THE MERCURY ERA OF ELECTROCHEMISTRY

Mercury has more to reveal about the structure of electrochemical interfaces and its effect on electrochemical electron transfer

26-11-2024, JUN HUANG

Winter School for Theoretical Chemistry and Spectroscopy

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Forschungszentrum

OUTLINE

- **Motivation for revisiting the Mercury era**

- **The EDL structure**

- **EDL effects on electron transfer**

'ONE THING IS CERTAIN …

It's a great time to have a degree in electrochemistry'. Jack Ewing and Ivan Penn in New York Times, 2021

Indeed, there is a risk today that electrochemistry may lose its status as a fundamental science and merely become a branch of materials science.

From our point of view, however, at least two branches of electrochemistry will act as bulwarks against such a transformation.

These are the detailed study of charged interfaces and the detailed study of charge transfer.
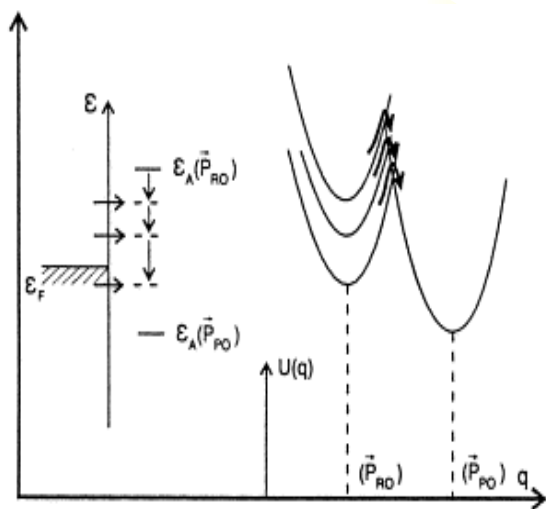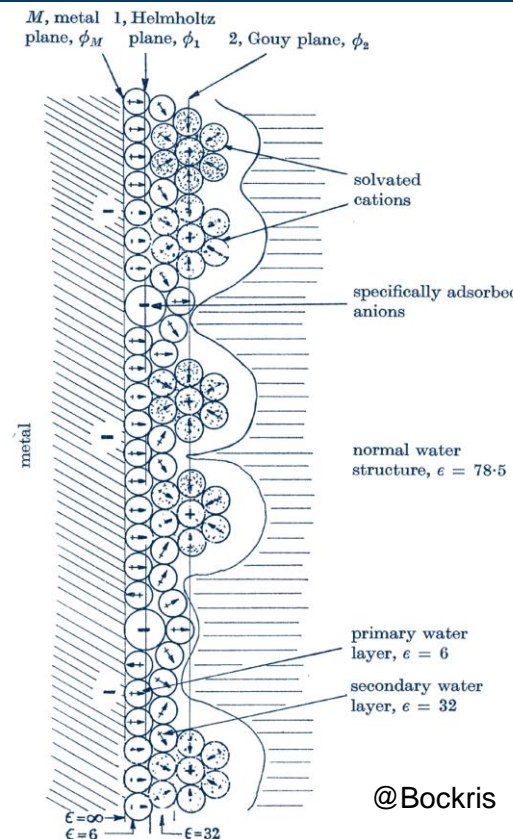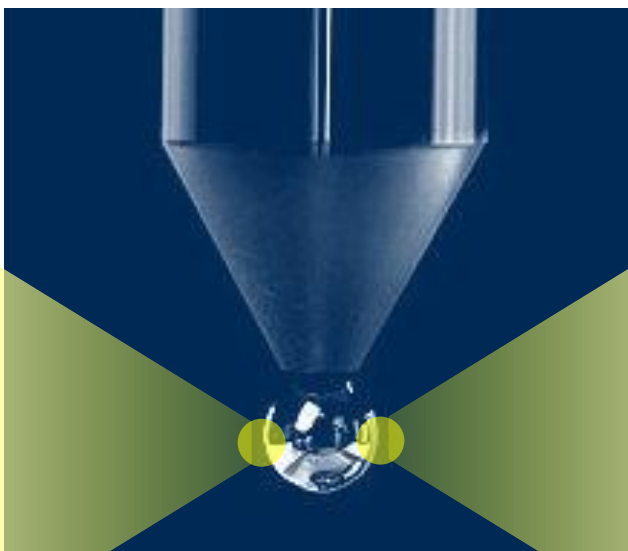
B. Damaskin
(1932-2019)

O. Petrii
(1937-2021)

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WHY MERCURY

"Nearly everything one desires to know about the electrical double layer is ascertainable with mercury surfaces if it is ascertainable at all." DC Grahame 1947
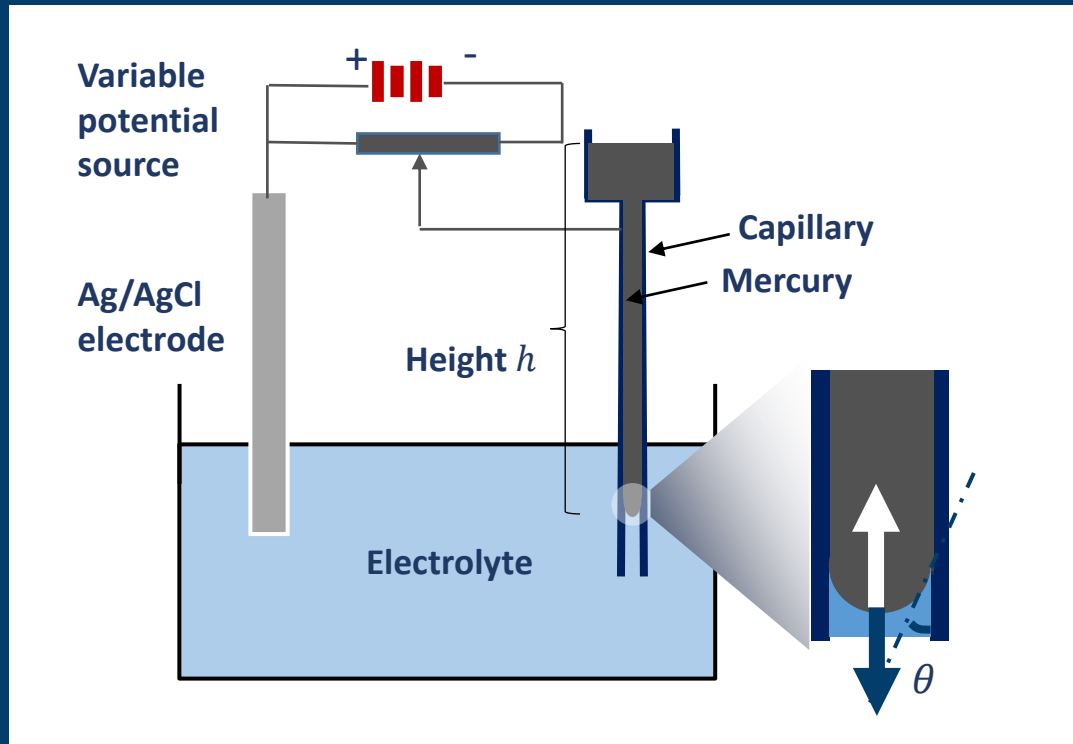

@ Kuznetsov

@Bockris

OUTLINE

- **Motivation for revisiting the Mercury Era**

- **The EDL structure**

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POTENTIAL-DEPENDENT SURFACE TENSION

Electrode potential is electrochemist's joystick

Mechanic equilibrium gives the measured surface tension

$$\gamma = \frac{\rho h g r}{2}$$

r, radius of capillary tube
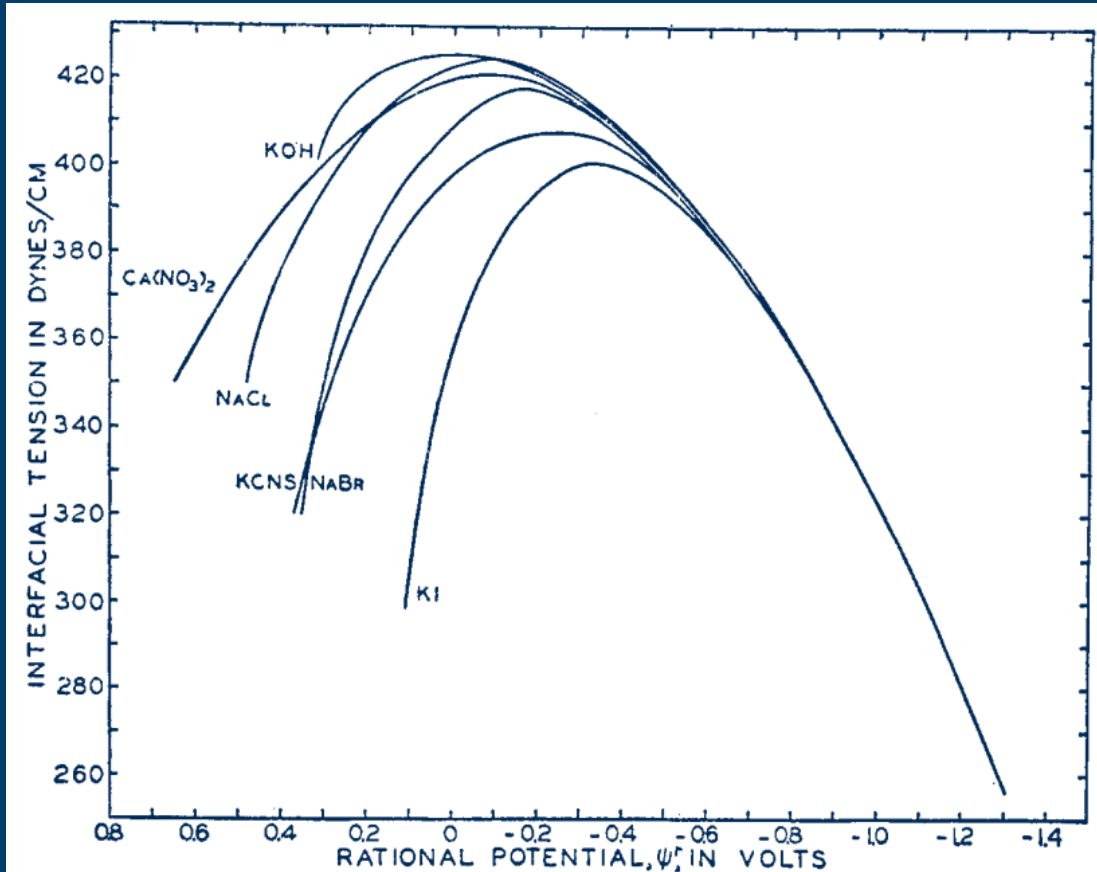$\rho = 13546 \text{ kg/m}^3$, density of Hg
r_c, radius of curvature of the mercury meniscus
$g = 10 \text{ N/kg}$, gravity constant

Bard A J, Faulkner L R, White H S. Electrochemical methods: fundamentals and applications[M]. John Wiley & Sons, 2022, pp. 11 and 23.

POTENTIAL-DEPENDENT SURFACE TENSION

**Mercury-aqueous solution interface at T = 18°C (Gouy, 1903-1017)**

"Until the thermodynamic theory of electrocapillarity has been discussed, there is not much to be learned from the electrocapillary curves"

D.C. Grahame, 1947

DYNE, unit of force, 1 DYNE $= 10^{-5}$ N and 1 DYNE/cm $= 1$ mN/m

Jun Huang - **Revisit Mercury Era**

LIPPMANN EQUATION

Nobel laureate in Physics for his method of reproducing colours photographically
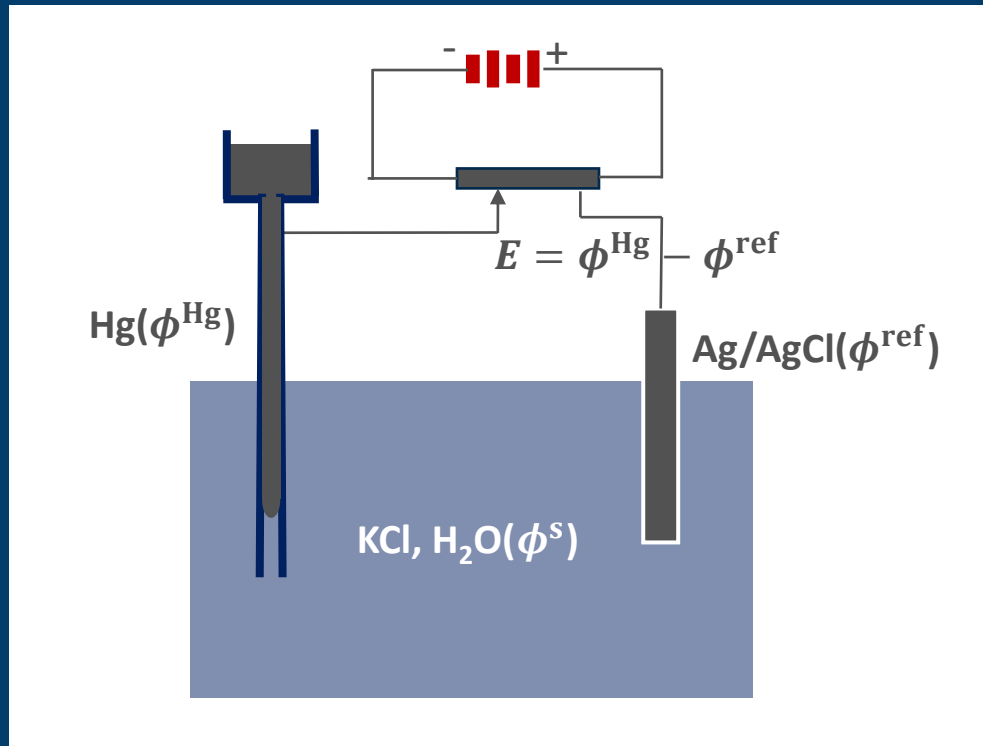
Gibbs adsorption isotherm

$$-d\gamma = \sum_i \Gamma_i d\tilde{\mu}_i \ (\text{cons.} \, T, P)$$

Bard book, Chapter 13

Lippmann equation

$$-d\gamma = \sigma dE + \Gamma_{K^+(H_2O)} d\mu_{KCl}$$

γ, surface tension

σ, surface excess charge

E, electrode potential vs Ag/AgCl electrode

μ_{KCl}, chemical potential of the salt KCl

$\Gamma_{K^+(H_2O)} = \Gamma_{K^+} - \Gamma_{H_2O} \frac{X_{KCl}}{X_{H_2O}}$, relative excess of the ion K^+, with X_{KCl} and X_{H_2O} being the mole fractions of the salt KCl and H_2O in bulk solution

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THERMODYNAMICS OF EDL

Lippmann equation

$$-d\gamma = \sigma dE + \Gamma_{K^+(H_2O)} d\mu_{KCl}$$

Surface excess charge

$$\sigma = -\left(\frac{\partial \gamma}{\partial E}\right)_{\mu_{KCl}}$$

Differential capacitance

$$C_{\mathrm{dl}} = \left(\frac{\partial \sigma}{\partial E}\right)_{\mu_{KCl}} = -\left(\frac{\partial^2 \gamma}{\partial E^2}\right)_{\mu_{KCl}}$$
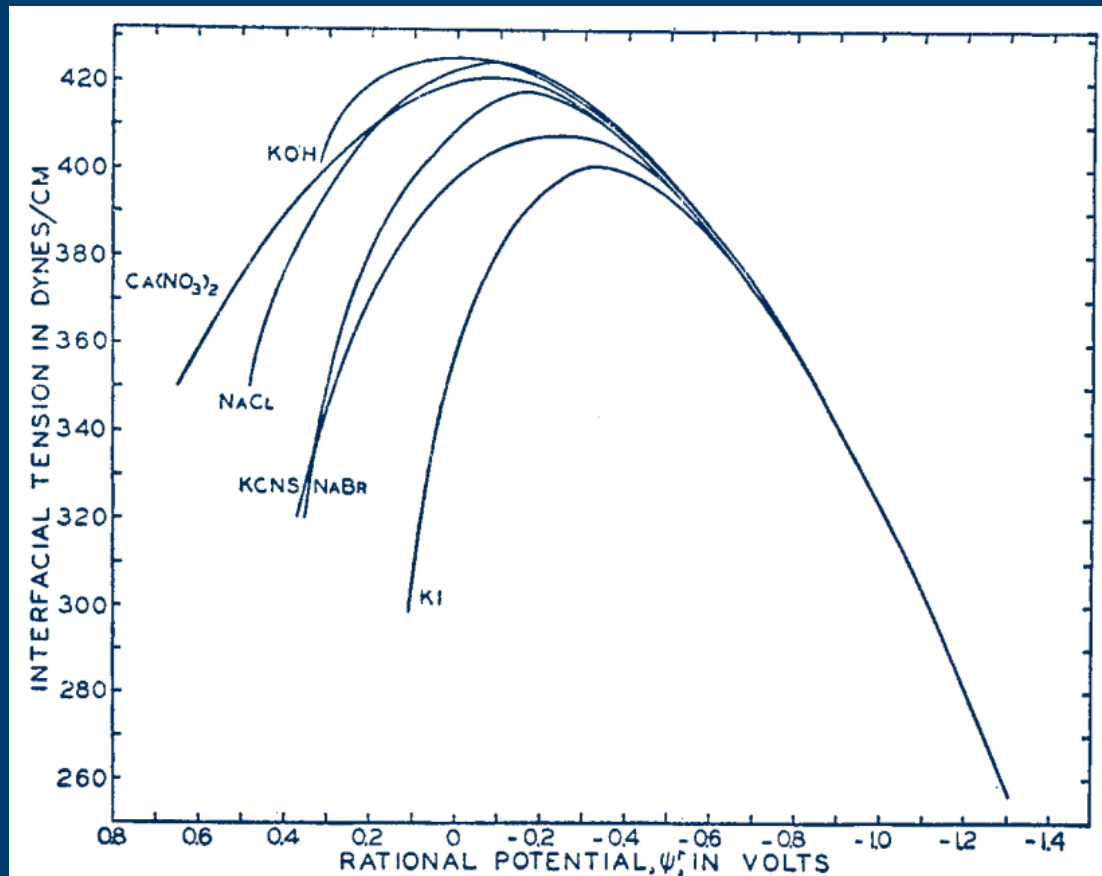
Relative surface excess of ions

$$\Gamma_{K^+(H_2O)} = -\left(\frac{\partial \gamma}{\partial \mu_{\mathrm{KCl}}}\right)_E = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial (\ln a_{\mathrm{KCl}})}\right)_E$$
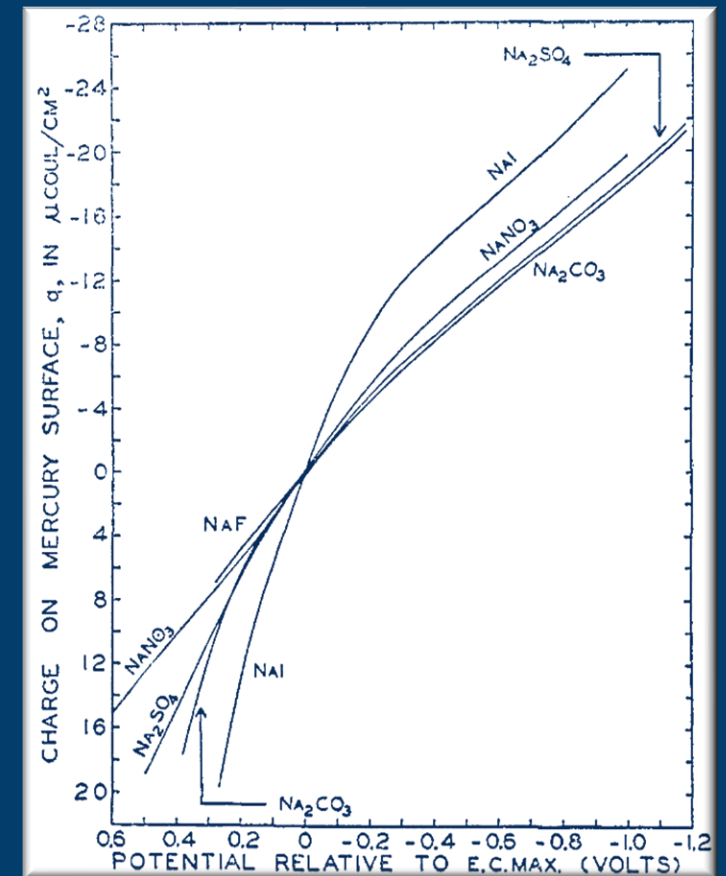
a_{KCl} is the activity of KCl

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SURFACE EXCESS CHARGE

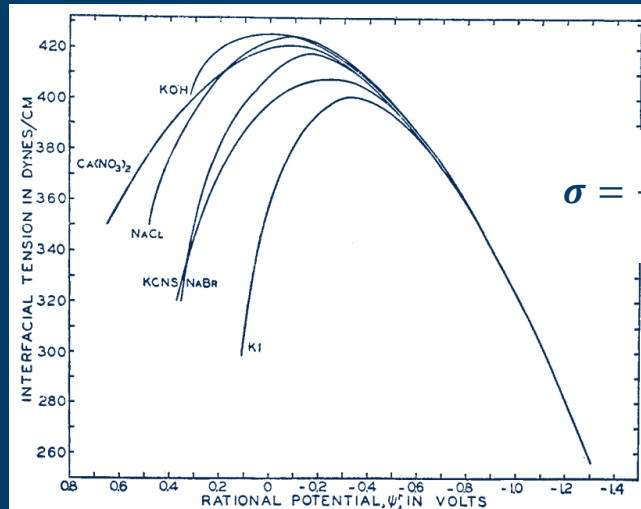**"Gouy, whose extraordinarily precise measurements make possible …" DC Grahame 1941**

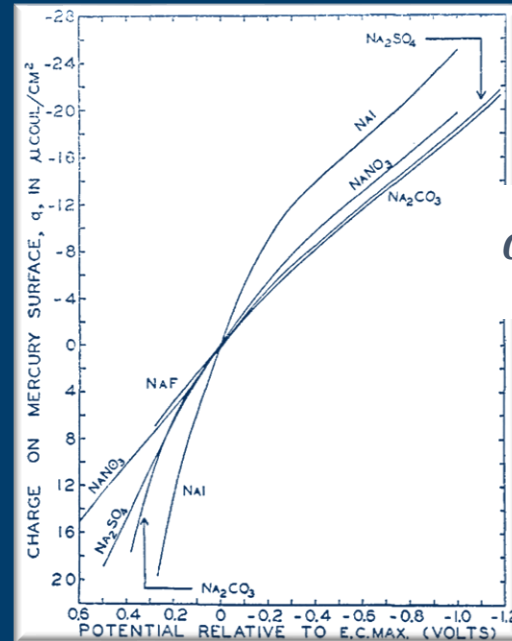$$\sigma = -\left(\frac{\partial \gamma}{\partial E}\right)_{\mu_{salt}}$$

Grahame D C. Chemical Reviews, 1947, 41(3): 441-501.

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DIFFERENTIAL DOUBLE LAYER CAPACITANCE

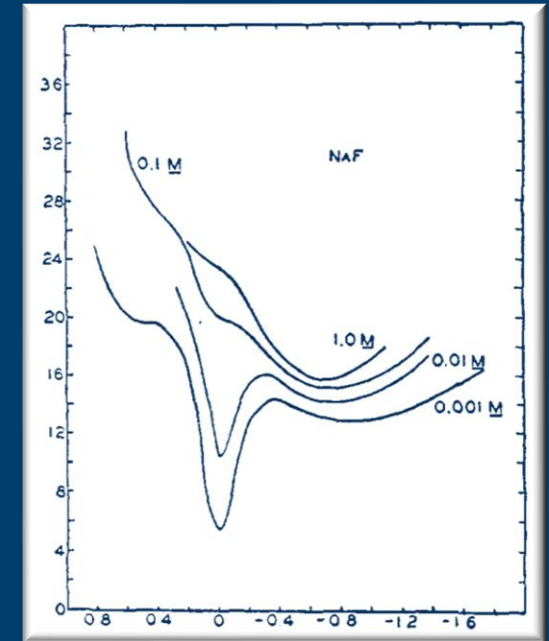**"Gouy, whose extraordinarily precise measurements make possible …" DC Grahame 1941**

$$\sigma = -\left(\frac{\partial \gamma}{\partial E}\right)_{\mu_{salt}}$$

$$C_{dl} = \left(\frac{\partial \sigma}{\partial E}\right)_{\mu_{salt}}$$

Grahame D C. Chemical Reviews, 1947, 41(3): 441-501.

GRAHAME'S METHODS OF MEASURING C_{DL}

"he took the polarography as a starting point and used the dropping mercury electrode to develop a method of measuring the interfacial capacity with an accuracy previously unattainable." R. Parsons 1998
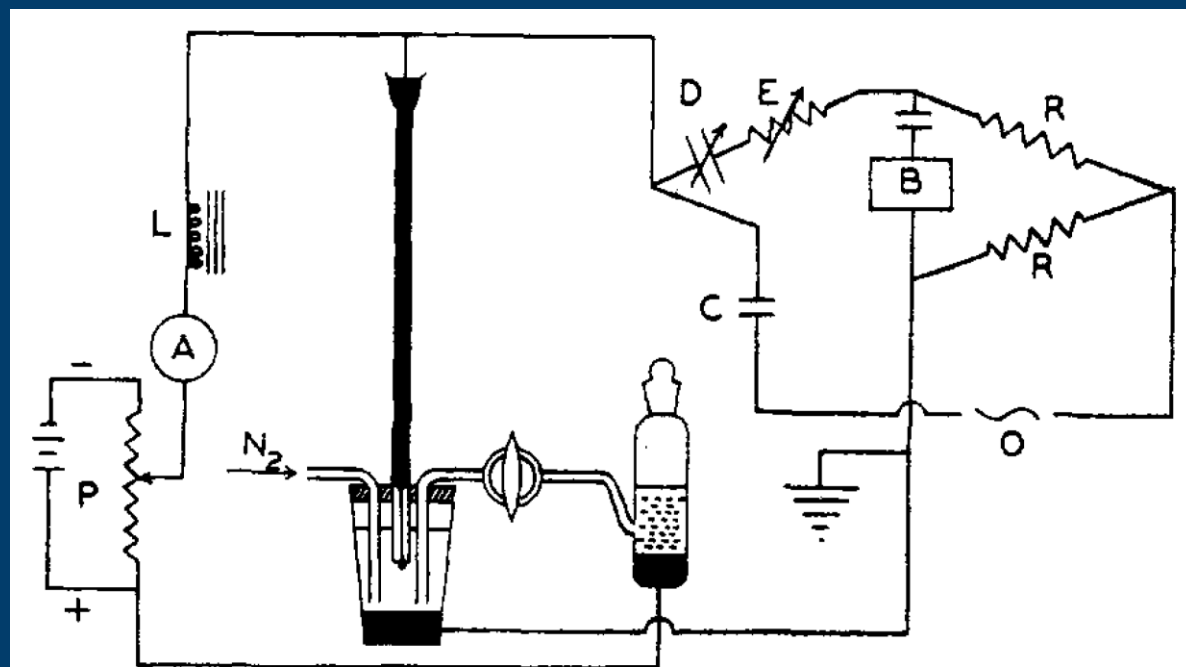

Fig. 1.—Apparatus for measuring the differential capacity of the electrical double layer.

Grahame D C. JACS, 1941

"Both the capacity and resistance of the system depend upon the size of the mercury droplet, which is continuously changing.

In order to overcome this difficulty, E and D were adjusted until an instant of silence occurred during the formation of each droplet."

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GRAHAME'S METHODS OF MEASURING C$_{DL}$

"he took the polarography as a starting point and used the dropping mercury electrode to develop a method of measuring the interfacial capacity with an accuracy previously unattainable." R. Parsons 1998
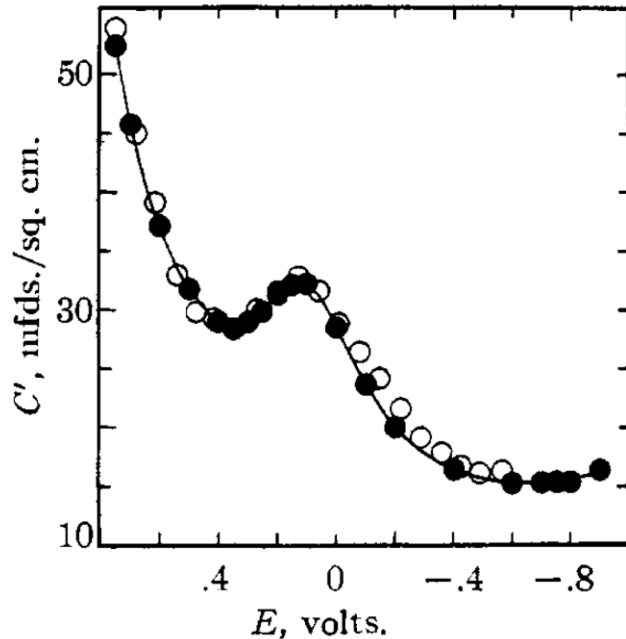

Fig. 5.—●, Differential capacity of the electrical double layer between mercury and 1 N H$_2$SO$_4$; O, d$^2\sigma$/dE^2 according to Gouy.

"It is possible in principle to obtain all of the significant thermodynamic properties of mercury solution interfaces by measurements of the interfacial tension, but as a practical matter the precision required in such measurements for the calculation of the differential capacity is so great that direct measurement of this quantity is generally to be preferred.

In addition, measurements of differential capacity and resistance under non-equilibrium conditions give information not derivable from the electrocapillary curves and reveal interesting and important properties of the surfaces studied."

Grahame D C. JACS, 1941

Grahame D C. JACS, 1946

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DAVID C. GRAHAME

"His work was his life and his life was work; not just any work but measurements of the capacitance of the double layer, and what they meant." J.O.C. Bockris, 2000
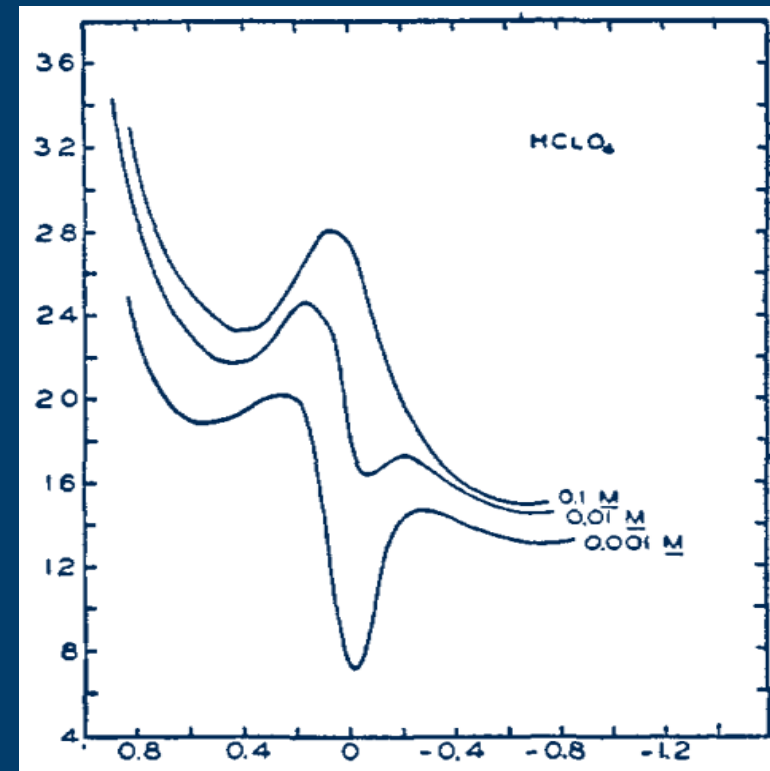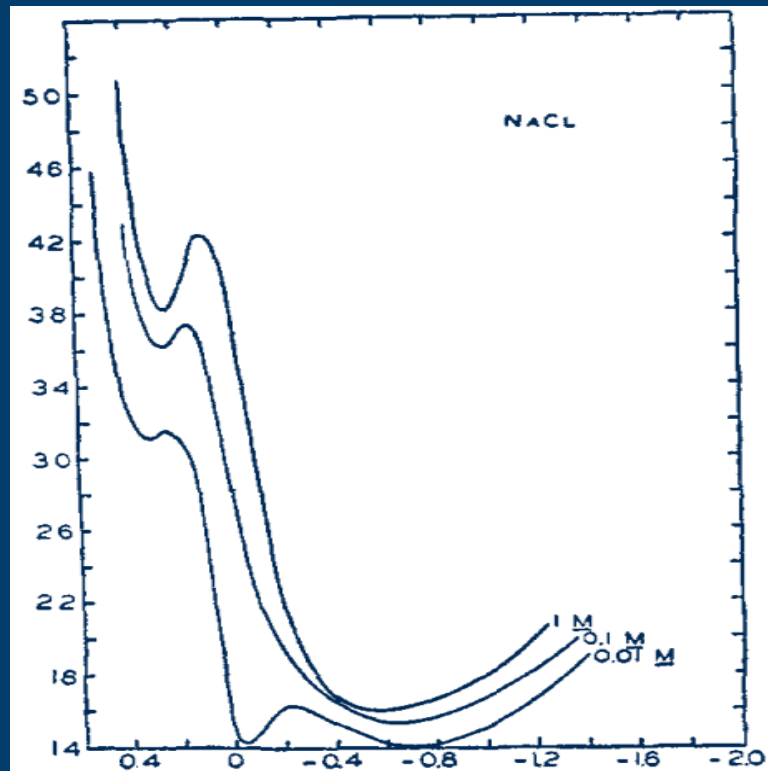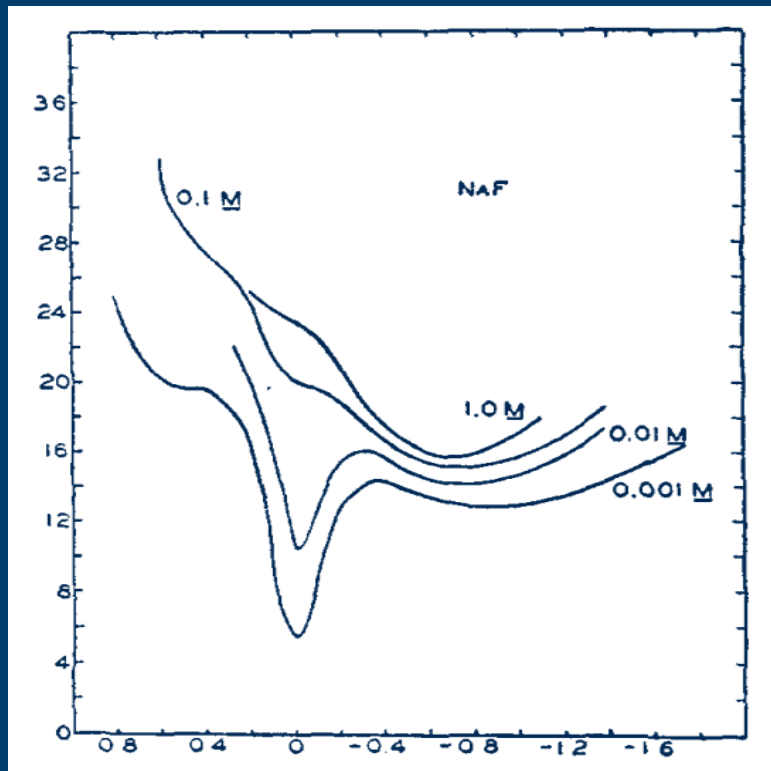
David C. Grahame
1912-1958

"There seems no doubt that
the person who made the most significant contribution to
experimental work on the double layer
in this century was
David C. Grahame of Amherst College in Massachusetts"

J.O.C. Bockris

A footnote in Chapter 6 of Modern Electrochemistry 2A

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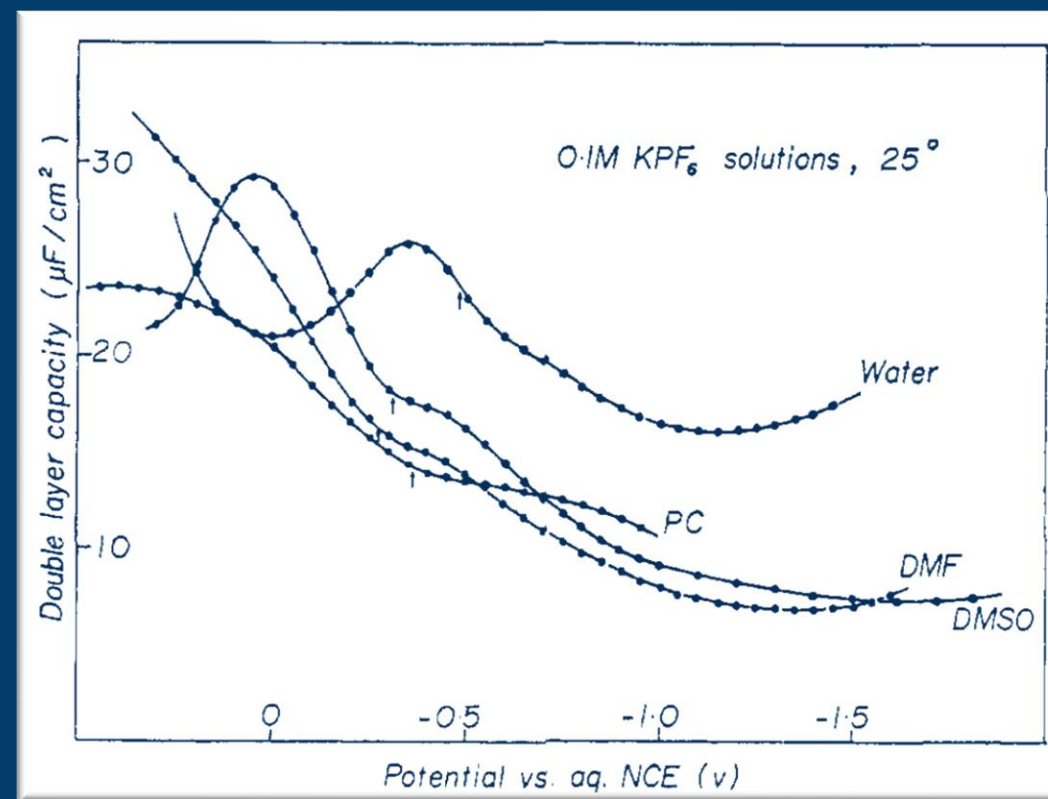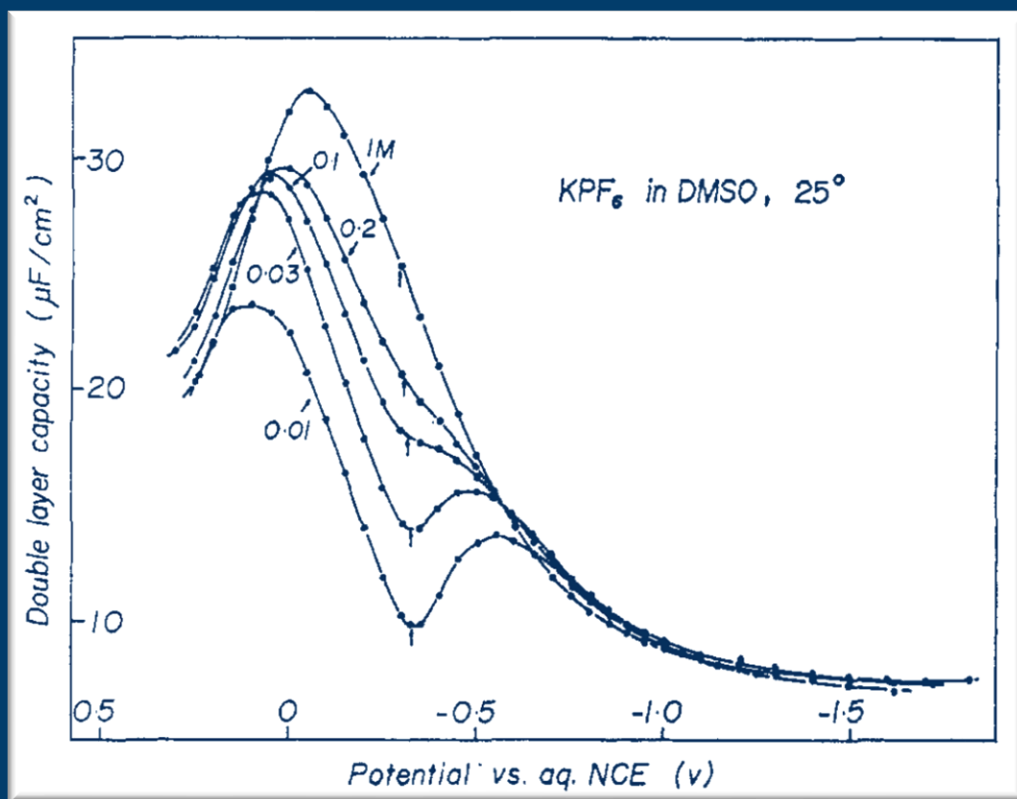
GALLERY OF C_{DL} OF MERCURY: ION EFFECTS

"Nearly everything one desires to know about the electrical double layer is ascertainable with mercury surfaces if it is ascertainable at all." DC Grahame 1947

Potential relative to E. C. MAX (V)

GALLERY OF C_{DL} OF MERCURY: SOLVENT EFFECTS

"Nearly everything one desires to know about the electrical double layer is ascertainable with mercury surfaces if it is ascertainable at all." DC Grahame 1947

Payne R. JACS, 1967

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GALLERY OF C_{DL} OF MERCURY: TEMPERATURE EFFECTS

"Nearly everything one desires to know about the electrical double layer is ascertainable with mercury surfaces if it is ascertainable at all." DC Grahame 1947

Grahame D C. JACS, 1957

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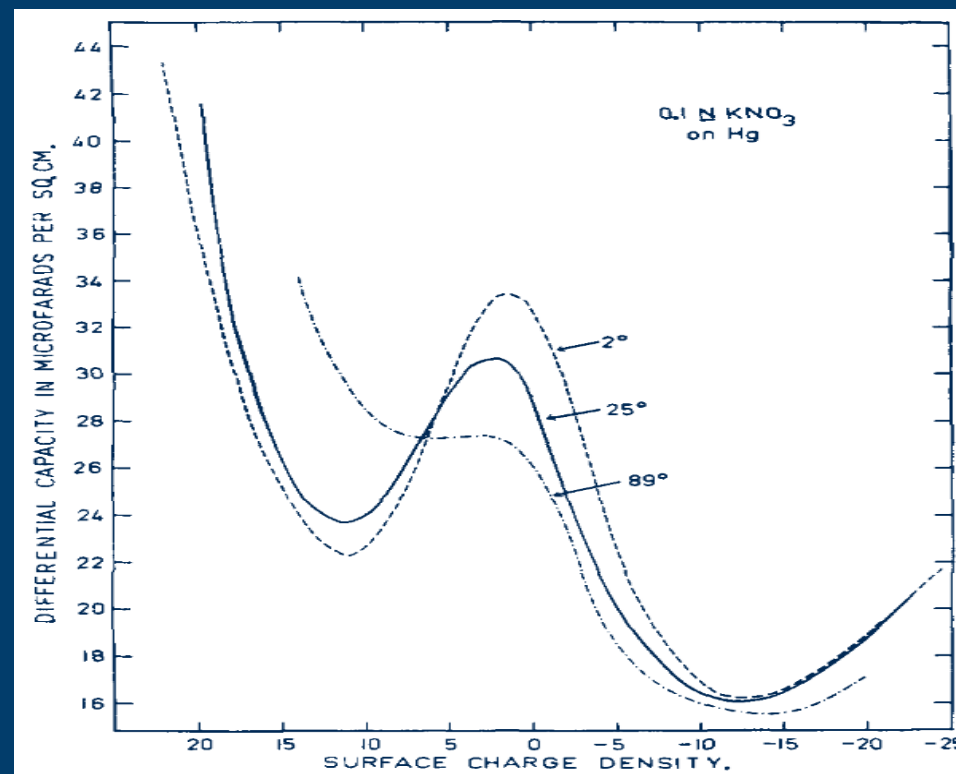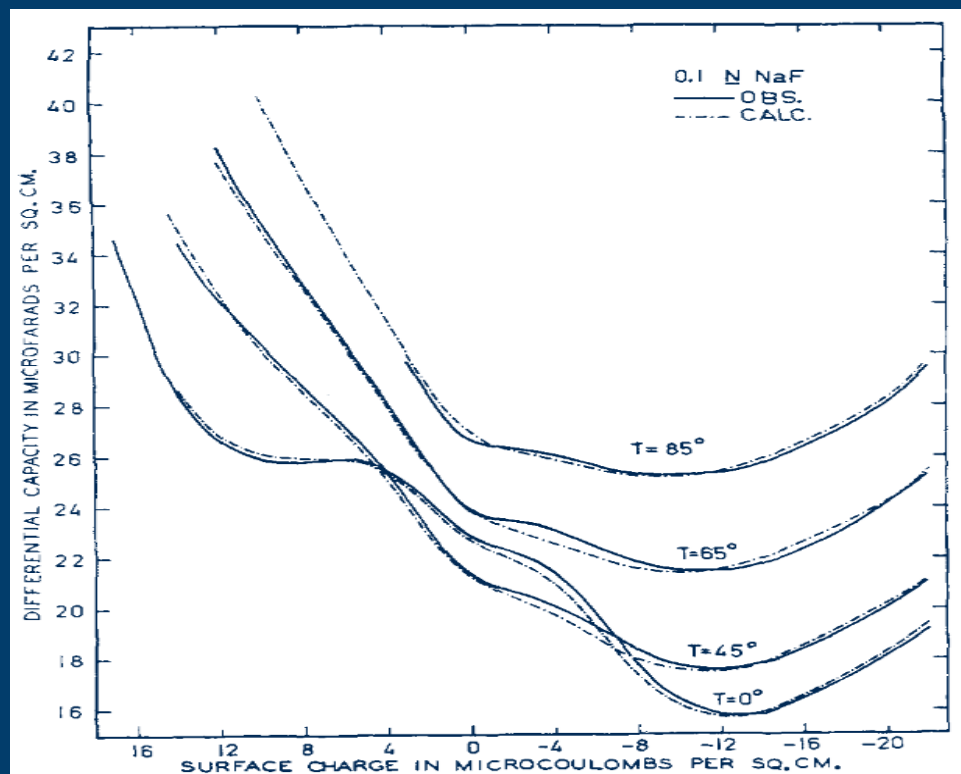
HELMHOLTZ MODEL 1874 (NOT 1853 OR 1879)

"Not only Helmholtz but also scientists like Nernst, Maxwell, and Pellat made their contribution to the double layer model." V.D. Ivanov 2024

"In so weit dies der Fall ist, — und meine Versuche zeigen, dafs man in gasfreien Flüssigkeiten und bei gasfreien Elektroden einem solchen Zustande wenigstens sehr nahe kommen kann, — wirkt die Zersetzungszelle wie ein Condensator von sehr grofser Capacität. In der That, wenn man nach der gewöhnlichen Vorstellungsweise negativ geladenen Sauerstoff der einen Elektrode, positiv geladenen Wasserstoff der anderen Elektrode genähert denkt, aber so, dafs ein Austausch der Elektricität zwischen der Elektrode und den genannten Bestandtheilen des Wassers nicht möglich ist, so wird sich auf der Elektrode selbst die entsprechende Menge der entgegengesetzten Elektricität anhäufen können, und jede Elektrode würde dann mit der Flüssigkeit einen Condensator von verschwindend kleiner Dicke der isolirenden Schicht, und eben deshalb von ungeheurer Capacität bilden."

"In so far as this is the case – and my experiments show that in gas-free liquids and with gas-free electrodes one can at least come very close to such a state – the electrolysis cell acts like a capacitor of very high capacitance.

In fact, if we think of the negatively charged oxygen of one electrode and the positively charged hydrogen of the other electrode, as approaching each other, but in such a way that an exchange of electricity between the electrode and the aforementioned components of water is not possible.

Then the corresponding amount of the opposite electricity will accumulate on the electrode itself, and each electrode would then form a capacitor with the liquid, of an infinitesimally small thickness of the insulating layer, and precisely for this reason of enormous capacitance."

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HELMHOLTZ MODEL 1874 (NOT 1853 OR 1879)

"its inability to provide any explanation for the dependence of the electrode charge (or of the capacitance) on the electrolyte concentration," Kornyshev 2007
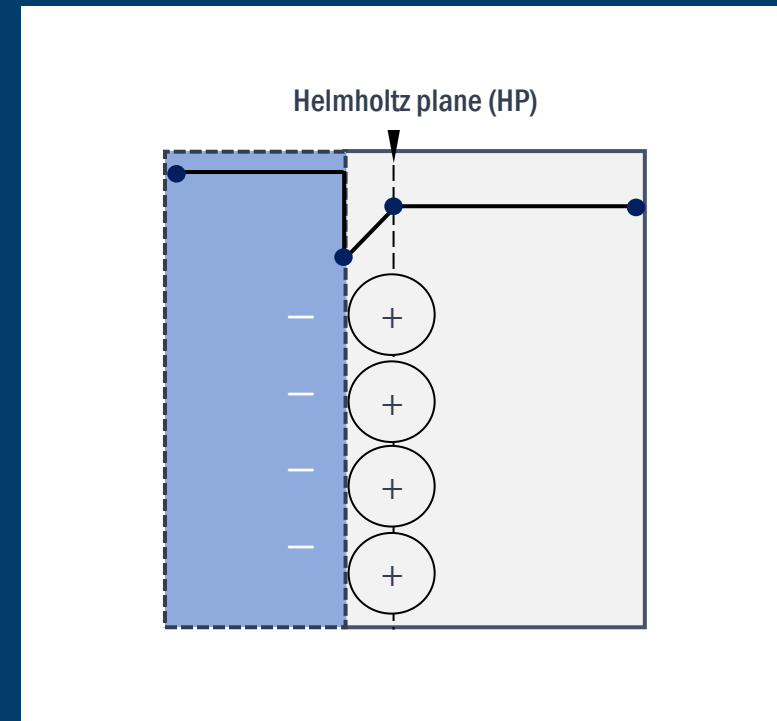
Key points
- The metal is a perfect conductor, and its excess charge is distributed on the surface
- The counter charge in solution resides at a surface (Helmholtz plane, HP), with a distance d from the metal surface

Capacitance

$$C_{dl} = \frac{\epsilon \epsilon_0}{d}$$

with the dielectric constant ϵ between two surfaces, the vacuum permittivity ϵ_0

$\epsilon = 78.5, \epsilon_0 = 9 \times 10^{-12}$ F/m, $C_{dl} = 50$ μF/cm^2 gives $d = 1.4$ nm

Helmholtz plane (HP)

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GOUY-CHAPMAN THEORY

"Gouy complicates the reading of his work by frequently failing to define the variables." V.D. Ivanov, 2023

The metal is a perfect conductor, and its excess charge is distributed on the surface

The solvent is a dielectric continuum, characterized by a dielectric constant ϵ

The ions are point-like charged particles, whose distribution is determined by the Poisson-Boltzmann equation
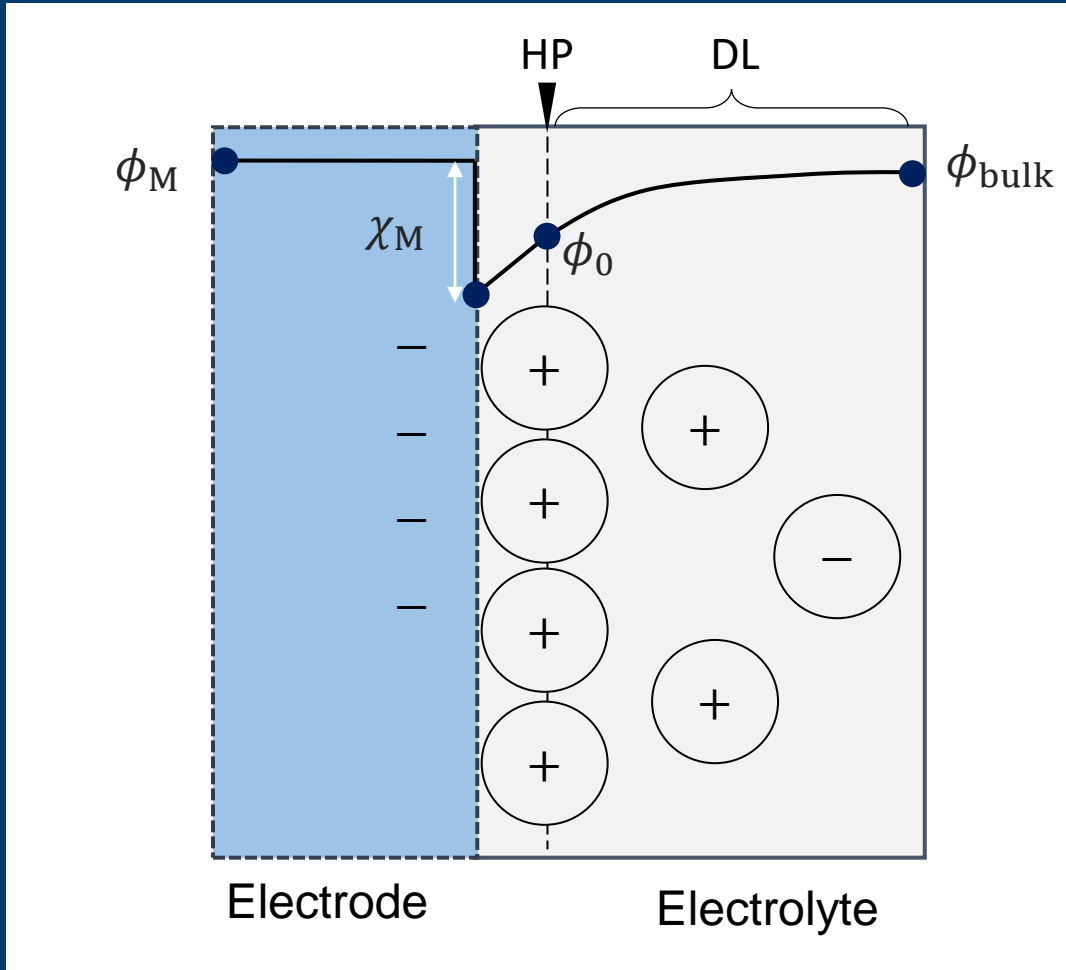
The region where ions distribute is called diffuse layer
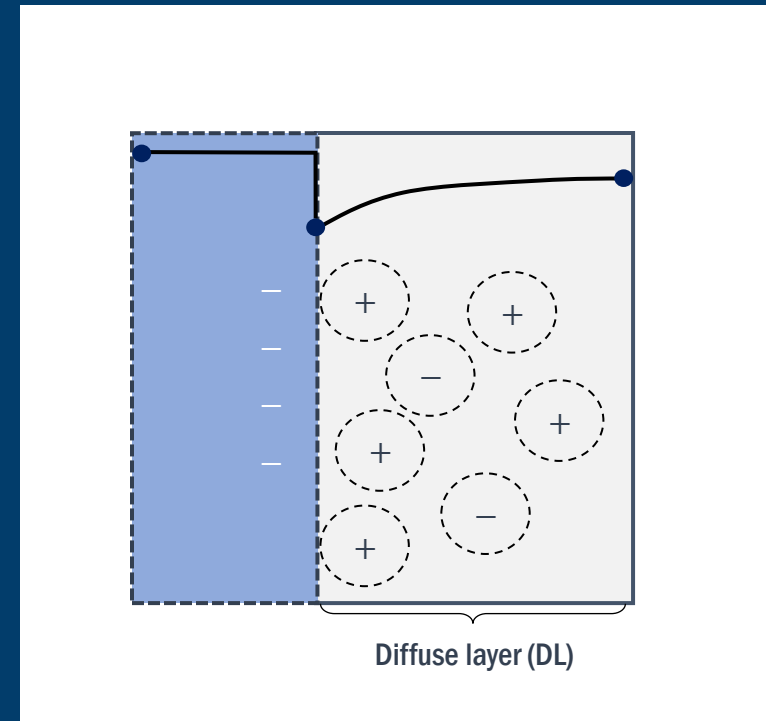
Diffuse layer (DL)

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GOUY-CHAPMAN THEORY

"Gouy complicates the reading of his work by frequently failing to define the variables." V.D. Ivanov, 2023

Capacitance of metal/z-z electrolyte

$$C_\mathrm{d} = \left(\frac{2z^2 e_0^2 \epsilon \epsilon_0 n^0}{k_B T} \right)^{\frac{1}{2}} \cosh \left(\frac{z e_0 (E_\mathrm{M} - E_\mathrm{PZC})}{2 k_B T} \right)$$

e_0, elementary charge
n^0, bulk number density of ions
k_B, Boltzmann constant
E^M, electrode potential
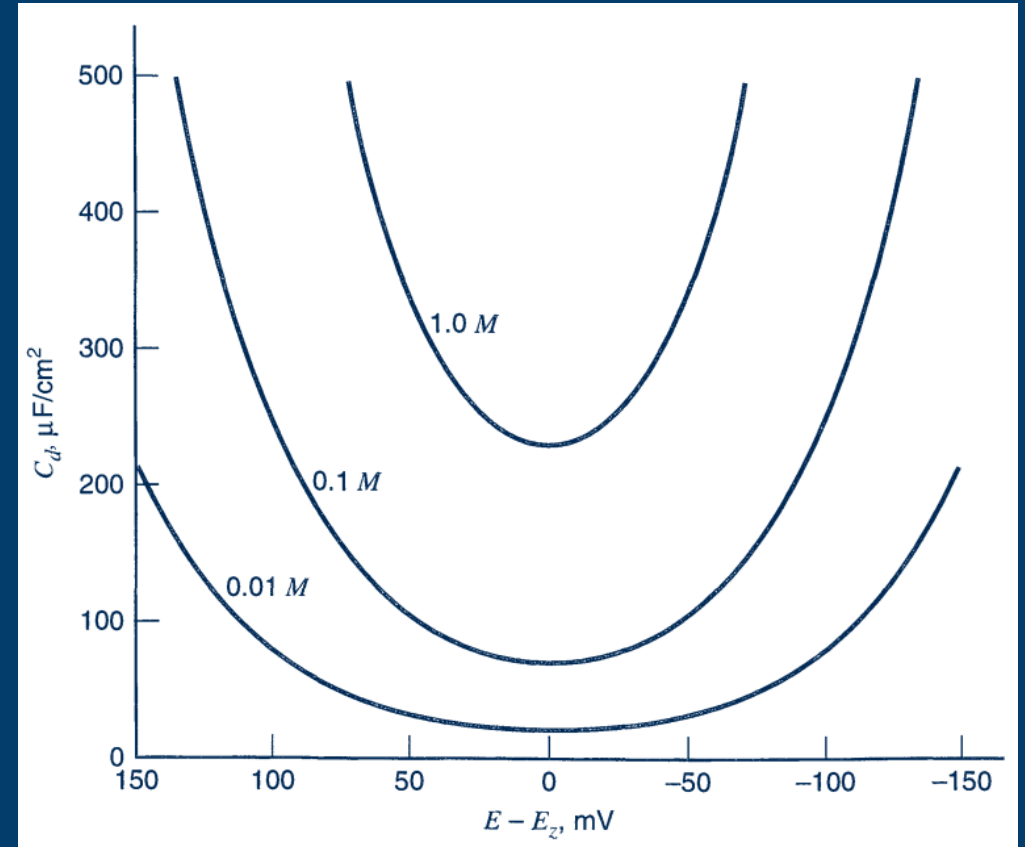
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GOUY-CHAMPAN-STERN MODEL

"The model of charged interface has advanced little since that of Stern (1924)" Bockris 1963

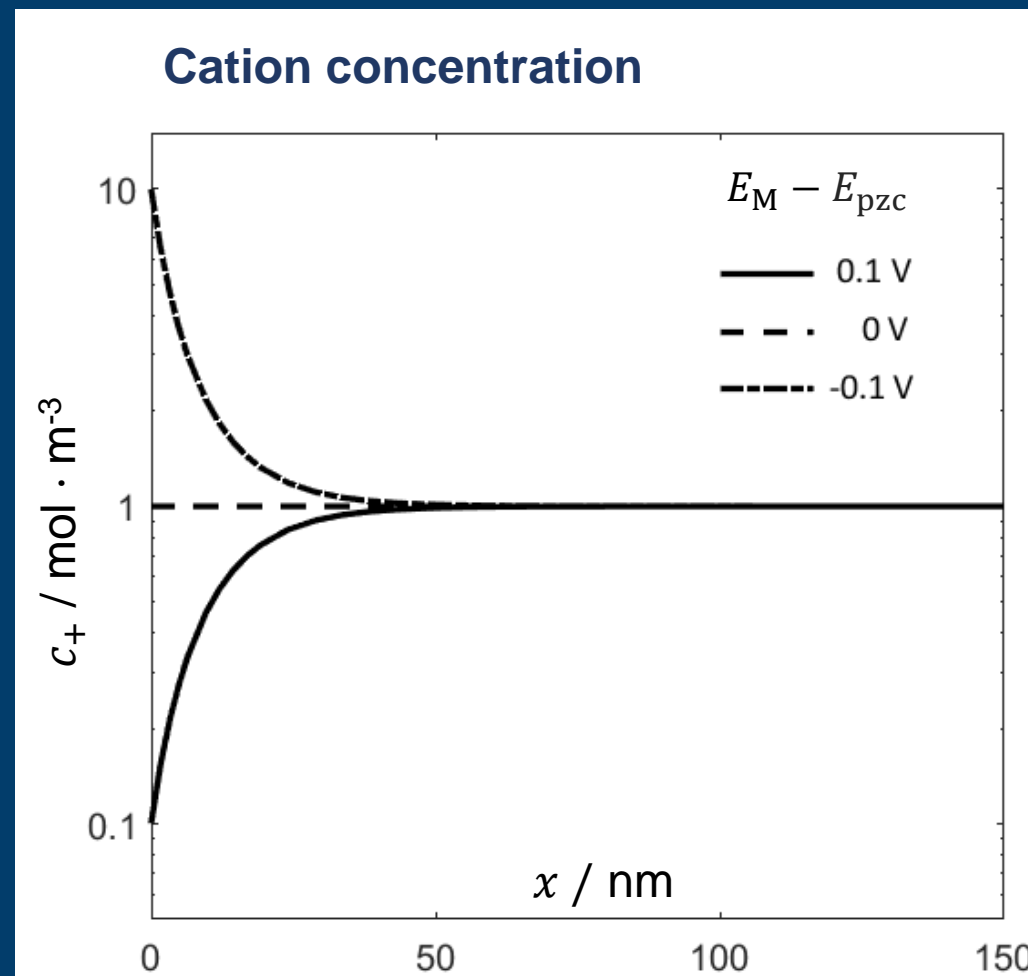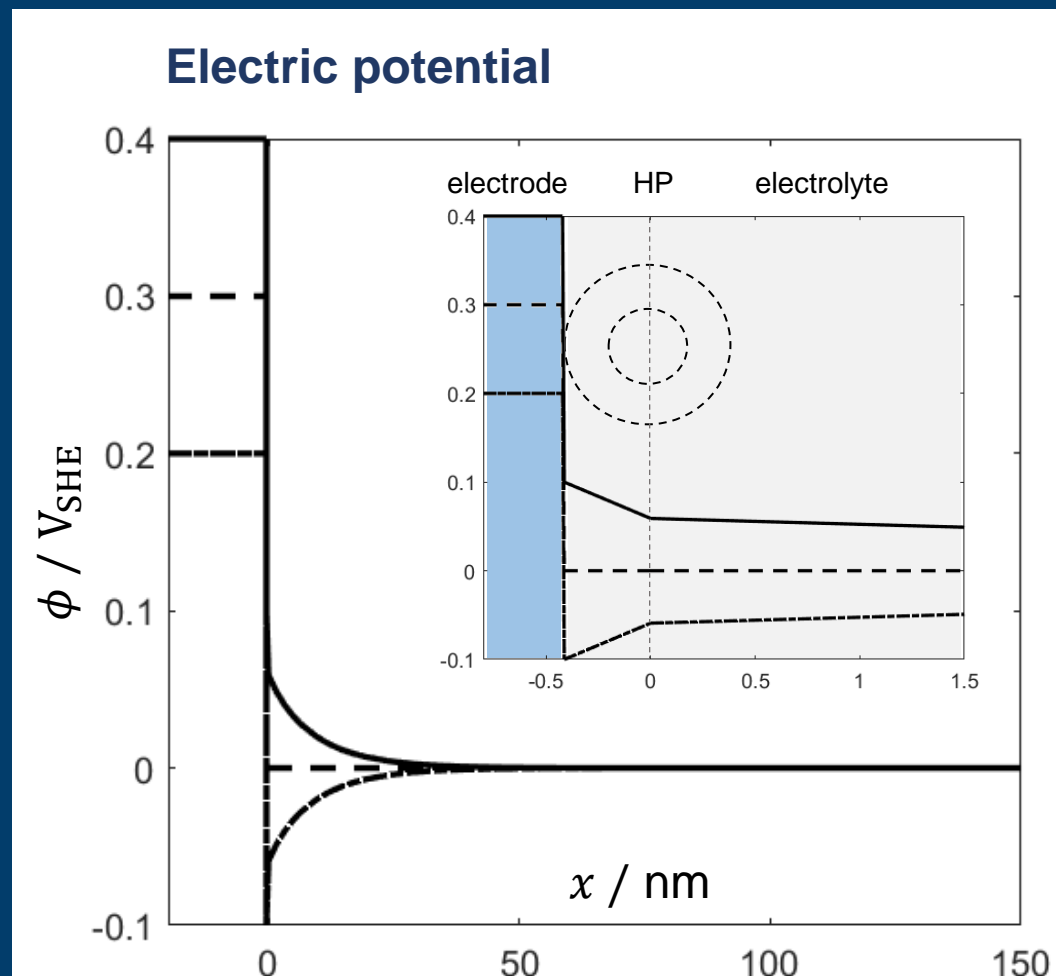$$\sigma_{\text{free}} = -\epsilon_S \left(\frac{\partial \phi}{\partial x}\right)_{x=+HP} = -\epsilon_{HP} \left(\frac{\partial \phi}{\partial x}\right)_{x=-HP}$$

$$\phi_0 = (\phi_M - \chi_M) + \left(\frac{\partial \phi}{\partial x}\right)_{x=+HP} \frac{\epsilon_S}{\epsilon_{HP}} \delta_{HP}$$

Reference to the standard hydrogen electrode, SHE

$$\phi_M - \chi_M \quad \Longrightarrow \quad E_M - E_{\text{pzc}}$$

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GOUY-CHAMPAN-STERN MODEL

"The model of charged interface has advanced little since that of Stern (1924)" Bockris 1963
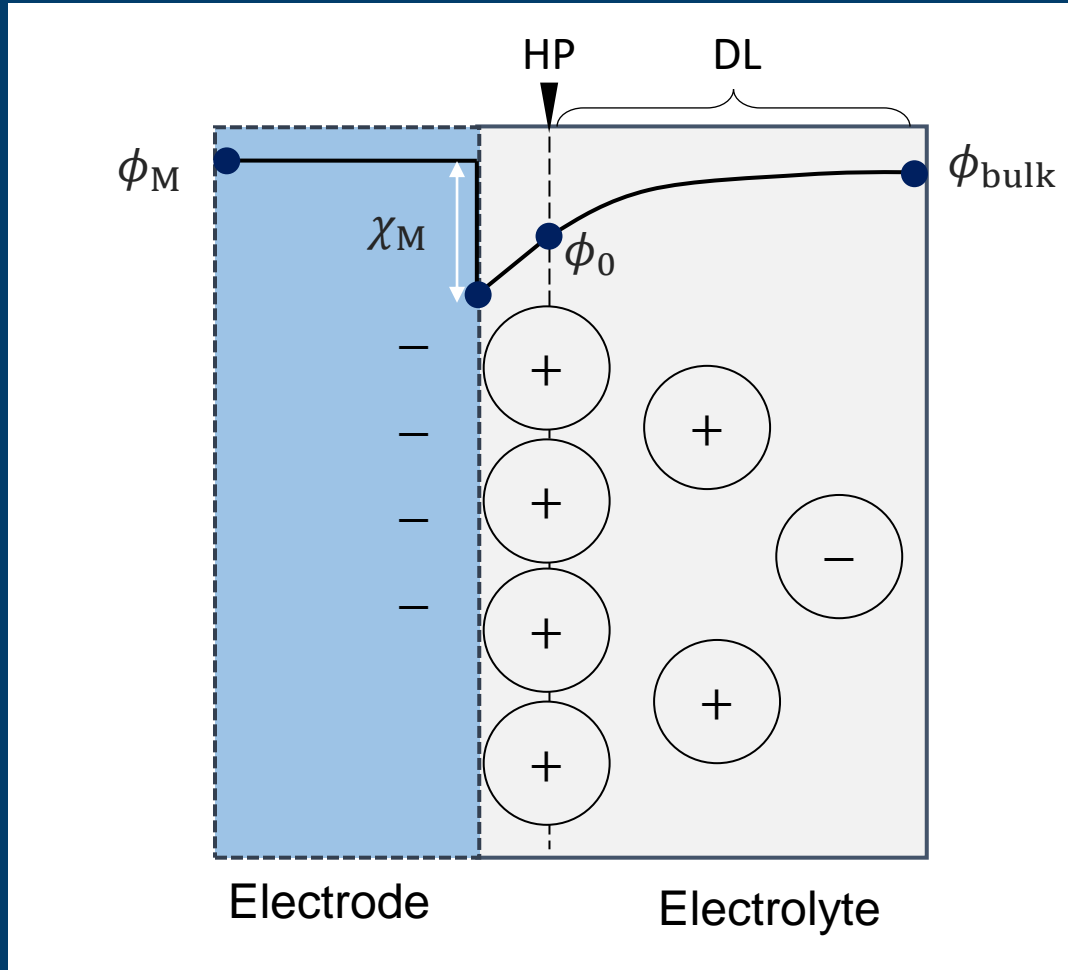
$$(C_{dl})^{-1} = (C_H)^{-1} + (C_D)^{-1}$$
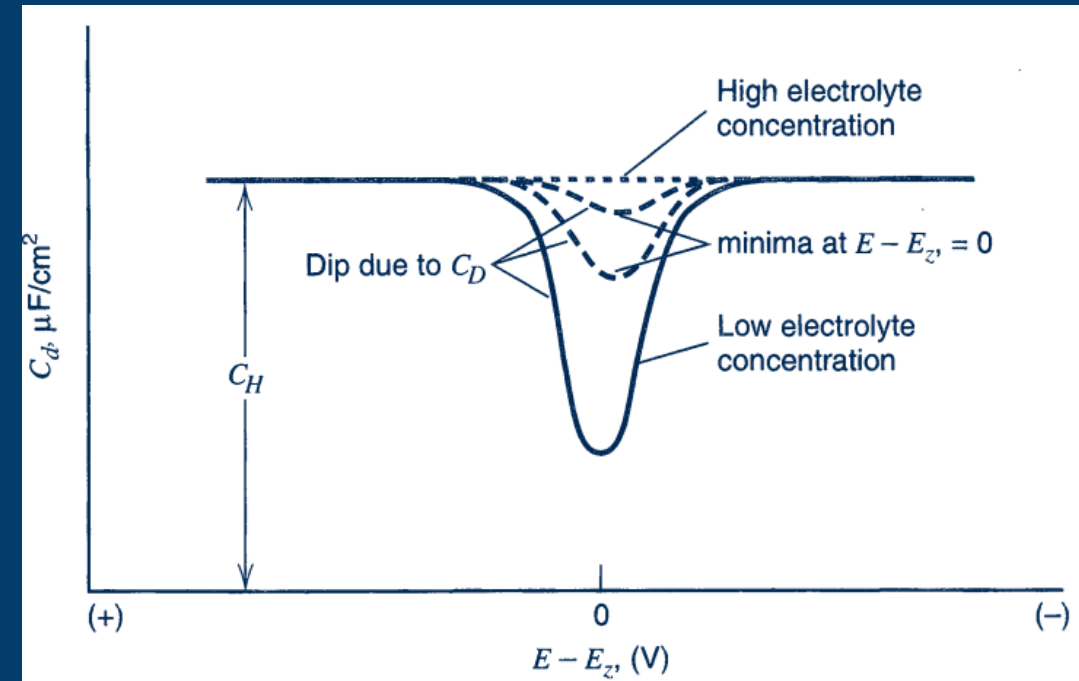
GOUY-CHAMPAN-STERN MODEL

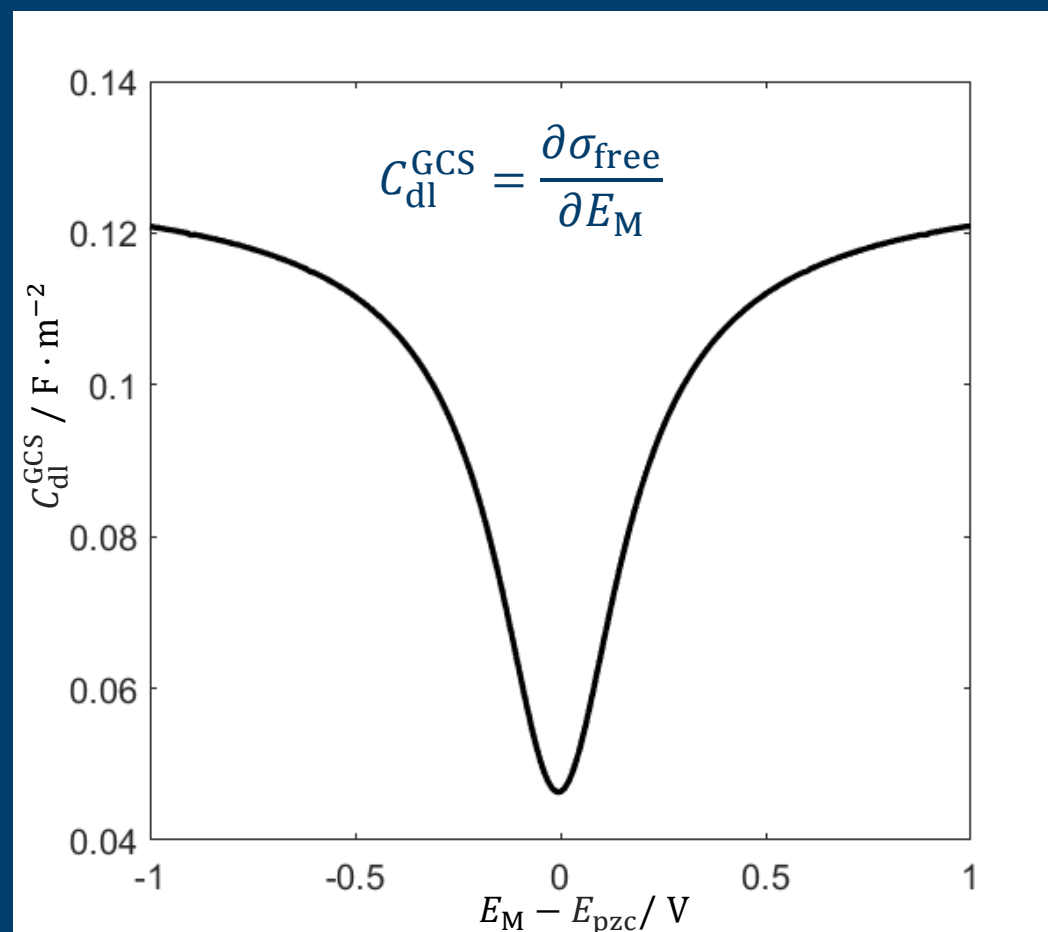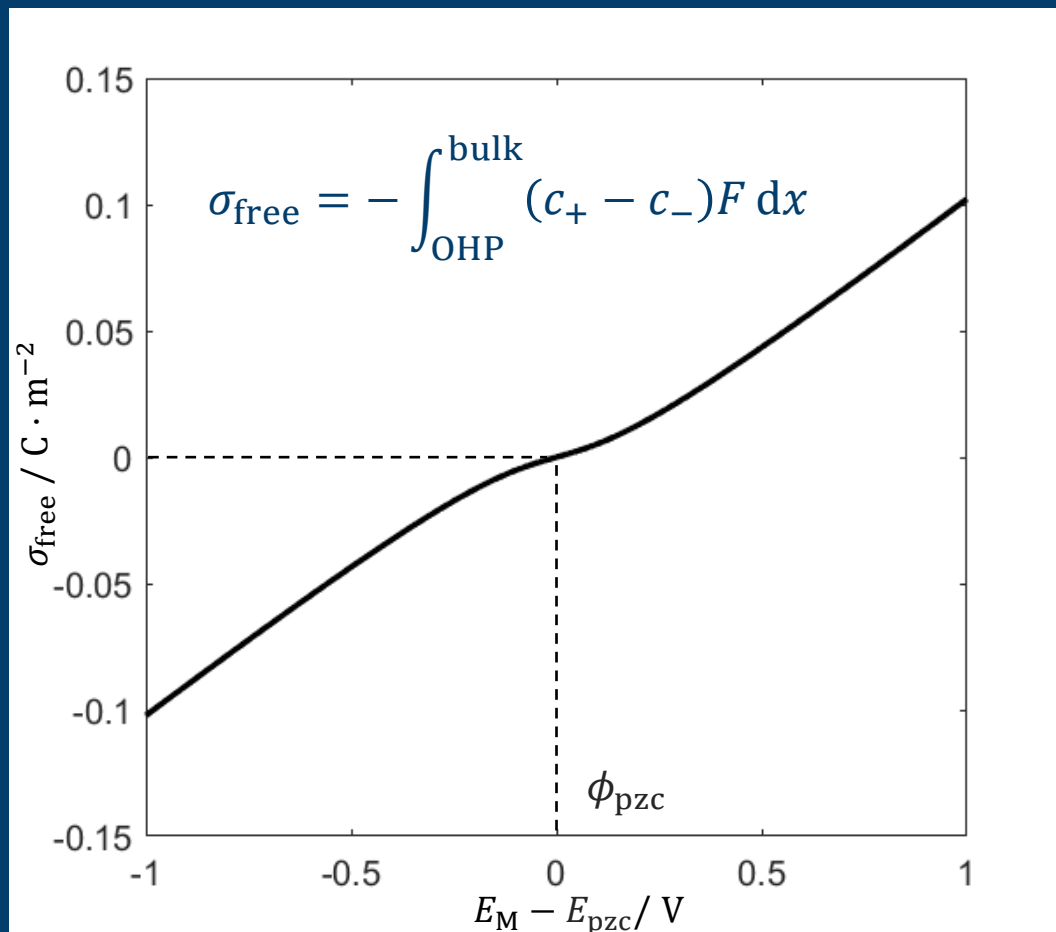**You will be surprised by many tricky issues when solving the GCS model on your own**

Zhang, Li, Huang, J. Electrochem. 2022

GOUY-CHAMPAN-STERN MODEL

$$\sigma_{\text{free}} = -\int_{\text{OHP}}^{\text{bulk}} (c_+ - c_-) F \, dx$$

$$C_{\text{dl}}^{\text{GCS}} = \frac{\partial \sigma_{\text{free}}}{\partial E_{\text{M}}}$$

Zhang, Li, Huang, J. Electrochem. 2022

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GRAHAME'S ANALYSIS

"the calculated values might be more nearly correct than the observed values where the two disagree."
D.C. Grahame 1954 JACS
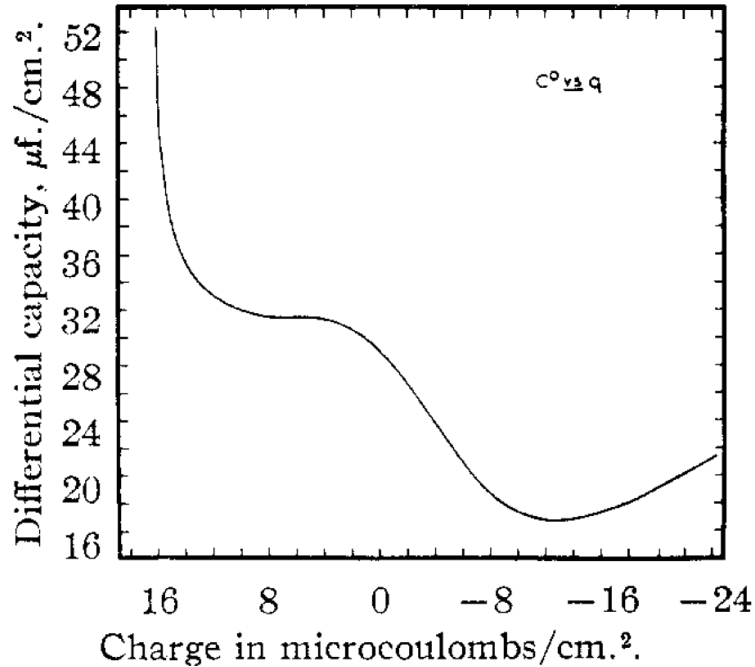
Fig. 6.—Differential capacity of the region lying between the metallic surface and the outer Helmholtz plane. Calculated from data on 0.916 M NaF at 25°.
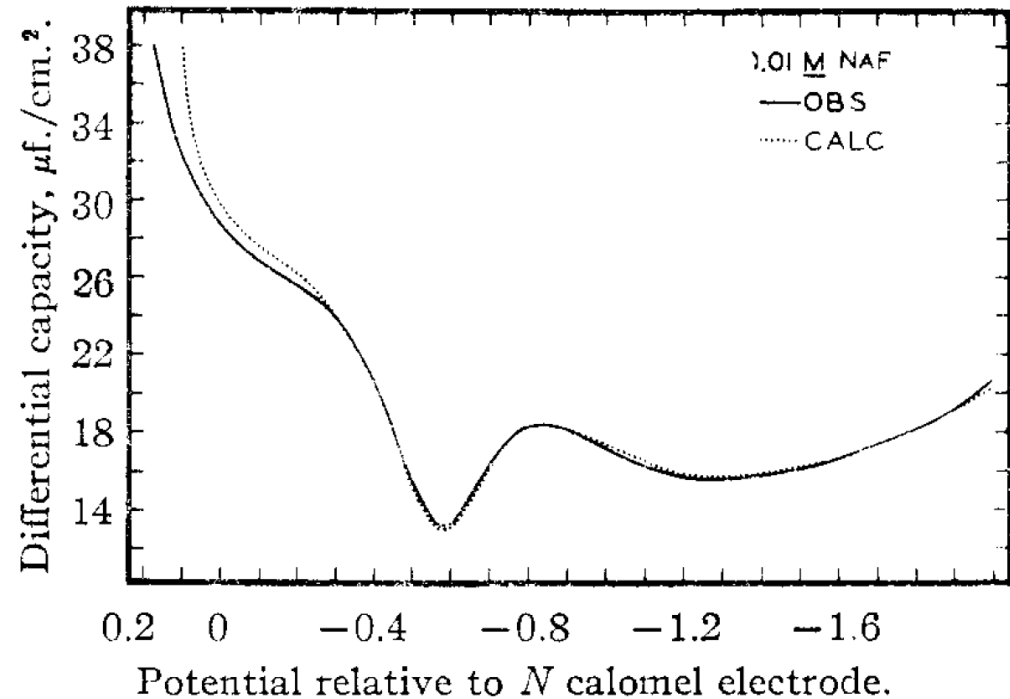
Fig. 4.—Differential capacity of mercury in contact with aqueous 0.01 M sodium fluoride solution at 25°.

KORNYSHEV'S ANALYSIS

$$(C_{\mathrm{dl}})^{-1} = (C_H)^{-1} + (C_D)^{-1}$$

"this (Parsons-Zobel) method has been used in a reduced form, where only the data for the p.z.c. are plotted." A. Kornyshev 2007

Fig. 4 Parsons–Zobel plots, C^{-1} versus C_{GC}^{-1}, for the mercury electrode in contact with aqueous NaF solutions, at several constant values of the electrode charge density, σ, that are indicated at each graph (in µC cm^{-2}): 0 (plot 1), +1 (plot 2), +2 (plot 3) in Fig. 4(a), −3 (plot 1), −2 (plot 2), −1 (plot 3), +1 (plot 4), +2 (plot 5), +3 (plot 6) in Fig. 4(b).
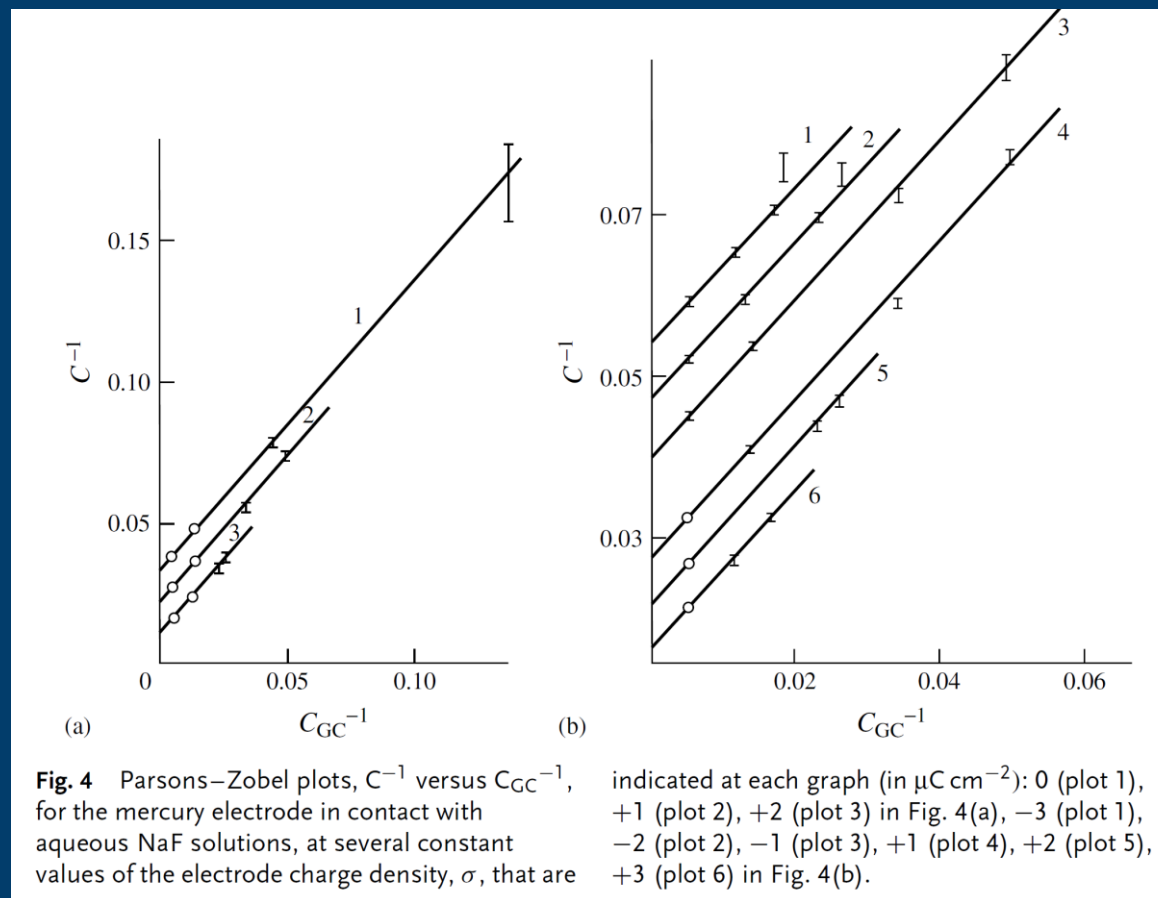
OVERVIEW OF DOUBLE LAYER MODELS

"The model of charged interface has advanced little since that of Stern (1924)" Bockris 1963
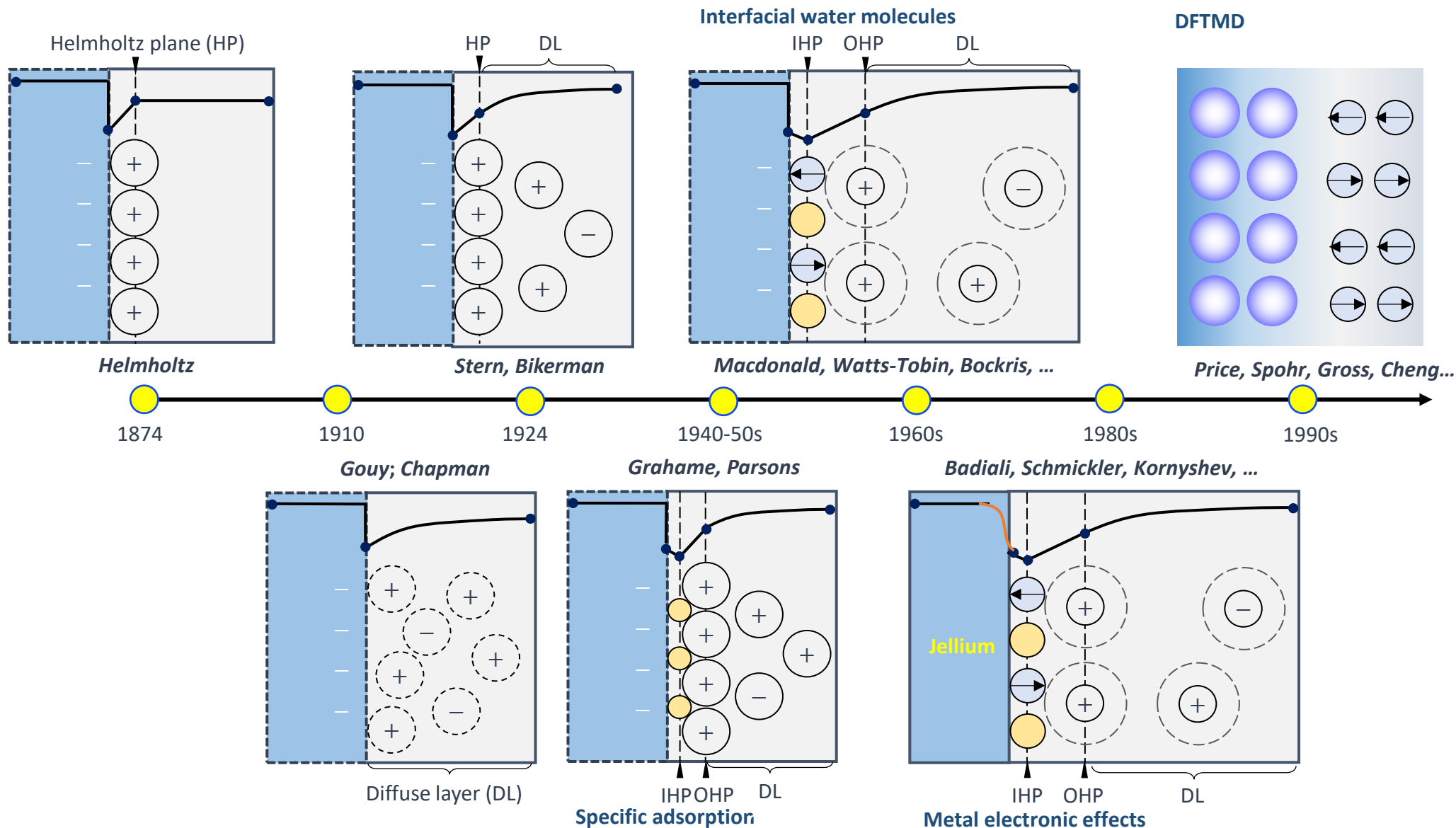
OUTLINE

- **Motivation for revisiting the Mercury Era**

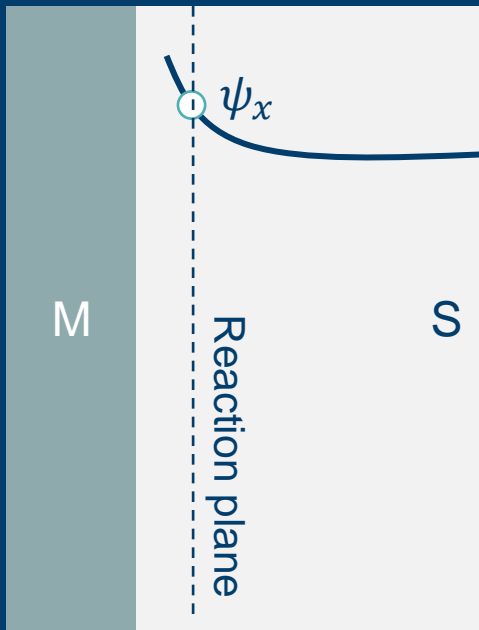- **The EDL structure**

- <u>**EDL effects on electron transfer**</u>

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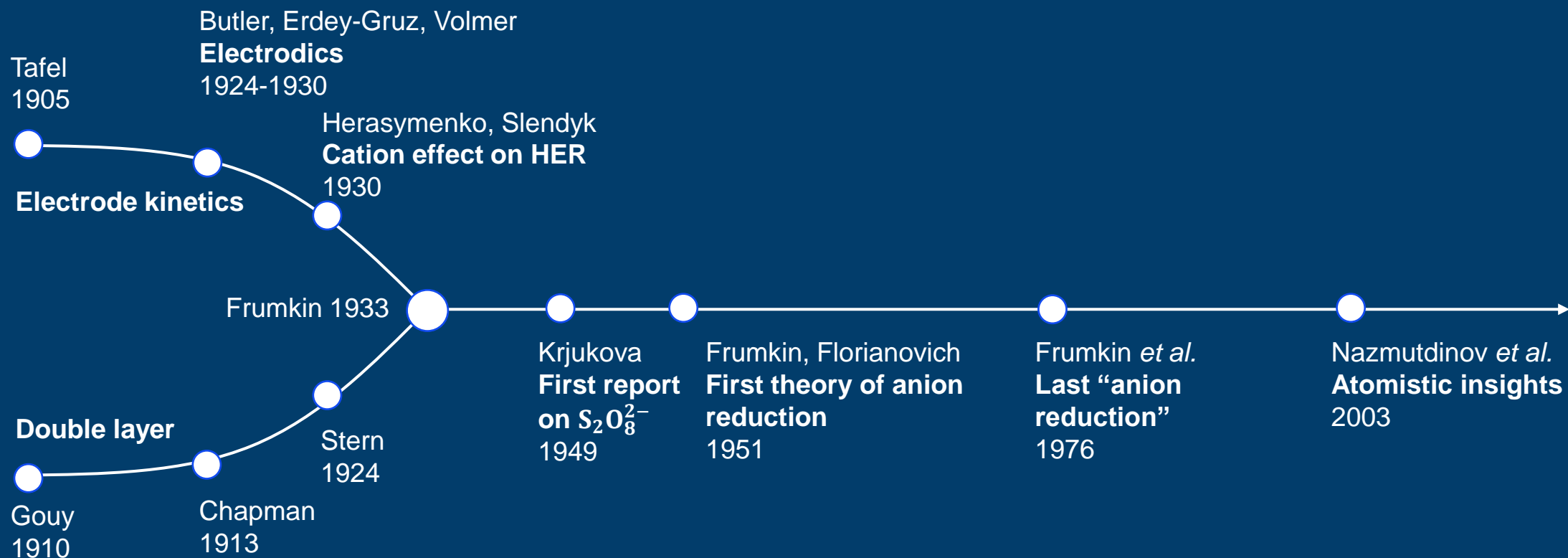
FRUMKIN CORRECTIONS OF EDL EFFECTS

Frumkin AN, Nikolaeva-Fedorovich NV, Berezina NP, Keis KE. *J. Electroanal. Chem.* 1975, 58(1):189-201

Cathodic reaction (R + e -> P)

$$j = nFk \left[C \exp\left(-\frac{zF\psi_x}{RT} \right) \right] \exp\left(\frac{\alpha F(|\eta| + \psi_x)}{RT} \right)$$

Local concentration of R (Boltzmann relation)

$$j = nFk \left[C \exp\left(-(z - \alpha)\frac{F\psi_x}{RT} \right) \right] \exp\left(\frac{\alpha F|\eta|}{RT} \right)$$

Electrostatic effects

How does ψ_x change with electrode potential?

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ψ_x AT VARYING POTENTIALS

Where EDL models matter

$E>E_{pzc}$

$\psi_x > 0$

$E=E_{pzc}$

$\psi_x = 0$

$E<E_{pzc}$

$\psi_x < 0$
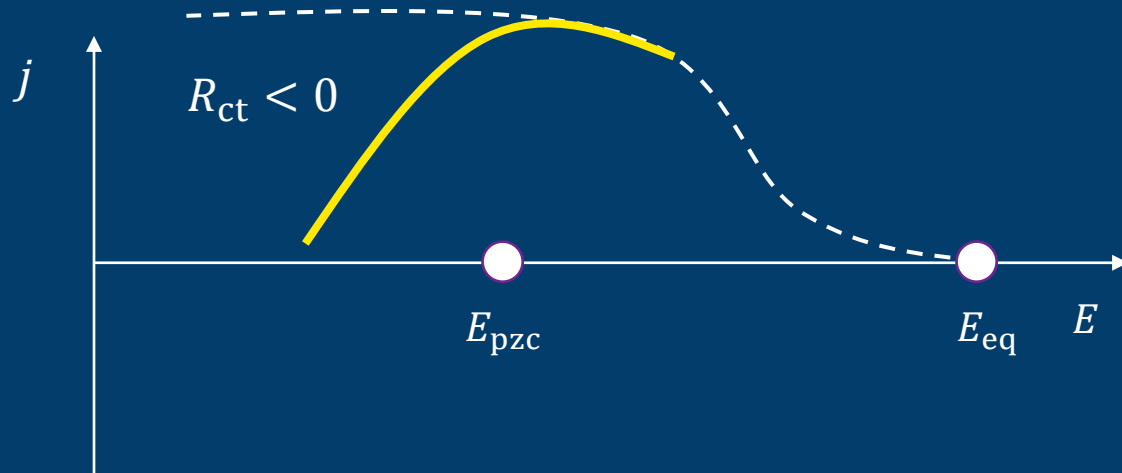
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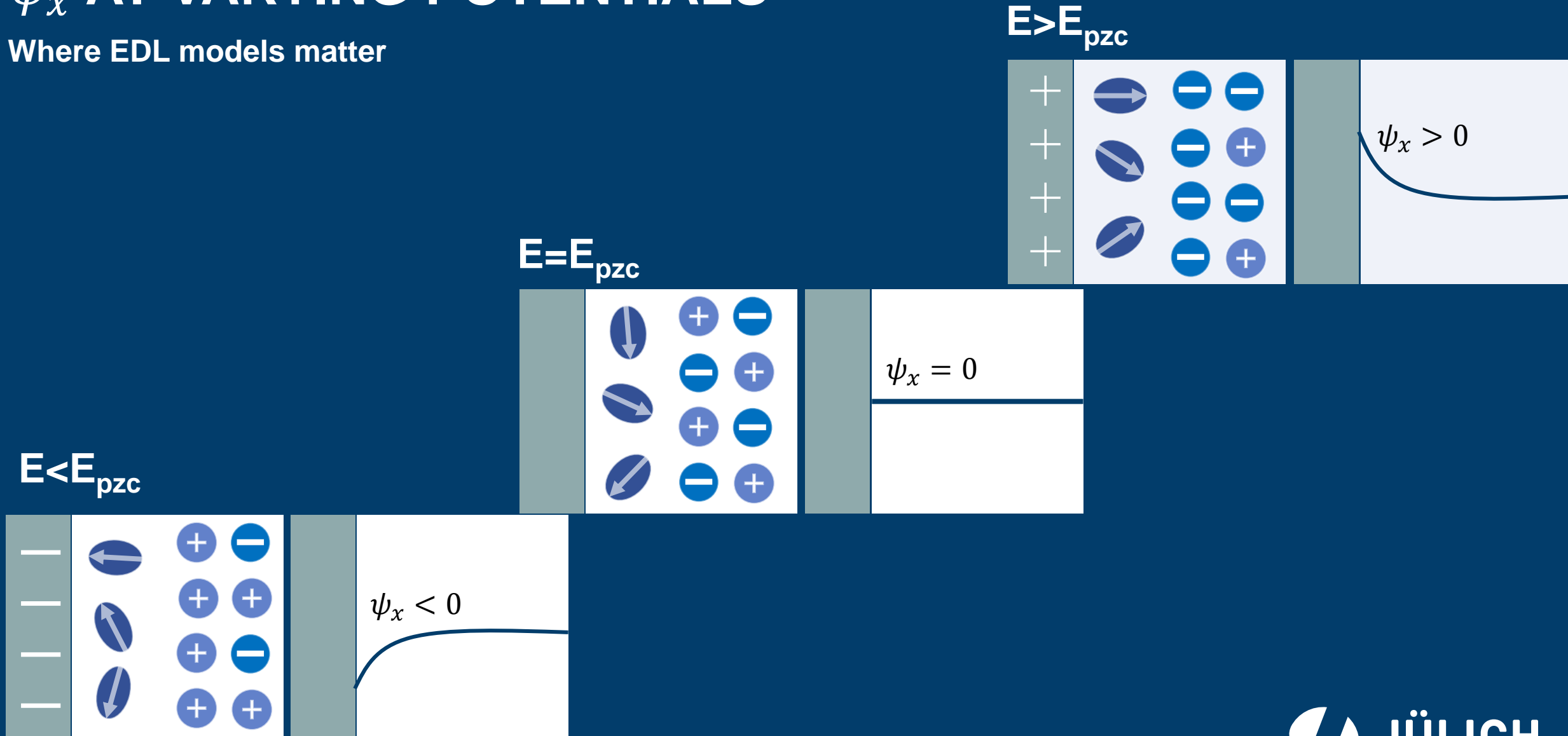
SUPPRESSED REDUCTION AT MORE NEGATIVE POTENTIALS
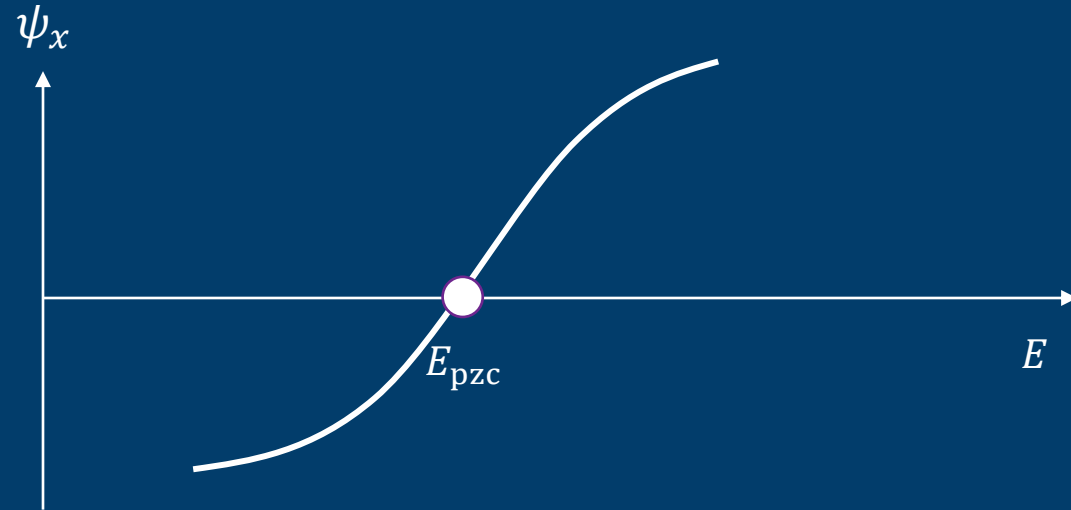
$$j = nFk \left[C \exp\left(-(z - \alpha)\frac{F\psi_x}{RT} \right) \right] \exp\left(\frac{\alpha F |\eta|}{RT} \right)$$
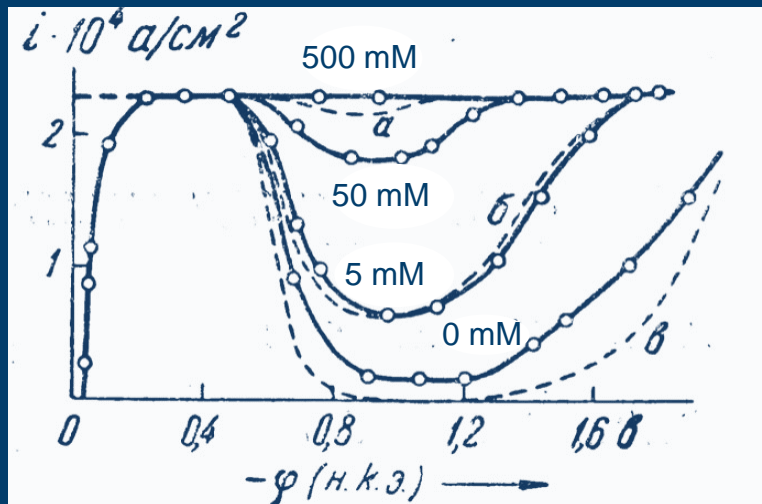
$$z = -2, \alpha \approx 0.2 \text{ for } S_2O_8^{2-}$$

Competition between overpotential driving and electrostatic repulsion

$$\frac{z - \alpha}{\alpha}$$

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PEROXODISULFATE ANION REDUCTION ON MERCURY

$$| \longrightarrow \psi_x < 0, \text{ repelling } S_2O_8^{2-}$$

1 mM $K_2S_2O_8 + x \, Na_2SO_4$ on dropping mercury electrode (Kryukova TA, 1949)

Why is there an initial decrease? Why is it suppressed in more concentrated solutions?

    Frumkin (1933, 1951): static EDL effects

    Levich (1949, 1959): dynamic EDL effects

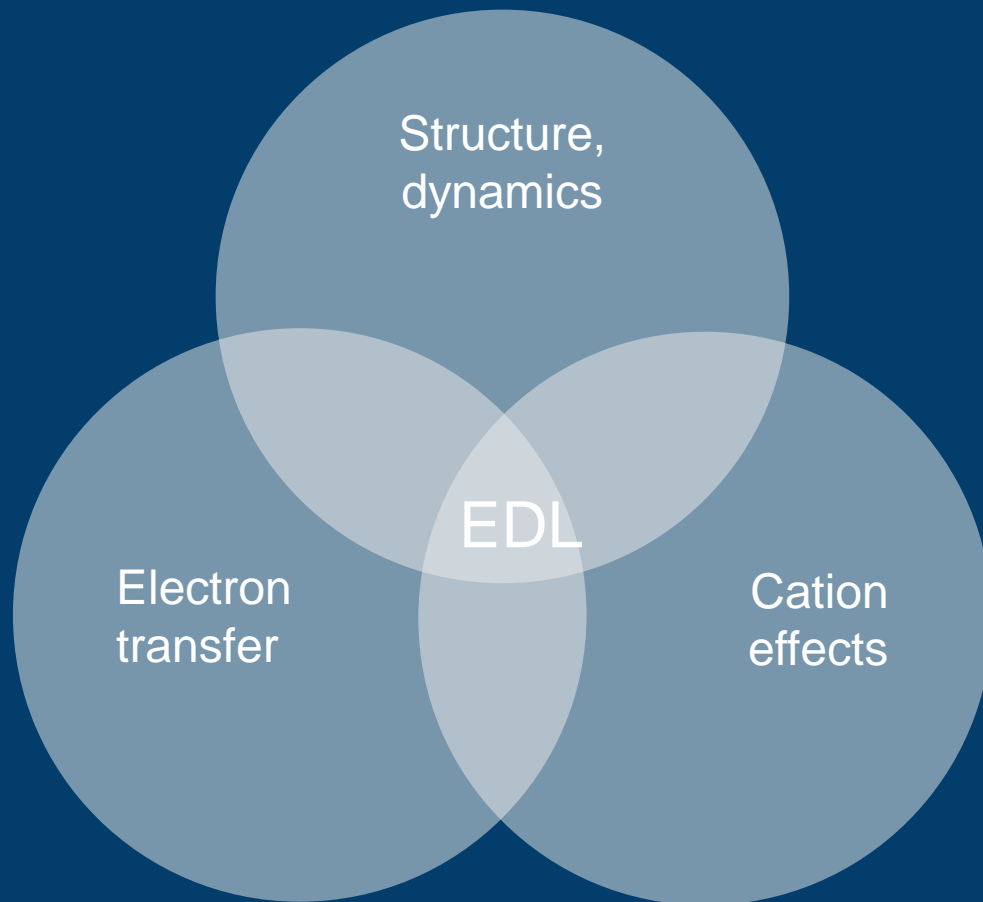**Why does the current increase again at large overpotentials?**

    Frumkin (1951): EDL saturation

    Nazmutdinov, Tsirlina, Petrii, *et al.* (2003): Increased reaction volume

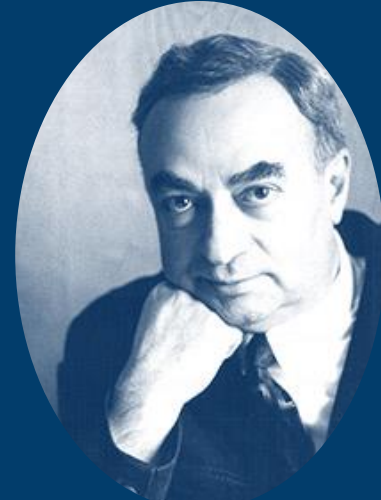**Why does the reduction rate follow the trend of $Cs^+ > K^+ > Na^+ > Li^+$?**

    Frumkin (1933): potential distribution in EDL

    Heyrovsky (1934): ion-pairing, local electric field effects

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PEROXODISULFATE ANION REDUCTION ON MERCURY

Structure, dynamics

Electron transfer

EDL

Cation effects

Why is there an initial decrease? Why is it suppressed in more concentrated solutions?

Frumkin (1933, 1951): static EDL effects

Levich (1949, 1959): dynamic EDL effects

Why does the current increase again at large overpotentials?

Frumkin (1951): EDL saturation

Nazmutdinov, Tsirlina, Petrii, *et al.* (2003): Increased reaction volume

Why does the reduction rate follow the trend of $Cs^+ > K^+ > Na^+ > Li^+$?

Frumkin (1933): potential distribution in EDL

Heyrovsky (1934): ion-pairing, local electric field effects

Jun Huang - **Revisit Mercury Era**

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WHY IS THERE AN INITIAL DECREASE?
WHY IS IT SUPPRESSED IN MORE CONCENTRATED SOLUTIONS?

A.N. Frumkin
(1895-1976)

B. Levich
(1917-1987)

WHY IS THERE AN INITIAL DECREASE?

A.N. Frumkin
(1895-1976)

Anions are repelled by negative surface charge

$$\psi_x$$

$$E_{\text{pzc}}$$

$$E$$

$$j$$

$$R_{\text{ct}} < 0$$

$$E_{\text{pzc}}$$

$$E_{\text{eq}}$$

$$E$$

$$j = nFk\left[C\exp\left(-(z-\alpha)\frac{F\psi_x}{RT}\right)\right]\exp\left(\frac{\alpha F|\eta|}{RT}\right)$$

$$z = -2, \alpha \approx 0.2 \text{ for } S_2O_8^{2-}$$

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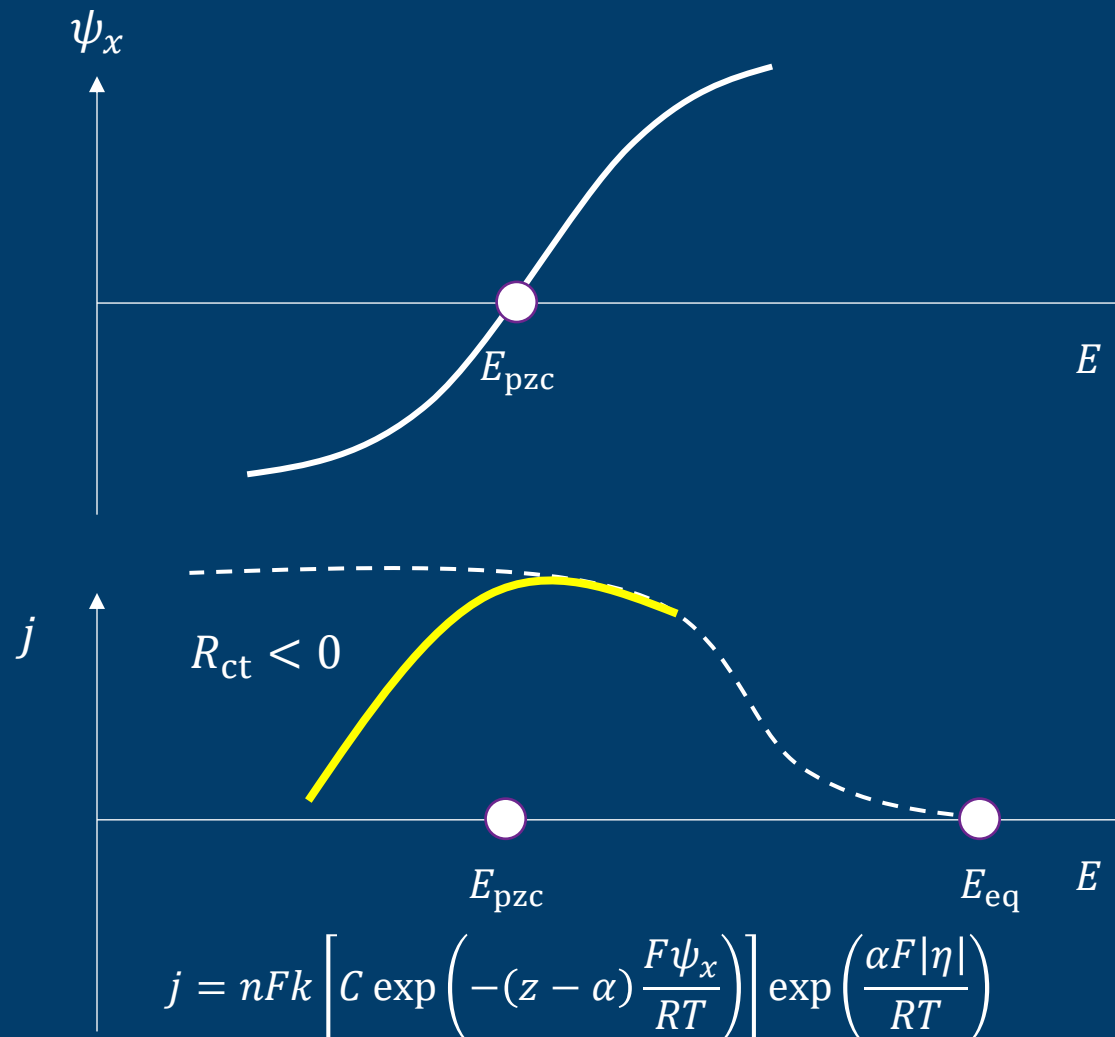
WHY IS THERE AN INITIAL DECREASE?

B. Levich
(1917-1987)

Anions are difficult to go through the EDL

B. Levich, *Dokl. Akad. Naak SSSR*
67, 309 (1949); 124,869 (1959).

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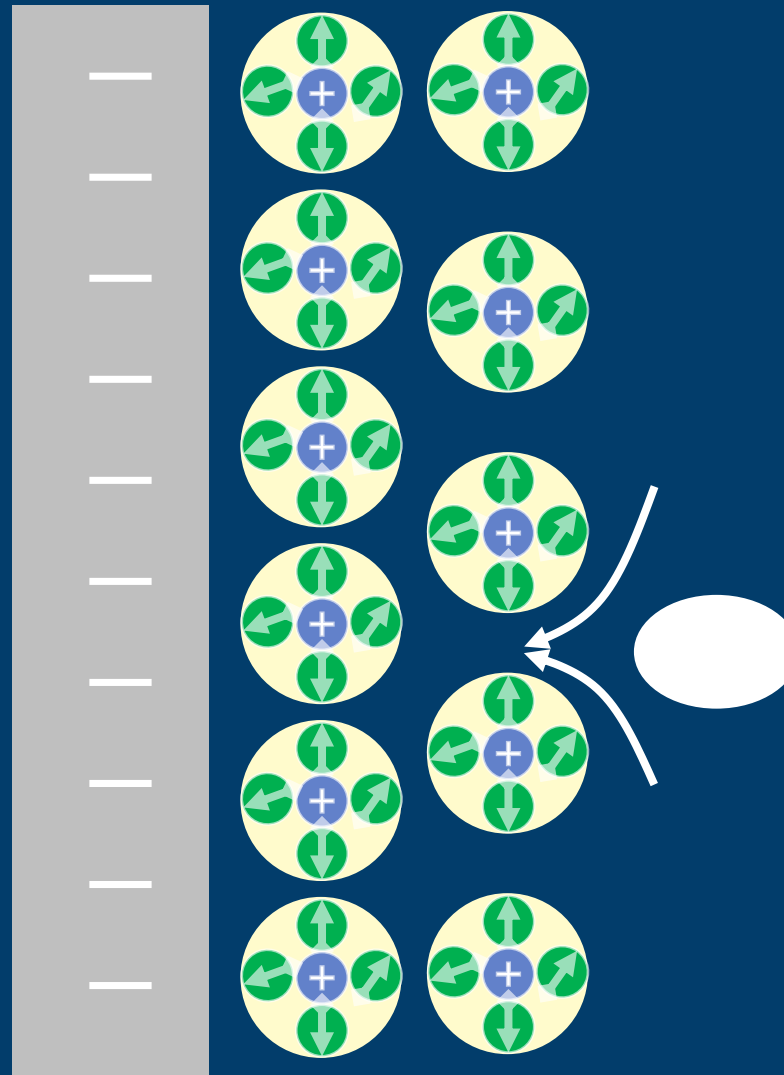
WHY IS IT SUPPRESSED IN MORE CONCENTRATED SOLUTIONS?

A.N. Frumkin, O.A. Petry, N.V. Nikolaeva-Fedorovich, *Electrochim. Acta.* **8,177 (1963).**
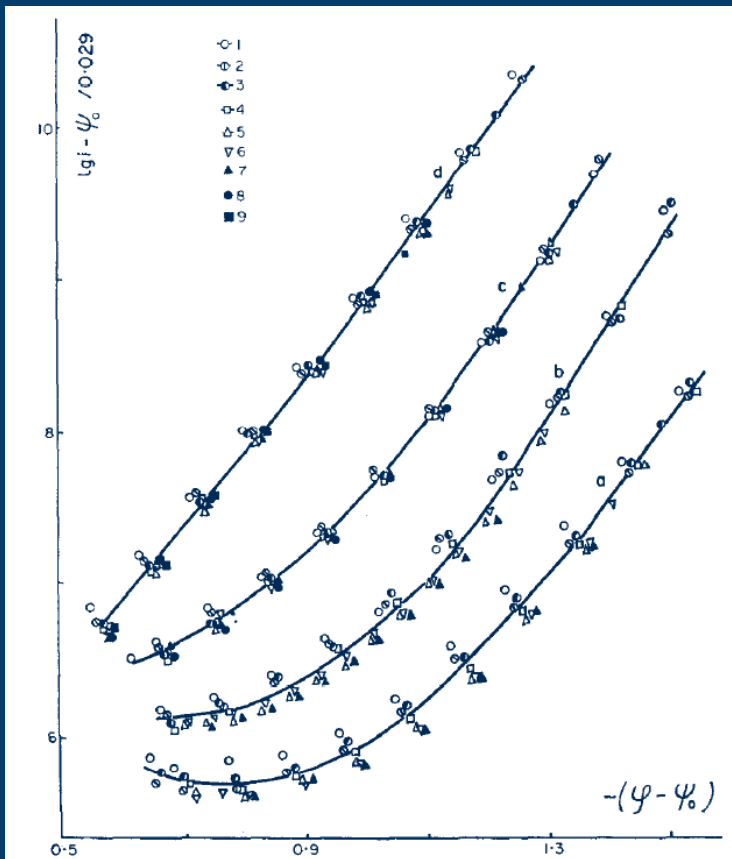
(d) 10^{-3} N $Cs_2S_2O_8$ in the presence of CsCl in concentrations 0 (1); 5×10^{-4} N (2); 10^{-3} N (3); 1.5×10^{-3} N (4); 2×10^{-3} N (5); 2.5×10^{-3} N (6); 3×10^{-3} N (7); 4×10^{-3} N (8); 5×10^{-3} N (9).

$$j = nFk \left[C \exp\left(-\frac{zF\psi_x}{RT} \right) \right] \exp\left(\frac{\alpha F(|\eta| + \psi_x)}{RT} \right)$$

Corrected Tafel plot

$$\ln j + \frac{zF\psi_x}{RT} = \text{const} - \frac{\alpha F(\varphi - \psi_x)}{RT}$$

K. Asada, P. Delahay, A. Sundaram, *J. Am. Chem. Soc.* 83,3396 (1961).

ψ_x **in the EDL is affected by the bulk concentration, while z and α should be concentration-independent, as demonstrated by Frumkin** *et al.* **(1963)**

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PEROXODISULFATE ANION REDUCTION ON AU

Samec Z, Doblhofer K. *J. Electroanal. Chem.*1994; 367(1-2):141-7.
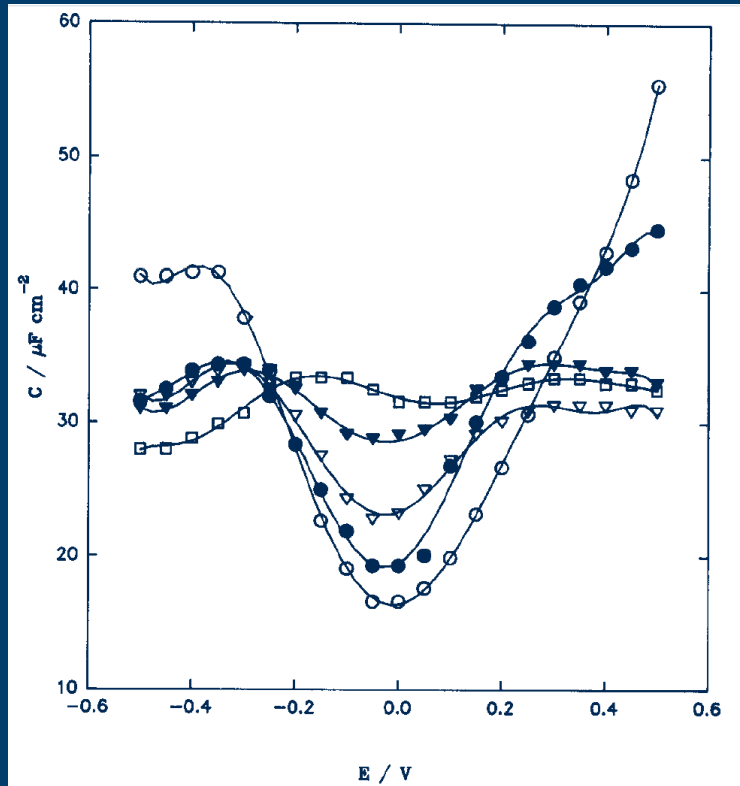
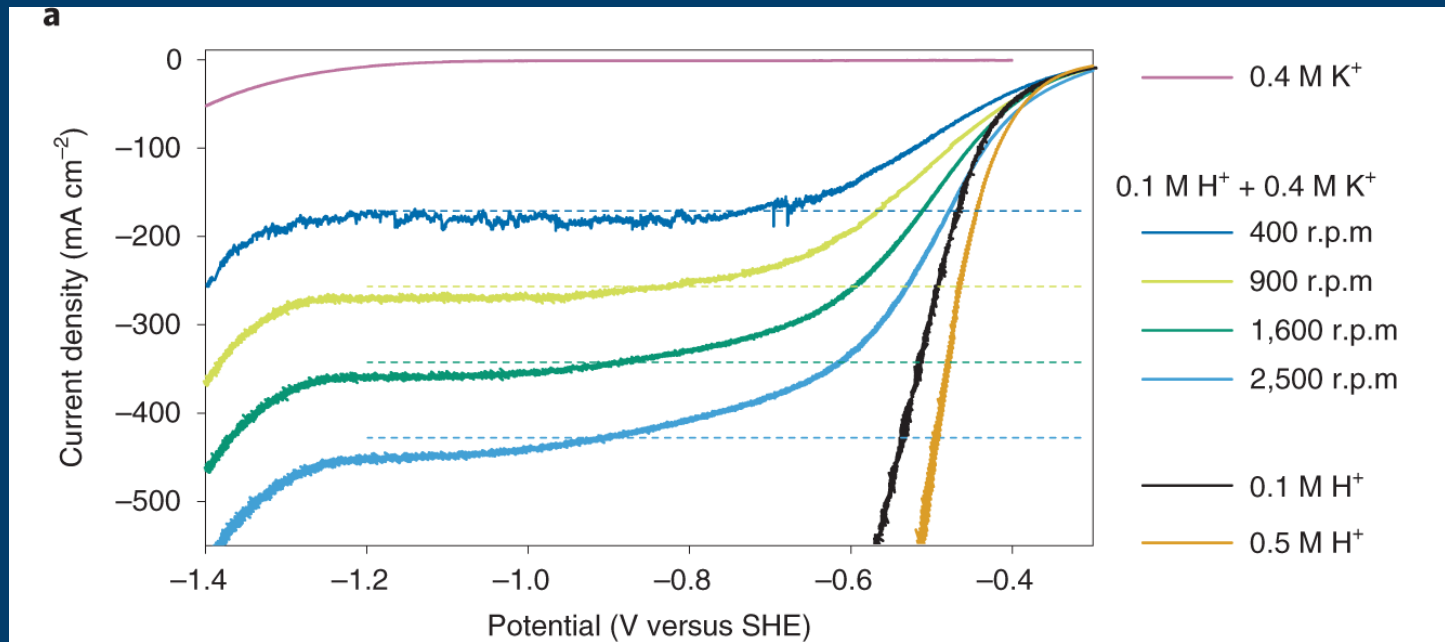C_{dl} (200 Hz) of Au in x M $HClO_4$
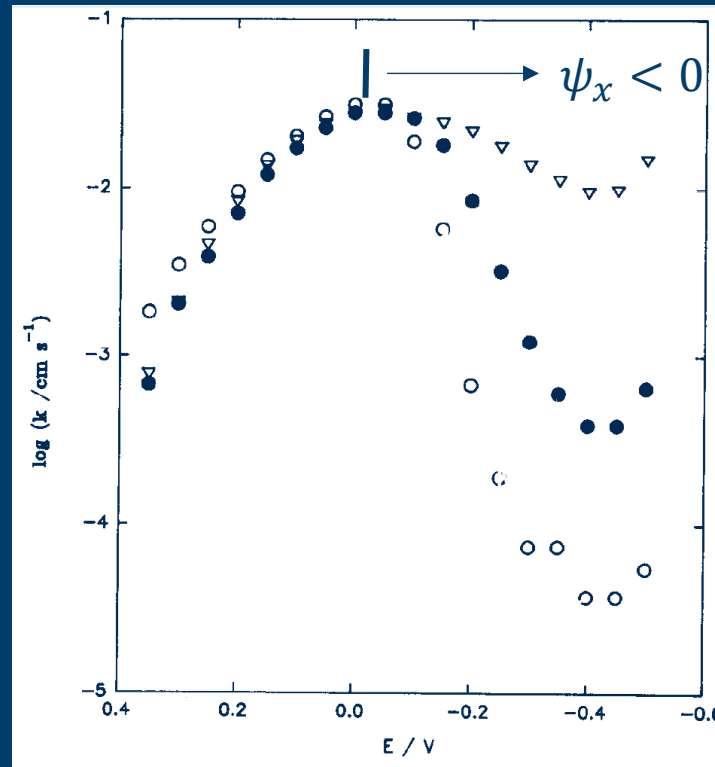
x M $HClO_4$ with 1 mM $Na_2S_2O_8$

Electrostatic effects are suppressed in more concentrated solutions.

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LEVICH'S IDEA IS REINVIGORATED

frustrated proton transport in EDL
J. Gu, S. Liu, W. Ni, W. Ren, S. Haussener, X. Hu, *Nat. Catal.* **2022, 5, 268–276;**

LSV curves for Au RDE in N_2 saturated solutions
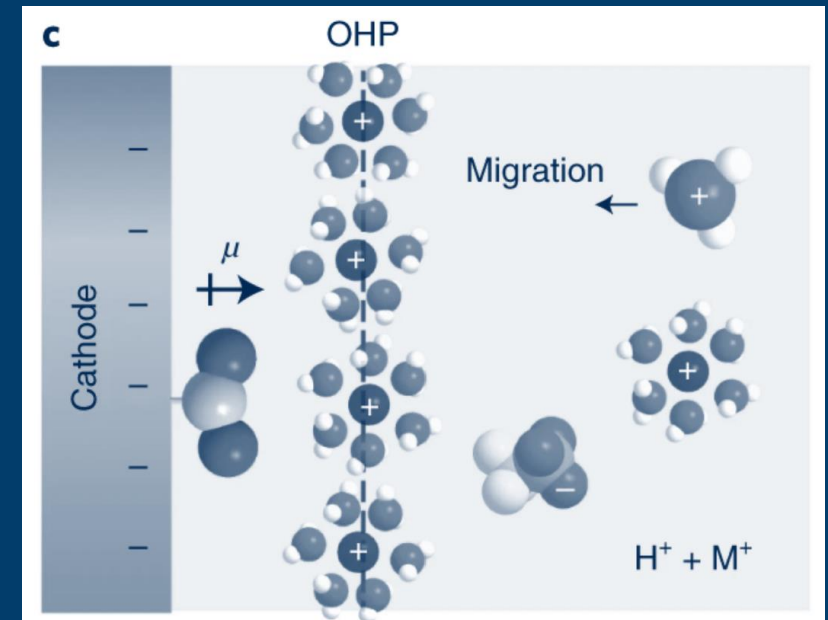
"In K^+-containing medium, due to the competitive adsorption of hydrated K^+ ions against hydronium ions at OHP, **a chemically inert hydrated K^+ layer formed at OHP** and shielded the electric field from the cathode in a long potential window. Thus, **migration of hydronium ions was dramatically suppressed**."

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LEVICH'S IDEA IS REINVIGORATED

frustrated proton transport in EDL

Li, X.-Y., Wang, T., Cai, Y.-C., Meng, Z.-D., Nan, J.-W., Ye, J.-Y., Yi, J., Zhan, D.-P., Tian, N., Zhou, Z.-Y., Sun, S.-G., *Angew. Chem. Int. Ed.* 2023, 62, e202218669
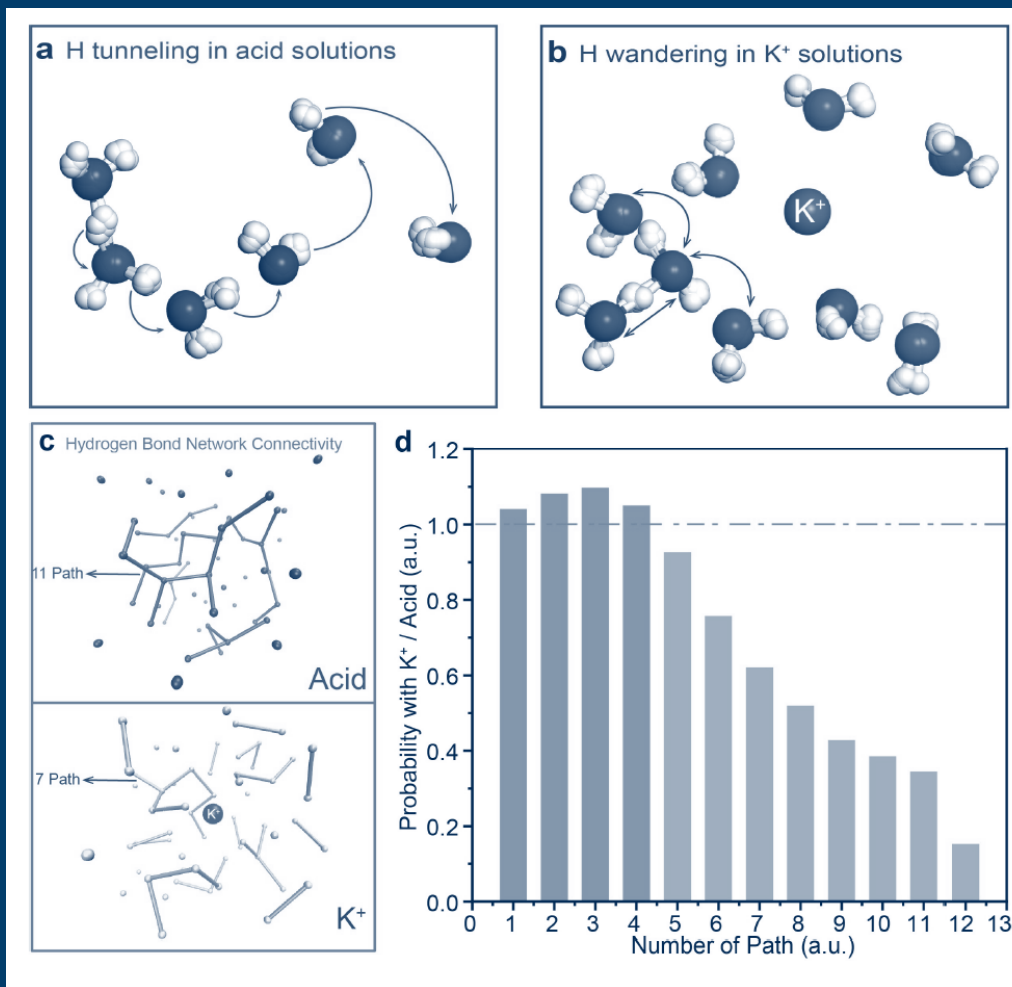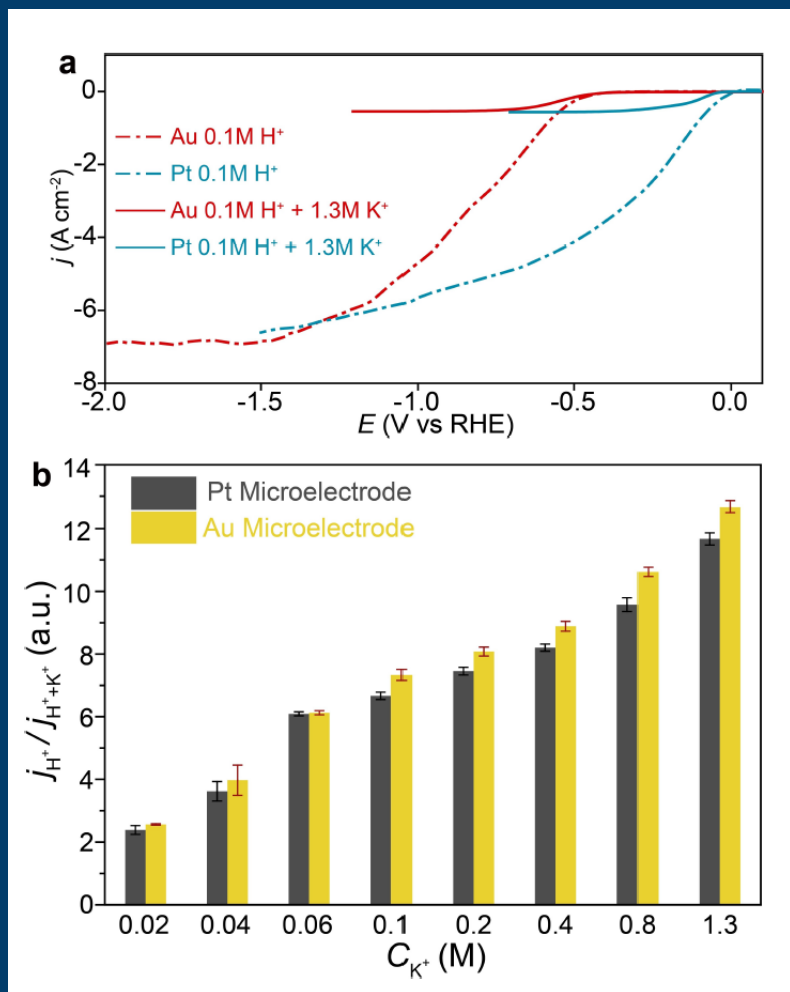
WHY DOES THE CURRENT INCREASE AGAIN AT LARGE OVERPOTENTIALS?
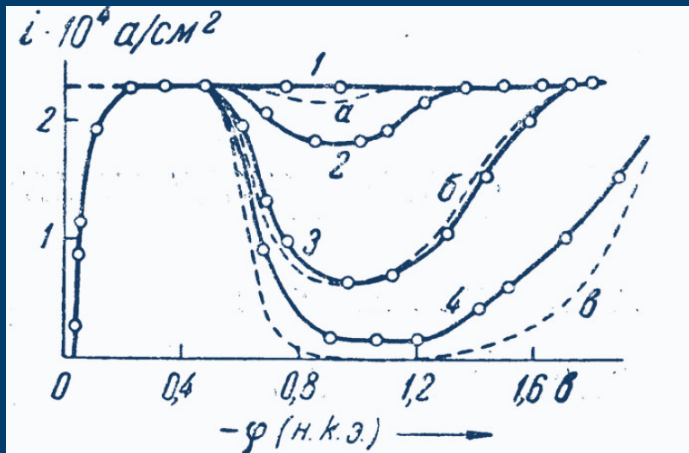
A.N. Frumkin
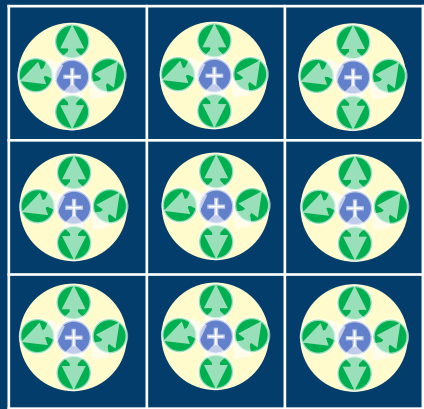(1895-1976)

O. Petrii
(1937-2021)

G. Tsirlina
(Active)

R. Nazmutdinov
(Active)

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WHY DOES THE CURRENT INCREASE AGAIN AT LARGE OVERPOTENTIALS?

Increased reaction volume

R.R. Nazmutdinov et al. *Journal of Electroanalytical Chemistry* 552 (2003) 261/278

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Journal of **Electroanalytical Chemistry**

Journal of Electroanalytical Chemistry 552 (2003) 261–278

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ELSEVIER

Contemporary understanding of the peroxodisulfate reduction at a mercury electrode

Renat R. Nazmutdinov [a], Dmitrii V. Glukhov [a], Oleg A. Petrii [b], Galina A. Tsirlina [b,*], Galina N. Botukhova [b]

[a] *Kazan State Technological University, Kazan, Republic Tatarstan, Russia*
[b] *Moscow State University, Chemical Faculty, Leninskie Gory, GSP-L, Moscow 119992, Russia*

Received 2 October 2002; received in revised form 19 February 2003; accepted 24 March 2003

Dedicated to Professor Boris B. Damaskin on the occasion of his 70th birthday

Four limitations of Frumkin theory

- Point charge assumption

- Butler-Volmer kinetics is problematic in a wide potential range

- Neglect of other electrostatic factors, i.e., changes in both the solvent reorganization energy and the electrode/reactant electronic coupling.

- Reaction plane assumption

WHY DOES THE CURRENT INCREASE AGAIN AT LARGE OVERPOTENTIALS?

Increased reaction volume

R.R. Nazmutdinov et al. *Journal of Electroanalytical Chemistry* **552 (2003) 261/278**
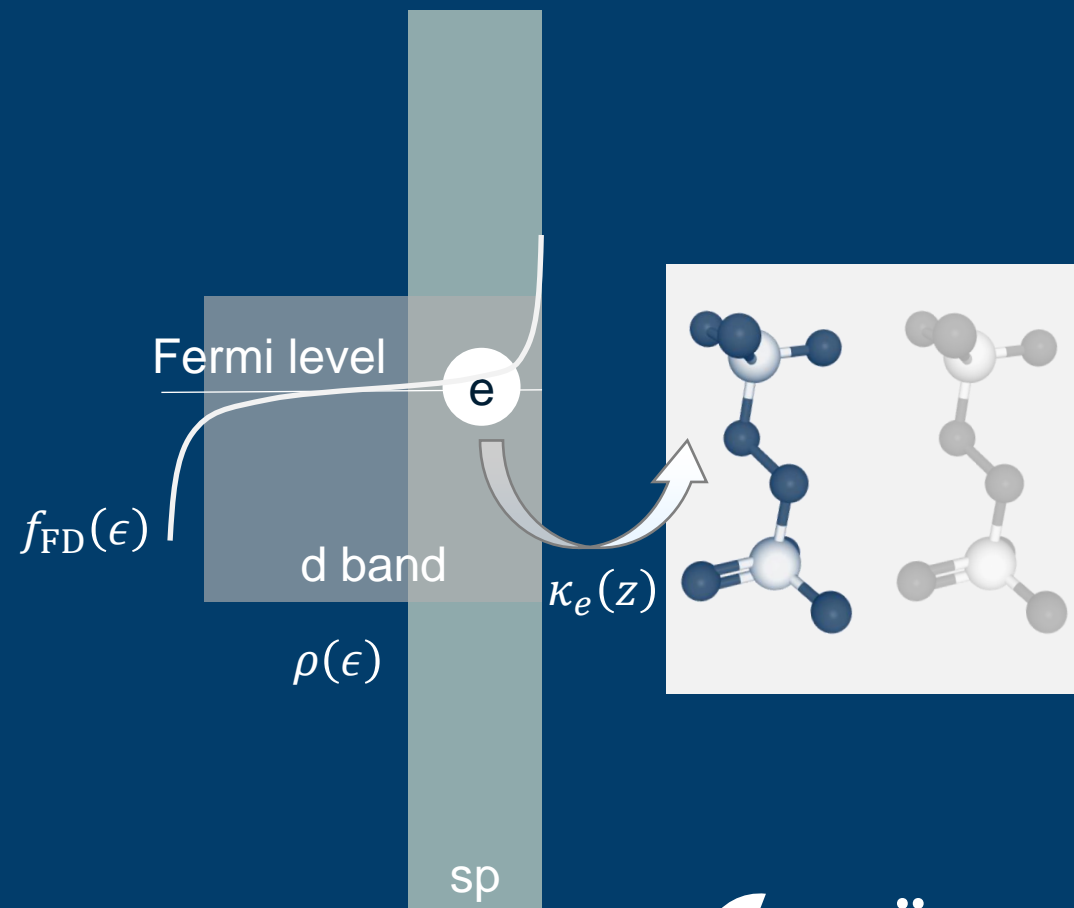
A general formalism of electron transfer

$$j = F[\text{Ox}]\left(\frac{\omega_{\text{eff}}}{2\pi}\right)$$

$$\int_{-\infty}^{+\infty} d\varepsilon \int_{z_{\min}}^{\infty} dz \rho(\varepsilon) f_{\text{FD}}(\varepsilon) \kappa_e(z) \exp\{-\Delta E_a(\varepsilon,\ z)/kT\}$$

A compact formalism

$$j = \text{const } j(\varepsilon_{\text{F}},\ z^*)\delta z \delta \varepsilon^*$$

δz: effective reaction volume
$\delta \epsilon$: effective energy interval

Fermi level

$f_{\text{FD}}(\epsilon)$

e

d band

$\rho(\epsilon)$

$\kappa_e(z)$

sp

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MODERN FRUMKIN THEORY

ion pair, atomistic charge, reaction volume

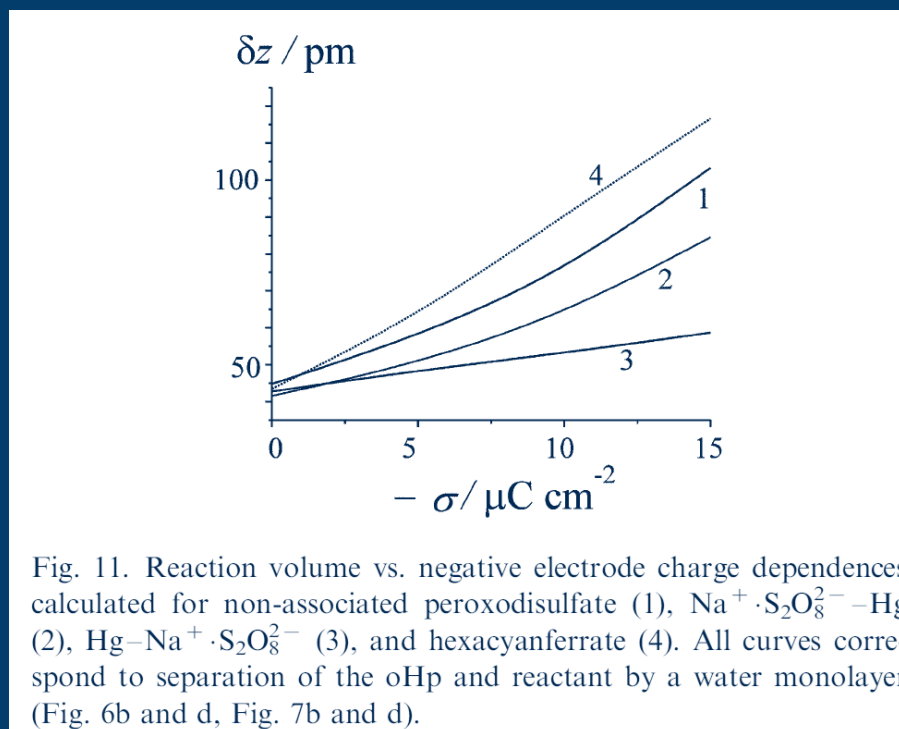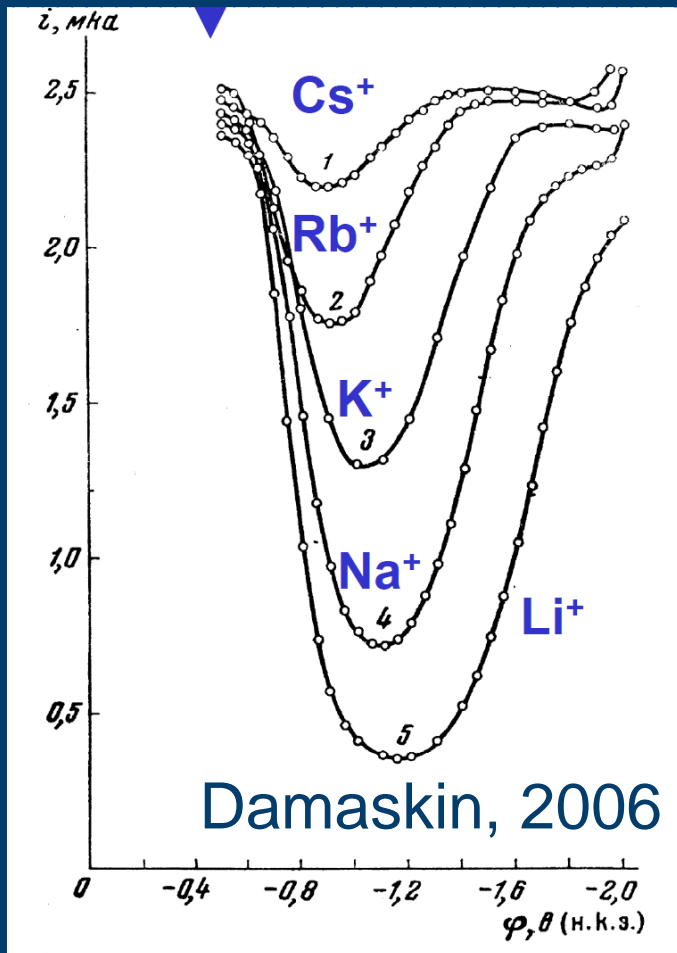**R.R. Nazmutdinov et al.** *Journal of Electroanalytical Chemistry* 552 (2003) 261/278

Fig. 11. Reaction volume vs. negative electrode charge dependences calculated for non-associated peroxodisulfate (1), $Na^+ \cdot S_2O_8^{2-} - Hg$ (2), $Hg-Na^+ \cdot S_2O_8^{2-}$ (3), and hexacyanferrate (4). All curves correspond to separation of the oHp and reactant by a water monolayer (Fig. 6b and d, Fig. 7b and d).

Transmission coefficients vs. distance decays simulated for various forms of peroxodisulfate reactants at electrode charge densities 0 (1), 5 (2), 10 (3), and 15 (4) mC/cm². Solid curves are for the non-associated anion, dotted curves are for $Na^+ - S_2O_8^{2-} - Hg$, and dashed curves for $Hg - Na^+ - S_2O_8^{2-}$

$$j = \text{const } j(\varepsilon_F, \ z^*)\delta z \delta \varepsilon^*$$

WHY DOES THE REDUCTION RATE FOLLOW THE TREND OF $Cs^+ > K^+ > Na^+ > Li^+$?

Damaskin, 2006

A.N. Frumkin
(1895-1976)

J. Heyrovsky
(1890-1967)

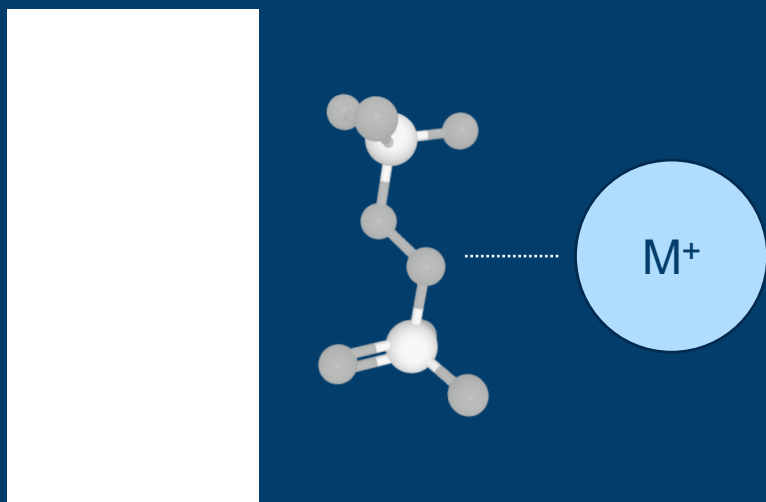# HEYROVSKY'S THEORIES OF CATION EFFECTS
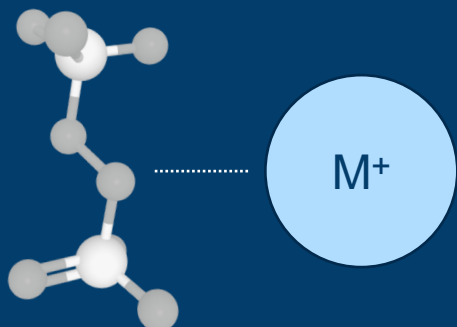
Ion pair
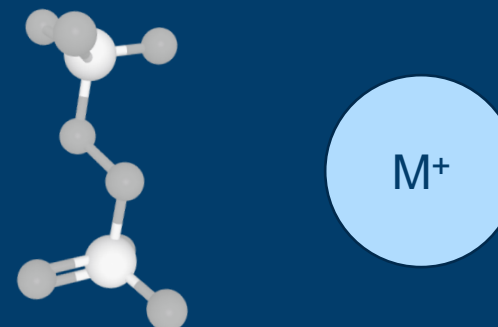
Activation by local electric field of the cation
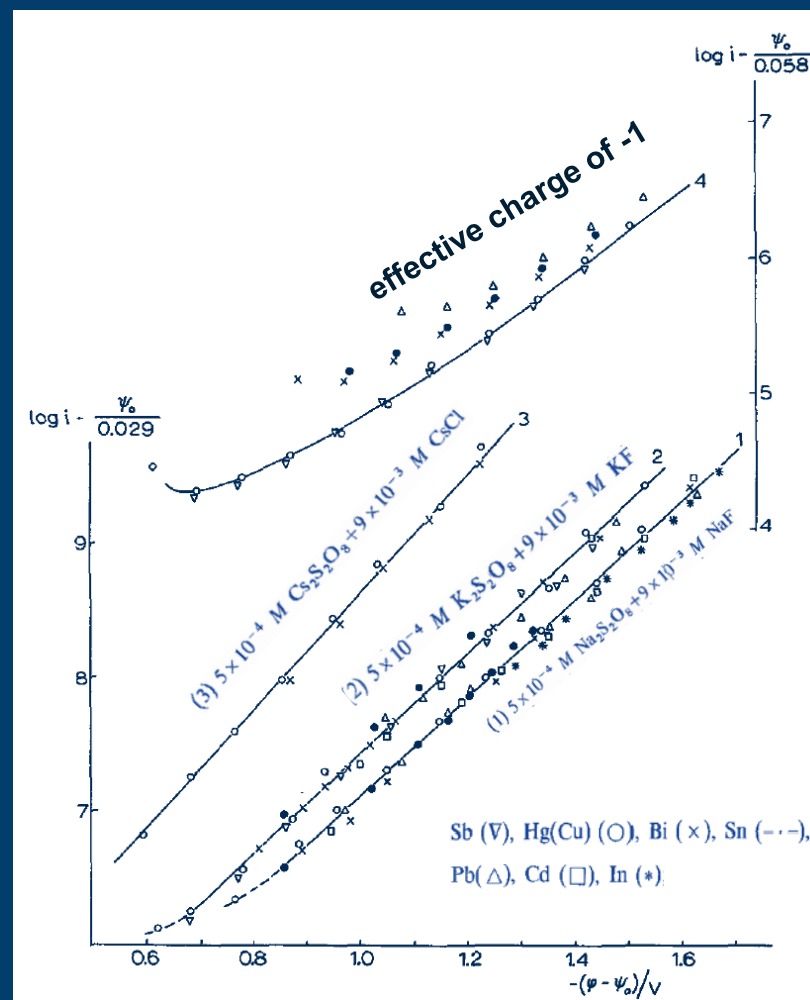
FRUMKIN RENOUNCED THE ION-PAIR THEORY

Frumkin AN, Nikolaeva-Fedorovich NV, Berezina NP, Keis KE. *J. Electroanal. Chem.* 1975, 58(1):189-201.
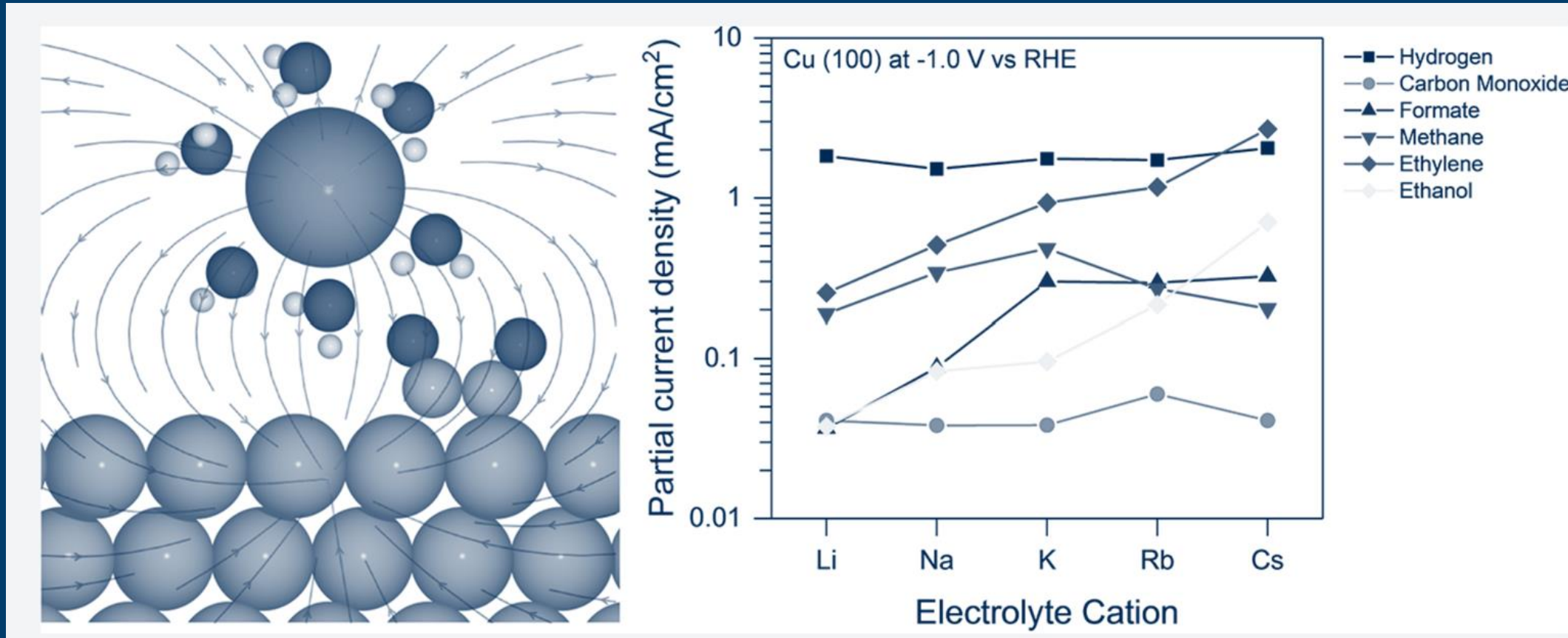
Ion pair -> effective charge of -1

$$\ln j + \frac{zF\psi_x}{RT} = \text{const} - \frac{\alpha F(\varphi - \psi_x)}{RT}$$

"the decisive role of the formation of ion pairs will raise objections" (Frumkin 1976)

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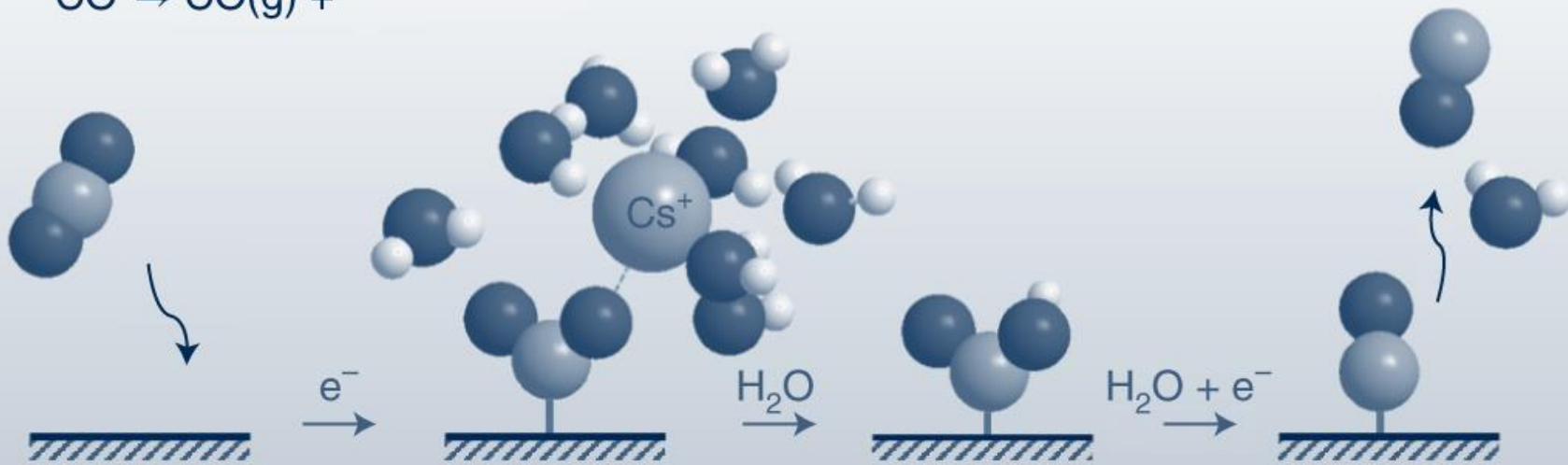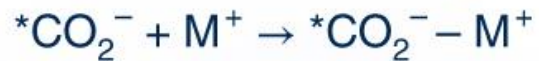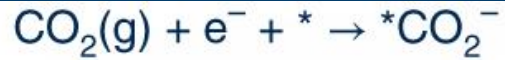
REINVIGORATION OF HEYROVSKY'S THEORIES

Resasco, J. , Chen, L. D. , Clark, E. , Tsai, C. , Chan K. & Bell, A. T. *JACS*, 139(32), 2017

Activation by local electric field of the cation -> field-dependent binding energy of adsorbate

REINVIGORATION OF HEYROVSKY'S THEORIES

Monteiro, M.C.O., Dattila, F., Hagedoorn, B. et al. *Nat Catal* 4, 654–662 (2021).

$$CO_2(g) + e^- + * \rightarrow *CO_2^-$$

$$*CO_2^- + M^+ \rightarrow *CO_2^- - M^+$$

$$*CO_2^- - M^+ + H_2O \rightarrow *COOH + M^+ + OH^-$$

$$*COOH + e^- \rightarrow *CO + OH^-$$

$$*CO \rightarrow CO(g) + *$$

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SUMMARY OF EDL EFFECTS

Why is there an initial decrease? Why is it suppressed in more concentrated solutions?
Frumkin (1933, 1951): static EDL effects
Levich (1949, 1959): dynamic EDL effects

Why does the current increase again at large overpotentials?
Frumkin (1951): EDL saturation
Nazmutdinov, Tsirlina, Petrii, *et al.* (2003): Increased reaction volume

Why does the reduction rate follow the trend of $Cs^+ > K^+ > Na^+ > Li^+$?
Frumkin (1933): potential distribution in EDL
Heyrovsky (1934): ion-pairing and local electric field effects

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TO SEE THE WAY FORWARD, LOOK BACK

Revisiting your founding ideals can help sharpen your purpose and values
by Ranjay Gulati, 2022 In Harvard Business Review

The Archivo di Stato in Vienna/Massimo Listri