

Impedance under forced convection conditions. Measurements and analysis

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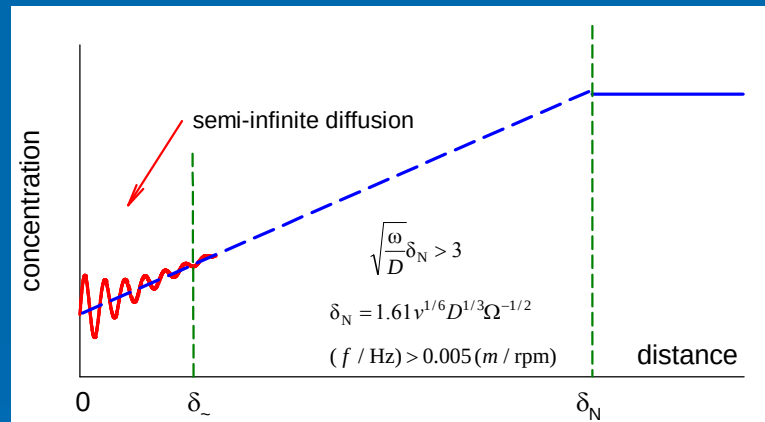
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THE MODEL



Premises

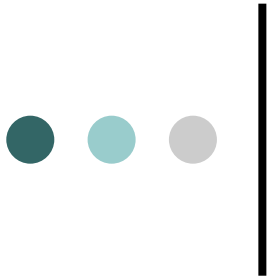
- The applied constant potential is superimposed by an alternating (sinusoidal) potential signal of small amplitude
- The depth of penetration of the concentration wave is considerably lower as compared with the thickness of the steady-state diffusion layer



- The intensity of forced convection is varied at the constant steady-state potential
- The impedance, as the function of the steady-state current, is recorded and analyzed

Quantitative description





General

When a sinusoidal voltage signal of low amplitude

$$V(\omega t) = V_0 \sin(\omega t)$$

is applied, the response of the electrochemical system is:

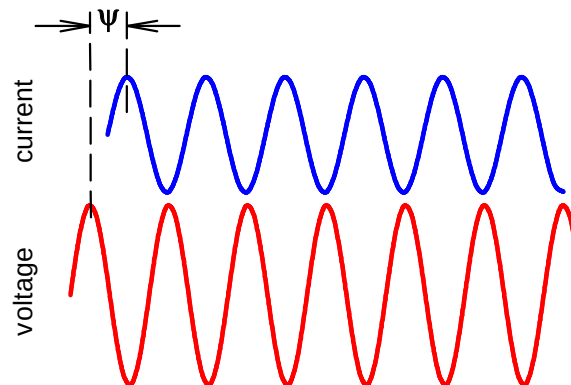
$$I(\omega t) = I_0 \sin(\omega t + \psi) = a \sin(\omega t) + b \cos(\omega t),$$

where

$$I_0 = \sqrt{a^2 + b^2}$$

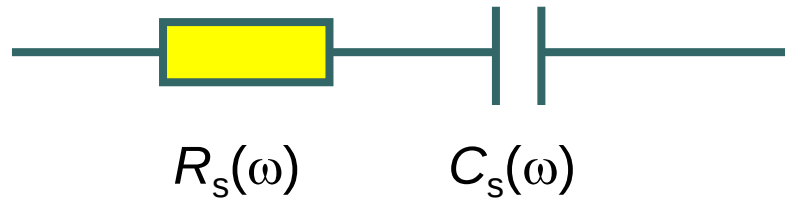
and the phase-angle between current and potential

$$\psi = \arctan(b / a).$$



General

The faradaic impedance $Z_F = Z' - j Z'' = R_s - j / \omega C_s$



$$R_s = Z \cos \psi = a V_0 / (a^2 + b^2)$$

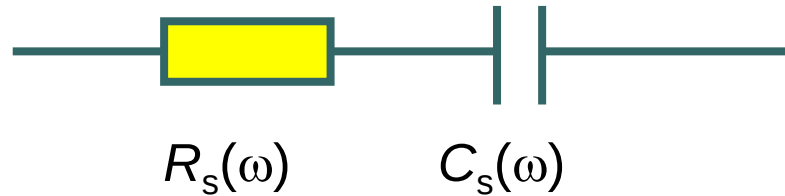
$$1/\omega C_s = Z \sin \psi = b V_0 / (a^2 + b^2)$$

$$\frac{a}{b} = 1 + \frac{\sqrt{2\omega}}{\lambda}$$

$$\psi = \arctan \left(1 + \frac{\sqrt{2\omega}}{\lambda} \right)^{-1}$$



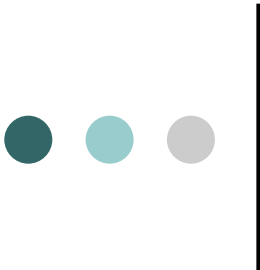
General equations



$$R_s = \frac{R_0}{A} \left(1 + \frac{\sqrt{2\omega}}{\lambda} \right)$$

$$R_0 = \lim_{k_s \rightarrow \infty} R_s$$

$$\frac{1}{\omega C_s} = \frac{R_0}{A}$$



Introduction of kinetic parameters

(an example of the redox process $O + n e \rightarrow R$)

- Kinetic equation is written:

$$i(t) = nFk_s \{c_{R,s} \exp[\alpha_a f \eta_0(t)] - c_{O,s} \exp[-\alpha_c f \eta_0(t)]\} \quad (1)$$

with $f = nF/RT$ and surface concentrations:

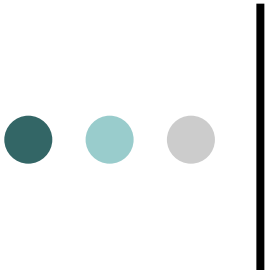
$$c_{R,s} = c_{R,b} - \int_0^t \frac{i(t-u)}{nF \sqrt{D_R \pi u}} du, \quad c_{O,s} = c_{O,b} + \int_0^t \frac{i(t-u)}{nF \sqrt{D_O \pi u}} du \quad (2)$$

- Eq. (2) and the overvoltage $\eta_0(t) = \eta_0 + V_0 \sin(\omega t)$ (3) are inserted into Eq. (1).

- The alternating component of the resulting relationship is identified with

$$i(\omega t) = a \sin(\omega t) + b \cos(\omega t), \quad (4)$$

to obtain expressions for the impedance parameters a and b .



The relationships obtained

(redox process $O + n e \rightarrow R$)

$$R_0 = \frac{4RT \cosh^2(f\eta_{1/2}/2)}{n^2 F^2 \sqrt{2\omega} (c_O \sqrt{D_O} + c_R \sqrt{D_R})} \quad (5)$$

$$A = 1 - \frac{\alpha_c \exp(-\alpha_a f\eta_{1/2}) - \alpha_a \exp(\alpha_c f\eta_{1/2})}{c_O \sqrt{D_O} + c_R \sqrt{D_R}} \times \frac{i\sqrt{D}}{nFk_s} \quad (6)$$

$$\lambda = \frac{k_s}{\sqrt{D}} \times [\exp(-\alpha_c f\eta_{1/2}) + \exp(\alpha_a f\eta_{1/2})] \quad (7)$$

$$D = D_O^{\alpha_a} D_R^{\alpha_c} \quad (8)$$

Special cases:

- a) At $c_O = 0$ (or $c_R = 0$) Eqns (5)-(8) are in line with these reported in: D.E. Smith, *Analyt. Chem.* **36**, 962 (1964).
- b) At $E = E_{eq}$, $i = 0$ and Eqns (5)-(8) transform into well-known relationships published earlier.



The relationships obtained

(electrodeposition $M^{n+} + n e \rightarrow M$)

$$R_0 = \frac{RT \exp(-f\eta_0)}{n^2 F^2 \sqrt{2\omega D_O}} \quad (9)$$

$$A = 1 - \alpha_c \exp(-\alpha_a f\eta_0) \times \frac{i}{nFk_s} \quad (10)$$

$$\lambda = \frac{k_s \exp(-\alpha_c f\eta_0)}{\sqrt{D_O}} \quad (11)$$

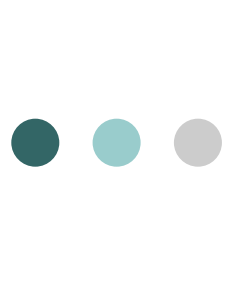
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The concentration of M^{n+} ions is outside the equations obtained

GENERALIZATION





The main general regularities

At constant E and ω , the capacitance is a linear function of current density:

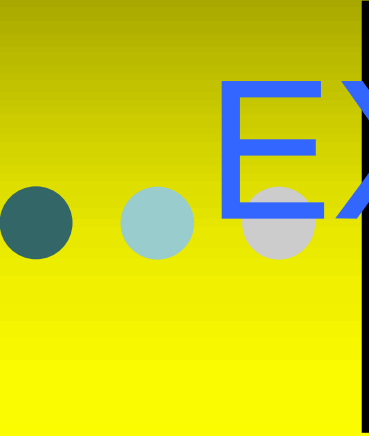
$$C_s = C_0 - k i$$

(anodic $i > 0$).

The term C_0 is specified by diffusion parameters, whereas the quantity k depends on the kinetic parameters of the charge transfer process.

Both C_0 and k vary linearly with $1 / \sqrt{\omega}$

Both C_0 and k are exponential functions of the electrode potential

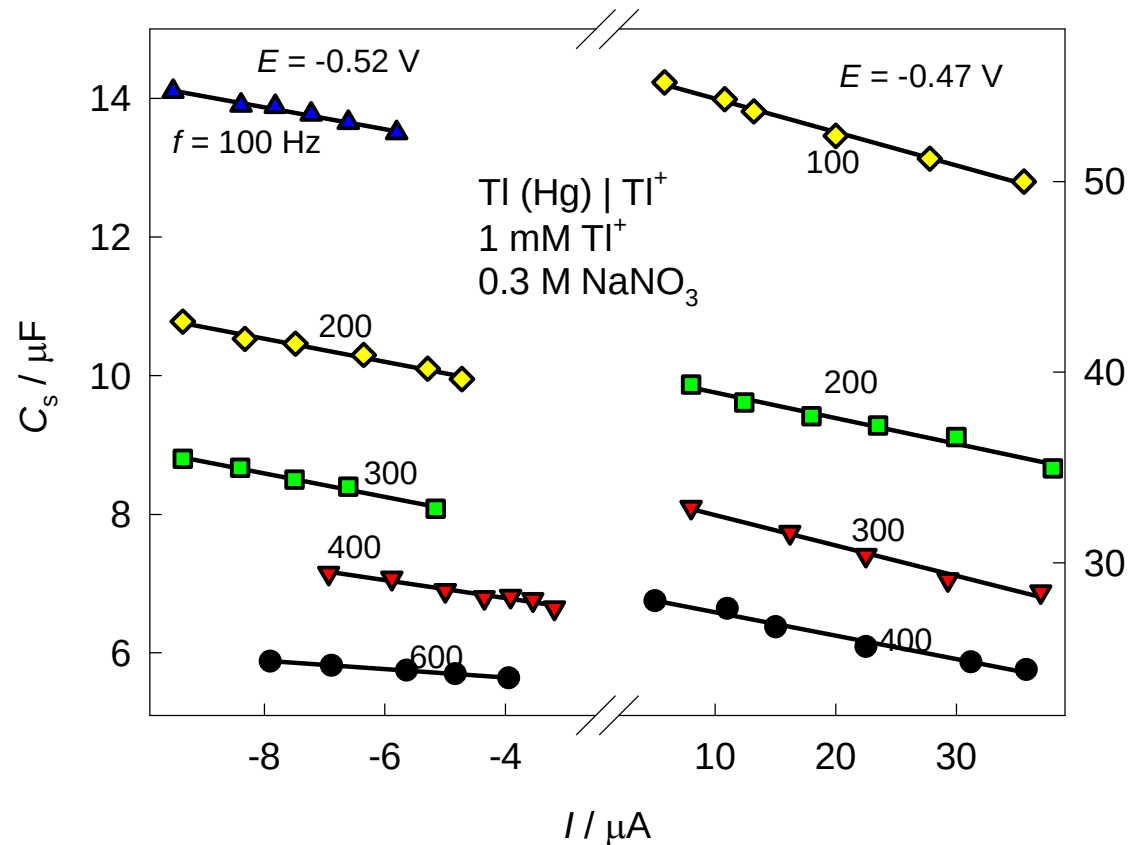


EXPERIMENTAL DATA

Moderate frequencies

Experimental data

System Tl | Tl⁺



In line with the theory,

C_s varies linearly with I

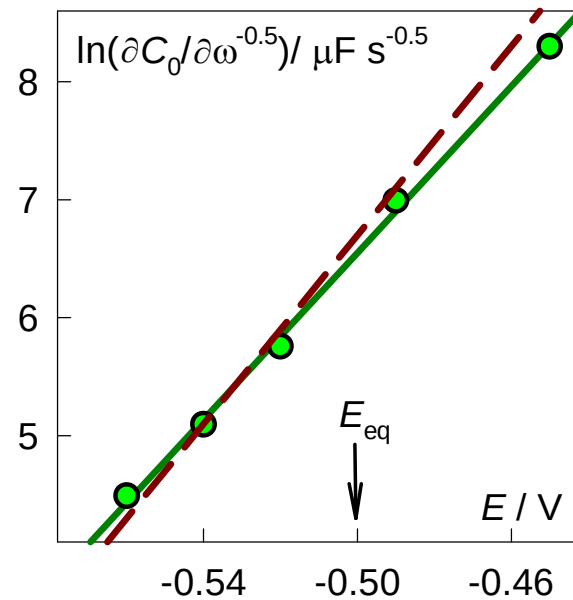
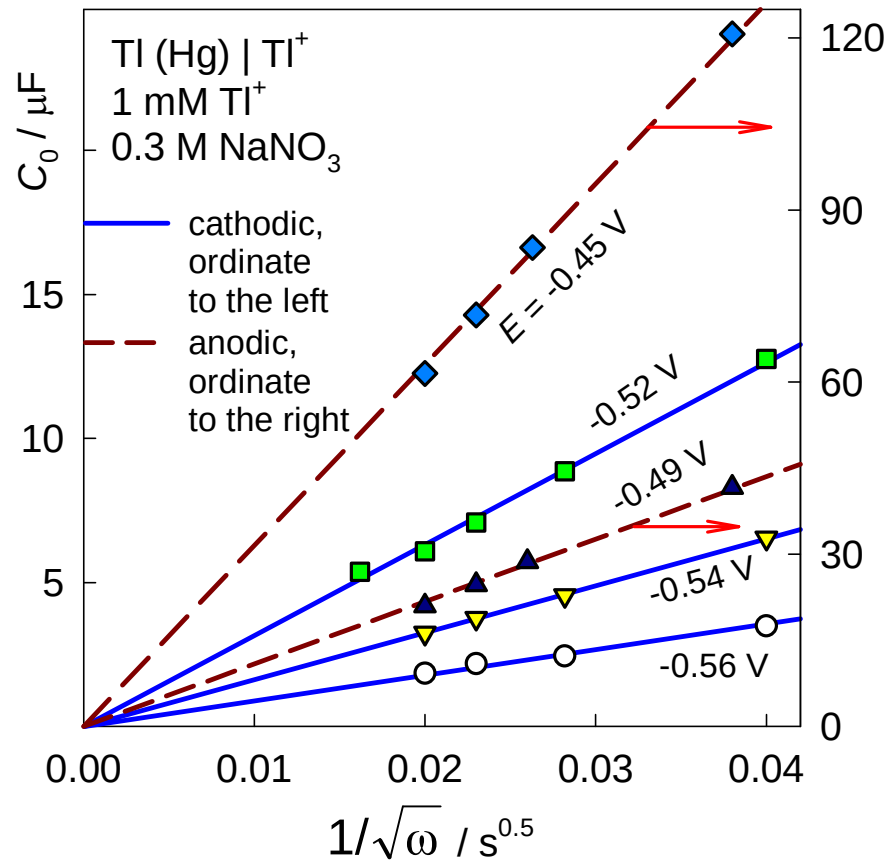
C_s increases with
cathodic current

C_s decreases with
anodic current

The electrode surface area is ignored

Experimental data

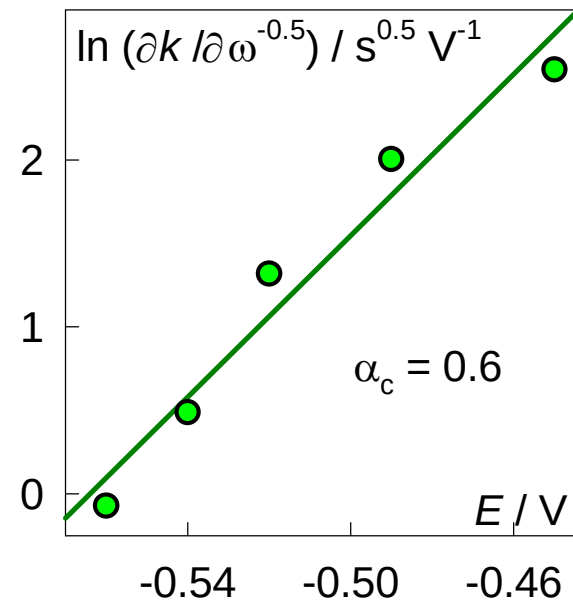
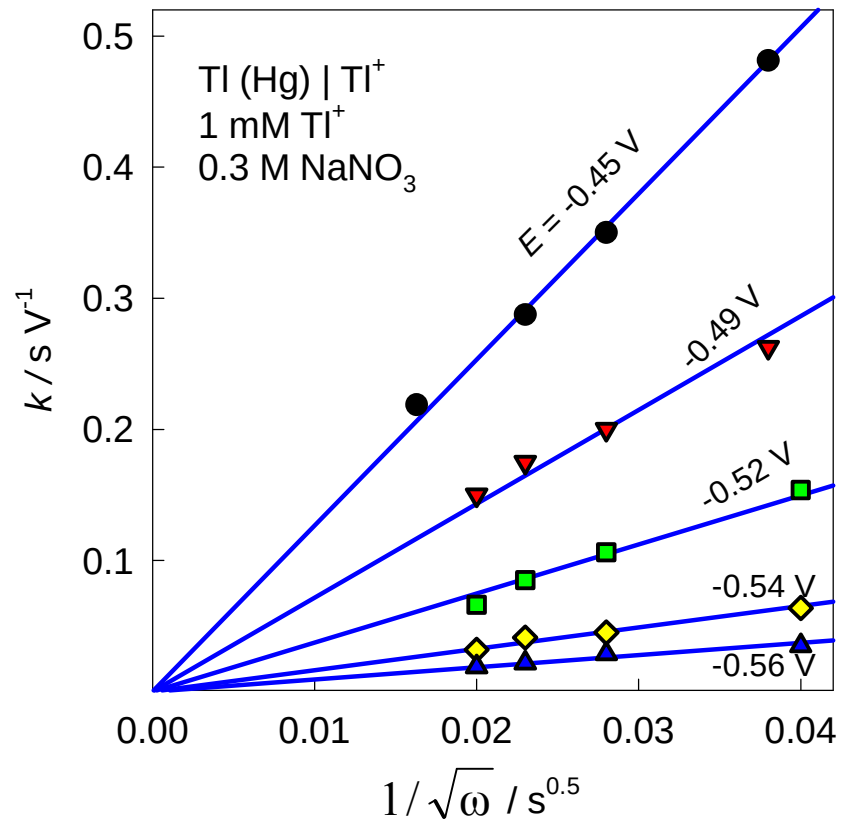
System TI | TI⁺



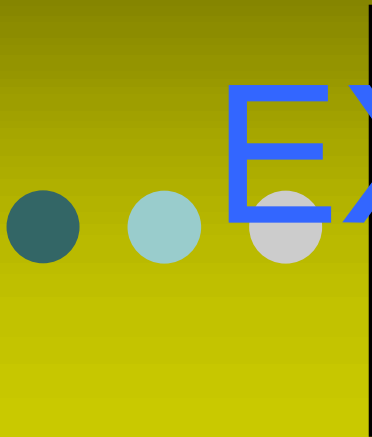
In line with the theory,
 C_0 varies linearly with $1/\sqrt{\omega}$
Slope is the exponential of E

Experimental data

System TI | TI⁺



In line with the theory,
 k varies linearly with $1/\sqrt{3}$
Slope is the exponential of E

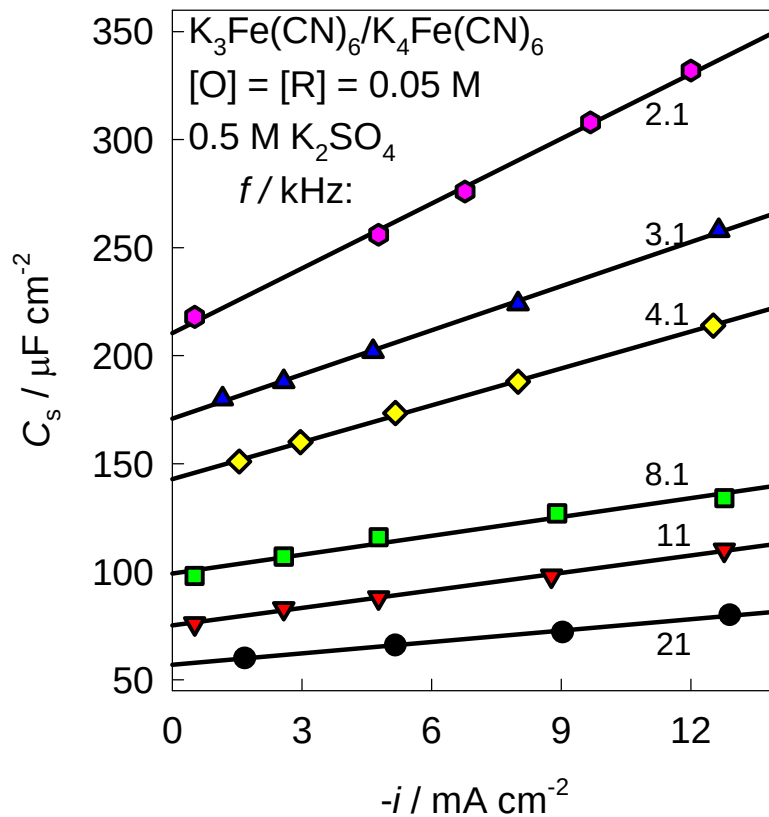


EXPERIMENTAL DATA

Higher frequencies

Experimental data

System $\text{K}_3\text{Fe}(\text{CN})_6 \mid \text{K}_3\text{Fe}(\text{CN})_6$



C_s varies linearly with i

C_s increases with cathodic current

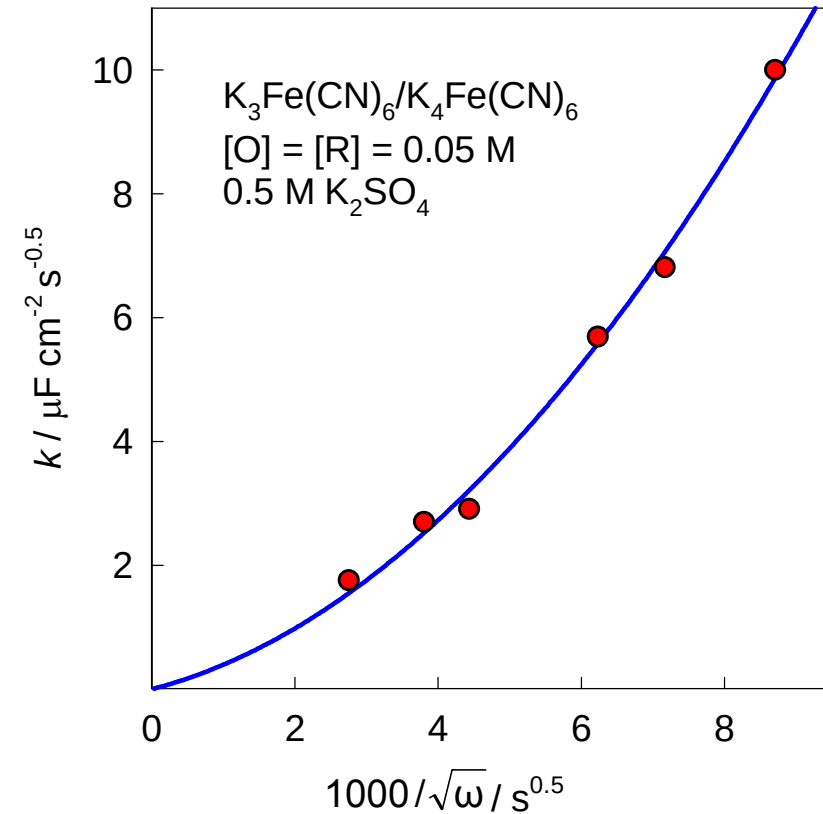
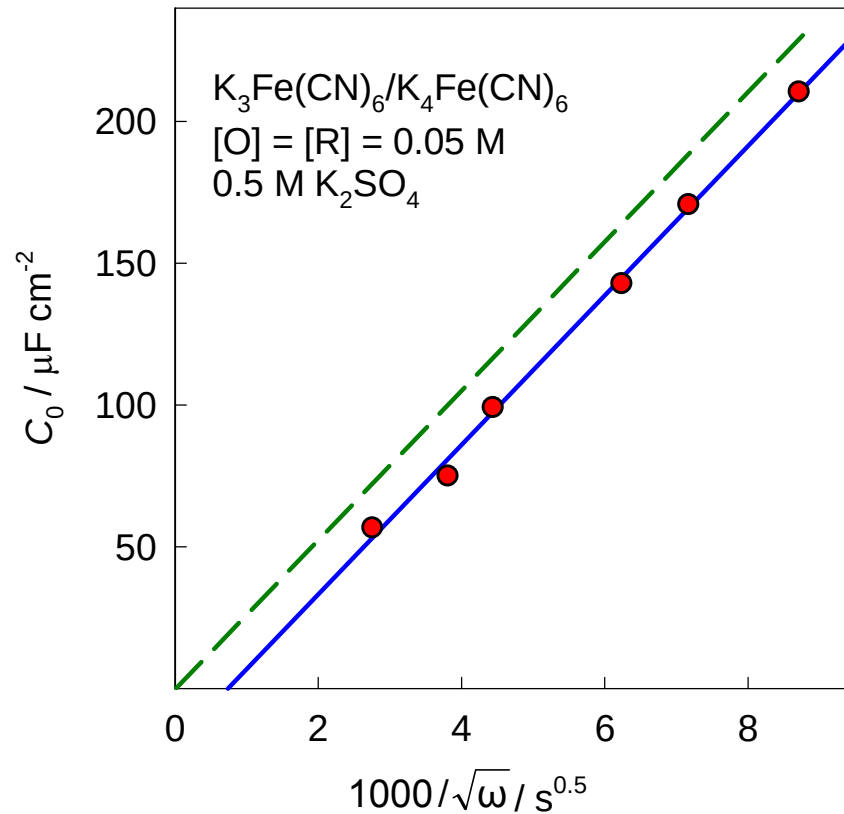
Slope decreases with frequency

No elimination of non-faradaic elements



Experimental data

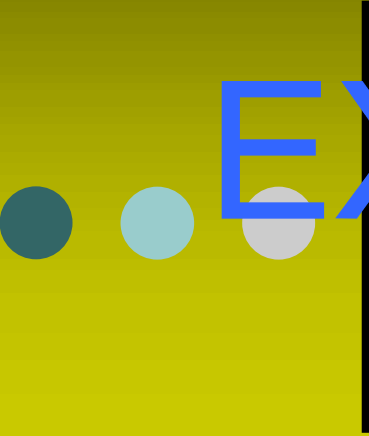
System $\text{K}_3\text{Fe}(\text{CN})_6$ | $\text{K}_4\text{Fe}(\text{CN})_6$



A shift of $C_0 - \omega^{-0.5}$ line occurs

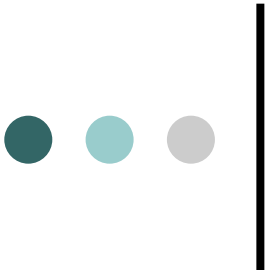
Curvature of $k - \omega^{-0.5}$ line is observed

Elimination of the double-layer impedance is desirable



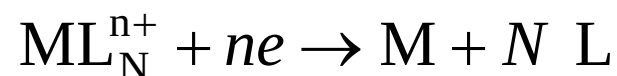
EXPERIMENTAL DATA

Complex systems

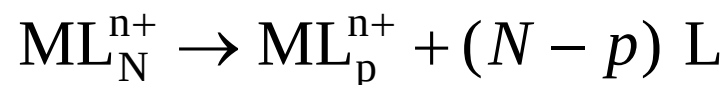


Systems involving metal complexes (The CE mechanism)

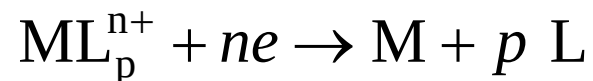
Overall electrochemical process



Preceding chemical reaction



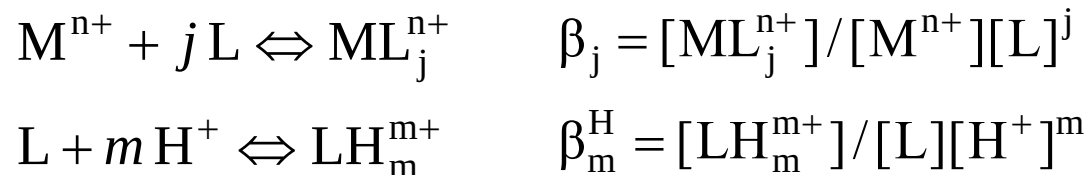
The charge transfer step involving the
electrochemically active complex (EAC)





Systems involving metal complexes

Chemical interactions



The total metal concentration

$$c_M = [M^{n+}] + [ML^{n+}] + [ML_2^{n+}] + \cdots + [ML_N^{n+}]$$

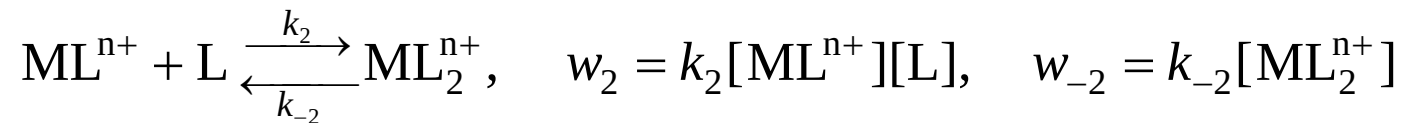
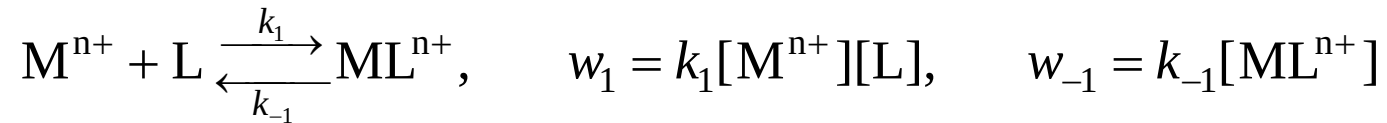
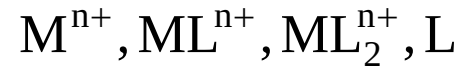
The total ligand concentration,

$$c_L = [L] + [ML^{n+}] + 2[ML_2^{n+}] + \cdots + N[ML_N^{n+}]$$



Systems involving metal complexes

Mass transport of chemically interacting species



$$\frac{\partial[M^{n+}]}{\partial t} = D \frac{\partial^2[M^{n+}]}{\partial x^2} - w_1 + w_{-1} \quad \frac{\partial[ML_2^{n+}]}{\partial t} = D \frac{\partial^2[ML_2^{n+}]}{\partial x^2} + w_2 - w_{-2}$$

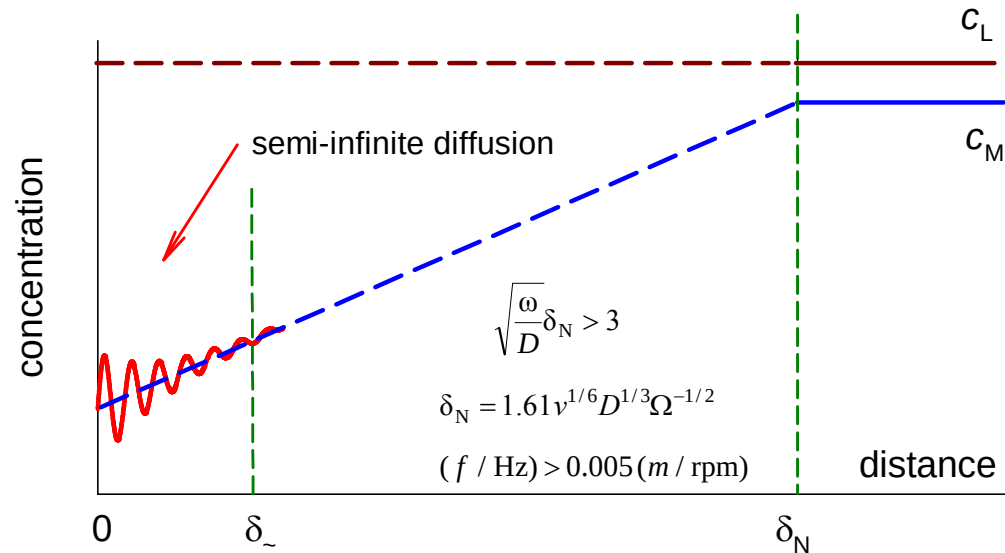
$$\frac{\partial[ML^{n+}]}{\partial t} = D \frac{\partial^2[ML^{n+}]}{\partial x^2} + w_1 - w_{-1} - w_2 + w_{-2}$$

$$\frac{\partial[L]}{\partial t} = D \frac{\partial^2[L]}{\partial x^2} - w_1 + w_{-1} - w_2 + w_{-2}$$

Systems involving metal complexes

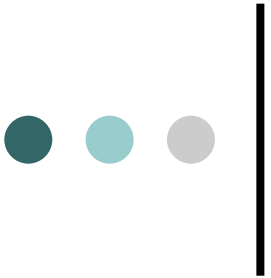
Mass transport of chemically interacting species

1) A linear profile of the total metal concentration arises in the Nernst-type diffusion layer



2) The total ligand concentration remains constant and equal to that in the bulk of solution

3) The latter is also valid for proton donors and acceptors



The relationships obtained at the excess of ligand

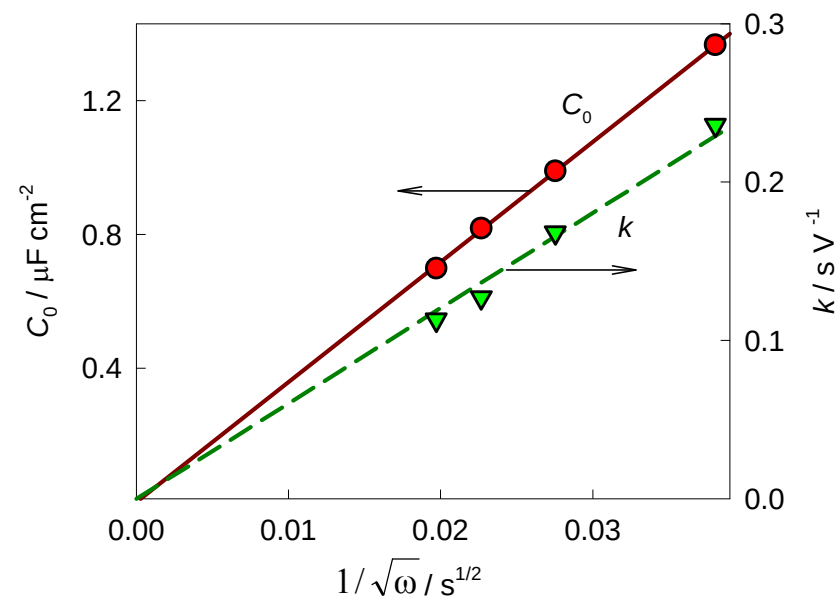
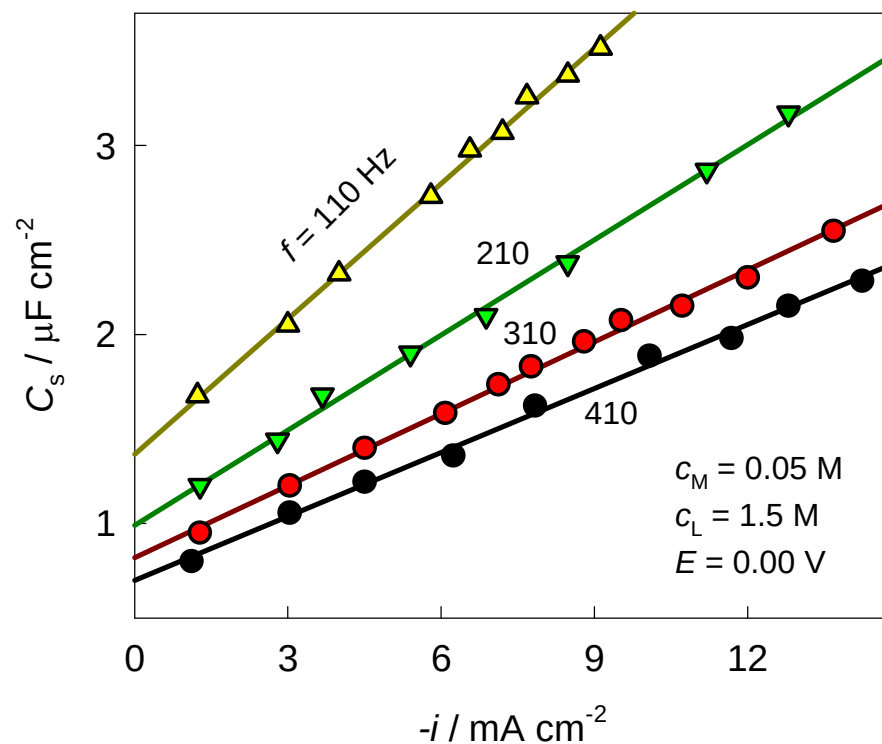
$$C_0 = \frac{n^2 F^2 \beta_N c_L^N \sqrt{\frac{2D}{\omega}}}{RT} \exp\left(\frac{nF}{RT} \eta_{00}\right)$$

$$k = \frac{nF \beta_N c_L^{N-p} \alpha_c \sqrt{\frac{2D}{\omega}}}{RT \beta_p^{\alpha_a} k_s} \exp\left(\frac{\alpha_c nF}{RT} \eta_{00}\right)$$

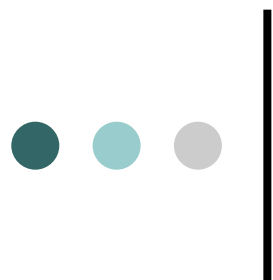
η_{00} is the overvoltage reckoned from the formal potential of the $M | M^{n+}$ electrode.

Experimental data

System Ag | Ag(I), KSCN

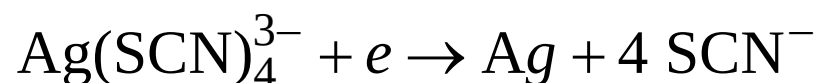


C_s varies linearly with i
 C_s increases with cathodic current
 Slope k decreases with frequency

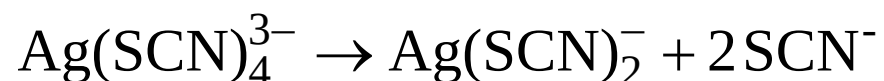


Results

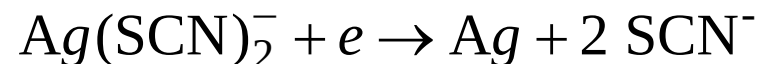
Overall electrochemical process



Preceding chemical reaction



The charge transfer step involving the electrochemically active complex (EAC)





Results

Stability constants of EAC and
predominating complex :

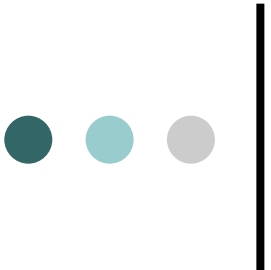
$$\log \beta_2 = 7.6 \quad \log \beta_4 = 10.3$$

Effective diffusion coefficient

$$D = 9.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$$

Kinetic parameters

$$\alpha_c = 0.5 \quad k_s = 0.4 (\text{cm s}^{-1}) \times (\text{mol cm}^{-3})^{-0.5}$$



CONCLUSIONS

- The suggested EIS modification involves impedance measurements at constant electrode potential and different intensities of the forced convection.
- The resulting faradaic impedance is represented by the frequency-dependent resistance R_s and capacitance C_s in series.
- Easy-to-analyze linear dependences of C_s vs. i and others are obtained.
- The experimental data obtained for redox processes $O + n e \rightarrow R$, $M^{n+} + n e \rightarrow R$ are in line with the derived analytical expressions.
- To obtain analytical relationships for processes involving labile complexes of metals, simplifying conditions should be accepted.

THANK YOU FOR YOUR
KIND ATTENTION

