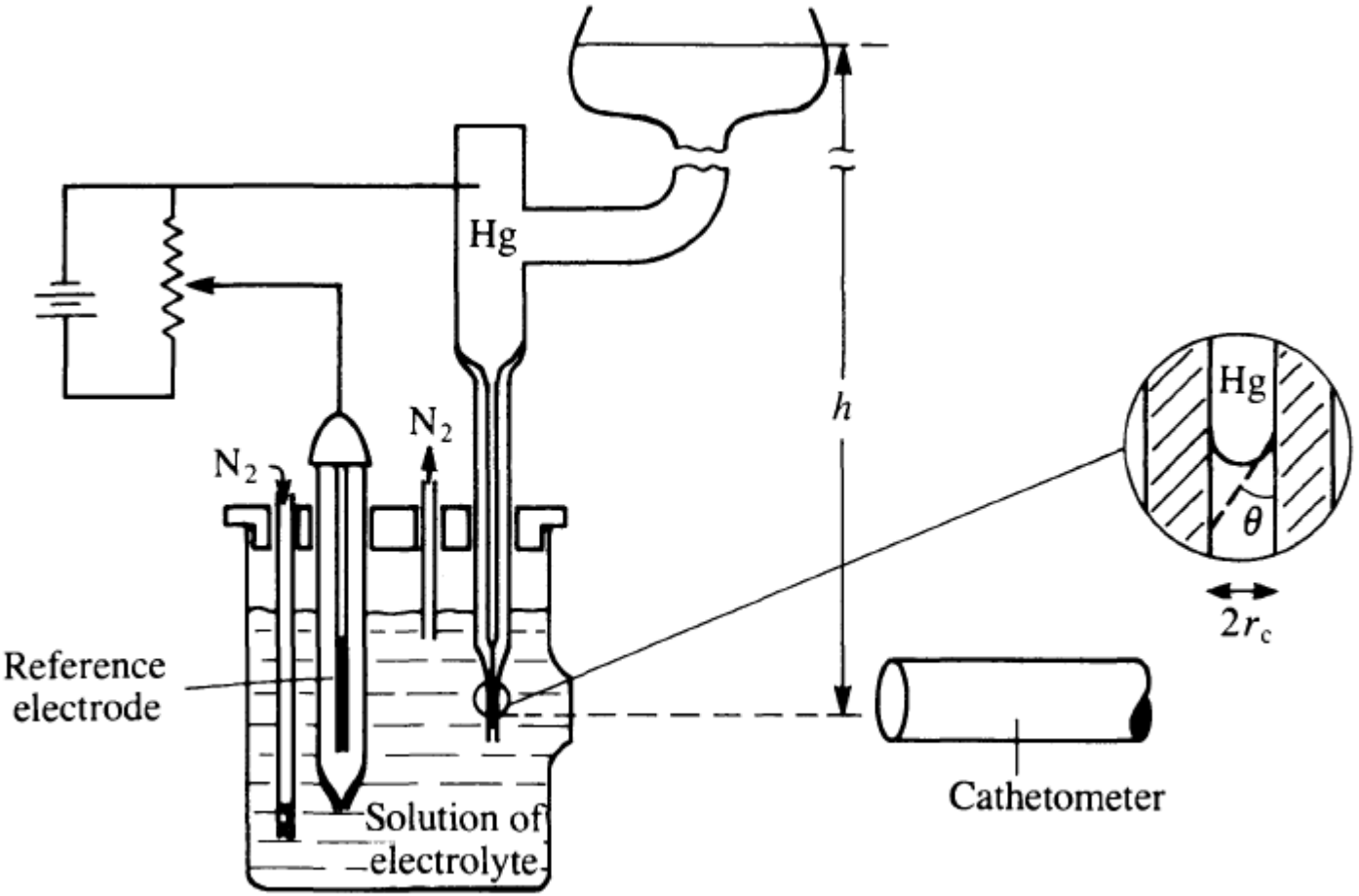
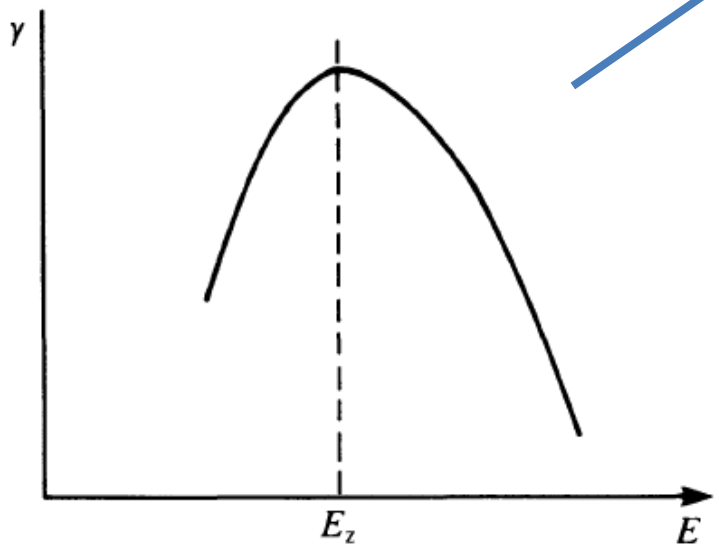
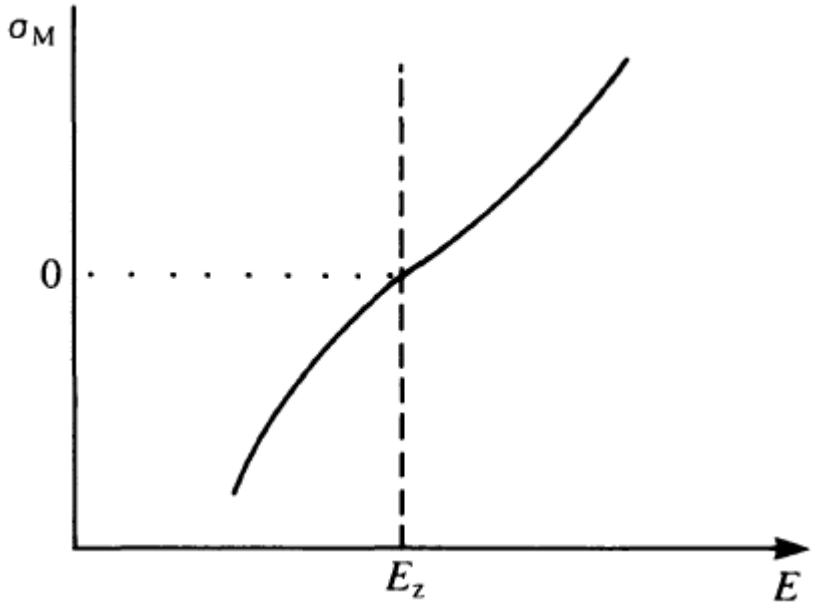
Elektrodová dvojvrstva

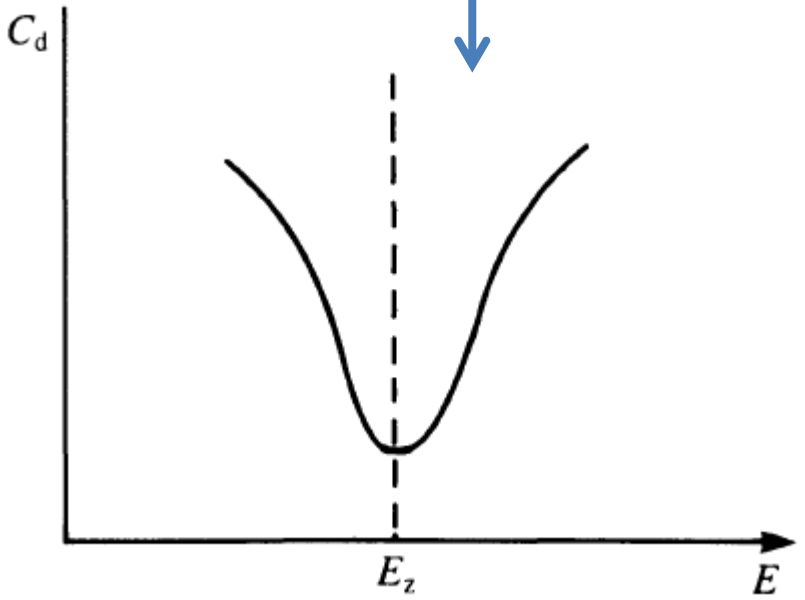


Elektrodová dvojvrstva

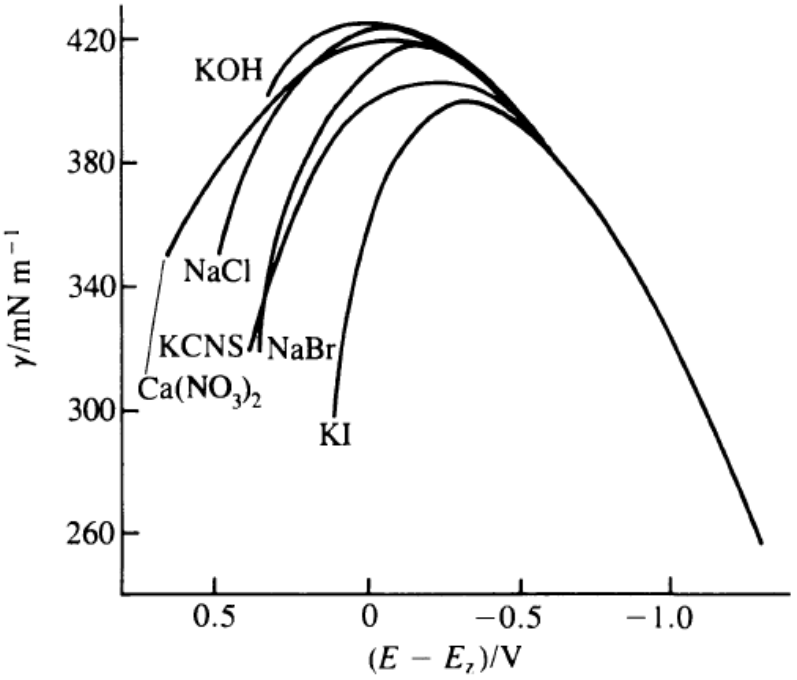
Lippmannova rovnice



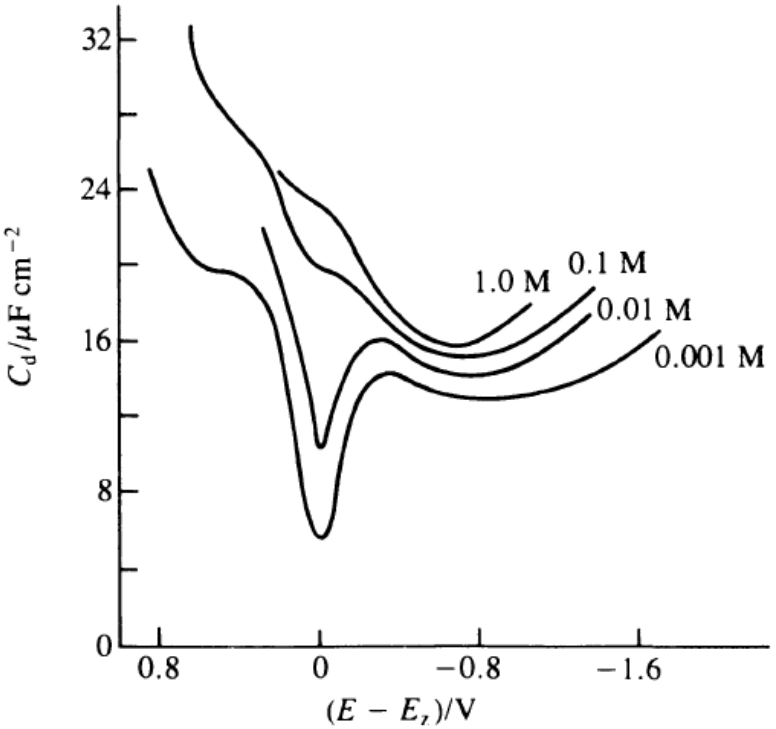




Elektrodová dvojvrstva

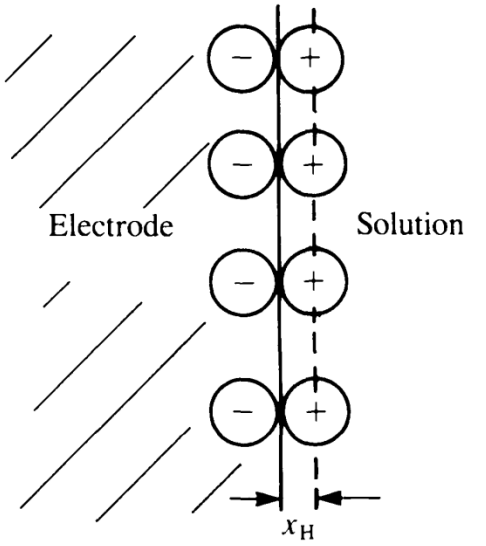


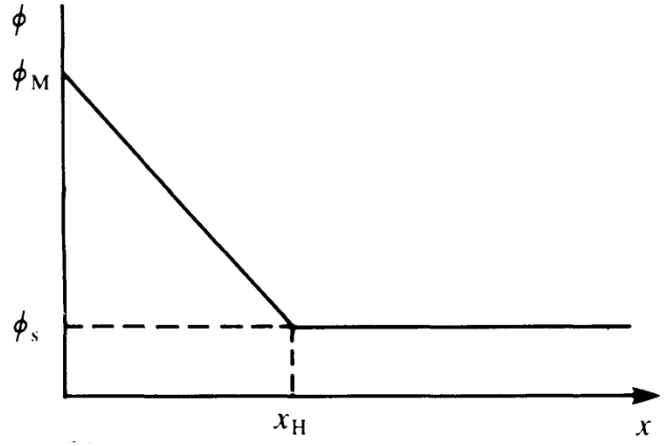
Ez pro NaF



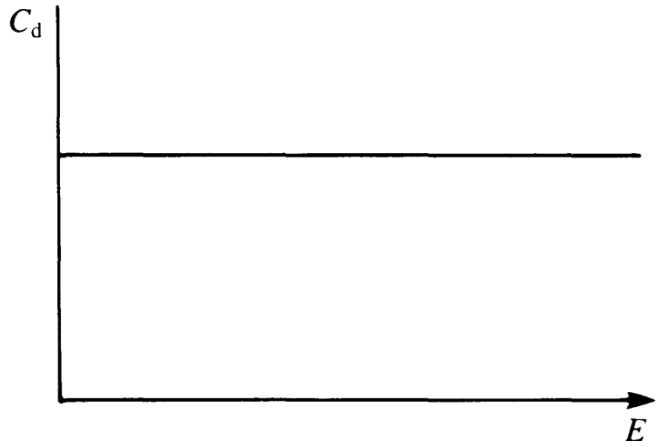
NaF

Helmholtzův model (1873)



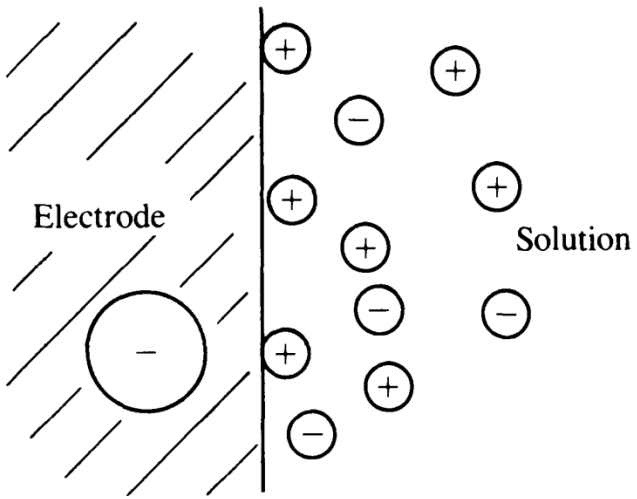


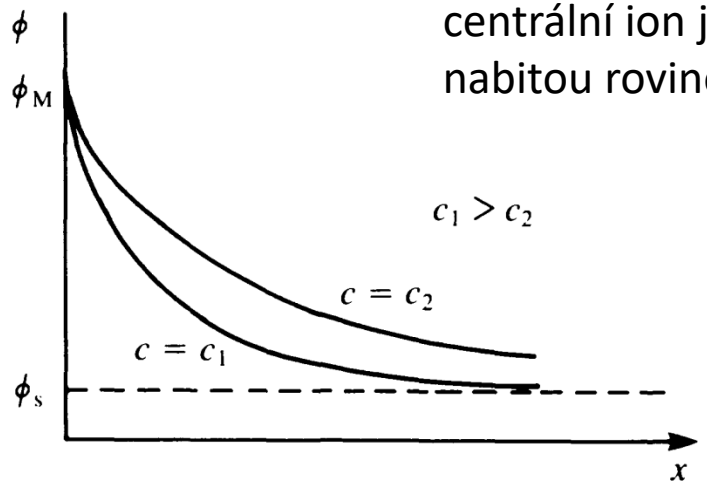
V realitě:
0.1 nm ze strany elektrody
1-10 nm ze strany elektrolytu

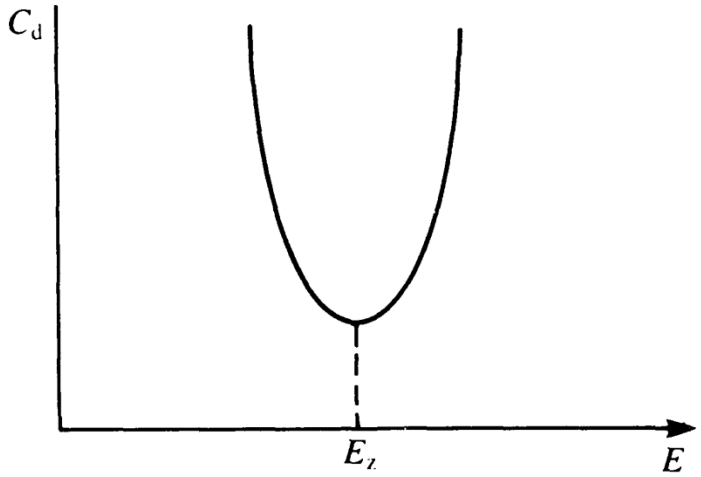


Guy-Chapmanův model (1910-1913)

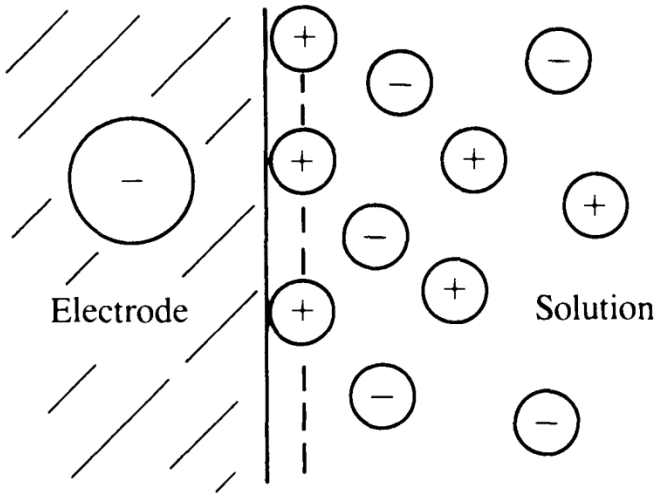
Odvození je podobné jako u Debye-Huckelovy teorie, centrální ion je nahrazen nabitou rovinou (elektrodou)

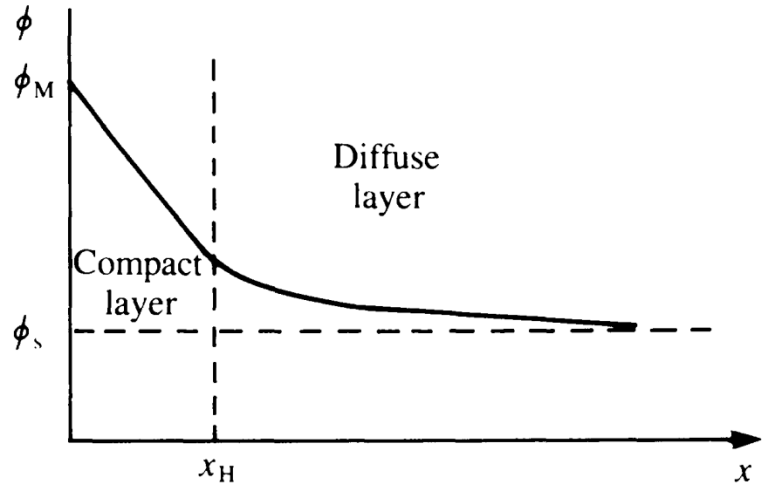


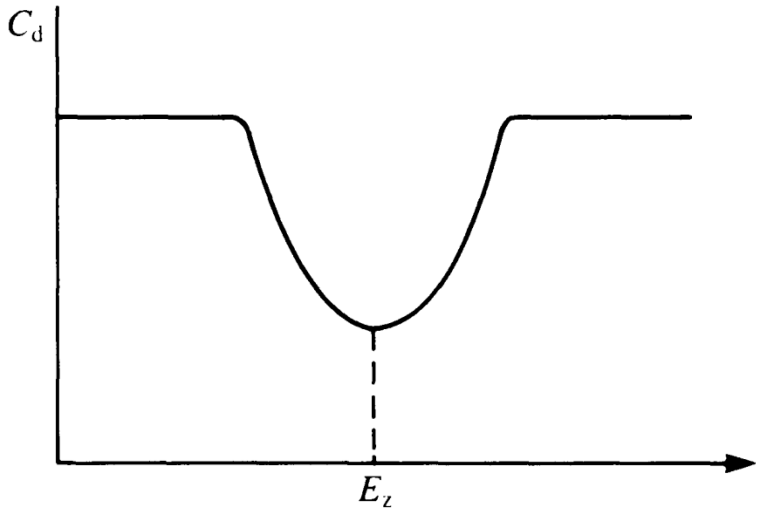




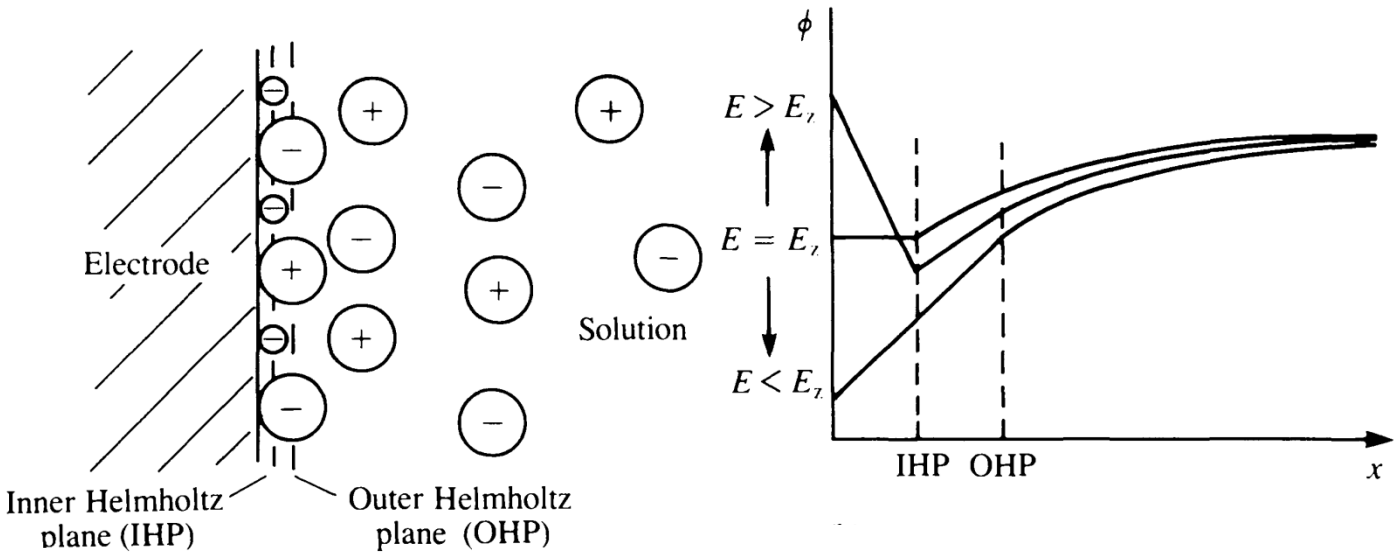
Sternův model (1924)

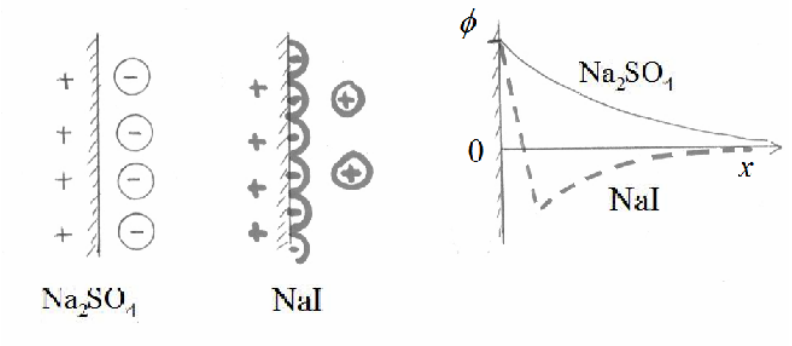


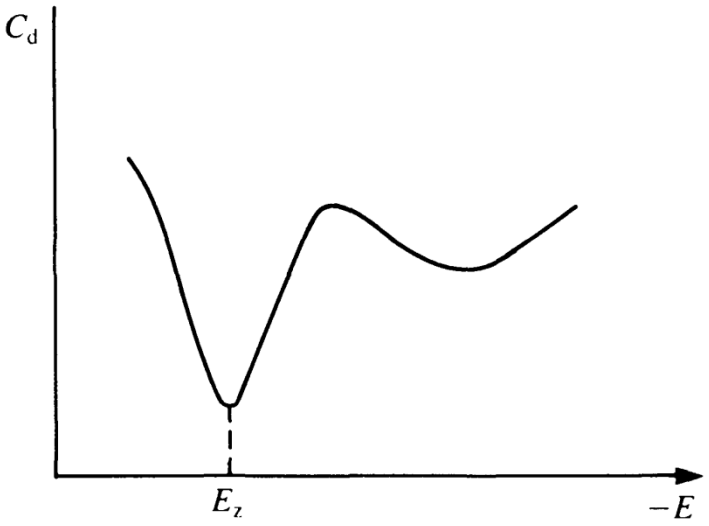




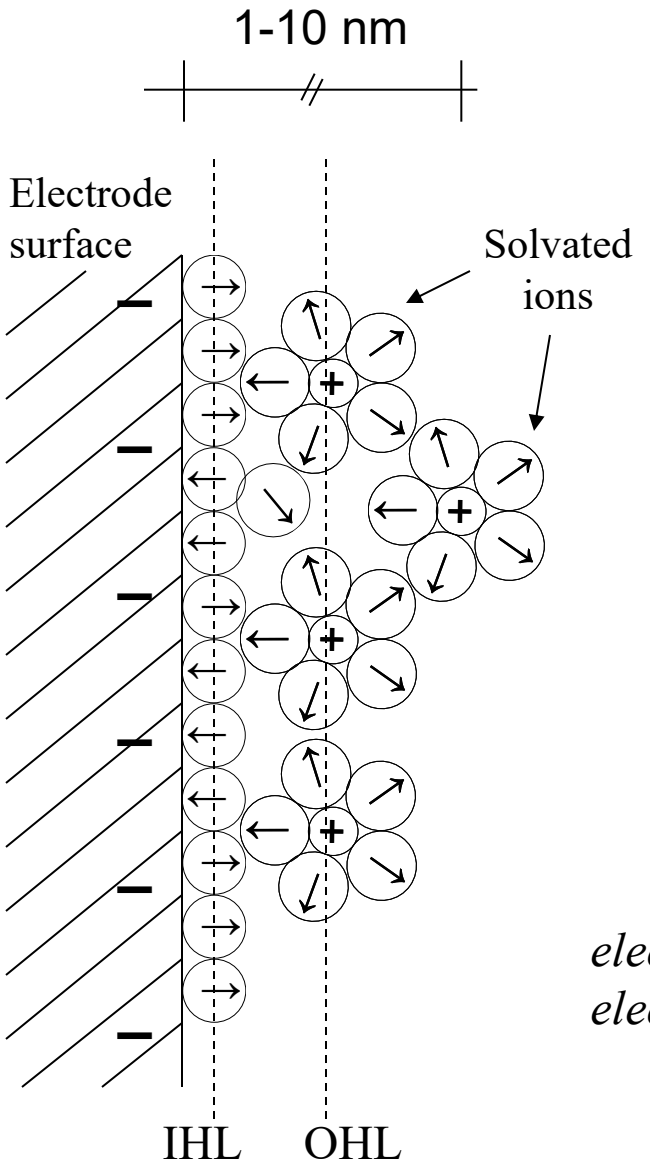
Grahamův model (1947)







ELECTRON TRANSFER PHENOMENON



The double-layer region is:

Where the truncation of the metal's Electronic structure is compensated for in the electrolyte.

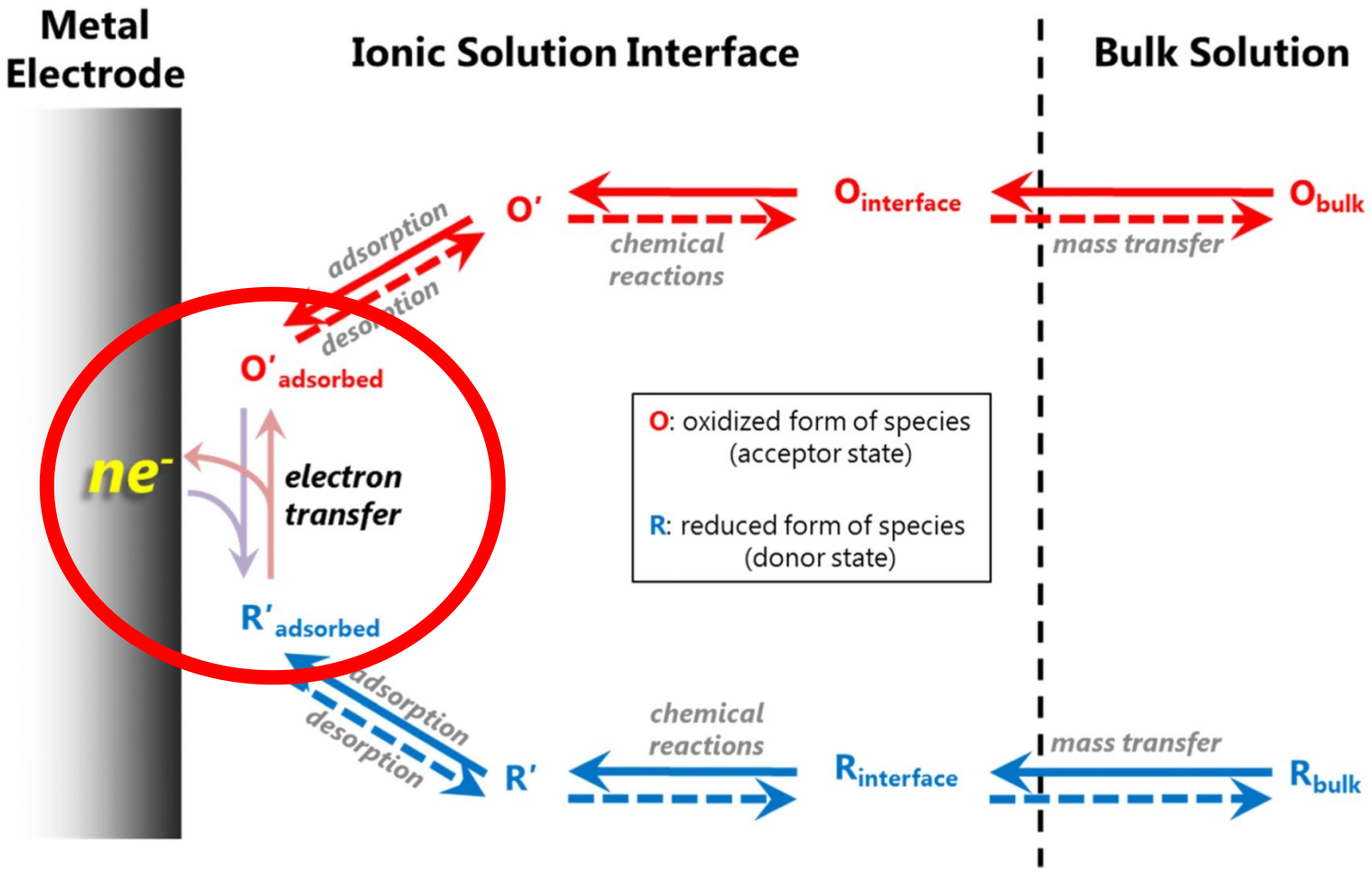
1-10 nm in thickness

~1 volt is dropped across this region…

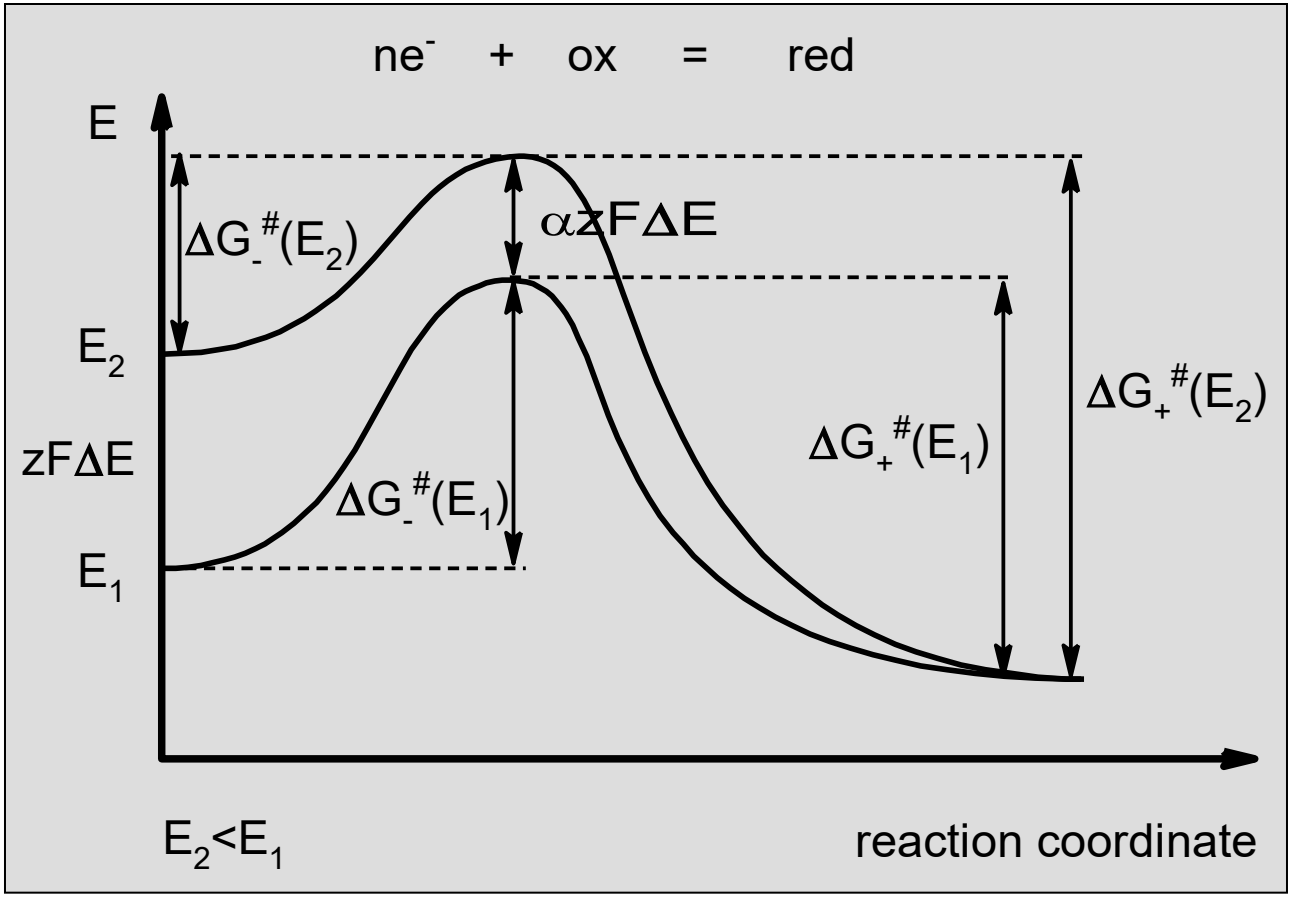
Which means fields of order $10^{7\text{-}8}$ V/m

"The effect of this enormous field at the electrode-electrolyte interface is, in a sense, the essence of electrochemistry." [1]

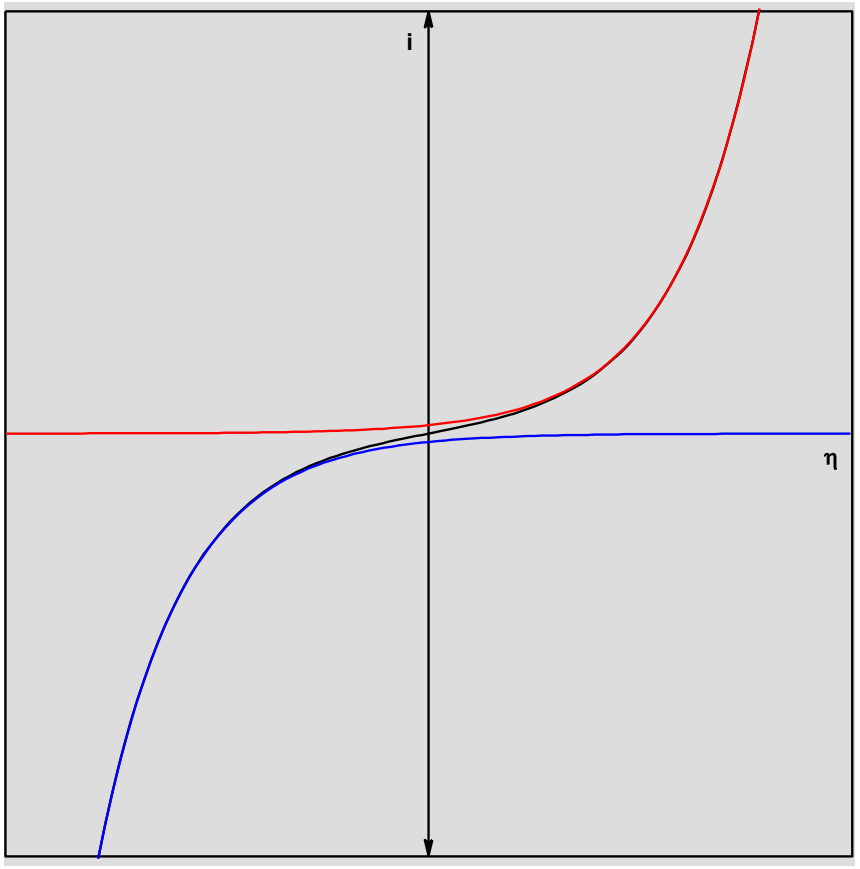
[1] Bockris, Fundamentals of Electrodics, 2000

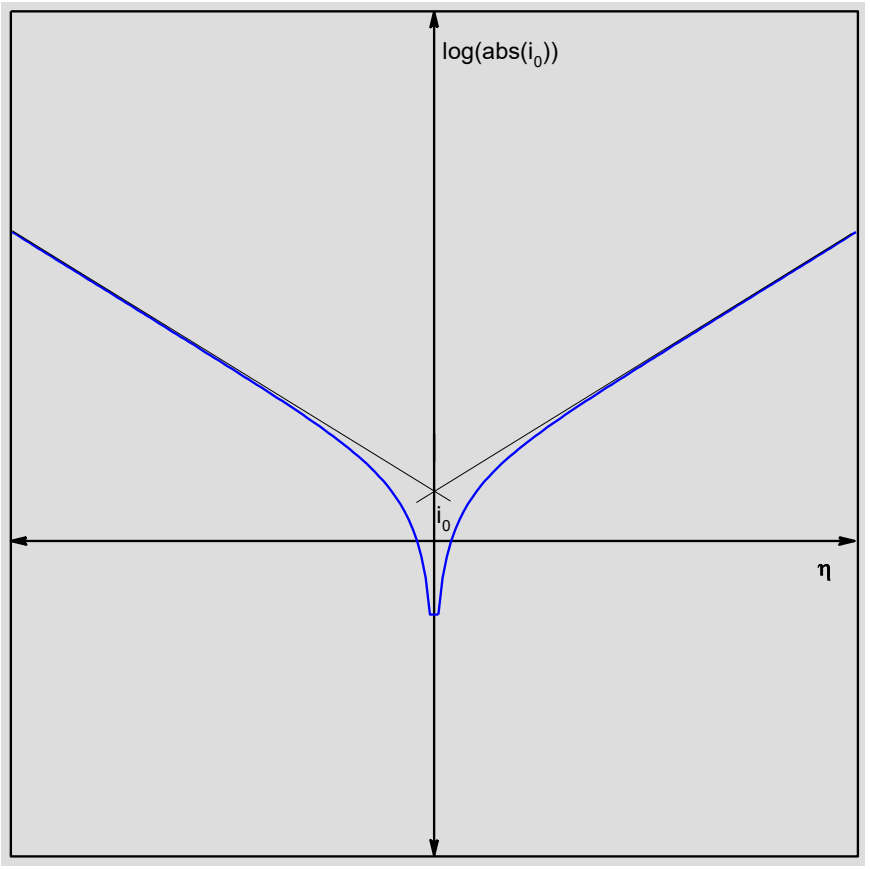

Metal Electrode
Ionic Solution Interface
Bulk Solution
O'
O interface
O bulk
adsorption
desorption
chemical reactions
mass transfer
O' adsorbed
ne-
electron transfer
R' adsorbed
O: oxidized form of species (acceptor state)
R: reduced form of species (donor state)
adsorption
desorption
R'
chemical reactions
R interface
mass transfer
R bulk

BUTLER-VOLMER AND TAFEL EQUATIONS



BUTLER-VOLMER AND TAFEL EQUATIONS

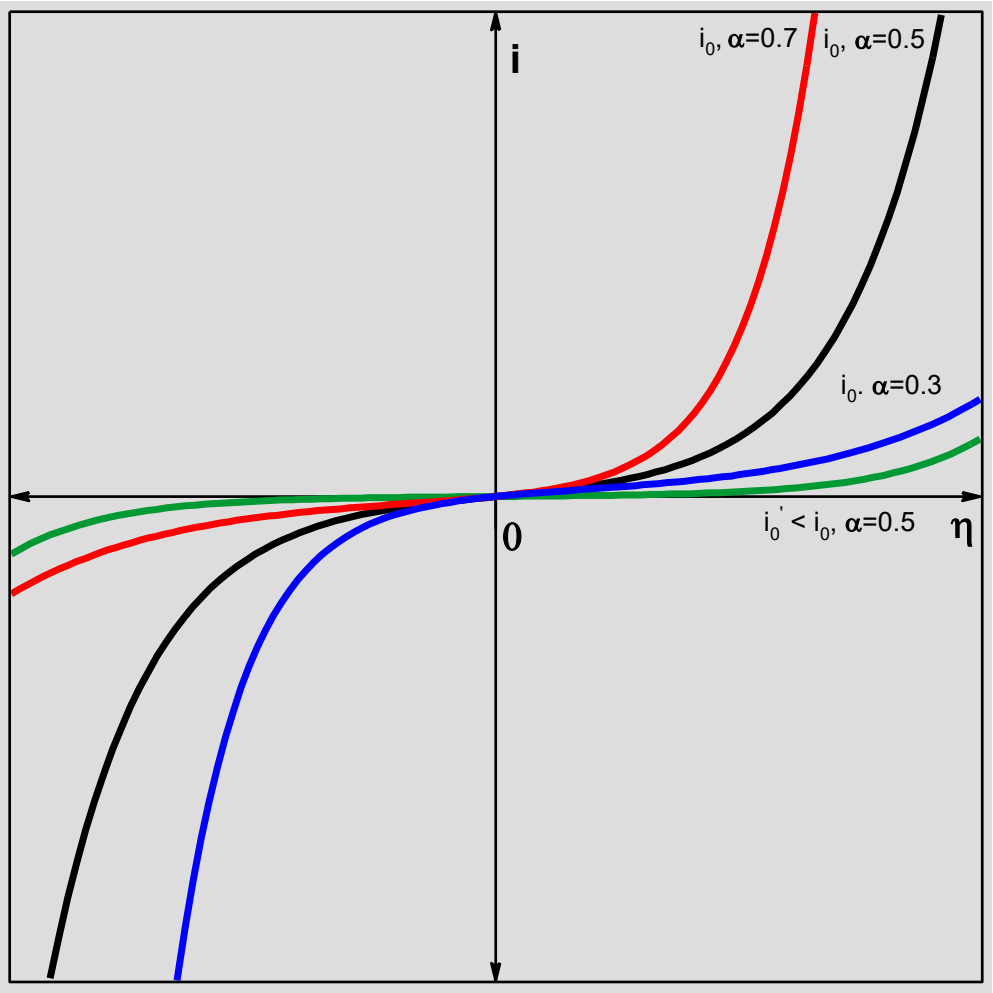




$$i = i_0\left(\exp\left(\frac{(1-\alpha)zF}{RT}(E-E^\circ)\right)-\exp\left(\frac{-\alpha zF}{RT}(E-E^\circ)\right)\right)$$

$$\log(i) = \log(i_0)-\left(\frac{2.303\alpha zF}{RT}(E-E^\circ)\right)$$

BUTLER-VOLMER AND TAFEL EQUATIONS



$$i = i_0\left(\exp\left(\frac{(1-\alpha)nF}{RT}(E-E^\circ)\right)-\exp\left(\frac{-\alpha nF}{RT}(E-E^\circ)\right)\right)$$

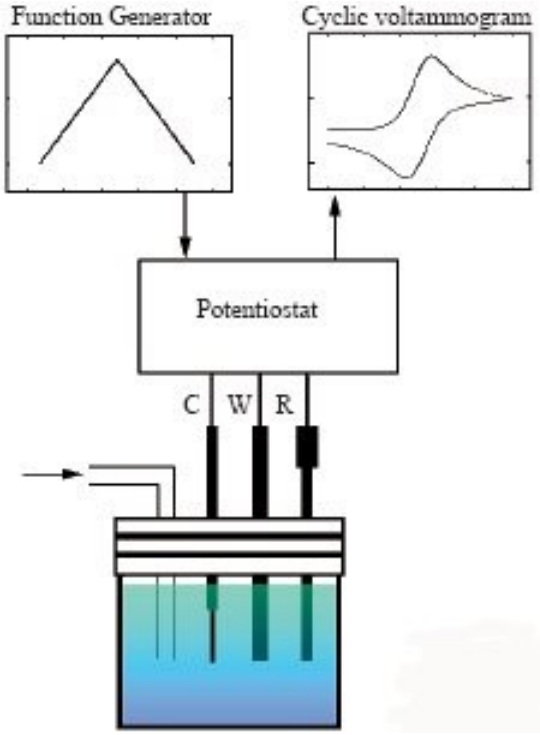
Exchange current density

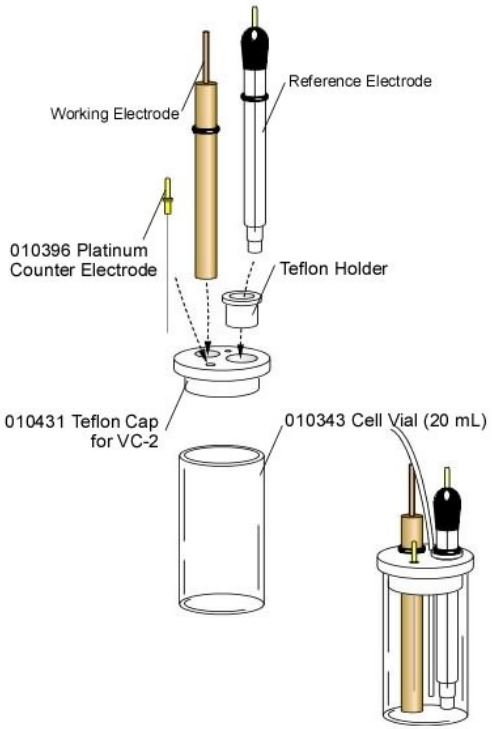
Depends on the species undergoing redox transformation and on the electrode material

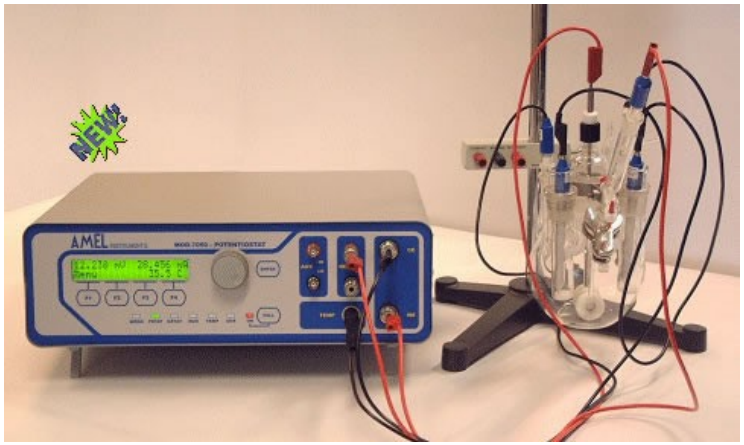
In fact, large overpotential for hydrogen evolution on Hg surfaces enables us to observe reductions in aqueous solutions

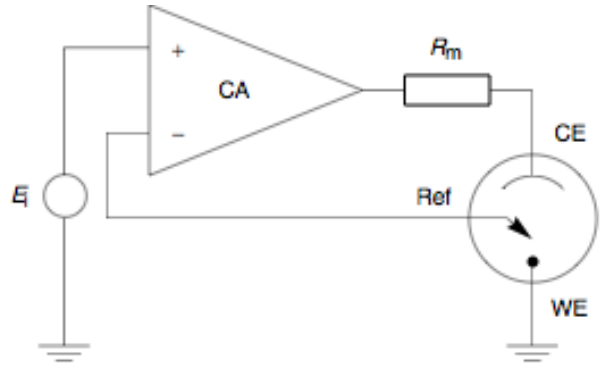
Also, the development of modern modified electrodes is based on finding the modifying layer which increase the exchange current density on the electrode surface

3-ELECTRODE CELLS AND POTENTIOSTATS









Polarizable and nonpolarizable

-Smíšený (korozní) potenciál: příklad Fe v HCl:

-Katodická reakce: 2 H^+ + 2e = H_2

-Anodická reakce: Fe = Fe^{2+} +2e