Theory of Charge Transport in Mixed Conductors: Description of Interfacial Contributions Compatible with the Gibbs Thermodynamics

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Content

- Introduction: mixed transport.
- Randles impedance. Interfacial capacitance. Formulation of the problem.
- Thermodynamics of charged interfaces. Conditions at interfaces for transport.
- Analytical expressions for impedance. Graphical illustrations.
- New systems: "mixed interfacial exchange".
- Conclusions.

medium 1

film : 2 mobile species plus fixed charges

medium 2

Film (f) :

- conducting or redox polymers,
- electron-ion conducting oxides/hydrids/sulfides,
- Li^{+} & Mg^{++} intercalation layers,
- solid electrolytes,
- thin layers of a binary solution.

Species :

- electronic and ionic (e, i) plus fixed charge,
- cations and anions.

Media 1 et 2 :

- electronic conductor (m),
- ionic conductor (s).

Tree types of systems :

- **m/f/m'** : between two electronic conductors,
- **s'/f/s** : "membrane geometry",
- **m/f/s** : "modified electrode"

Electrochemical Impedance Spectroscopy

- transport properties,
- interfacial characteristics

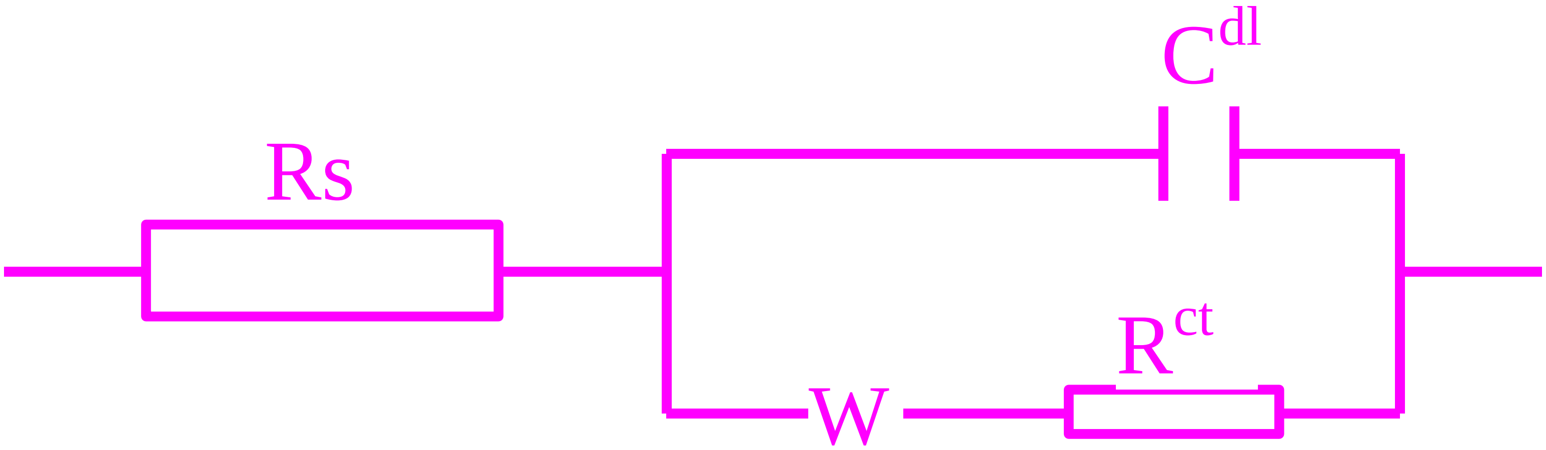
Based on :

- analytical analysis,
- equivalent circuit.

To be included :

- bulk film transport,
- charge transfer across the interfaces ("faradaic"),
- charge of interfaces (charge of "double layers")

Randles Impedance : metal / solution
Supporting electrolyte + Redox species



General hypothesis :

- consider the process without interfacial charge,

- add "double layer capacitance" C^{dl} parallel to the "faradaic branch".

System containing only **two** mobile species:

- no supporting electrolyte,

- the **same** species participate at each interface

- in the "**faradaic" process**

(redox reaction or ion exchange)

as well as

- in the **interfacial charge**

⇨ these two processes are coupled to the same transport process (Warburg element).

Another complication :

metal	EDL	diffusion layer	bulk solution
σ	σ_+ ,σ_-		$i_k = t_k\, i$

Composition of the double layer (charges σ_+ , σ_-) is determined by **properties of the interface**.

Partial currents i_k in the bulk solution are determined by **transport numbers t_k** .

This discrepancy of the partial currents and the variation of charges σ_+ , σ_- must be compensated by the **diffusion layer**

$\Rightarrow$ its impedance (analogue of W) must be a **function of t_k** as well as **of parameters determining σ_+ and σ_-**

Conclusion : **capacitance C^{dl} is not sufficient** to characterize the charging of interfaces !

Thermodynamics of interfaces – binary solution:

2 independent variables, e.g. σ & $\mu = \mu_+/z_+ - \mu_-/z_-$

solution: μ

EDL: σ_+ , σ_-

metal: σ

$$dE_+ = (C^{dl})^{-1}\, d\sigma - t_-^{dl}\, d(\mu/F)$$

$$d\sigma_+ = - t_+^{dl}\, d\sigma - C_\mu^{dl}\, d(\mu/F)$$

$$d\sigma_- = - t_-^{dl}\, d\sigma + C_\mu^{dl}\, d(\mu/F)$$

THREE independent interfacial parameters:

(1) $\mathbf{C^{dl}}$, interfacial capacitance ("capacitance of the electrical double layer"),

(2) $\mathbf{t_+^{dl}}$ et $\mathbf{t_-^{dl}}$, "interfacial numbers of species" :

$\sigma_+ + \sigma_- = - \sigma \quad \Rightarrow \quad t_+^{dl} + t_-^{dl} = 1$

The same coefficient t_-^{dl} for dE_+ et for $d\sigma_-$,

(3) $\mathbf{C_\mu^{dl}}$, "asymmetry factor of the interfacial charge"

Electrolyte without specific adsorption :

theory of Gouy-Chapman-Grahame

- these parameters are functions of σ and μ ,
- generally, $C_\mu^{dl} \sim C^{dl}$; $0 \leq t_+^{dl}, t_-^{dl} \leq 1$

Specific adsorption : $t_k^{dl} < 0$ or $t_k^{dl} > 1$

$$i_k(0,t) = i_k^{dl} + i_k^{ct}$$

$$i_k^{dl} = - d\sigma_k / dt$$

$$i_k^{ct} = [\mu_k^{ext} - \mu_k(0,t)] / z_k F R_k^{ct} \equiv (E_k - E_k°) / R_k^{ct}$$

Transport equations + conditions at interfaces

Their combined solution gives analytical expressions of impedance $Z(\omega)$ for 3 geometries of the system : **m/f/m'** (different metals), **m/f/s**, **s'/f/s**.

m/f/m : film between two identical metals

$$Z^{m/f/m} = R_f + 2\,Z^{m/f} + 4\,W_f\,(\,\delta t_i\,)^2\,[\coth \nu + F^{m/f}]^{-1}$$

$$Z^{m/f} = (\,1\,/\,R_e^{m/f} + j\omega\,C^{m/f}\,)^{-1}$$

$$W_f = \Delta R_f\ \ \nu^{-1}\,; \qquad \nu = (\,j\omega\,L^2\,/\,4D\,)^{1/2}$$

$$\delta t_i = t_i - t_i^{m/f}\,(1 - g^{m/f}\,)\,;\ \ g^{m/f} = (1 + j\omega\,R_e^{m/f}\,C^{m/f}\,)^{-1}$$

$$F^{m/f} = 2\,W_f\,j\omega\,[\,(\,t_i^{m/f}\,)^2\,g^{m/f}\,C^{m/f} - C_\mu^{m/f}\,]$$

m/f/s : film between a metal and a solution

$$Z^{m/f/s} = R_s + R_f + Z^{m/f} + Z^{f/s} + 2\, W_f\; Z_a / Z_b$$

$$Z_a = (\delta t_i)^2 (\coth 2\nu + F^{f/s}) + 2\, \delta t_i\, \delta t_e (\sinh 2\nu)^{-1}$$
$$+ (\delta t_e)^2 (\coth 2\nu + F^{m/f}) ;$$

$$Z_b = 1 + (F^{m/f} + F^{f/s}) \coth 2\nu + F^{m/f} F^{f/s}$$

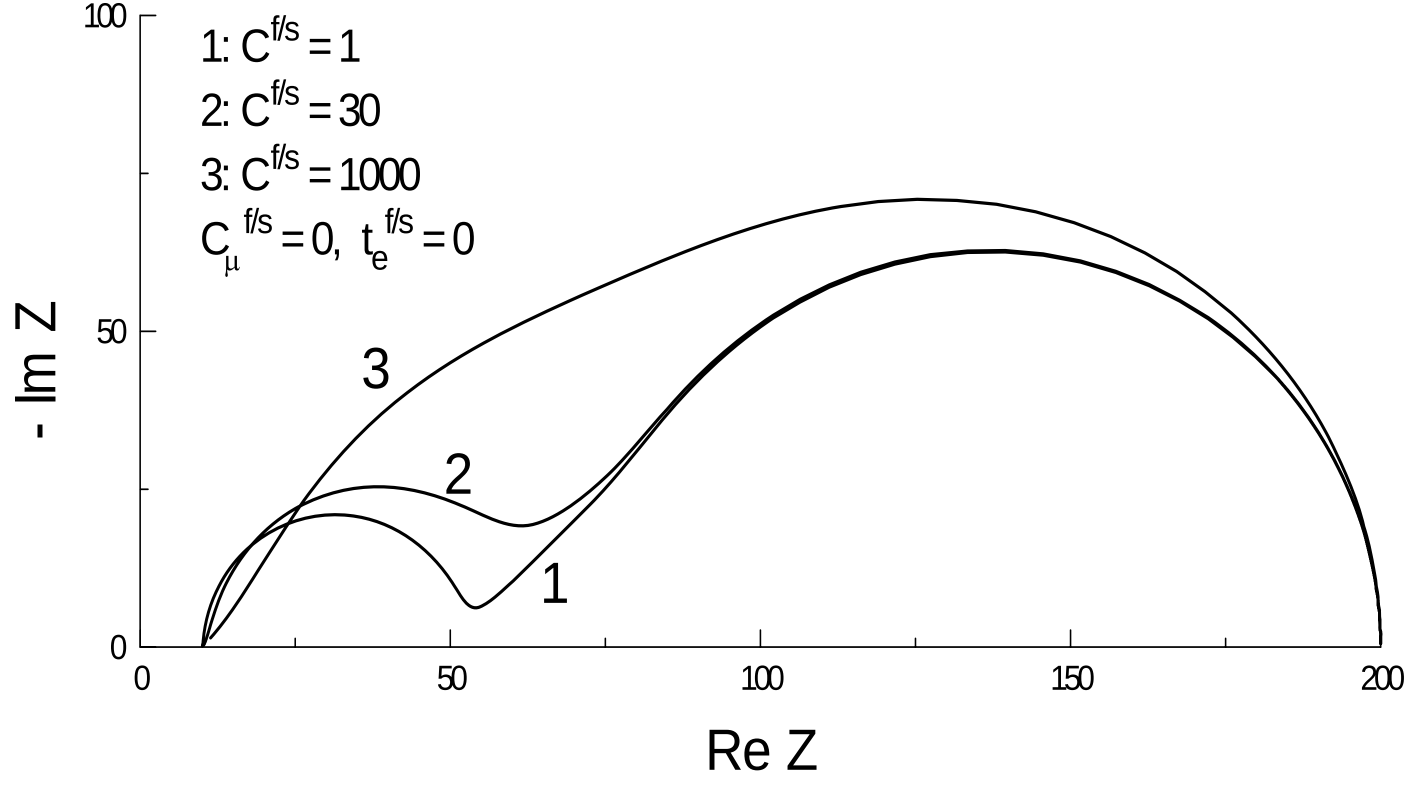
s/f/s : particular case, $t_e^{f/s} = 0$, $C_\mu^{f/s} = 0$

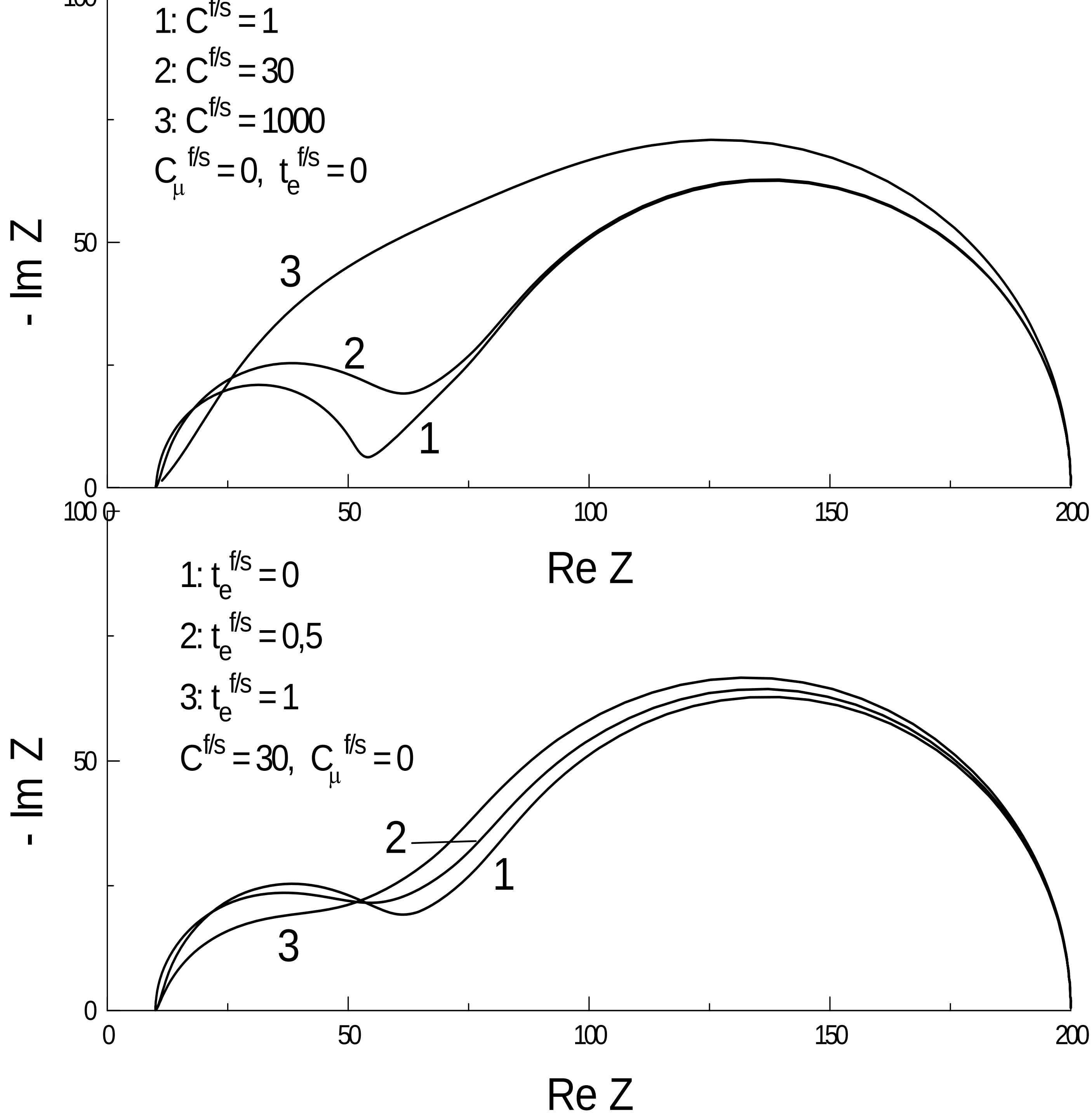
$$Z^{s/f/s} = R_f + 2\, Z^{f/s} + 4\, W_f\, t_e^2 \tanh \nu$$

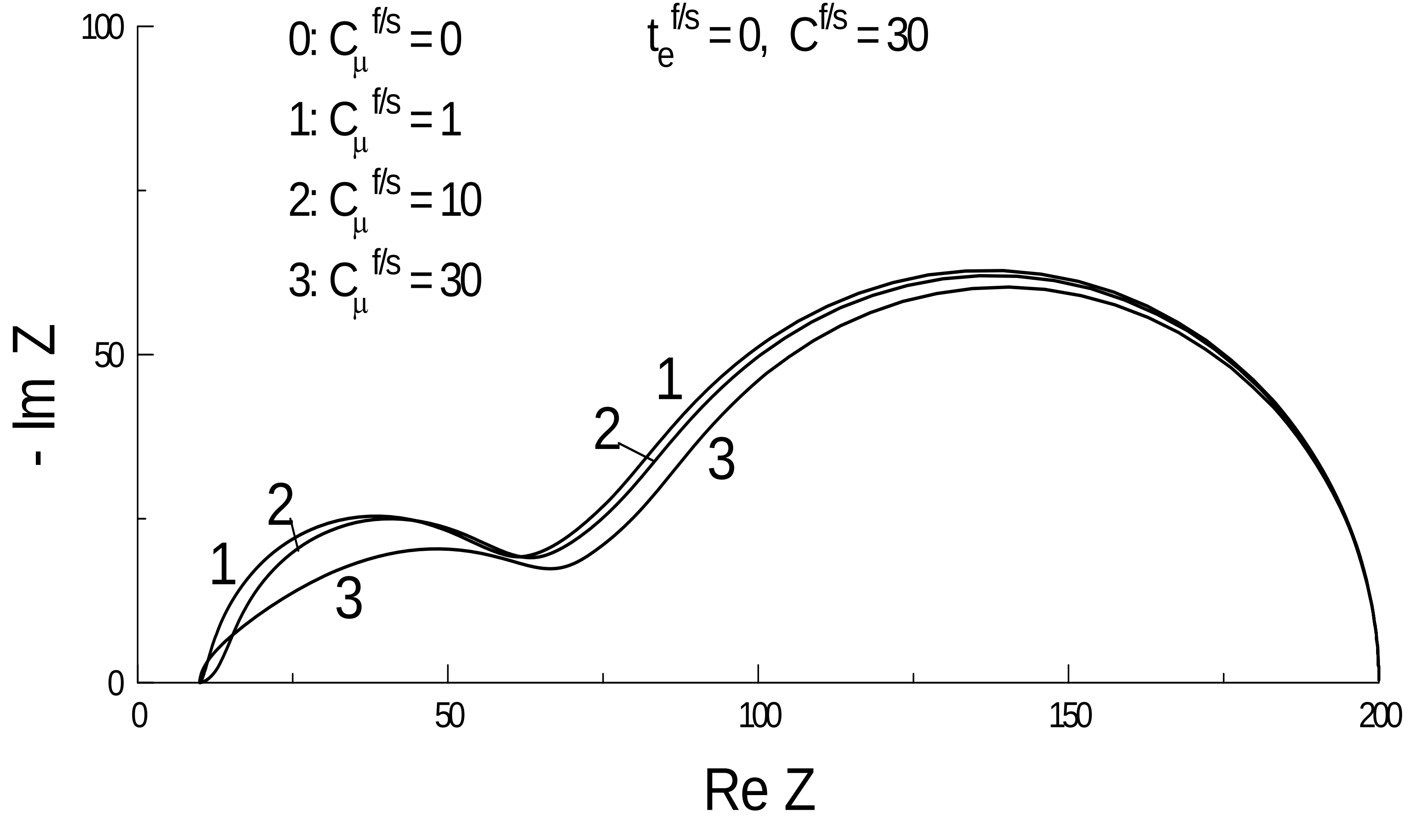
$$Z^{f/s} = \left(1 / R_i^{f/s} + j\omega\, C^{f/s} \right)^{-1}$$

$W_f = \Delta R_f\ \nu^{-1}$; $\nu = \left(j\omega\, L^2 / 4D \right)^{1/2}$

Symmetrical membrane geometry: film between two identical solutions, s/f/s



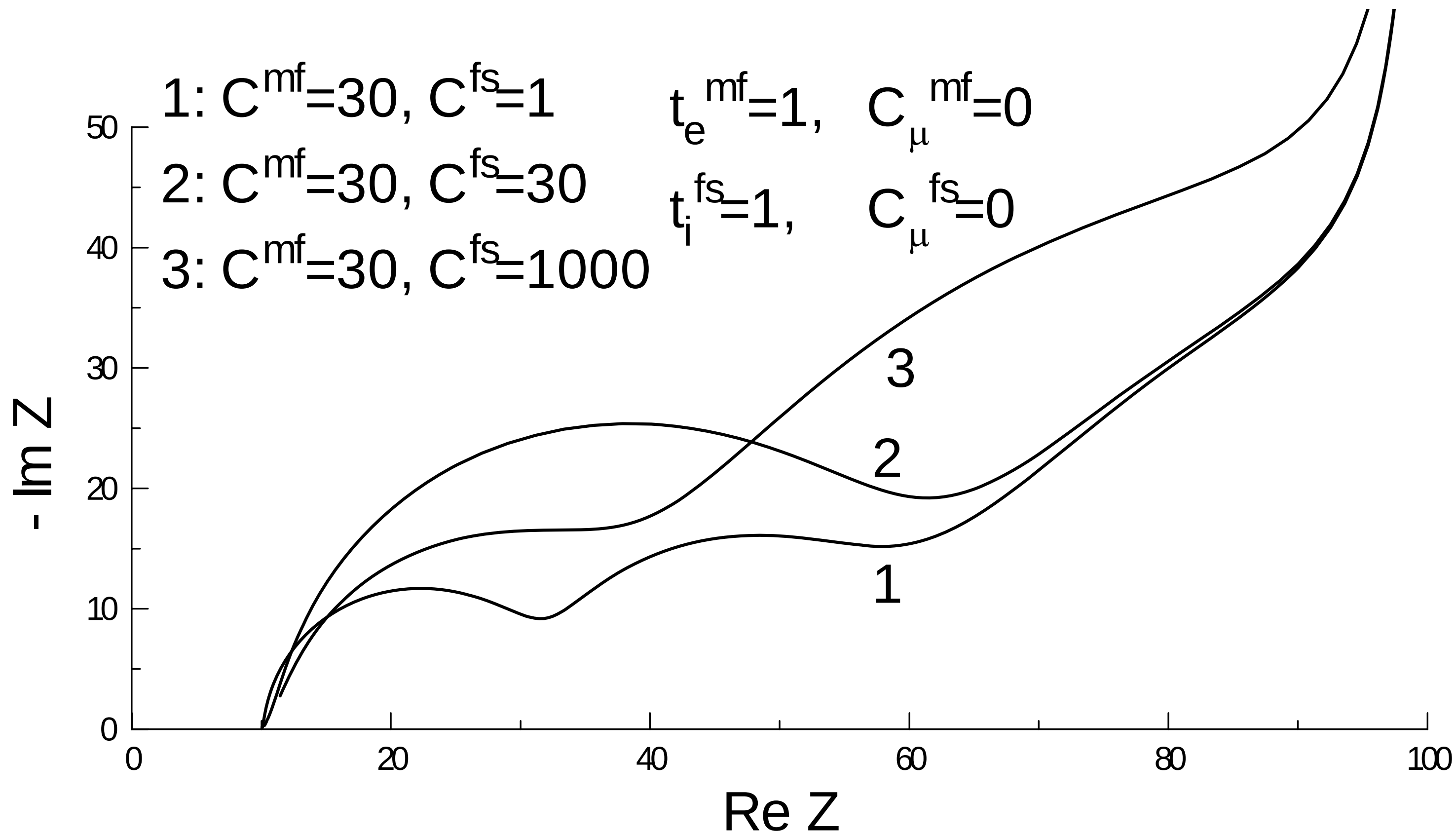

1: C^f/s = 1
2: C^f/s = 30
3: C^f/s = 1000
C_μ^f/s = 0, t_e^f/s = 0
- Im Z
Re Z
0
50
100
150
200
1
2
3
1: t_e^f/s = 0
2: t_e^f/s = 0,5
3: t_e^f/s = 1
C^f/s = 30, C_μ^f/s = 0
- Im Z
Re Z
0
50
100
150
200
1
2
3

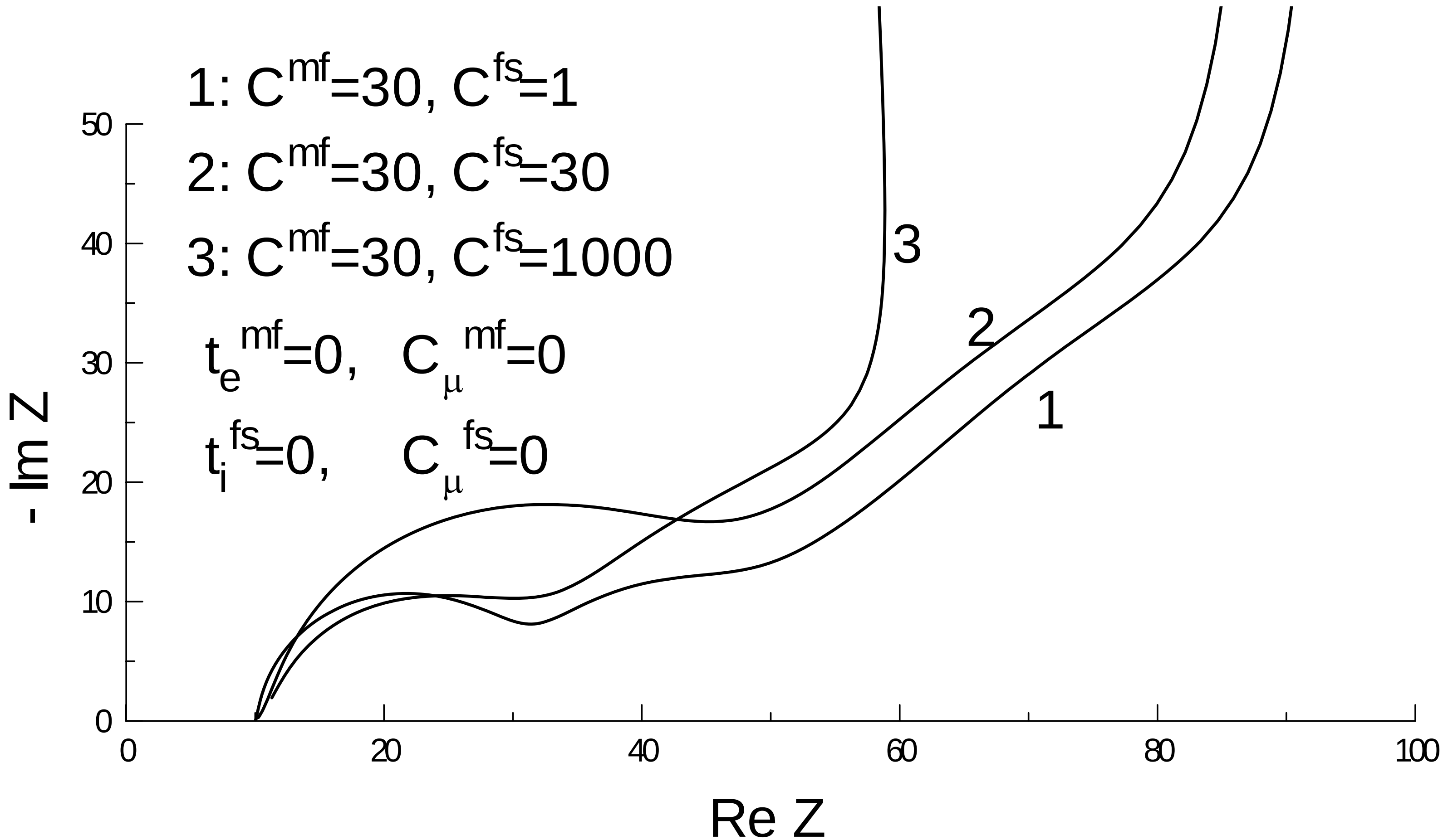


0: $C_\mu^{f/s} = 0$
1: $C_\mu^{f/s} = 1$
2: $C_\mu^{f/s} = 10$
3: $C_\mu^{f/s} = 30$
$t_e^{f/s} = 0$, $C^{f/s} = 30$
- Im Z
Re Z
100
50
0
0
50
100
150
200
1
2
3
1
2
3

Modified Electrode Geometry:

film between a metal and a solution, m/f/s





1: C^{mf}=30, C^{fs}=1
2: C^{mf}=30, C^{fs}=30
3: C^{mf}=30, C^{fs}=1000
t_e^{mf}=0, C_μ^{mf}=0
t_i^{fs}=0, C_μ^{fs}=0
3
2
1
- Im Z
Re Z
0
10
20
30
40
50
0
20
40
60
80
100

metal (e)

electron exchange

film : e + i

ion exchange

solution (i)

metal (e)

electron exchange

film : e + i

electron + ion exchange

electroactive solution (e,i): Red $\leftrightarrow$ Ox + ne

New geometries: m/f/es, es'/f/es, s/f/es

Similar treatment of boundary conditions for transport

Analytical solutions for all new geometries

New experimental possibilities: one can obtain impedance data for numerous systems having the same values of the bulk film and interfacial parameters

CONCLUSIONS

- there is no simple way to insert the contribution of the interfacial charge in the final expression for complex impedance.

- contrary to expectations, interfacial capacitance C^{dl} is not sufficient to characterize this contribution : impedance also depends on interfacial numbers $t_{\pm}^{dl}$ as well as parameter C_{μ}^{dl}.

- thin film with a mixed conductivity : one can obtain analytical expressions Z(ω) in the cases :

1. between two metals (identical or different),
2. between two solutions ("membrane geometry"),
3. between a metal and a solution ("modified electrode").

- if the charging of the double layer is realized completely by the "faradaic" species, the effect of the interfacial charge is very simple : capacitance C^{dl} in parallel to $R_e^{m/f}$ or $R_i^{f/s}$.

- general case : impedance plots are markedly deformed with respect to this simple case.

Application of simplified formulae can lead to serious errors in the value of capacitance C^{dl} found from the treatment of experimental data.

- new prospects to extract the bulk-film and interfacial parameters of the system are provided by "non-traditional" arrangements, films in contact with "electroactive solutions".

Analytical formulae for complex impedance are now available for all possible 1D geometries:

m'/f/m, s'f/s, m/f/s, m/f/es, es'/f/es, s/f/es