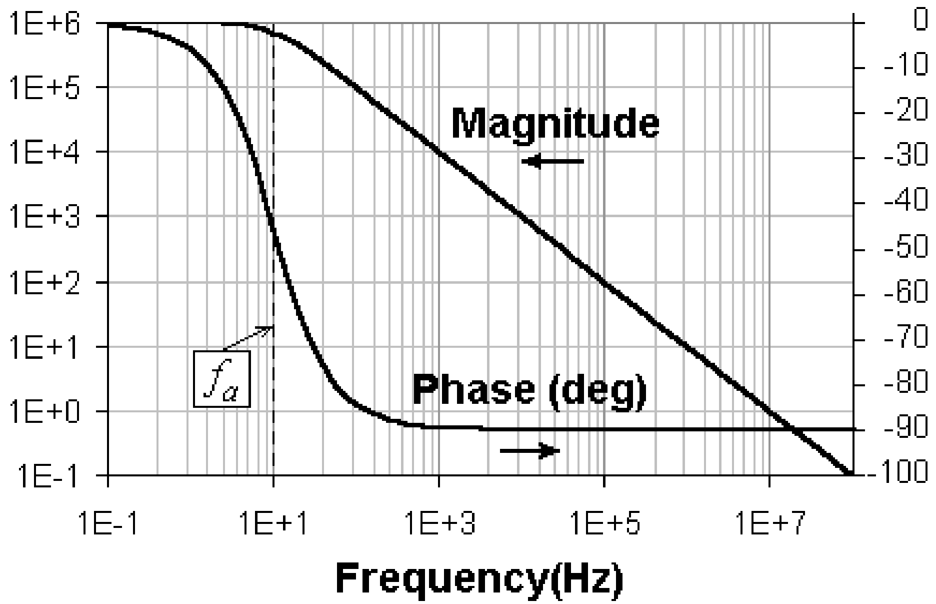
Impedance :
Other Transfer Functions (TF)



CONTENTS

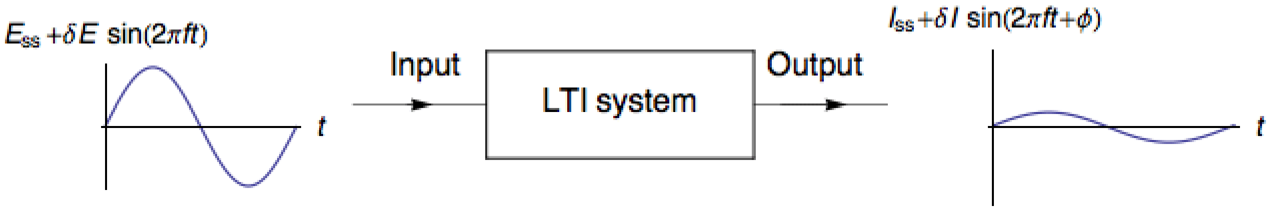
Background on EIS

Other Transfer Functions:

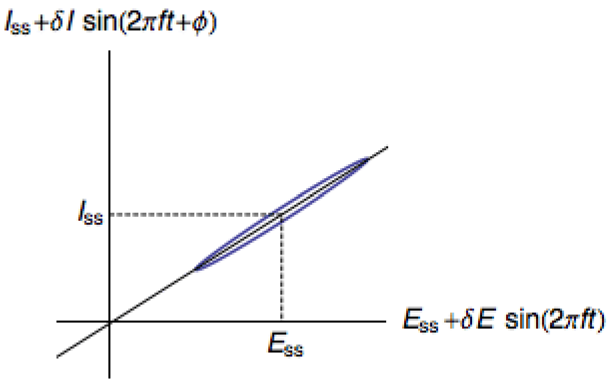
- Photo-electrochemical TF (IMVS/IMPS)
- Electro-hydrodynamic TF (EHD)
- Magneto-hydrodynamic TF
- Electro-gravimetric TF
- Raman spectro TF
- Thermo-electrochemical TF (TEC)
- Pneumato-chemical Impedance Spectroscopy (PIS)
- …

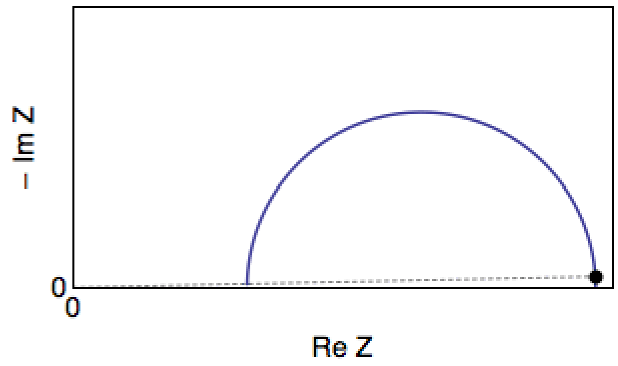
Summary

BACKGROUND



Current response has a the same frequency with an **amplitude δI** and **phase Φ**
Perturbation in potential, (it is also possible to perform the same in Galvano)





Increasing the frequency → moving away from the steady state I_{ss} vs E curve

$Z(f) = \mathcal{L}E(t)/\mathcal{L}I(t)$

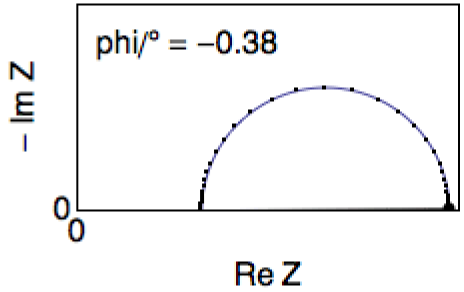
$\mathcal{L}$: Laplace Transform

The impedance is a complex number:

$Z = a + jb = Re(Z) + jIm(Z)$ (with $j^2 = -1$)

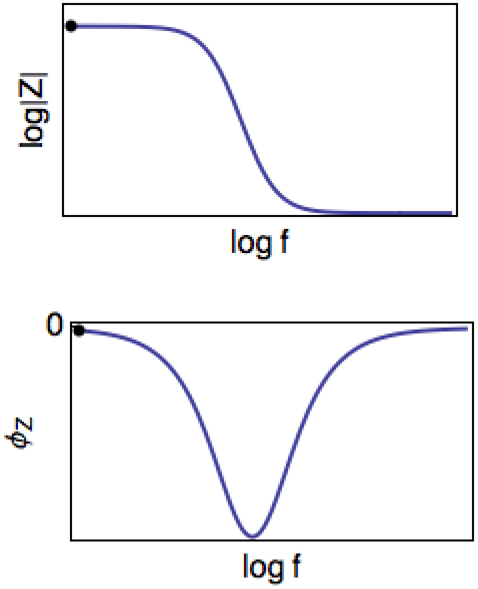
$Z = \rho(\cos\varphi + j\sin\varphi)$ with ρ the modulus and φ the phase

Nyquist diagram



In the Nyquist plot, the impedance for each frequency is plotted in the complex plane -Im(Z) *vs* Re(Z).

Bode diagram



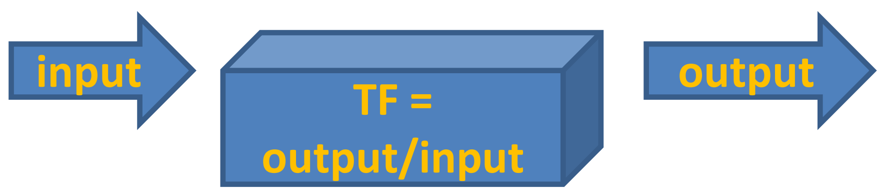
In the Bode Plot, the modulus and the phase of the impedance are plotted against the frequency of the modulation.

What if we replace U and/or I by other input/output quantities? Not only electrical quantities.

It chemical Impedance Spectroscopy but Transmittance spectroscopy
This allows one to study the dependence (output) of the system to an input

It is a measurement of magnitude and phase of the output as a function of frequency, in comparison to the input.

Unit is not in Ohm but is the *ratio* of the two quantities
H = output/input



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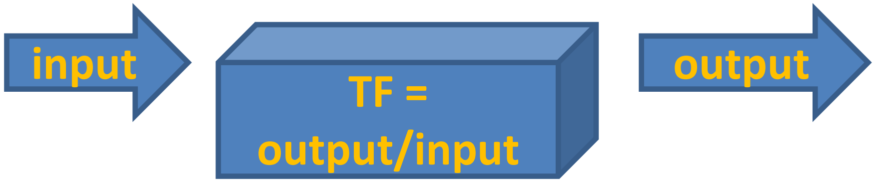
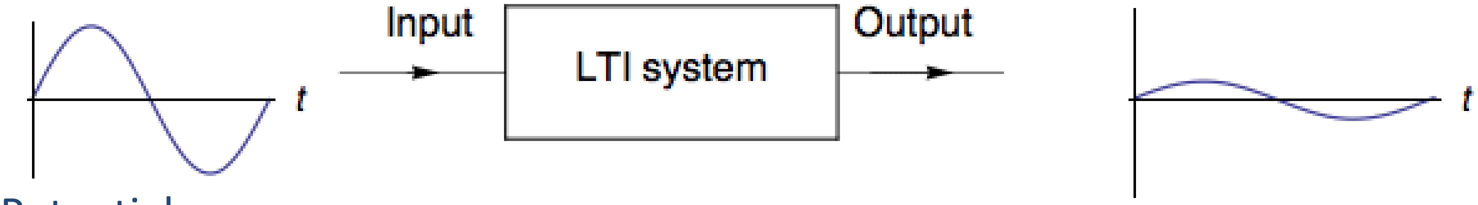


$$F(\text{input}) = \text{input} \times \text{TF} = \cancel{\text{input}} \times \frac{\text{output}}{\cancel{\text{input}}} = \text{output}$$

BACKGROUND

What about if we replace E and/or I by other input/output quantities?
Not only electrical quantities.



Potential
Current
Temperature
Pressure
Rotation speed of the electrode
Magnetic field
Light intensity
…

Potential
Current of the electrode
Current of the secondary electrode
Temperature
Pressure
Magnetic field
…

Other Transfer Functions:

	Input	Output	ref
IMPS/IMVS	Light intensity/ϕ	PhotoCurrent/I Photovoltage/E	Halme, J. Phys. Chem. Chem. Phys., 2011, 13, 12435–12446
Electro-hydrodynamic TF (EHD)	Rotation speed/Ω	Current/I Voltage/E	Tribollet *et al.* J. of Electroanal. Chem. , 2004, Vol. 572, 2, Pages 389–398
Magneto-hydrodynamic TF	Magnetic field/B	Current/I Voltage/E	Olivier *at al.* J. of Electrochem. Soc., 2004, Vol 151, 2, C112-C118,
Electro-gravimetric TF	Quartz resonator frequency/F or adsorbed mass/m Sauerbrey relationship: $\Delta F = k\Delta m$	Voltage/E	Perrot *et al*. The Journal of Physical Chemistry B, 2002, Vol. 106, 12, 3182-3191
Raman	Raman intensity/Count.s^{-1}	Current/I Voltage/E	Deslouis *et al.* Electrochimica acta, 2010, 55, 6299-6307
Thermo-electrochemical TF (TEC)	Temperature/T	Current/I Voltage/E	Olivier, A. *et al.* Electrochimica Acta, 1996, Vol 41, 17, 2731-2736
Pneumato-chemical Impedance Spectroscopy (PIS)	Pressure/P	Voltage/E	Millet, P. *et al.* J. Phys Chem B; 2005 109 24016-24024

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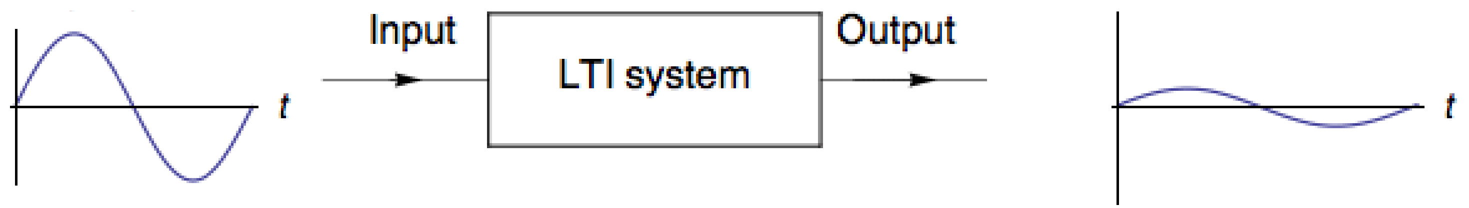
Each type of Transfer Functions is a disciplin itself.
We will see only the two first

IMVS/IMPS



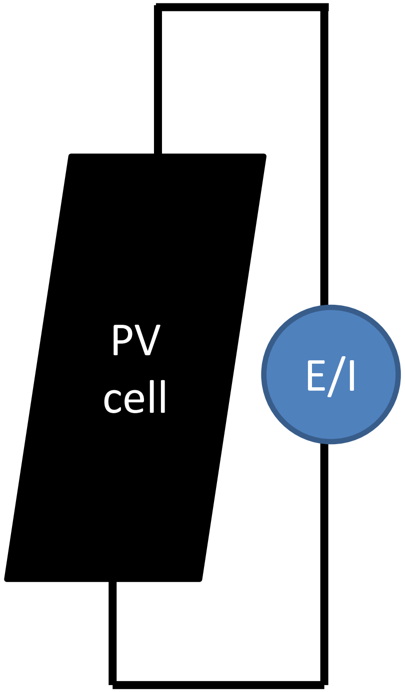
ϕ: light intensity

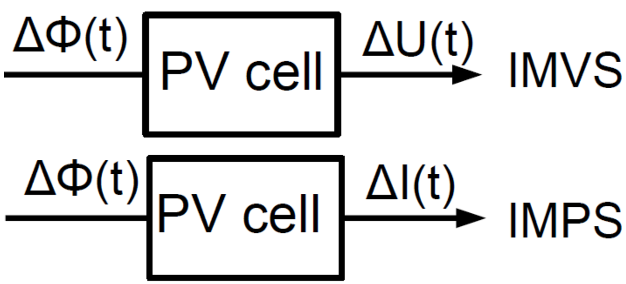
IMVS= $\mathcal{L}\Phi(t)/\mathcal{L}E(t)$

IMPS= $\mathcal{L}\Phi(t)/\mathcal{L}I(t)$

I: PhotoCurrent - IMPS
U: PhotoVoltage - IMVS

IMVS: **I**ntensity **M**odulated photo**V**oltage **S**pectroscopy
IMPS: **I**ntensity **M**odulated **P**hotocurrent **S**pectroscopy





Which system?

Solar cell, Grätzel cell,

Which information?

- $D \approx a \cdot d^2 / \tau_{IMPS}$

where a ≈ 0.393 for weakly absorbed modulated light

D: diffusion coefficient of electrons/$m^2.s^{-1}$

d: photoelectrode film thickness/m

- $\tau_{IMPS} \approx \tau$

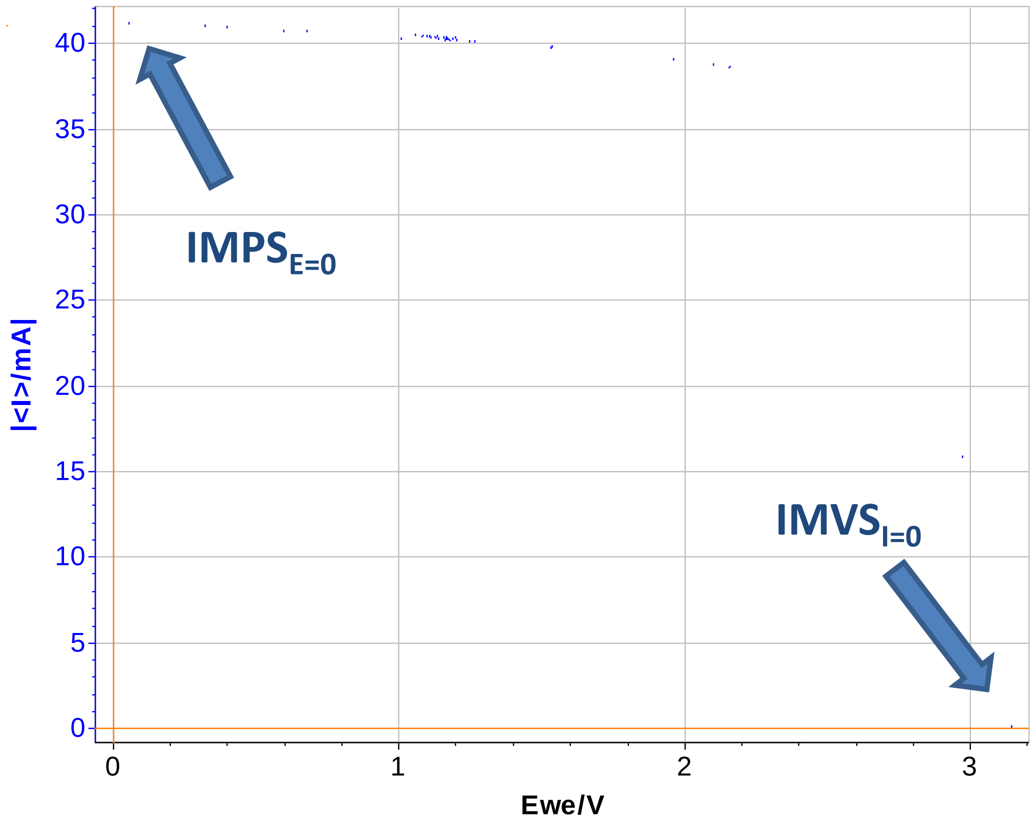
- $L = (D\ \tau)^{1/2}$

L: electron diffusion length/m

- $\eta_{COL} \approx 1 - (\tau_{IMVS} / \tau_{IMPS})$

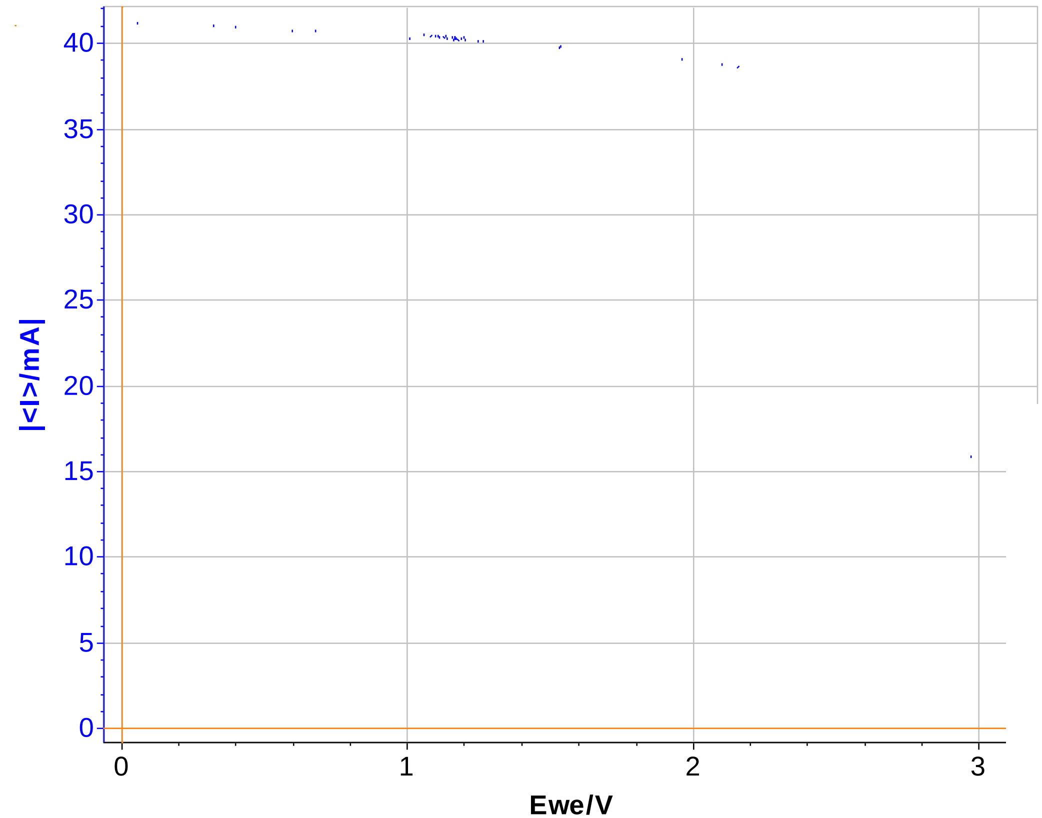
η_{COL} :Efficiency electron collection

IMVS/IMPS



IMVS= $\mathcal{L}\Phi(t)/\mathcal{L}E(t)$

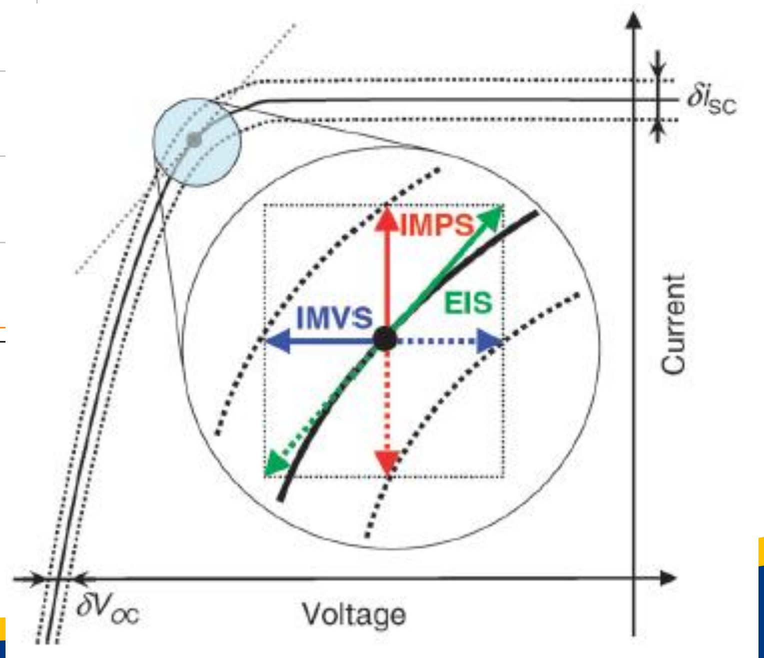
IMPS= $\mathcal{L}\Phi(t)/\mathcal{L}I(t)$



In that case, there is a relatiosnhip bewteen EIS, IMPS and IMVS.

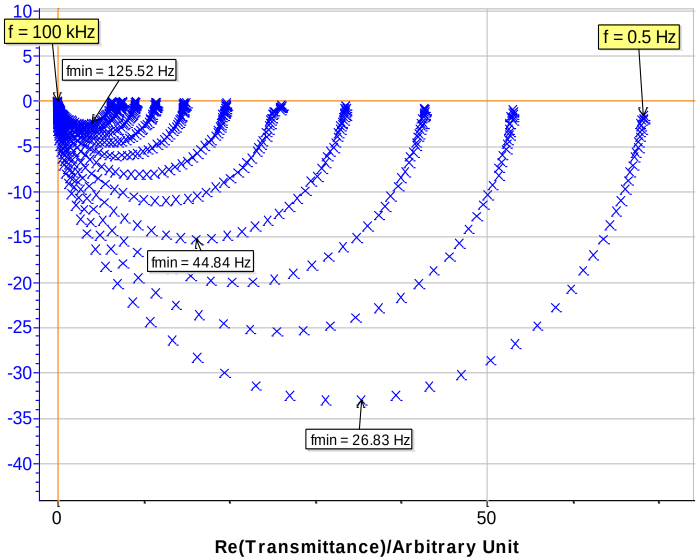
For the same condition (same E, same I, same light intensity),

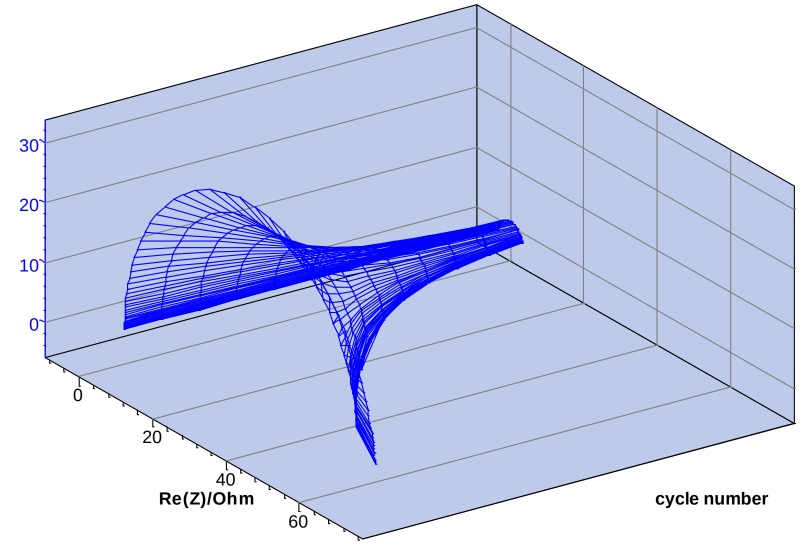
EIS = IMVS/IMPS



IMVS= ∠Φ(t)/∠E(t)

IMPS= ∠Φ(t)/∠I(t)





Lifetime of the electron τ_n is related to the characteristic frequency f_c by the following equation

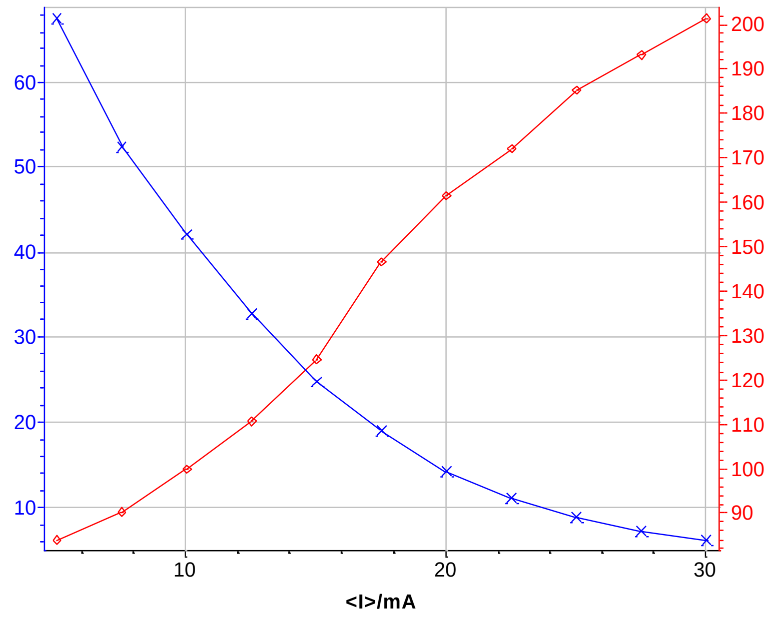
$$\tau_n = 1/(2\pi f_c)$$

IMVS/IMPS

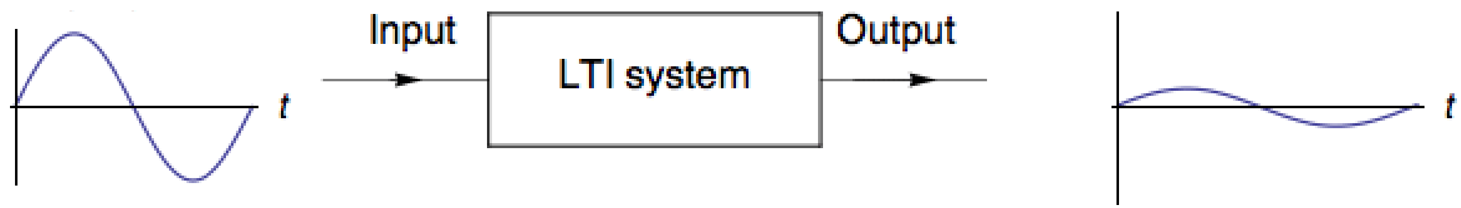
$$f_{min} = 1/(2\,\pi\,RC)$$

Resistance, Capacitor, Minimum frequency and Electron lifetim of white LED vs. light intensity.

Light intensity/ $W.m^{-2}$	R/ Ohm	C/ µF	f_{min}/ Hz	τ_n/ ms
0.500	67.55	84.04	28.05	5.94
0.750	52.45	90.48	33.56	4.59
1.000	42.12	99.91	35.32	4.04
1.250	32.84	110.78	43.77	3.55
1.500	24.73	124.73	51.62	3.12
1.750	18.95	146.48	57.36	2.74
2.000	14.27	161.35	69.20	2.41
2.250	11.09	172.00	83.52	1.87
2.500	8.83	185.32	97.29	1.64
2.749	7.22	193.07	114.30	1.45
2.999	6.14	201.40	128.69	1.27



Electro-HydroDynamic TF (EHD)



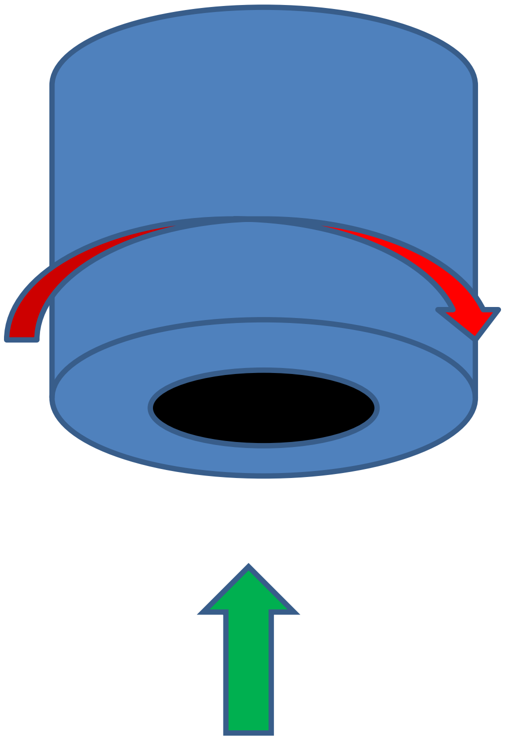
Ω: rotation speed

$EHD_E = \mathcal{L}E(t)/\mathcal{L}\Omega\,(t)$

$EHD_I = \mathcal{L}I(t)/\mathcal{L}\Omega\,(t)$

I: current
U: voltage

$Z = EHD_E \,/\, EHD_I$



Which system?

Useful for analysis electrochemical system that are either partially or completely limited by mass transport

Which information?

Method to isolate the influence of mass transfer from the electrochemical impedance response of a system

What was the aim of this overview?

EIS is only a part of what is possible to do with Function Transfer.
Other method exist and maybe other can be developed to investigate the dynamic behavior of the system.

User has to find the appropriate input and output.

SUMMARY

	System	Information
ElectroHydrodynamic TF (EHD)	• Electrochemical system that are either partially or completely limited by mass transport • Partially blocked electrode	• Mass transfer from the electrochemical impedance response of a system
PhotoElectrochemical TF (IMVS/IMPS)	• Solar cell	• Electron lifetime • Diffusion
MagnetoHydrodynamic TF	• Metal electrode deposition	• Kinetic of the processes
ElectroGravimetric TF	• Insertion in film • Reaction with adsorbed species	• Kinetic of the processes •Chemical identification of the species
Raman TF	• Reaction with adsorbed species	• dynamic information on the interface
ThermoElectrochemical TF (TEC)	• Redox system	• kinetic of mass transport
PneumatoChemical Impedance Spectroscopy	• Insertion reaction • Hydrogen insertion	• phase transformation

MORE INFO…….

Feel free to visit our web site, some application notes or EIS handbook may be helpful for your applications:

http://www.bio-logic.info/potentiostat/notesan.html

Thank you for your attention

Lets move to the instruments