe for the study of platinum single crystal/solution interphases

Victor Climent [a], M. Dolores Maciá [a], Enrique Herrero [a], Juan M. Feliu [a,*], Oleg A. Petrii

Picasso portrait:
manual to study the electrode kinetics



1965

Surface thermodynamics of the perfectly polarizable electrode

$$\mathrm{Ox} + n\bar{e} \rightleftarrows \mathrm{Red}$$

Nernst Equation $dE = d\mu_{Ox} - d\mu_{\mathrm{Red}}$

Gibbs Equation $d\sigma = -\Gamma_{ox} d\mu_{Ox} - \Gamma_{\mathrm{Red}} d\mu_{\mathrm{Red}} - \sum_i \Gamma_i d\mu_i$

When $\mu_{\mathrm{Ox}} = const$,

$$d\sigma = \Gamma_{\mathrm{Red}} dE - \sum_i \Gamma_i d\mu_i$$

When $\mu_{\mathrm{Red}} = const$,

$$d\sigma = -\Gamma_{Ox} dE - \sum_i \Gamma_i d\mu_i$$

Two Lippman Equations:

$$\left(\partial\sigma/\partial E\right)_{\mu_{Ox},\mu_i} = \Gamma_{\mathrm{Red}} \qquad \left(\partial\sigma/\partial E\right)_{\mu_{\mathrm{Red}},\mu_i} = -\Gamma_{Ox}$$

Total charges:

$$\Gamma_{\mathrm{Red}} = -\varepsilon + A_{\mathrm{Red}}, \; \Gamma_{ox} = \varepsilon + A_{Ox}$$

Hydrogen electrode (platinized platinum)

$$d\sigma = -\Gamma_H d\mu_H - \Gamma_{HA} d\mu_{HA} - \Gamma_{CA} d\mu_{CA}$$

$$\left(\partial E_r / \partial \mu_{H^+}\right)_{\Gamma_H, \mu_{CA}} = \left(\partial \Gamma_{H^+} / \partial E_r\right)_{\mu_{H^+}, \mu_{CA}} \Big/ \left(\partial \Gamma_H / \partial E_r\right)_{\mu_{H^+}, \mu_{CA}}$$

Double layer capacity

Isoelectric shift

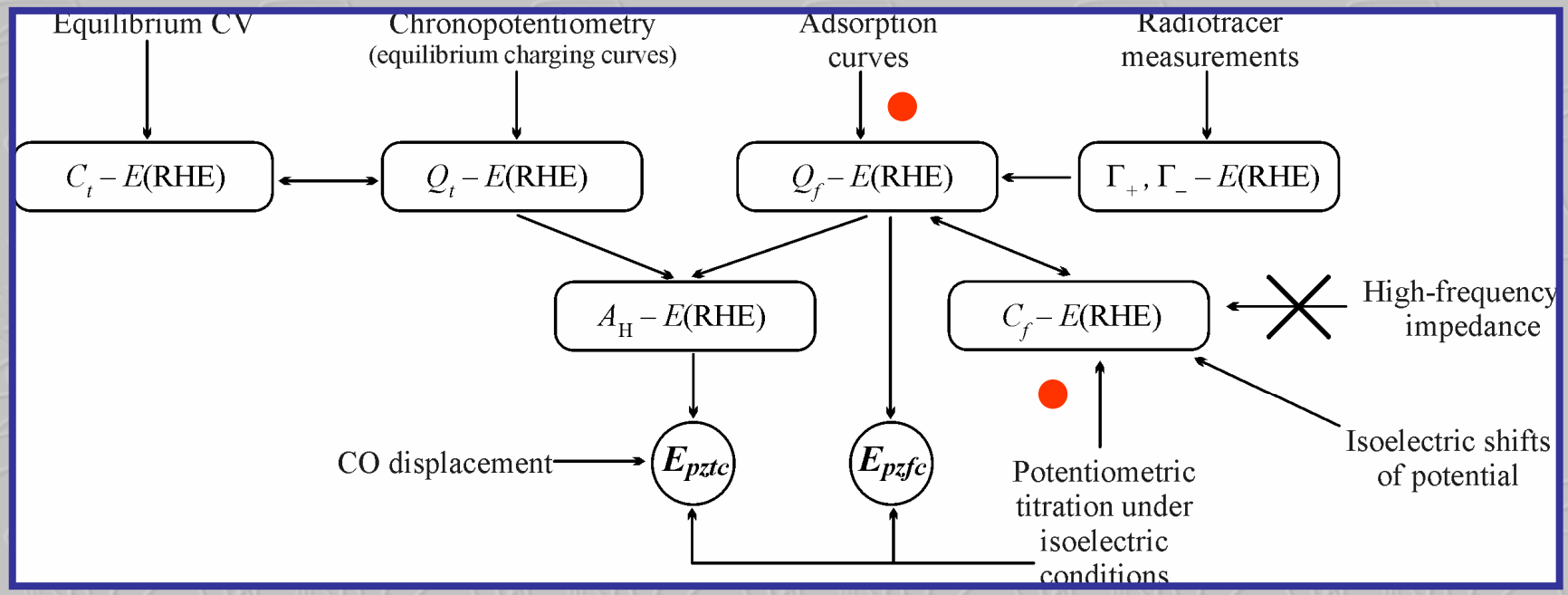
$$C_{dl} = C_{total} \left(\partial E_r / \partial \mu_{H^+}\right)_{\Gamma_H, \mu_{CA}}$$

Total capacity

Experimental techniques to verify surface thermodynamics concept

t – the quantities related to the total electrode charge

f – related to free electrode charge



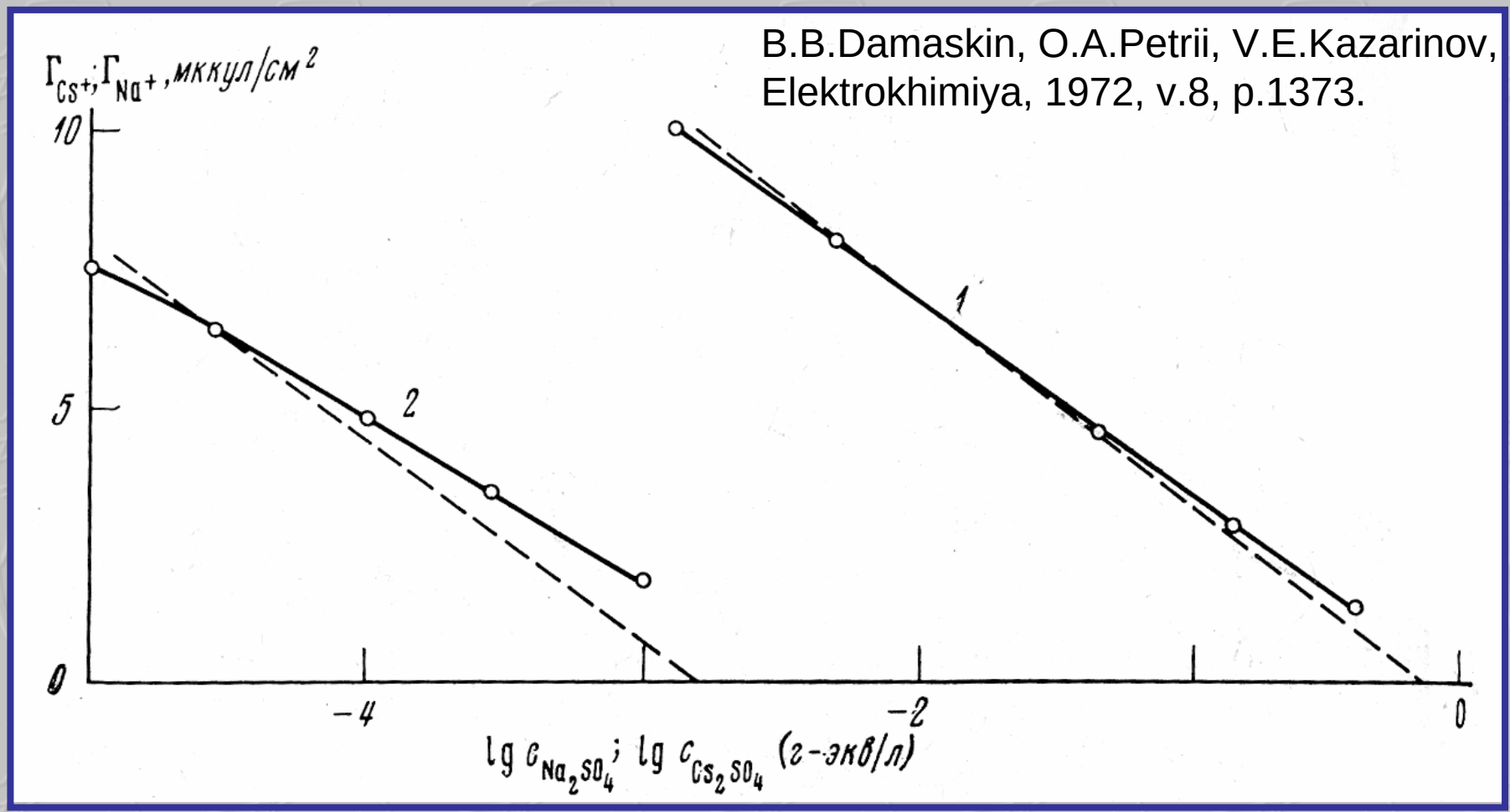
● Still possible to apply only to the electrodes of high true surface area

Coadsorption

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2$$

$$\left(\partial\Gamma_1 / \partial\mu_2\right)_{\mu_1} = \left(\partial\Gamma_2 / \partial\mu_1\right)_{\mu_2}$$

B.B.Damaskin, O.A.Petrii, V.E.Kazarinov, Elektrokhimiya, 1972, v.8, p.1373.



Free electrode charge: pH dependence

Hydrogen region, $A_{H^+} = 0$

$$\left(\partial E / \partial pH\right)_{\varepsilon=0} = -\frac{2.3RT}{F}\frac{1}{1-\left(\partial \Gamma_{H^+} / \partial A_H\right)_{E_r}}$$

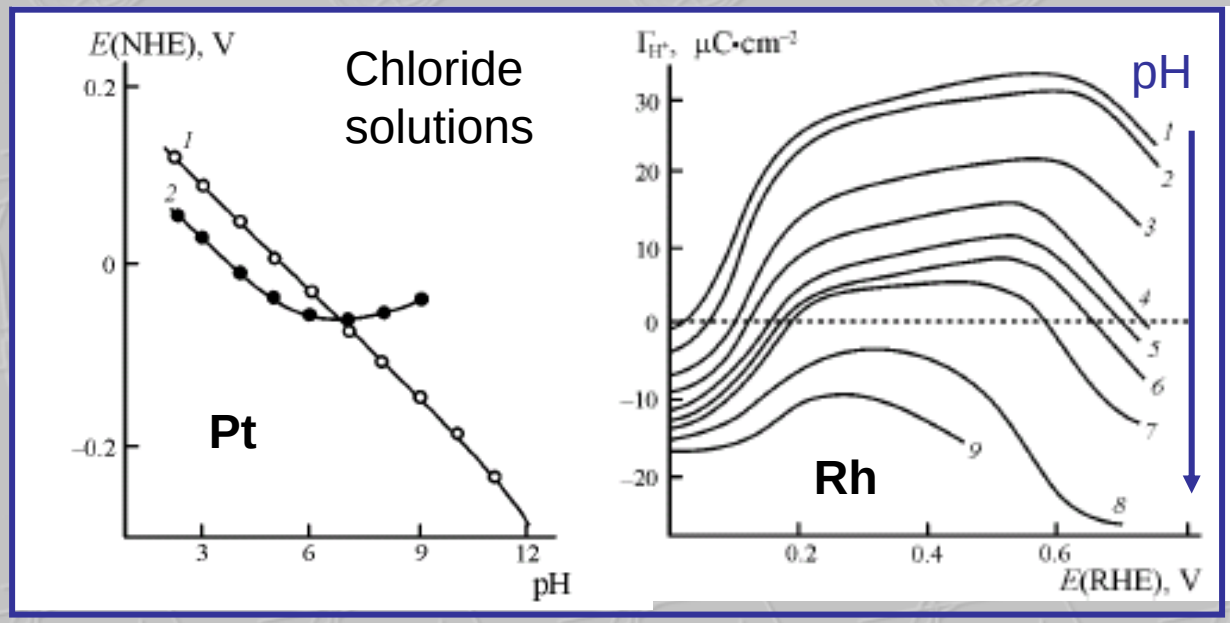
Oxygen region, $A_{OH^-} = 0$

$$\left(\partial E / \partial pH\right)_{\varepsilon=0} = -\frac{2.3RT}{F}\left(\partial A_{OH} / \partial \Gamma_{H^+}\right)_{E_r}\frac{1}{1+\left(\partial A_{OH} / \partial \Gamma_{H^+}\right)_{E_r}}$$

If $A_H = 0$ or $A_{OH} = 0$

$$\left(\partial E / \partial pH\right)_{\varepsilon=0} = 0$$

Doklady AN SSSR, 1975, v.222, 1159; 1976, v.226, 117



Partial charge transfer

$$n_1 = \left(\partial \Gamma_{\mathrm{Red}} \Big/ \partial \Gamma_{\Sigma} \right)_E$$

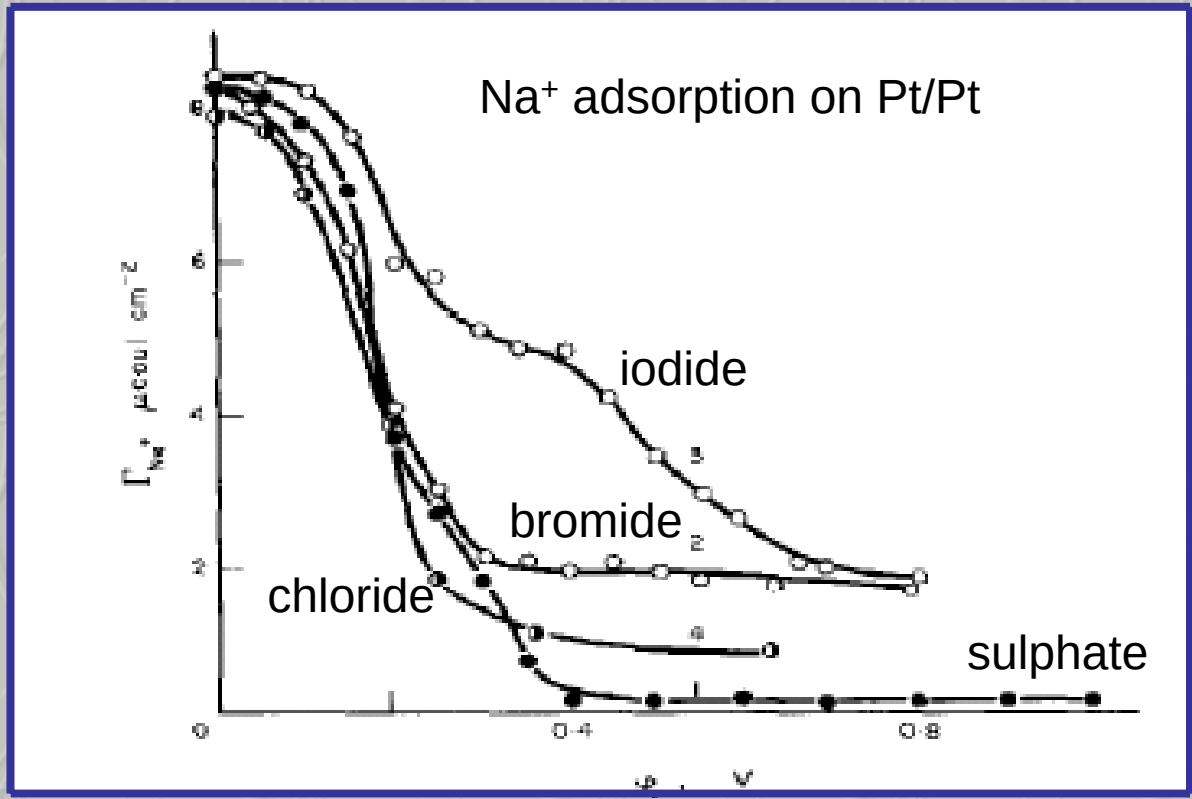
$$n_2 = \left(\partial \Gamma_{Ox} \Big/ \partial \Gamma_{\Sigma} \right)_E$$

$$\Gamma_{\Sigma} = \Gamma_{Ox} + \Gamma_{\mathrm{Red}}$$

$$\mathrm{Ox} + n\bar{e} \rightleftarrows \mathrm{Red}$$

$$\mathrm{Ox} + n_1\bar{e} \rightleftarrows \mathrm{Ad}$$

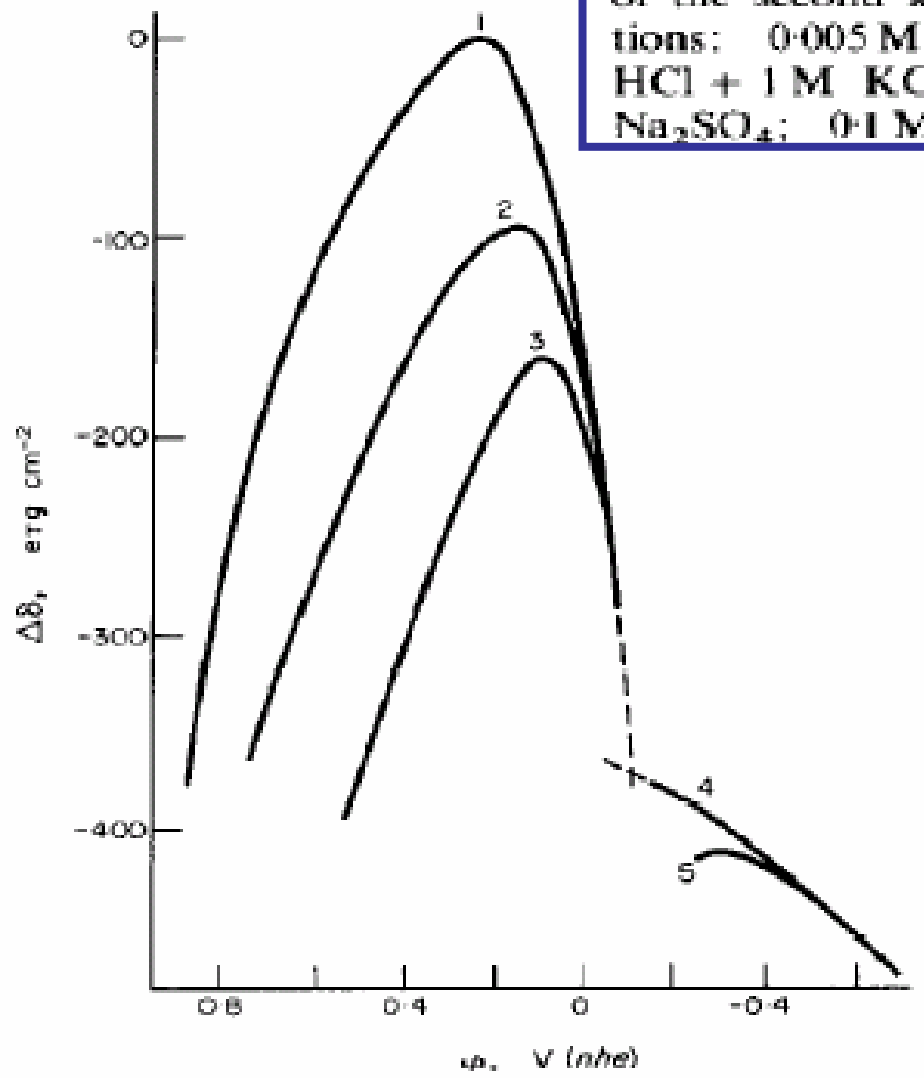
$$\mathrm{Ad} + n_2\bar{e} \rightleftarrows \mathrm{Red}$$

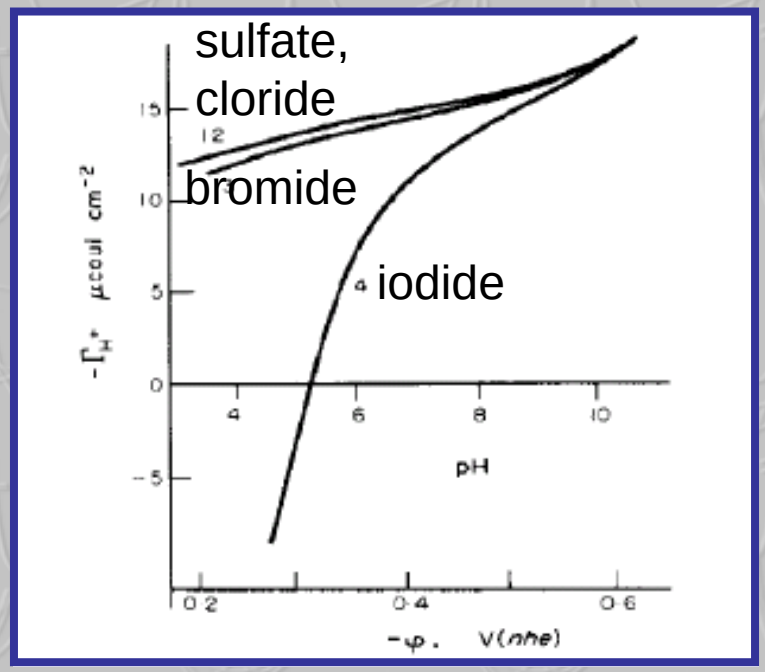


1974: Edward Kennedy visit to USSR

The intersect of 3D electrocapillary curve

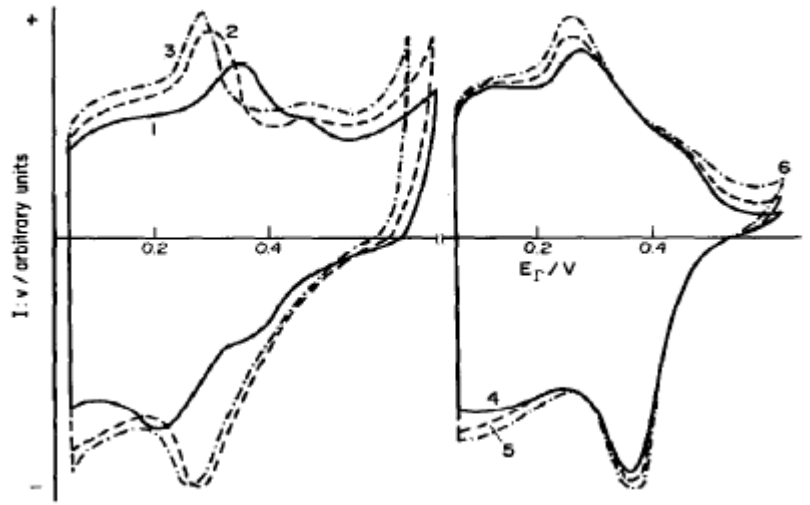
Electrocapillary curves of the first kind (1–3) and of the second kind (4,5) of Pt/Pt electrode in the solutions: 0·005 M H_2SO_4 + 0·5 M Na_2SO_4; $2–10^{-2}$ M HCl + 1 M KCl; $3–10^{-2}$ M HBr + 1 M KBr; 4–0·5 M Na_2SO_4; 0·1 M KCl ($\varphi_r = 0$); 5–0·1 M KI ($\varphi_r = 0$)





Charging curves of the 2nd kind

Electrochemical material science



ROLE OF CARBON DEFICIENCY AND ANODIC ACTIVATION IN THE ELECTROCHEMISTRY OF CARBIDE MATERIALS

G. A. TSIRLINA and O. A. PETRII

High temperature oxide superconductors

JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) 583–588

Anomalous features of thallium oxide electrodeposited layers and room temperature HTSC electrosynthesis*

O. A. PETRII, G. A. TSIRLINA, T. V. RAKOVA, S. YU. VASSILIEV

Tungsten and chromium carbides:

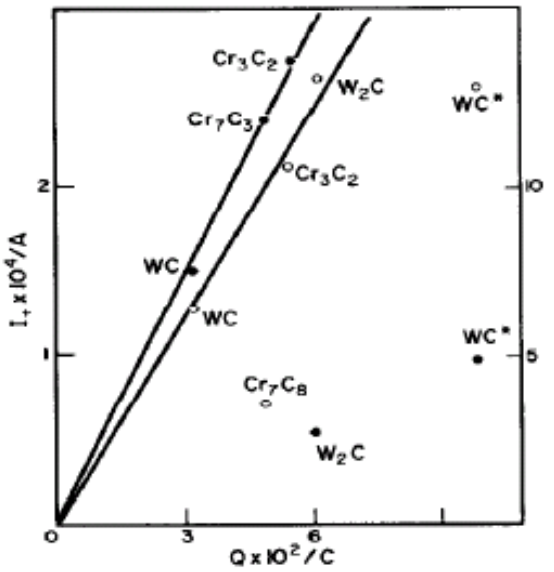
Electrochim. Acta, 1987, v.32, 37 and 649

Rechargeable oxides (a brief review):

SURFACE ELECTROCHEMISTRY OF OXIDES: THERMODYNAMIC AND MODEL APPROACHES

O. A. PETRII

Electrochim. Acta, 1996, v.41, 2307

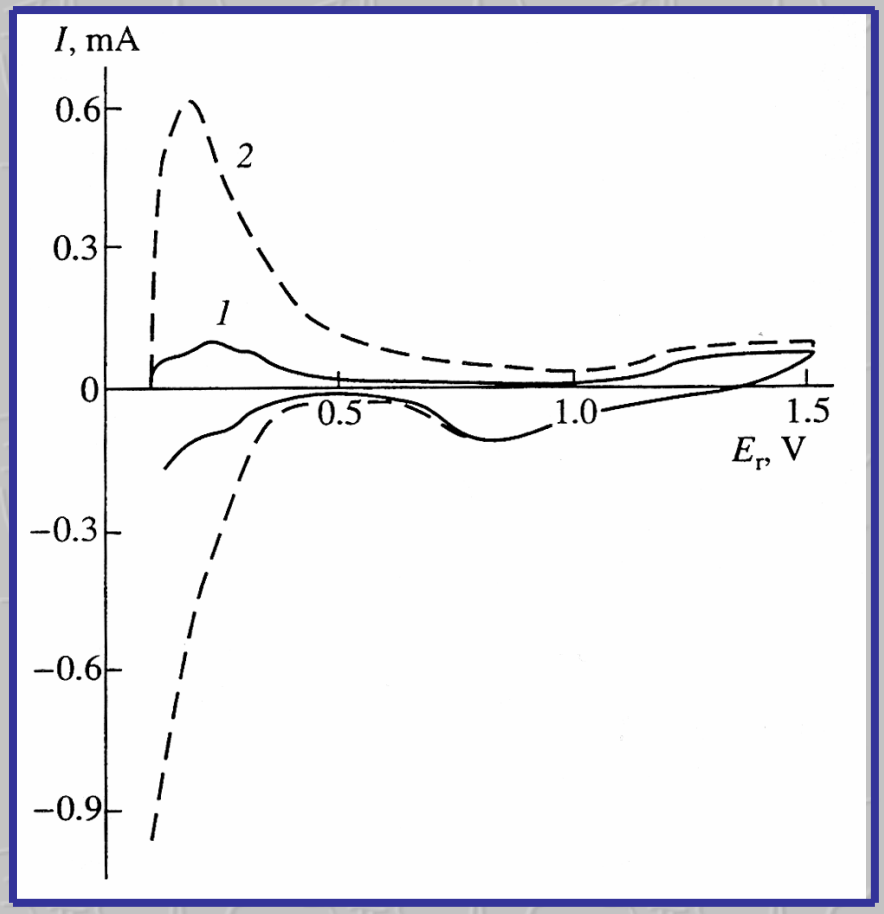


HYDROGEN EVOLUTION ON SMOOTH STOICHIOMETRIC TUNGSTEN AND CHROMIUM CARBIDES

G. A. TSIRLINA and O. A. PETRII

Electrochemical material science

Pt-ZrO2: spillover



O. A. Petrii, S. Ya. Vasina, Yu. D. Seropegin, Russ. J. Electrochem. 1995, v.31, 1274

CeNi3 – CeCo3 system:

Yu. M. Vol'fkovich, O. A. Petrii, A. A. Zaitsev, I.V. Kovrigina, Vestn. Mosk. Univ. Ser. 2, 1988, No29, 173

For review, see

O. A. Petrii, I. V. Kovrigina, S. Ya. Vasina, Mater. Chem. Phys. 1989, v.22, 51

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION
COMMISSION ON ELECTROCHEMISTRY*

J. Electroanal. Chem., 327 (1992) 353–376

REAL SURFACE AREA MEASUREMENTS IN ELECTROCHEMISTRY

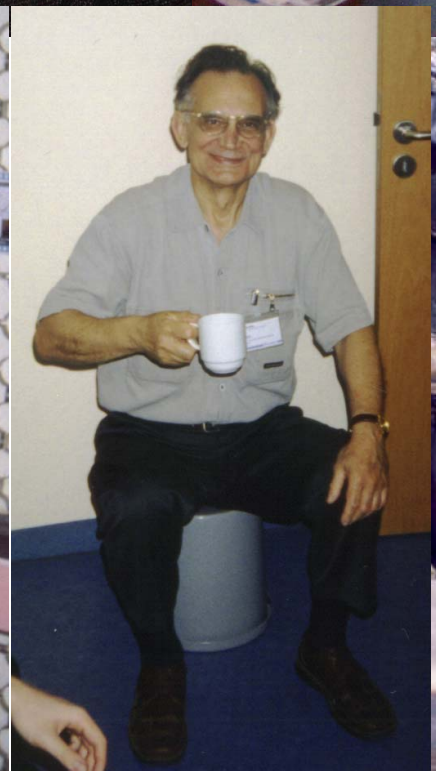
Prepared for publication by

S. TRASATTI[1] and O. A. PETRII[2]

1974, Horiuti and Frumkin

Alma-Ata, 1975


70 лет
КАФЕДРЕ ЭЛЕКТРОСВЯЗИ
СТОЛОВОЕ ВИНО
ПАНОРАЗМЕРНОЕ



1999

Roger Parsons

Lev Krishtalik

Sergio Trasatti

Boris Damaskin

Jean Clavilier

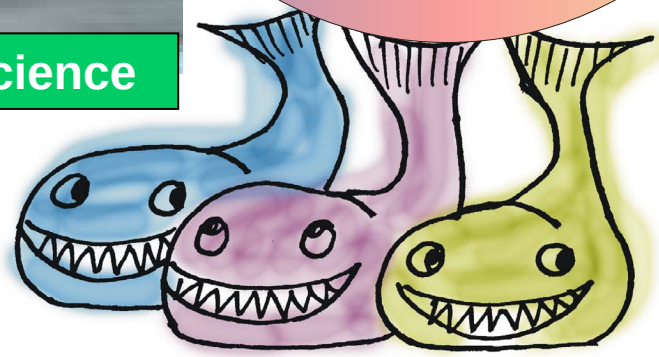
Oleg Petrii

2009

Bio

Electrochemistry on three foundations

Material science



«diffusion» «double layer»

«electron transfer»

Home-made movie, 1965