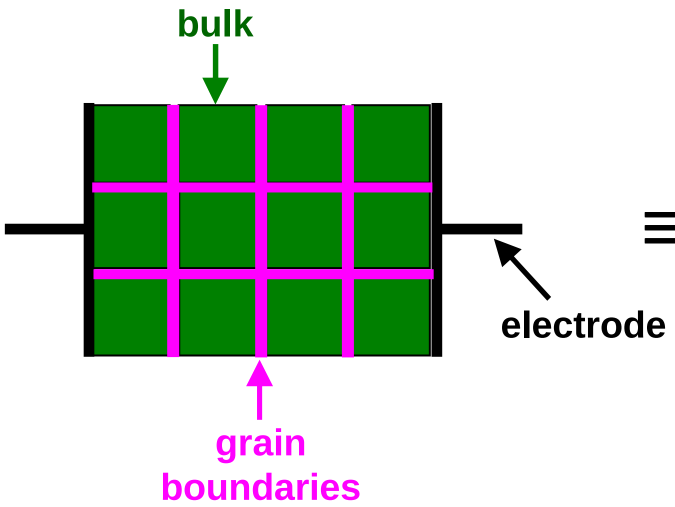
New graphical representation of impedance data

Investigation of bulk and grain boundaries conductivities

Anthony CHESNAUD

Centre des Matériaux Pierre-Marie FOURT
Mines-ParisTech, 91003 Evry Cedex

Bricklayer model



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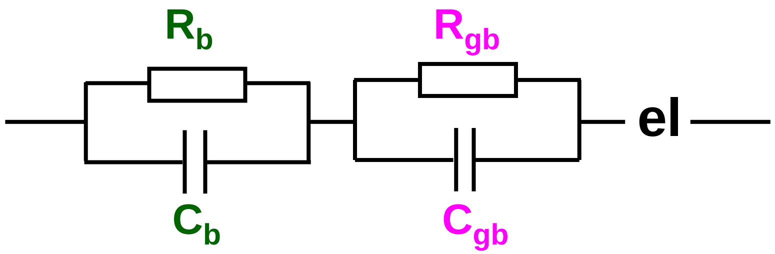
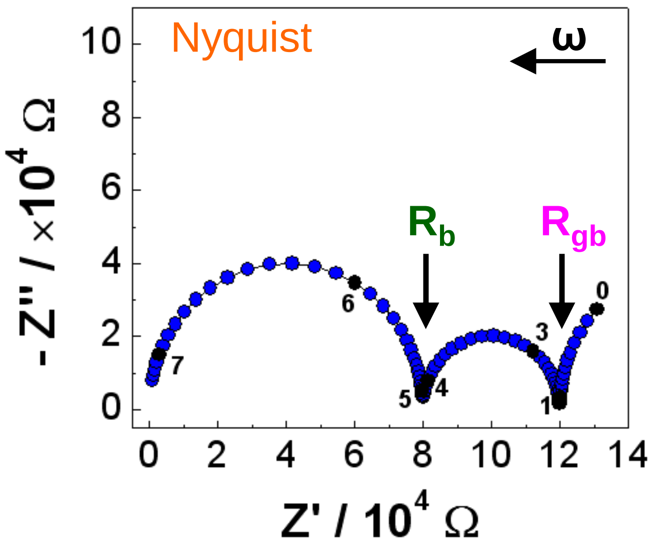
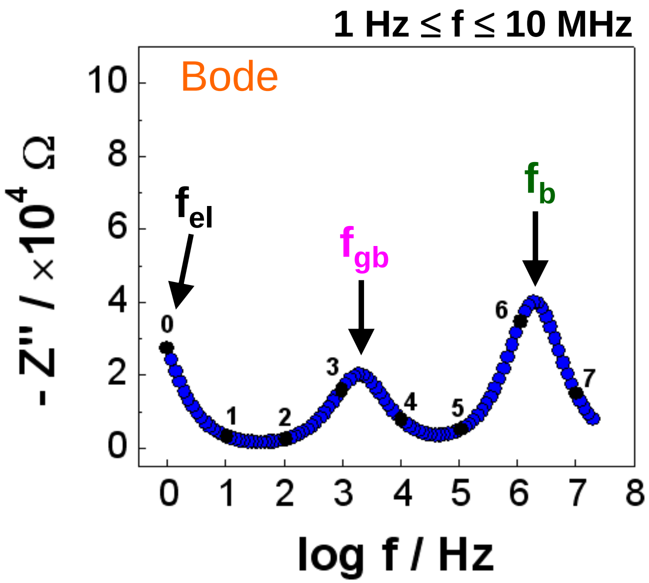
electrochemical system ≡ electrolyte material



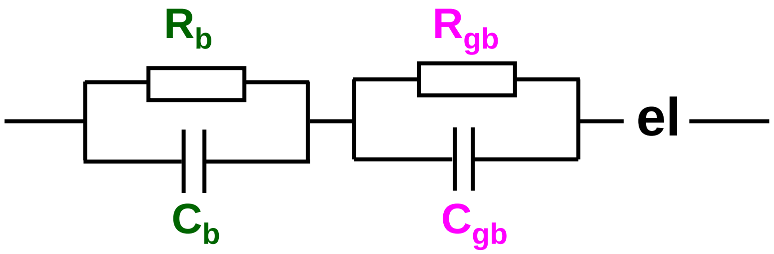
First case : $\frac{f_b}{f_{gb}} = 1000$



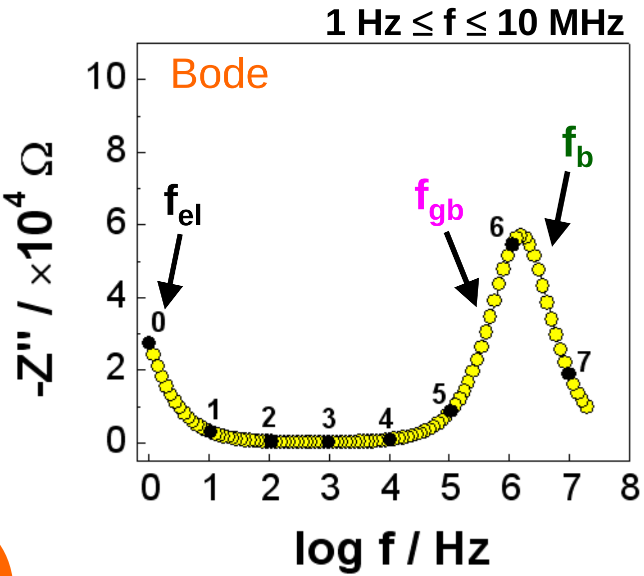


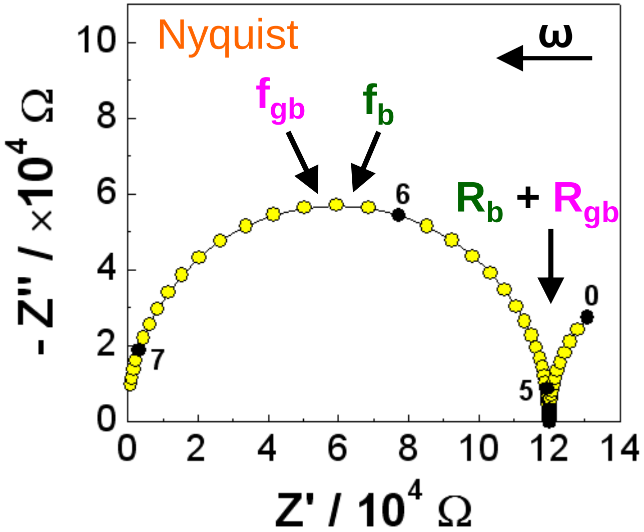
Bricklayer model

system ≡ electrolyte material



Second case : $\frac{f_b}{f_{gb}} = 2$

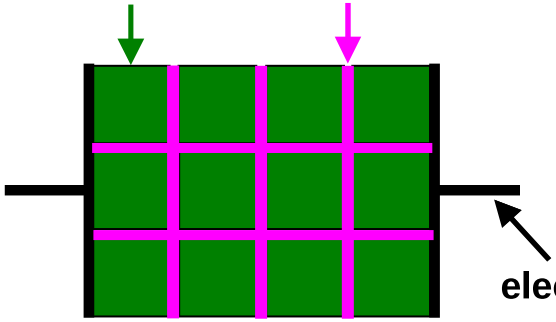




Bulk and grain boundaries processes are strongly overlapped

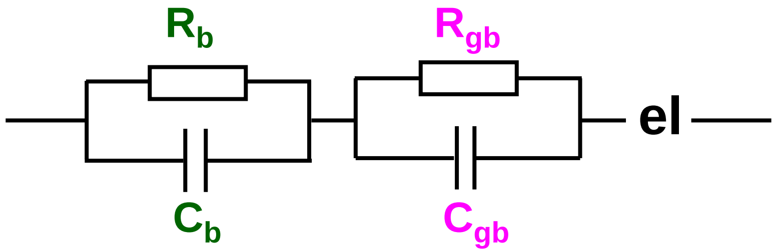
New complex plane

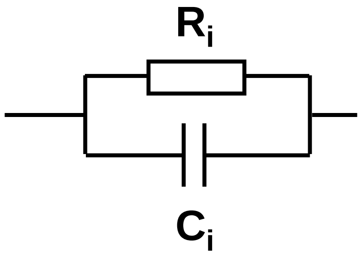
Theoretical approach



electrochemical system ≡ electrolyte material

≡





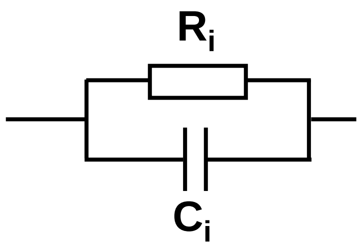
$$Z_{R//C} = \frac{R_i}{1+R_i^2 \times C_i^2 \times \omega^2} - j\frac{R_i^2 \times C_i \times \omega_i}{1+R_i^2 \times C_i^2 \times \omega^2}$$

with $j^2 = -1$

Relaxation frequency: $f_o = \frac{1}{2\pi \times R \times C}$

as $\omega_i = \frac{1}{R_i \times C_i}$ and $f_i = \frac{\omega_i}{2\pi}$ then $R_i^2 \times C_i^2 \times \omega^2 = \left(\frac{f}{f_i}\right)^2$

Theoretical approach

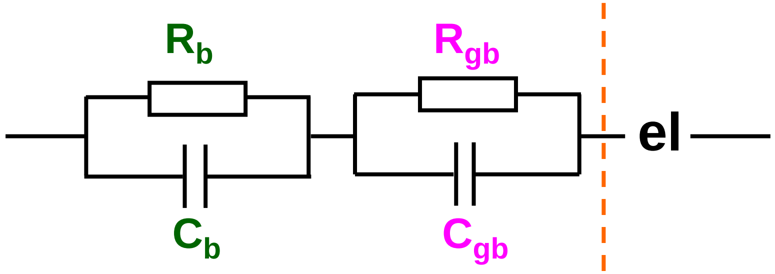


$$Z_{R//C} = \frac{R_i}{1+(f/f_i)^2} - j\frac{(f/f_i)\times R_i}{1+(f/f_i)^2} \qquad \text{with} \quad j^2 = -1$$

$f_i = f_o^{(i)}$ is the relaxation frequency associated with the phenomenon i

$$\text{with} \quad f_i = \frac{\omega_i}{2\pi} \ ; \ \omega_i = \frac{1}{R_i \times C_i} \ ; \ \tau_i = R_i \times C_i$$

system ≡ electrolyte material



$$Z_{system} = Z' - jZ'' = Z_{R_b//C_b} + Z_{R_{gb}//C_{gb}}$$

$$Z' = \frac{R_b}{1+(f/f_b)^2} + \frac{R_{gb}}{1+(f/f_{gb})^2} \quad \text{and} \quad Z'' = \frac{(f/f_b)\times R_b}{1+(f/f_b)^2} + \frac{(f/f_{gb})\times R_{gb}}{1+(f/f_{gb})^2}$$

Theoretical approach

$$L(\theta) = \log\left(\frac{Z'}{Z''}\right) = \log\left(\frac{\left(R_b/\left(1+(f/f_b)^2\right)\right) + \left(R_{gb}/\left(1+(f/f_{gb})^2\right)\right)}{\left((f/f_b)\times R_b/\left(1+(f/f_b)^2\right)\right) + \left((f/f_{gb})\times R_{gb}/\left(1+(f/f_{gb})^2\right)\right)}\right)$$

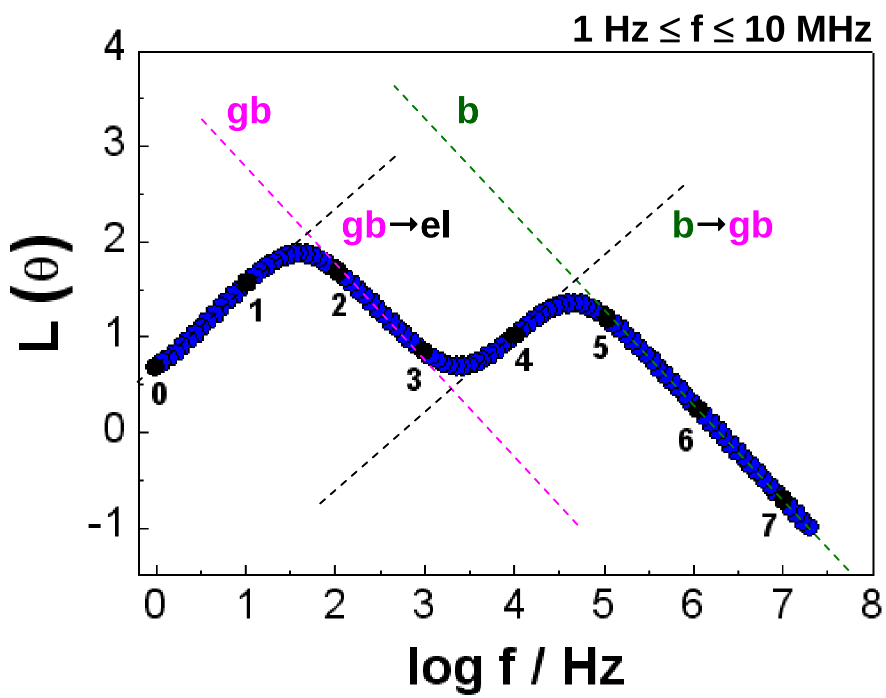
First case : $\frac{f_b}{f_{gb}} = 1000$

Semi-circles in the Nyquist plane (relaxation frequencies of R//C parallel circuits)

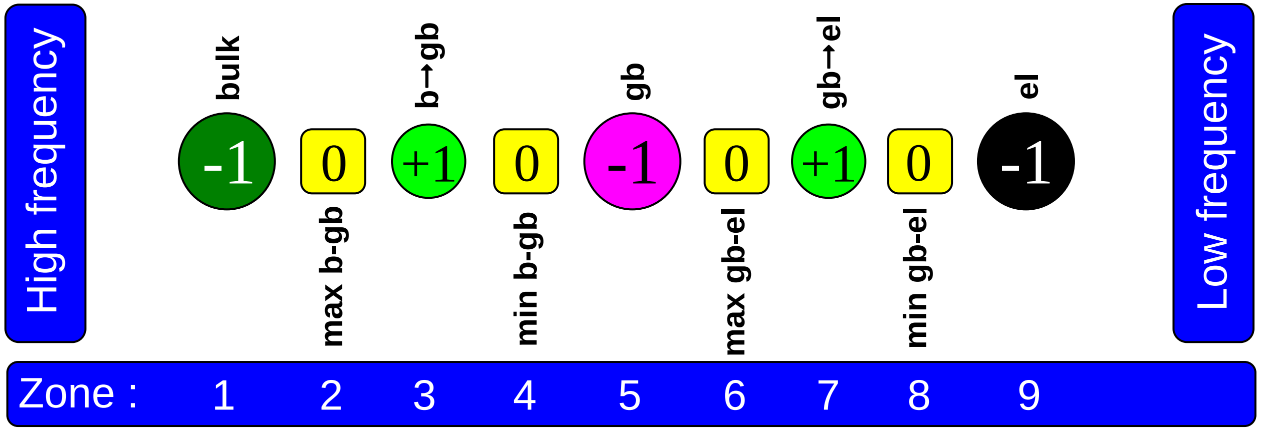
2 straight lines with slope -1

2 straight lines with slope +1

Transition zones (between two processes i)

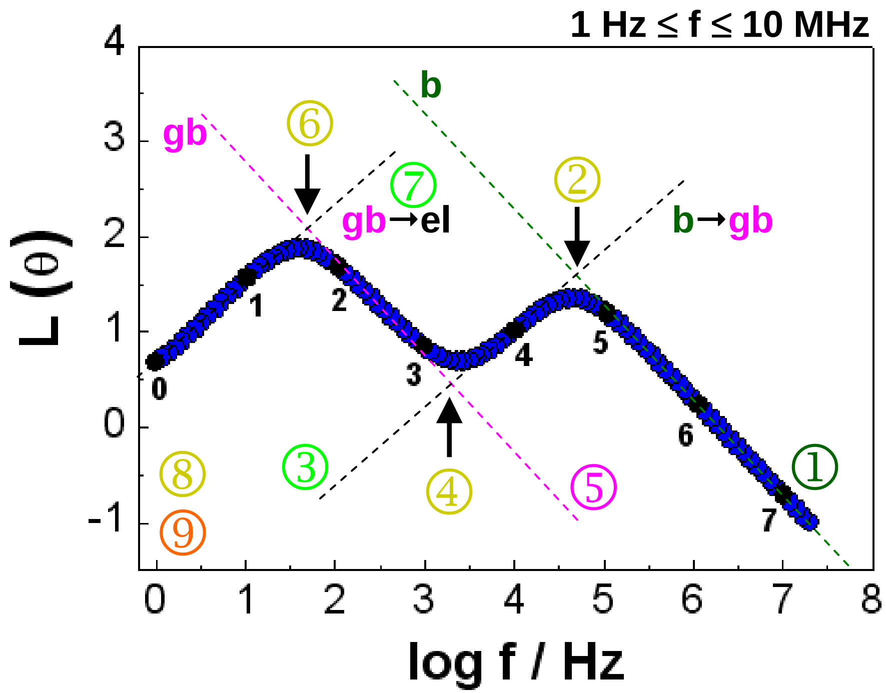


Theoretical approach and discussion



Sample in between 2 electrodes

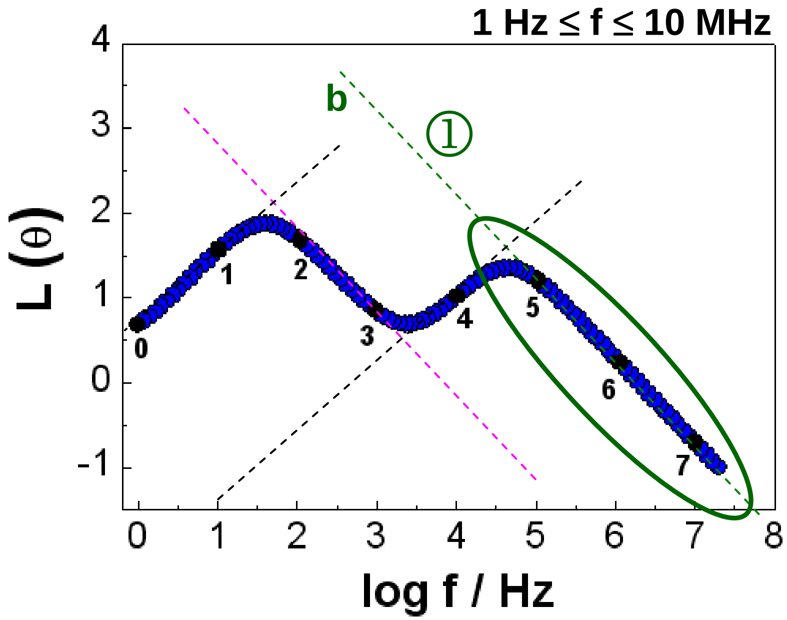
9 characteristic zones on the L(θ) = f (log f) representation



Equation associated with each zone

① Straight line with slope -1 (high frequency) $f >> f_{gb} >> f_{el}$

$$L(\theta) \approx \log\left(\frac{R_b}{R_b / f_b}\right) - \log(f) \quad \Rightarrow \quad L(\theta) = \log(f_b) - \log(f)$$



$L(\theta) = (\lambda_\theta) + (\alpha_\theta)\times\log(f)$

2 new representations

$(\alpha_\theta) = f(\log(f))$

slope of the function L(θ)

$(\lambda_\theta) = f(\alpha_\theta)$

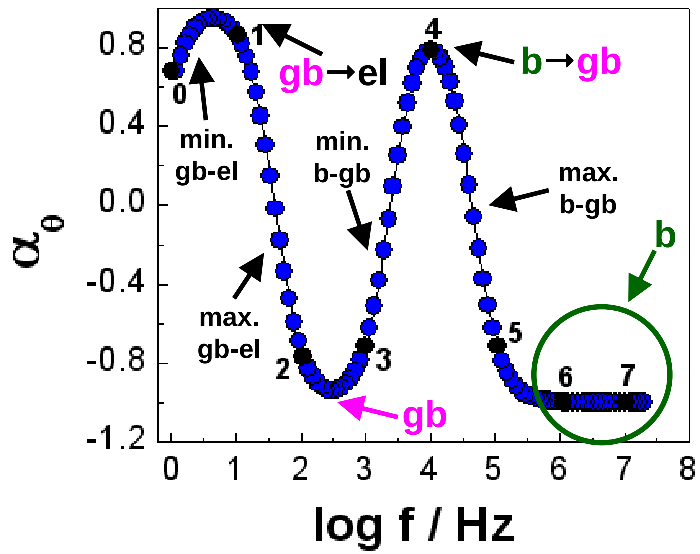
intercept of the function L(θ)

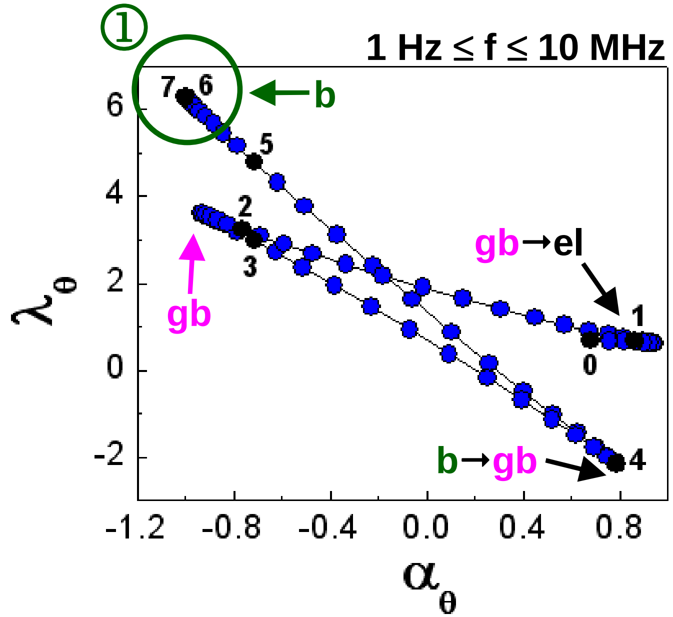
$$\alpha_\theta = \frac{d\log(\theta)}{d\log(f)} = \left(\frac{\Delta L(\theta)}{\Delta\log(f)}\right)_{\Delta\log(f)\to 0}$$

Equation associated with each zone

$(\alpha_\theta) = f(\log(f))$

$(\lambda_\theta) = f(\alpha_\theta)$





① $L(\theta) = \log(f_b) - \log(f)$ → Extrapolated value of λ_θ to slope $\alpha_\theta = -1$

↓

$\log(f_b) = 6.30$

← Relaxation frequency relative to bulk contribution

Extrapolated and theoretical values

$$\log(f_b) = \log\left(\frac{1}{2\pi \times R_b \times C_b}\right) = 6.30$$ → $R_b \times C_b = 8\times10^{-9}\ \Omega\ F$

Equation N°	slope / α_θ	r_f = 1000 (exp/th)	r_f = 100 (exp/th)	r_f = 10 (exp/th)	r_f = 2 (exp/th)
1	-1	6.30/6.30	-	-	-
3	+1	-	-	-	-
2	0	-	-	-	-
5	-1	-	-	-	-
4	0	-	-	-	-

$R_b \times C_b = 8.0\times10^{-9}$ ① → 1 equation and 2 unknowns

Equation associated with each zone

③ Straight line with slope +1 (b ➡ gb transition)

$f_{gb} << f << f_b$ and $f >> f_{el}$

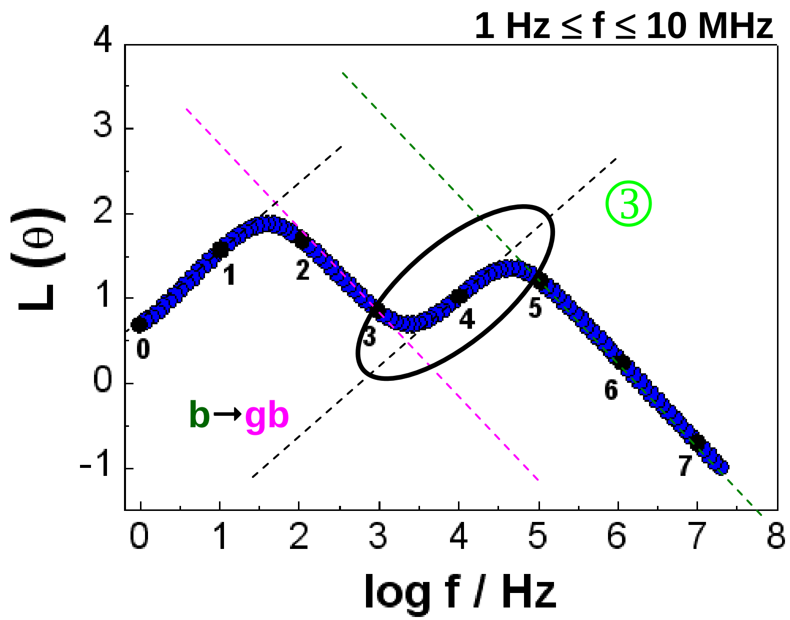
$$L(\theta) \approx \log\left(\frac{R_b + \left(R_{gb}/(f/f_{gb})^2\right)}{(f/f_b)\times R_b + \left((f/f_b)\times R_{gb}/(f/f_{gb})^2\right)}\right)$$

➡ $$L(\theta) \approx \log\left(\frac{R_b}{R_{gb}\times f_{gb}}\right) + \log(f)$$

$$L(\theta) = (\lambda_\theta) + (\alpha_\theta)\times\log(f)$$

➡ $$(\lambda_\theta) = \log\left(\frac{R_b}{R_{gb}\times f_{gb}}\right)$$

➡ $$(\alpha_\theta) = +1$$



Equation associated with each zone

③ Straight line with slope +1 (b→gb transition)

$$L(\theta) \approx \log\left(\frac{R_b + \left(R_{gb}/(f/f_{gb})^2\right)}{(f/f_b)\times R_b + \left((f/f_b)\times R_{gb}/(f/f_{gb})^2\right)}\right)$$

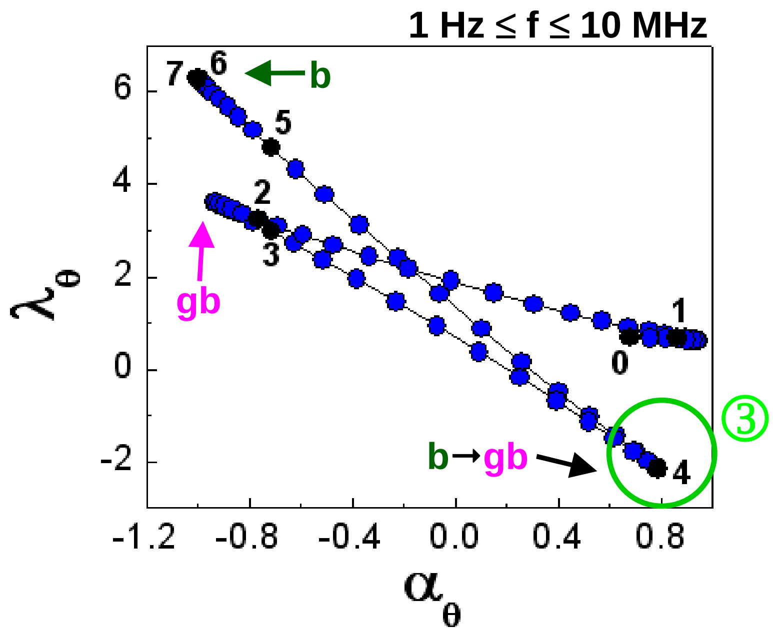
$f_{gb} << f << f_b$ and $f >> f_{el}$

$$\Rightarrow \quad L(\theta) \approx \log\left(\frac{R_b}{R_{gb}\times f_{gb}}\right) + \log(f)$$

Extrapolated value of λ_θ to slope $\alpha_\theta = +1$

↓

Relation between characteristic parameters of the electrical circuit



Extrapolated and theoretical values

$$\log\left(\frac{R_b}{R_{gb} \times f_{gb}}\right) = -3.00$$ → $2 \times \pi \times R_b \times C_{gb} = 1 \times 10^{-3}\ \Omega\ F$

Equation N°	slope / α_θ	r_f = 1000 (exp/th)	r_f = 100 (exp/th)	r_f = 10 (exp/th)	r_f = 2 (exp/th)
1	-1	6.30/6.30	-	-	-
3	+1	-3.00/-3.00	-	-	-
2	0	-	-	-	-
5	-1	-	-	-	-
4	0	-	-	-	-

$R_b \times C_b = 8.0 \times 10^{-9}$ ①

$R_b \times C_{gb} = 1.6 \times 10^{-4}$ ③

→ 2 equation and 3 unknowns

Equation associated with each zone

② Maximun between bulk and grain boundaries with slope 0

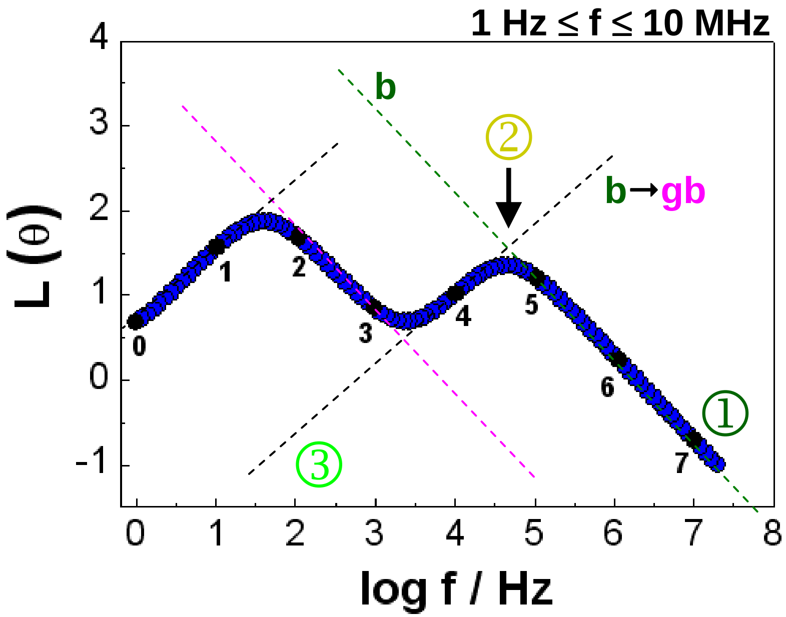
① $$\log(f_b) - \log\left(f_{b\to gb}^{max}\right) = \log\left(\frac{R_b}{R_{gb}} \times \frac{1}{f_{gb}}\right) + \log\left(f_{b\to gb}^{max}\right)$$ ③

$$\Rightarrow \log\left(f_{b\to gb}^{max}\right) = \frac{1}{2} \times \log\left(f_b \times f_{gb} \times \frac{R_{gb}}{R_b}\right) \Rightarrow \log\left(f_{b\to gb}^{max}\right) = 4.60$$

Intercept between the straight line of slope -1 (b process) with the straight line of slope +1 (b→gb transition)

↓

Relation between characteristic parameters of the electrical circuit



Extrapolated and theoretical values

$$\frac{1}{2}\times\log\left(f_b\times f_{gb}\times\frac{R_{gb}}{R_b}\right)=4.60 \rightarrow \frac{1}{4\times\pi^2\times R_b^2\times C_b\times C_{gb}}=1.6\times10^9\ \Omega^{-2}\ F^{-2}$$

Equation N°	slope / α_θ	r_f = 1000 (exp/th)	r_f = 100 (exp/th)	r_f = 10 (exp/th)	r_f = 2 (exp/th)
1	-1	6.30/6.30	-	-	-
3	+1	-3.00/-3.00	-	-	-
2	0	4.60/4.65	-	-	-
5	-1	-	-	-	-
4	0	-	-	-	-

$R_b\times C_b = 8.0\times10^{-9}$ ①

$R_b\times C_{gb} = 1.6\times10^{-4}$ ③

$R_b^2\times C_b\times C_{gb} = 1.6\times10^{-11}$ ②

→ 3 equations and 3 unknowns

R_b, C_b, C_{gb} can be deduced

② → R_{gb}

Equation associated with each zone

⑤ Straight line with slope -1 (intermediate frequency)

$$L(\theta) \approx \log\left(\frac{R_b + \left(1 + \left(1/f_{gb}\right)^2\right)}{\left(f/f_b\right) \times R_b + \left(\left(f/f_b\right) \times R_{gb} / \left(1 + \left(f/f_{gb}\right)^2\right)\right)}\right)$$

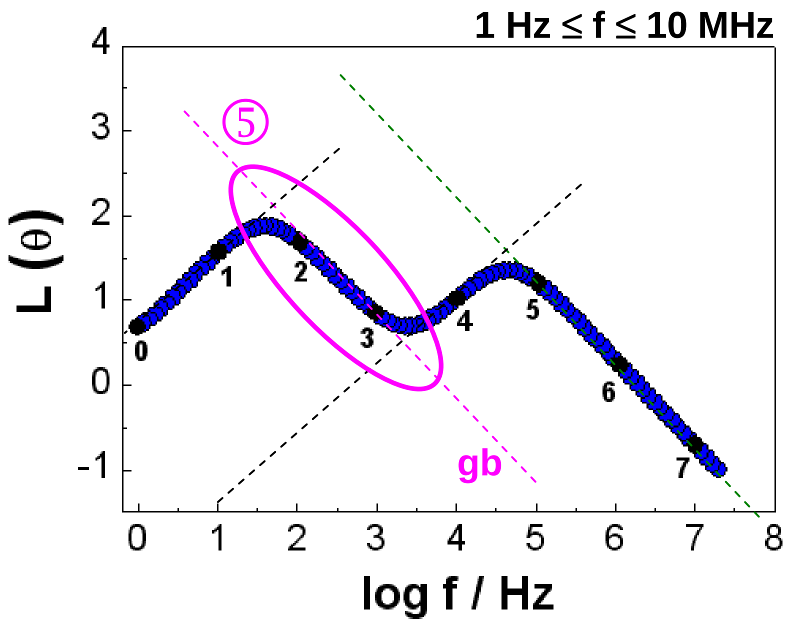
$f_{el} << f << f_b$ and $f < f_{gb}$

$$L(\theta) \approx \log\left(\frac{R_b + R_{gb}}{\left(R_b/f_b\right) + \left(R_{gb}/f_{gb}\right)}\right) - \log(f)$$

$$L(\theta) = (\lambda_\theta) + (\alpha_\theta) \times \log(f)$$

$$(\lambda_\theta) = \log\left(\frac{R_b + R_{gb}}{\left(R_b/f_b\right) + \left(R_{gb}/f_{gb}\right)}\right)$$

$$(\alpha_\theta) = -1$$



Equation associated with each zone

⑤ Straight line with slope -1 (intermediate frequency)

$$L(\theta) \approx \log\left(\frac{R_b + \left(1 + \left(1/f_{gb}\right)^2\right)}{\left(f/f_b\right) \times R_b + \left(\left(f/f_b\right) \times R_{gb} / \left(1 + \left(f/f_{gb}\right)^2\right)\right)} \right)$$

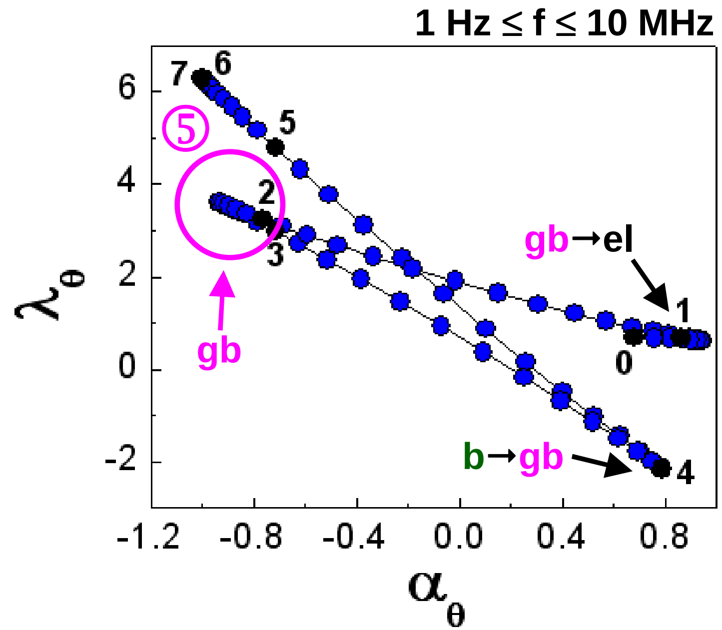
$f_{el} << f << f_b$ and $f < f_{gb}$

$$\Rightarrow \quad L(\theta) \approx \log\left(\frac{R_b + R_{gb}}{\left(R_b/f_b\right) + \left(R_{gb}/f_{gb}\right)} \right) - \log(f)$$

Extrapolated value of λ_θ to slope $\alpha_\theta = -1$

↓

Relation between characteristic parameters of the electrical circuit



Equation associated with each zone

④ Minimun between bulk and grain boundaries with slope 0

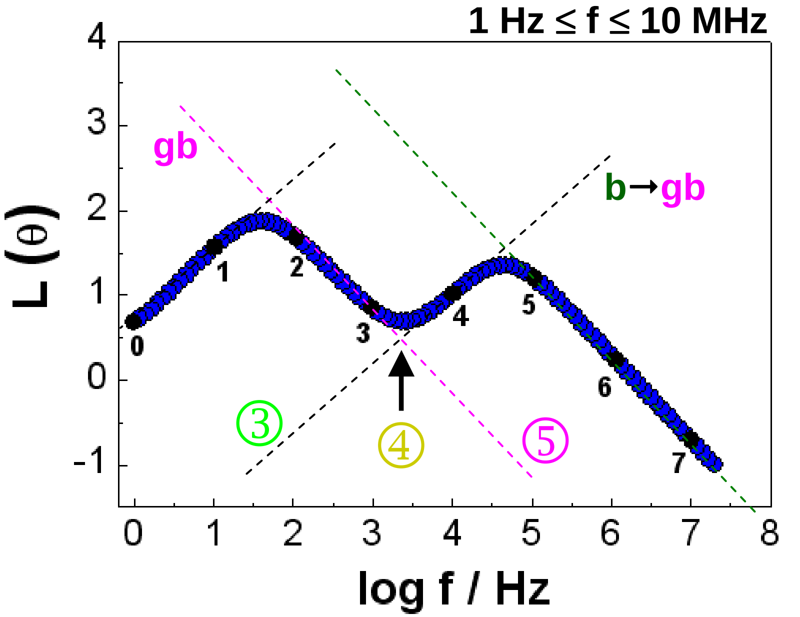
$$③\quad \log\left(\frac{R_b}{R_{gb}}\times\frac{1}{f_{gb}}\right)+\log\left(f_{b\to gb}^{min}\right)=\log\left(\frac{R_b+R_{gb}}{\left(R_b/f_b\right)+\left(R_{gb}/f_{gb}\right)}\right)-\log\left(f_{b\to gb}^{min}\right)\quad ⑤$$

$$\Rightarrow\quad \log\left(f_{b\to gb}^{min}\right)=\frac{1}{2}\times\log\left(\frac{R_{gb}}{R_b}\times f_{gb}\times\left(\frac{R_b+R_{gb}}{\left(R_b/f_b\right)+\left(R_{gb}/f_{gb}\right)}\right)\right)$$

Intercept between the straight line of slope +1 (b→gb transition) with the straight line of slope -1 (gb process)

↓

Relation between characteristic parameters of the electrical circuit



Extrapolated and theoretical values

⑤ $$\log\left(\frac{R_b + R_{gb}}{2\times\pi\times\left(R_b^2\times C_b + R_{gb}^2\times C_{gb}\right)}\right) = 3.78$$

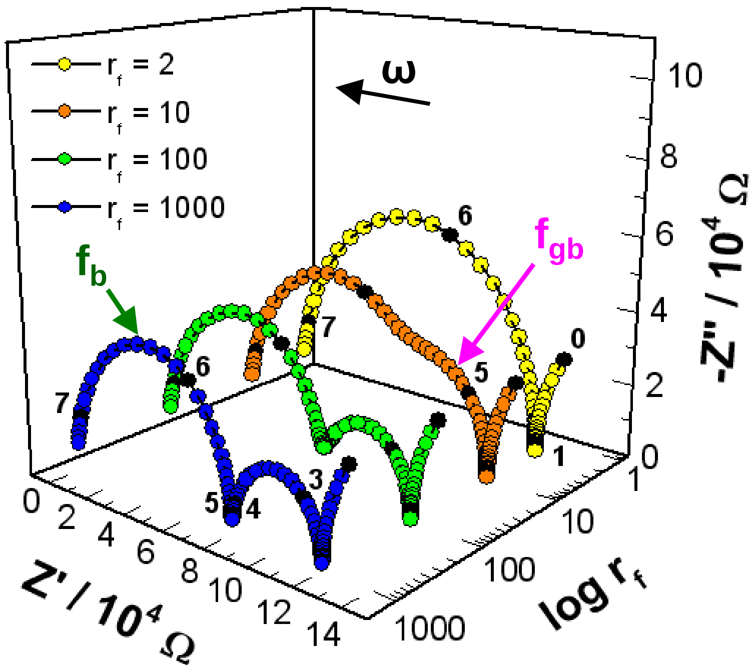
④ $$\frac{1}{2}\times\log\left(\frac{1}{4\times\pi^2\times R_b\times C_{gb}}\times\left(\frac{R_b + R_{gb}}{\left(R_b^2\times C_b + R_{gb}^2\times C_{gb}\right)}\right)\right) = 3.40$$

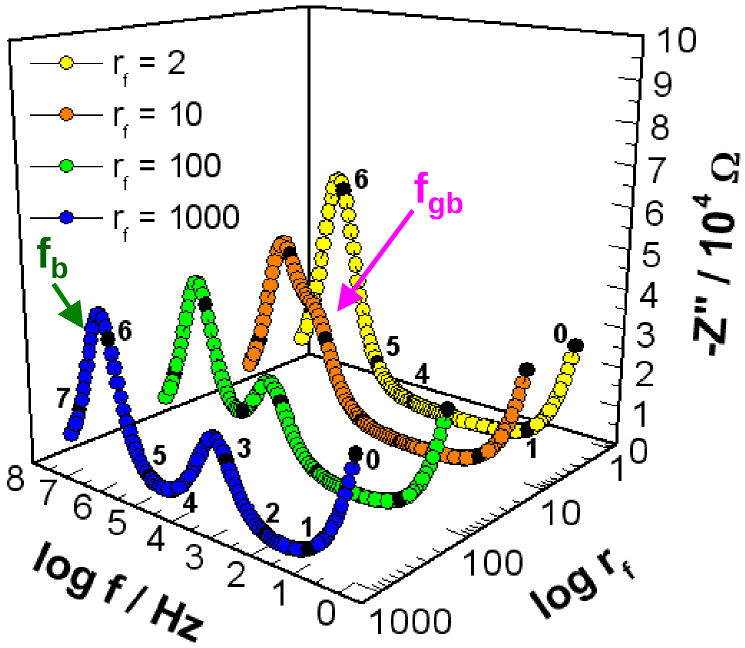
Equation N°	slope / α_θ	r_f = 1000 (exp/th)	r_f = 100 (exp/th)	r_f = 10 (exp/th)	r_f = 2 (exp/th)
1	-1	6.30/6.30	-	-	-
3	+1	-3.00/-3.00	-	-	-
2	0	4.60/4.65	-	-	-
5	-1	3.78/3.77	-	-	-
4	0	3.40/3.39	-	-	-

Perfect agreement between the theoretical values and the ones obtained by extrapolation or intercepts points

$r_f = f_b/f_{gb}$ dependency of impedance spectra

1 Hz ≤ f ≤ 10 MHz

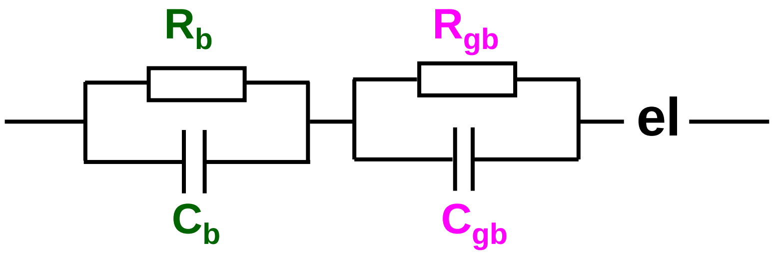


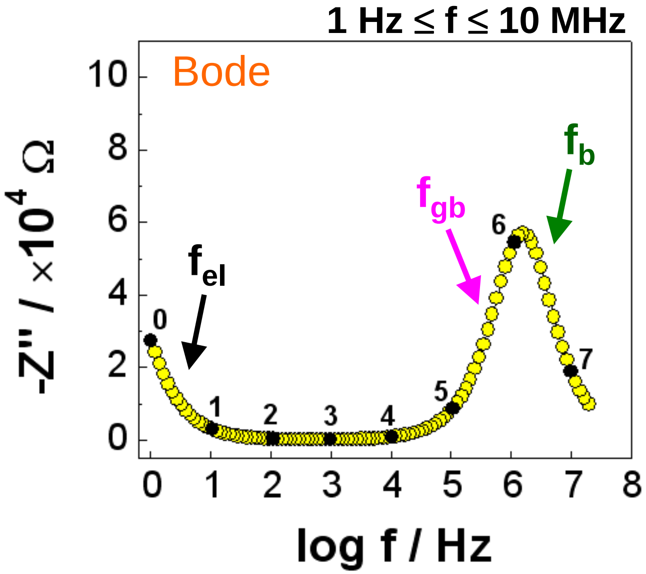


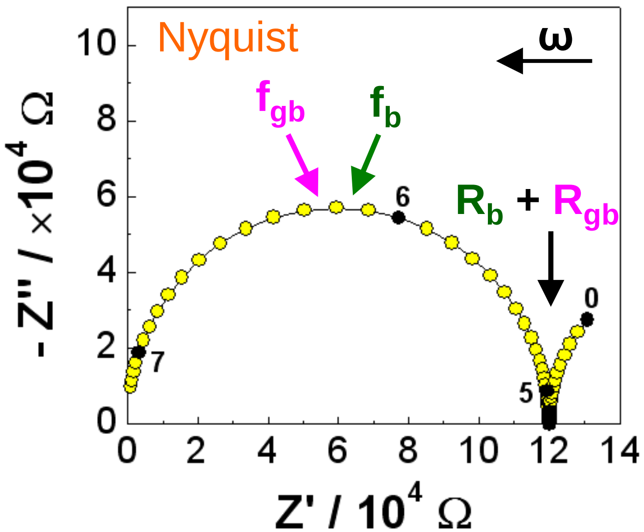
- Classical representations do not permit to separate bulk and grain boundaries processes when $r_f < 10$
- Starting characteristic parameters cannot be extracted for NLLS refinements

Case $r_f = f_b/f_{gb} = 2$

system ≡ electrolyte material







Bulk and grain boundaries processes are strongly overlapped

New complex plane

Case $r_f = f_b/f_{gb} = 2$: $L(\theta) = f(\log(f))$

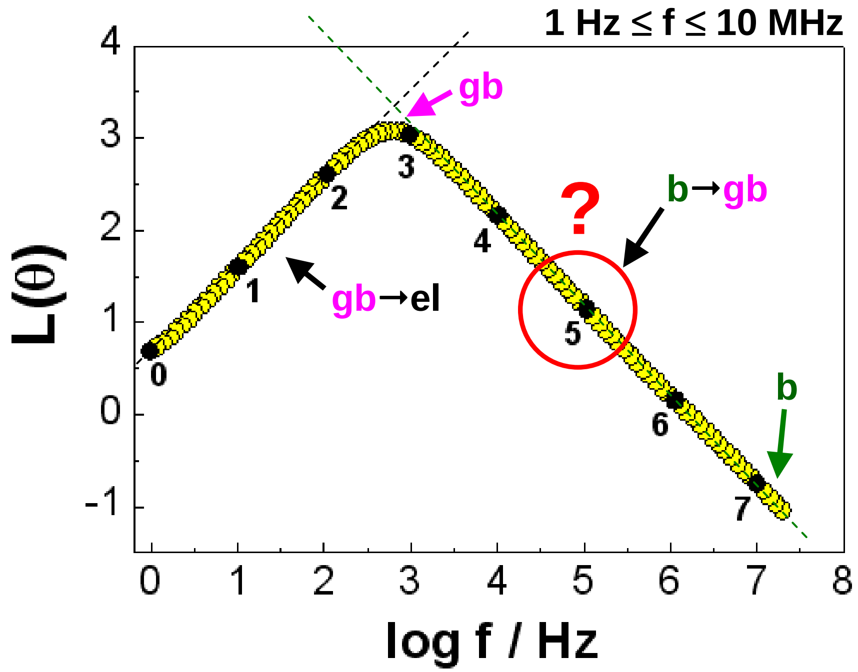
$$L(\theta) = \log\left(\frac{Z'}{Z''}\right) = \log\left(\frac{\left(R_b/\left(1+(f/f_b)^2\right)\right)+\left(R_{gb}/\left(1+(f/f_{gb})^2\right)\right)}{\left((f/f_b)\times R_b/\left(1+(f/f_b)^2\right)\right)+\left((f/f_{gb})\times R_{gb}/\left(1+(f/f_{gb})^2\right)\right)}\right)$$

Semi-circles in the Nyquist plane (relaxation frequencies of R//C parallel circuits)

1 straight line with slope -1

1 straight lines with slope +1

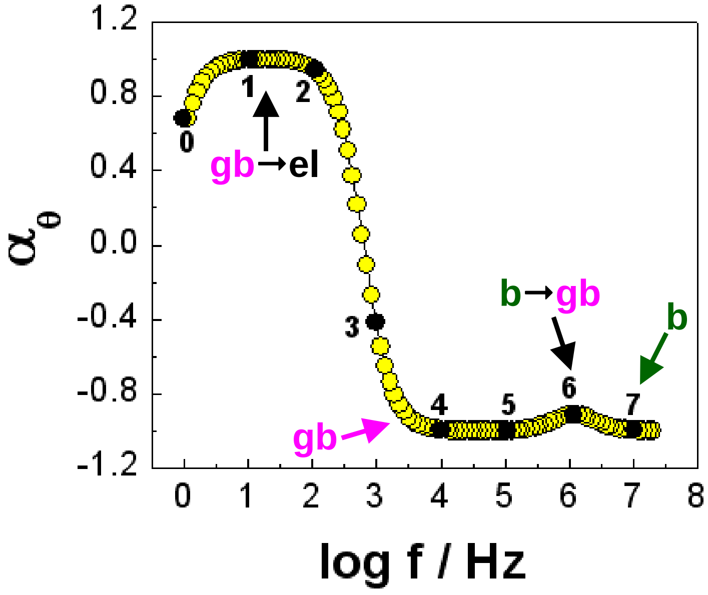
Transition zones (between two processes i)



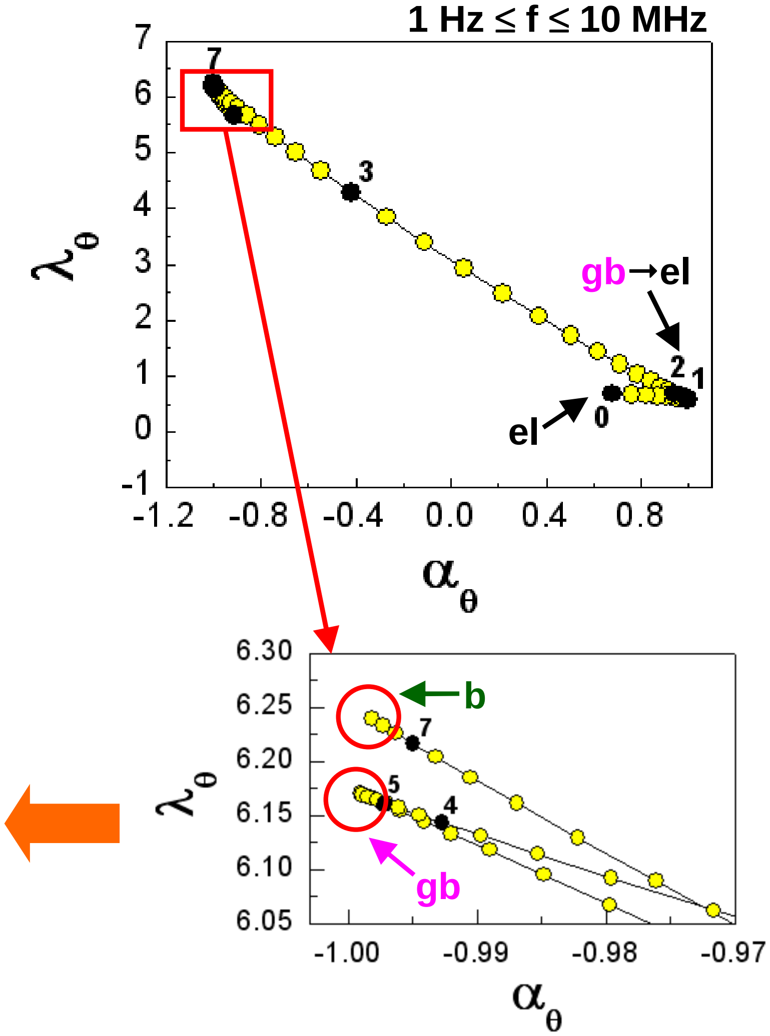
L(θ) = f(log(f)) not sensitive enough to detect the b→gb transition

Case $r_f = f_b/f_{gb} = 2$

$(\alpha_\theta) = f(\log(f))$



$(\lambda_\theta) = f(\alpha_\theta)$

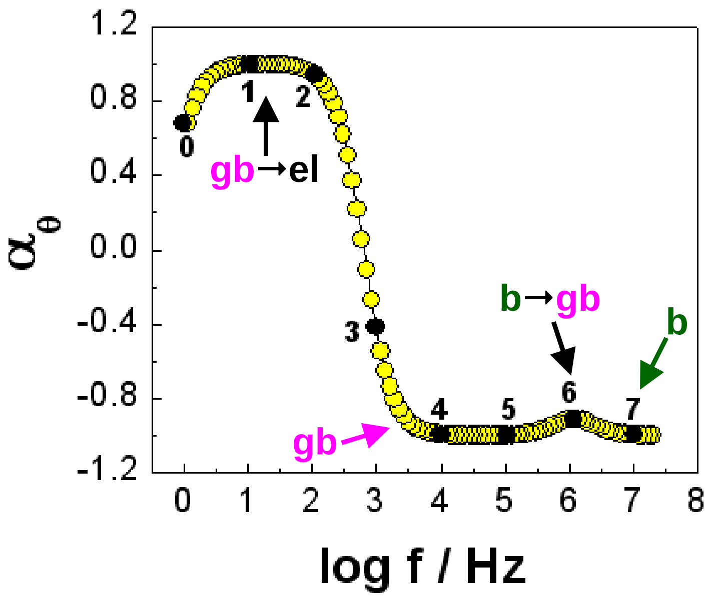


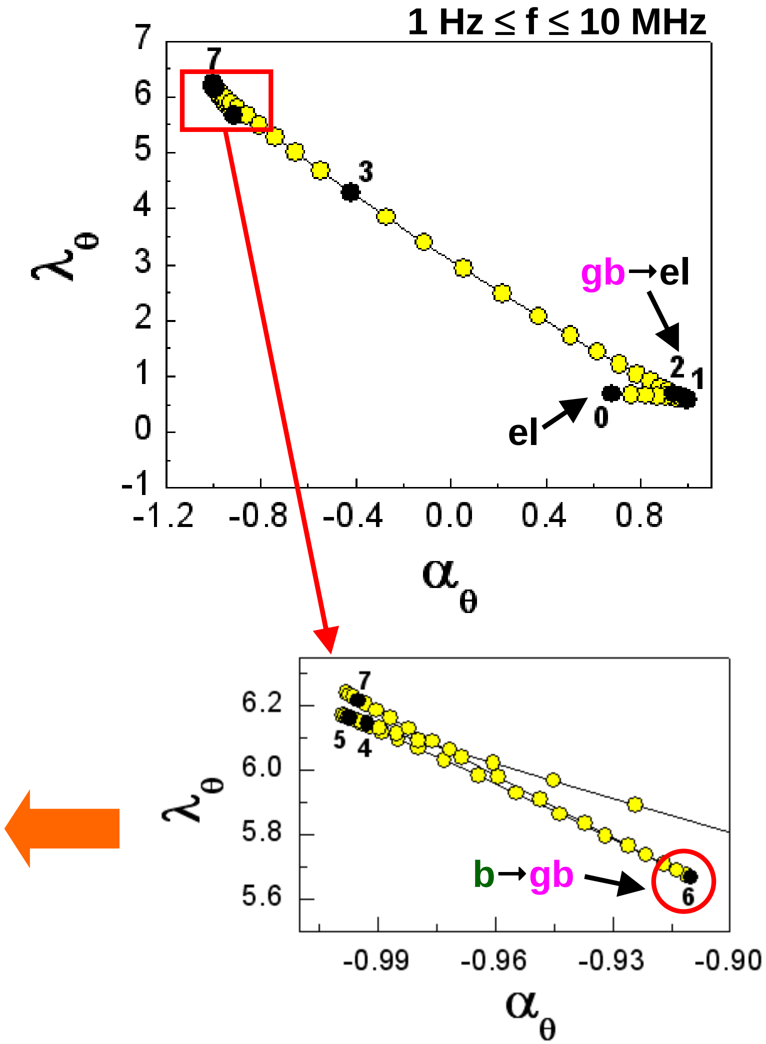
① Bulk (b) and ⑤ grain boundaries (gb) processes can be deconvoluted in the new impedance plane

Case $r_f = f_b/f_{gb} = 2$

$(\alpha_\theta) = f(\log(f))$

$(\lambda_\theta) = f(\alpha_\theta)$



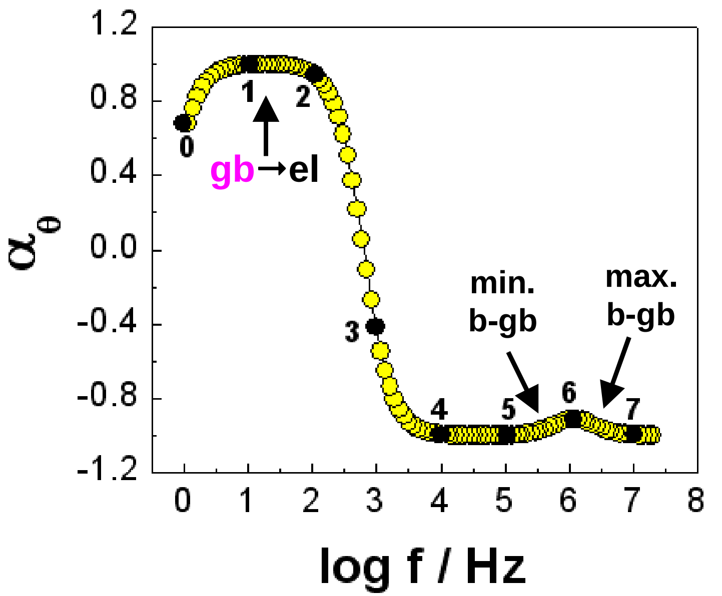


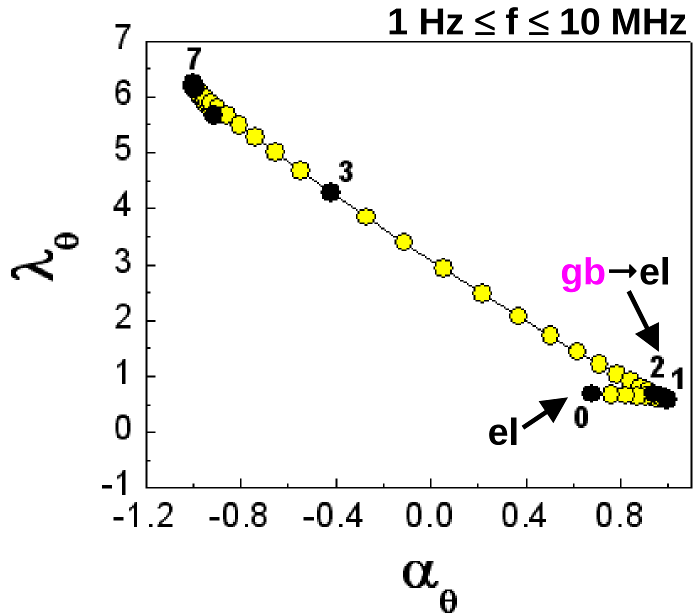
The transition ③ b→gb is detected in the $\alpha_\theta = \log(f)$ plane as well as in the $\lambda_\theta = f(\alpha_\theta)$ one

Case $r_f = f_b/f_{gb} = 2$

$(\alpha_\theta) = f(\log(f))$

$(\lambda_\theta) = f(\alpha_\theta)$





The ② max. b→gb and ④ min. b→gb zones are detected in the $\alpha_\theta = \log(f)$

Values of ② and ④ are deduced using tangents method

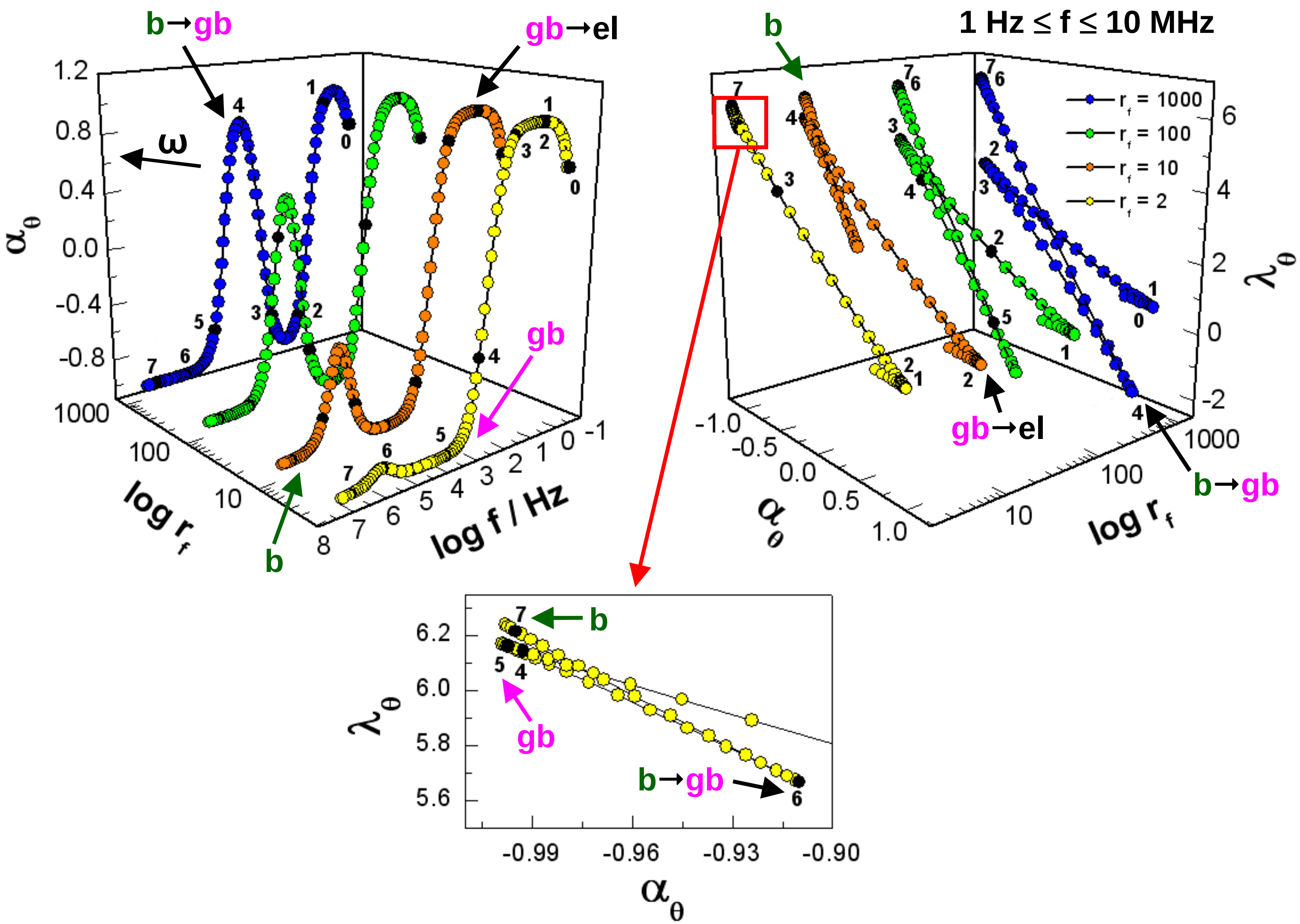
Extrapolated and theoretical values : case $r_f = 2$

Equations ① ② ③ ④ and ⑤ can be resolved and then R_b, R_{gb}, C_b, C_{gb} can be extracted even if relaxation frequencies of bulk and grain boundaries processes are very close

Equation N°	slope / α_θ	$r_f = 1000$ (exp/th)	$r_f = 100$ (exp/th)	$r_f = 10$ (exp/th)	$r_f = 2$ (exp/th)
1	-1	6.30/6.30	-	-	6.30/6.30
3	+1	-3.00/-3.00	-	-	-5.70/-5.70
2	0	4.60/4.65	-	-	6.00/6.00
5	-1	3.78/3.77	-	-	6.17/6.17
4	0	3.40/3.39	-	-	6.00/5.94

Perfect agreement between the theoretical values and the ones obtained by extrapolation or intercepts points

3D graphical representation of $\alpha_\theta = f(\log(f))$ and $\lambda_\theta = f(\alpha_\theta)$



Extrapolated and theoretical values : case r_f = 10 and r_f = 100

① bulk process (b)
② maximum between bulk and grain boundaries (max. b→gb)
③ transition between bulk and grain boundaries (b→gb)
④ minimum between bulk and grain boundaries (min. b→gb)
⑤ grain boundaries process (gb)

Equation N°	slope / α_θ	r_f = 1000 (exp/th)	r_f = 100 (exp/th)	r_f = 10 (exp/th)	r_f = 2 (exp/th)
1	-1	6.30/6.30	6.30/6.30	6.30/6.30	6.30/6.30
3	+1	-3.00/-3.00	-4.00/-4.00	-5.00/-5.00	-5.70/-5.70
2	0	4.60/4.65	5.20/5.15	5.50/5.80	6.00/6.00
5	-1	3.78/3.77	4.78/4.77	5.70/5.70	6.17/6.17
4	0	3.40/3.39	4.40/4.38	5.50/5.35	6.00/5.94

→ Perfect agreement between the theoretical values and the ones obtained by extrapolation or intercepts points

Experimental issues

Impedance spectra must be recorded on fully dense samples (> 95% of the theoretical density)

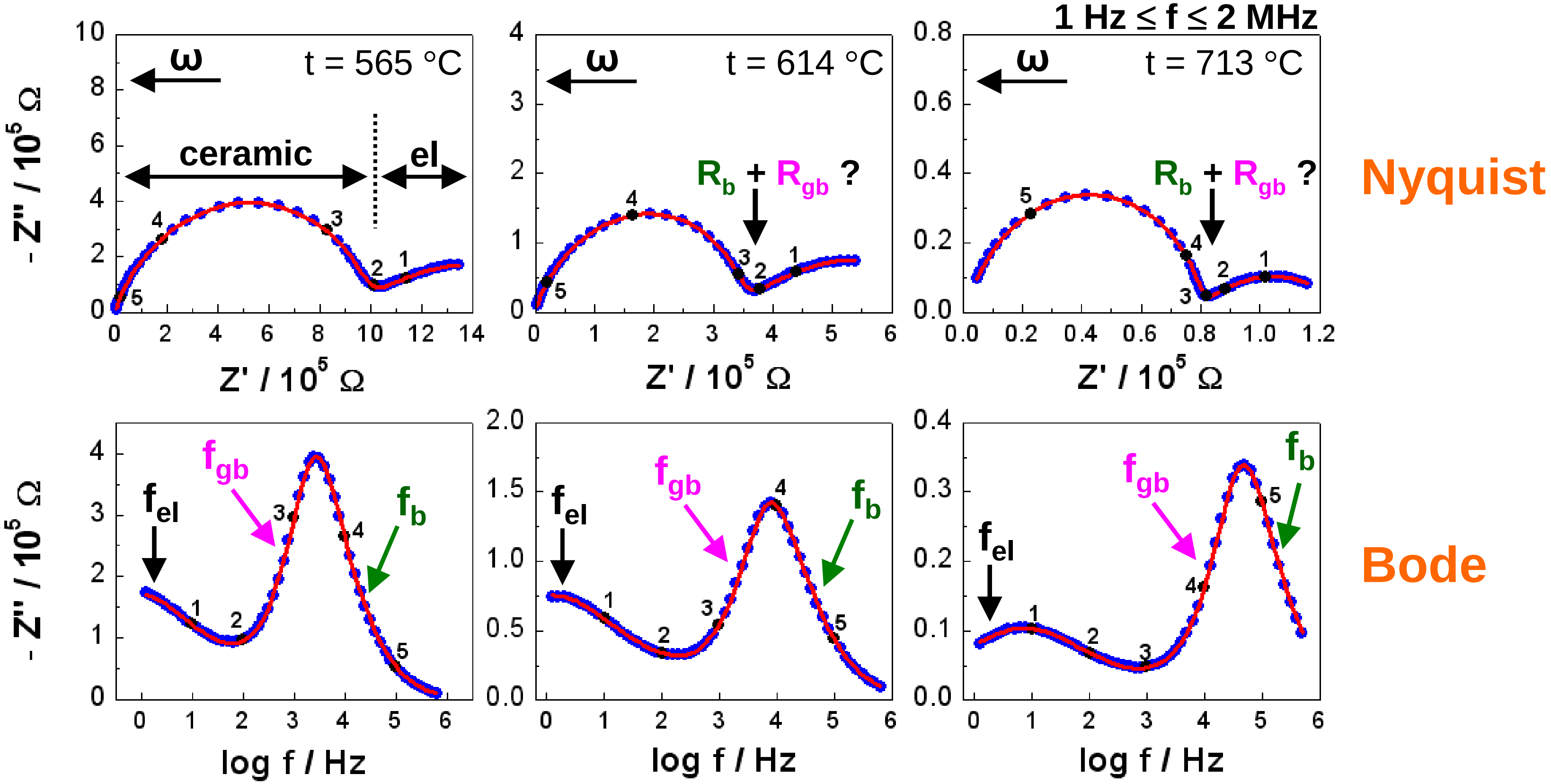
$$\alpha_\theta = \frac{d\log(\theta)}{d\log(f)} = \left(\frac{\Delta L(\theta)}{\Delta\log(f)}\right)_{\Delta\log(f)\to 0}$$

accurate values of α_θ if increments of $\Delta\log(f)$ is as small as possible
(12 points per decade of frequency are required)

Application to :

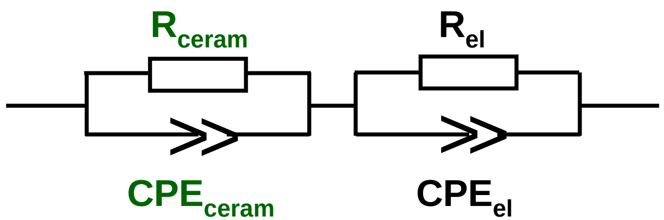
- $Nd_4Ga_{2(1-x)}Ti_{2x}O_{9+x}\square_{1-x}$ compounds
- $Nd_{2.955}Sr_{0.045}O_{1.9775}\square_{0.0225}(GaO_4)$

Electrical response of $Nd_4Ga_2O_9$



2 relaxation phenomena regardless of temperature ?

Equivalent circuit



Impedance of elements : CPE

CPE

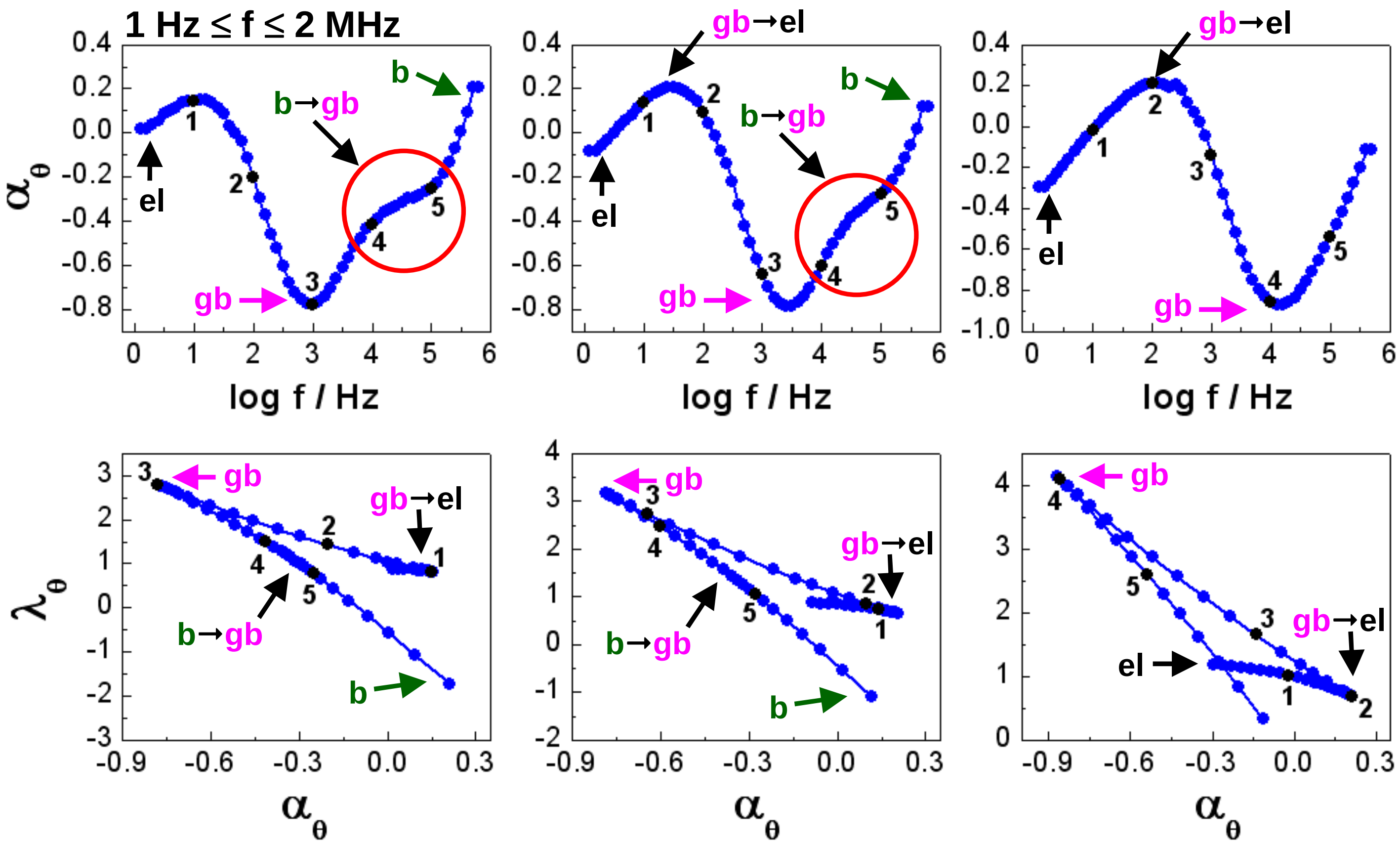
$$Z_{CPE}(\omega) = \frac{1}{T\times(j\times\omega)^p} = \frac{R}{(j\times R\times C\times\omega)^p} \quad \text{with} \quad C = \frac{T^{1/p}}{R^{(1-1/p)}}$$

➡ T and p are the characteristic parameters of the CPE

CPE
- Fractal dimension of the material's area
- Electrodes rugosity
- Change in the sample thickness
- Compositional or porosity dispersion inhomogeneity
- Dispersion of activation energy

p	Z'_{CPE} (ω)	Z''_{CPE} (ω)
-1.0	0	$R^2\times C\times\omega = L\times\omega$
-0.5	Z' = Z''	
0	R	0
+0.5	Z' = -Z''	
+1.0	0	

Electrical response of $Nd_4Ga_2O_9$

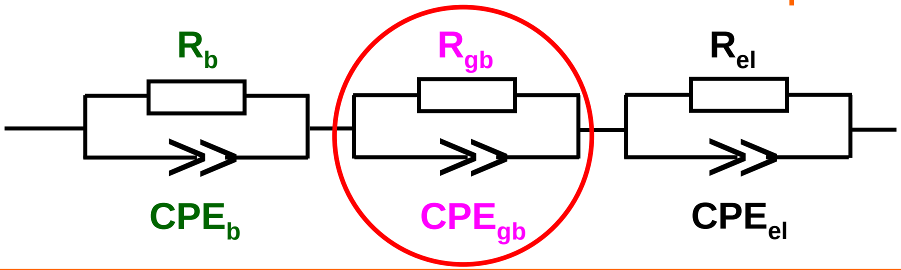


$\alpha_\theta = f(\log f)$

$\lambda_\theta = f(\alpha_\theta)$

3 relaxation phenomena are observed at low temperatures

Equivalent circuit



$$\frac{f_b}{f_{gb}} \approx 3$$

Electrical properties of $Nd_4Ga_2O_9$

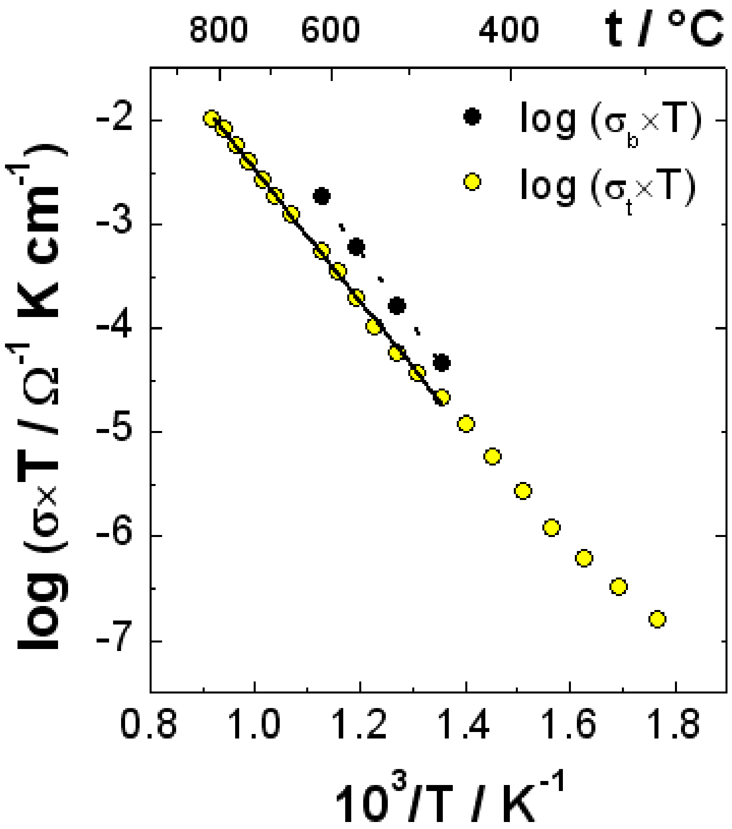
To opte for the electrical circuit which modelized accurately experimental data at low temperatures

↓

Modelisation of impedance spectra by Non-Linear Least Squares fitting

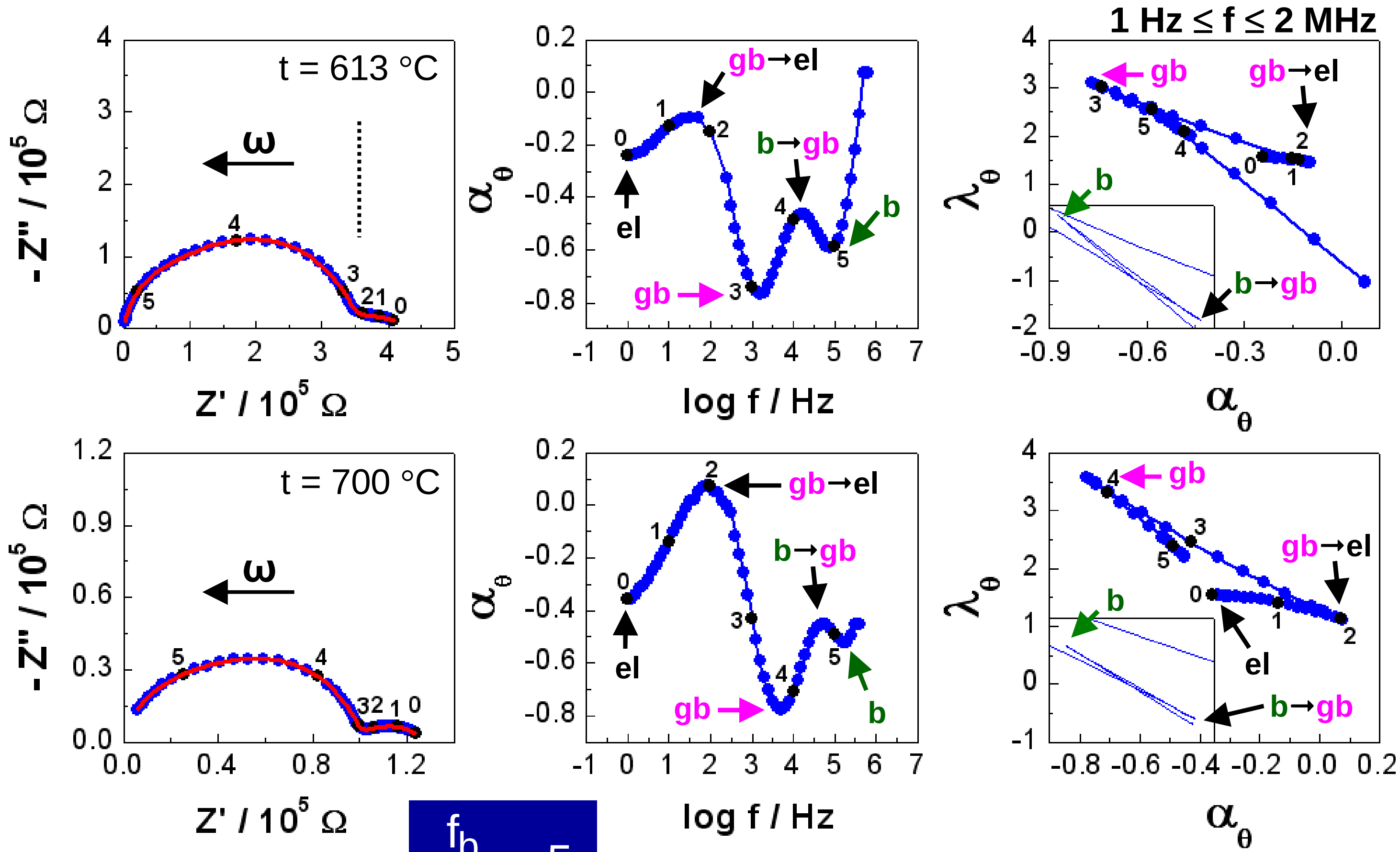
↓

Extraction of R_b, R_{gb}, R_{el}, CPE_b, CPE_{gb} and CPE_{el} starting parameters



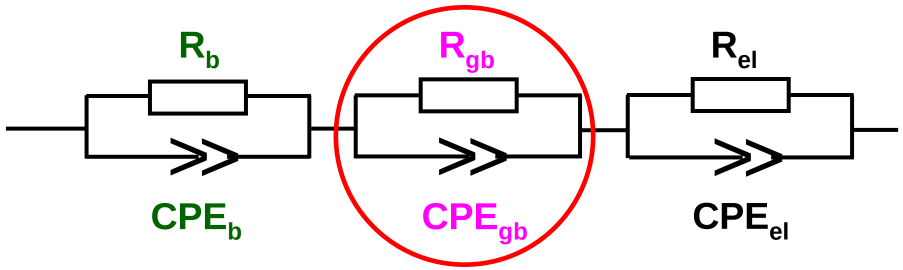
$\sigma_{bulk} = 3\times\sigma_{total}$

Electrical response of $Nd_4Ga_{1.2}Ti_{0.8}O_{9.4}\square_{0.6}$

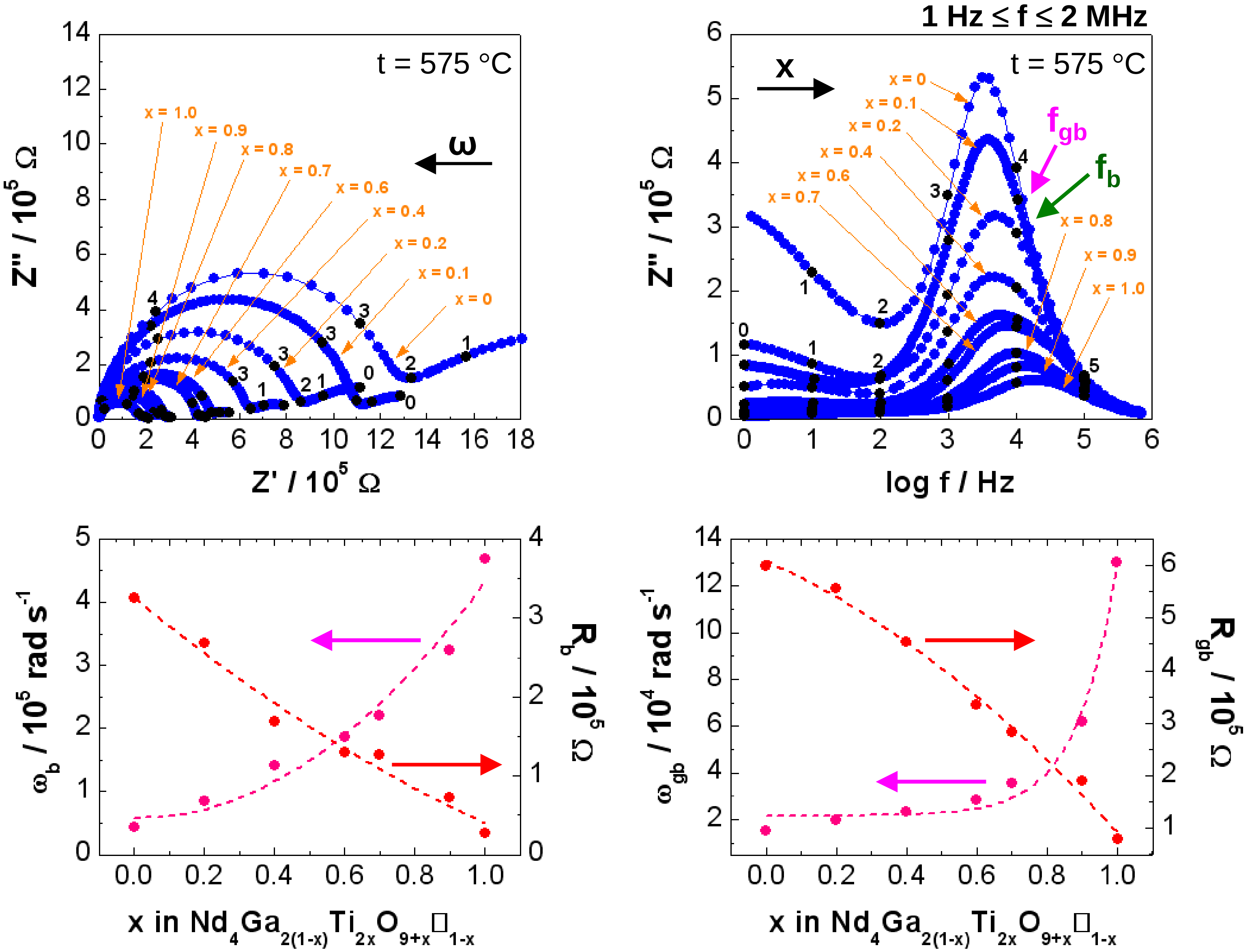


$$\frac{f_b}{f_{gb}} \approx 5$$

Equivalent circuit



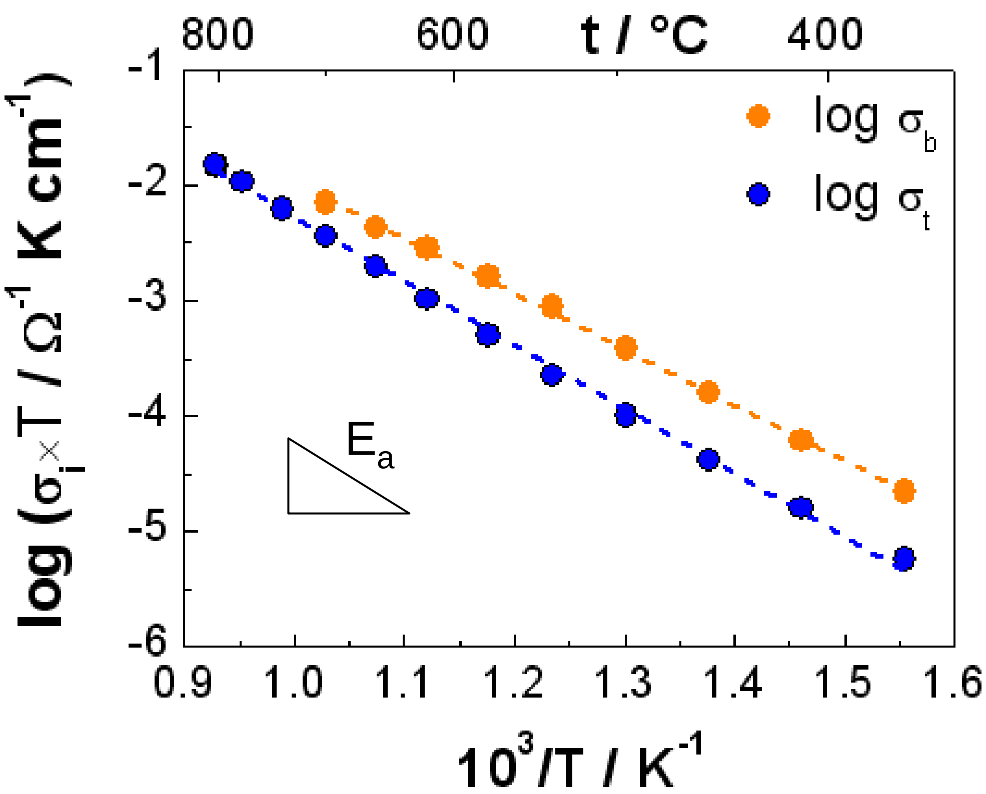
Electrical properties of $Nd_4Ga_{2(1-x)}Ti_{2x}O_{9+x}\square_{1-x}$



Electrical properties of $Nd_4Ga_{2(1-x)}Ti_{2x}O_{9+x}\square_{1-x}$

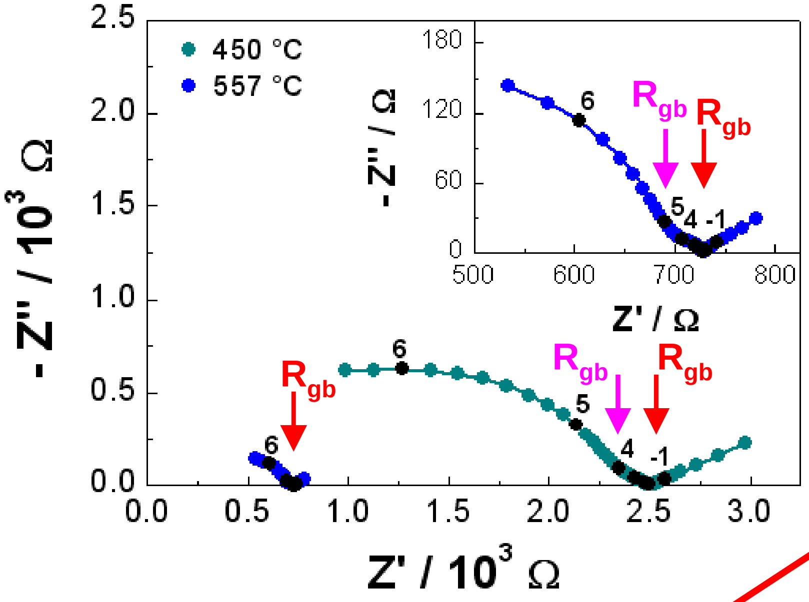
x	i	R_i / kΩ	C_i / pF	p_i	β_i / °	ω_i / rad s^{-1}	ω_b/ω_{gb}
0	b	325(3)	71(1)	0.99(1)	0.90	4.33×10^4	≈ 3
	gb	600(9)	108(8)	0.91(1)	8.1	1.54×10^4	
0.20	b	268(9)	44(4)	0.98(1)	1.8	8.44×10^4	≈ 4
	gb	557(9)	90(9)	0.90(1)	9.	1.99×10^4	
0.40	b	169(1)	43(2)	0.98(1)	2.3	1.42×10^5	≈ 6
	gb	455(9)	95(5)	0.89(1)	10.4	2.32×10^4	
0.60	b	130(3)	41(1)	0.97(1)	2.9	1.87×10^5	≈ 7
	gb	335(5)	104(3)	0.88(1)	10.9	2.86×10^4	
0.70	b	126(3)	36(1)	0.96(1)	3.2	2.20×10^5	≈ 6
	gb	283(4)	99(2)	0.91(1)	8.5	3.57×10^4	
0.90	b	73(1)	44(2)	0.98(1)	1.7	3.23×10^5	≈ 5
	gb	190(3)	85(2)	0.86(1)	12.2	6.19×10^4	
1.00	b	27(1)	79(1)	0.99(1)	0.90	4.69×10^5	≈ 4
	gb	100(9)	77(7)	0.86(1)	12.6	1.30×10^5	

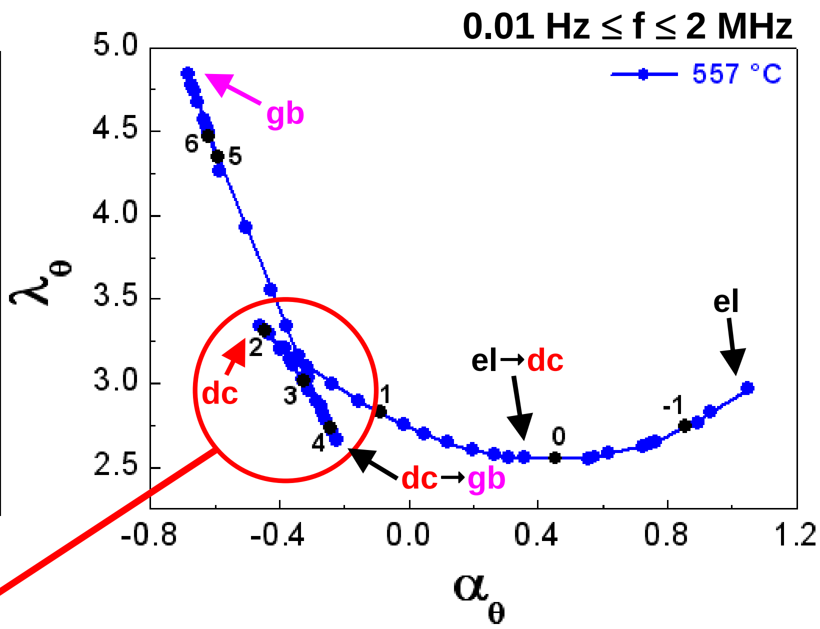
Electrical properties of $Nd_4Ga_{0.6}Ti_{1.4}O_{9.7}\square_{0.3}$

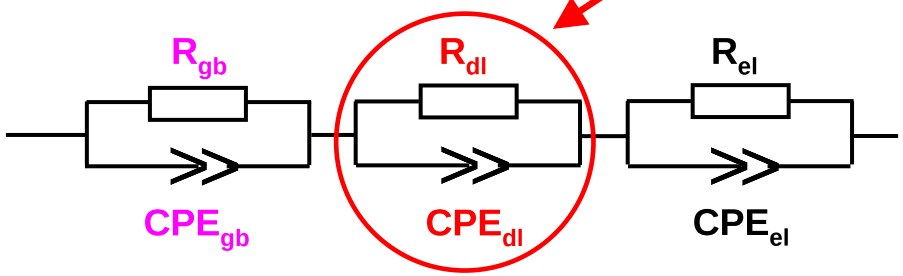


- $(E_a)_{bulk}$ = 0.95 eV vs $(E_a)_{total}$ = 1.10 eV
- At 700 °C, $\sigma_{bulk} = 7.72\times10^{-6}$ S cm^{-1} vs $\sigma_{total} = 3.69\times10^{-6}$ S cm^{-1} *i.e.* 2 times higher

Electrical response of $Nd_{2.955}Sr_{0.045}O_{1.9775}\square_{0.0225}(GaO_4)$







Electrical double layer phenomena "dc"

$10^2 < f(\mathrm{Hz}) < 10^4$

R_{dl} is small

$C_{dl} \approx 0.40\ \mu F\ cm^{-2}$

Conclusion

- Effectiveness of this new representation to separate processes even if their relaxation frequencies are very close

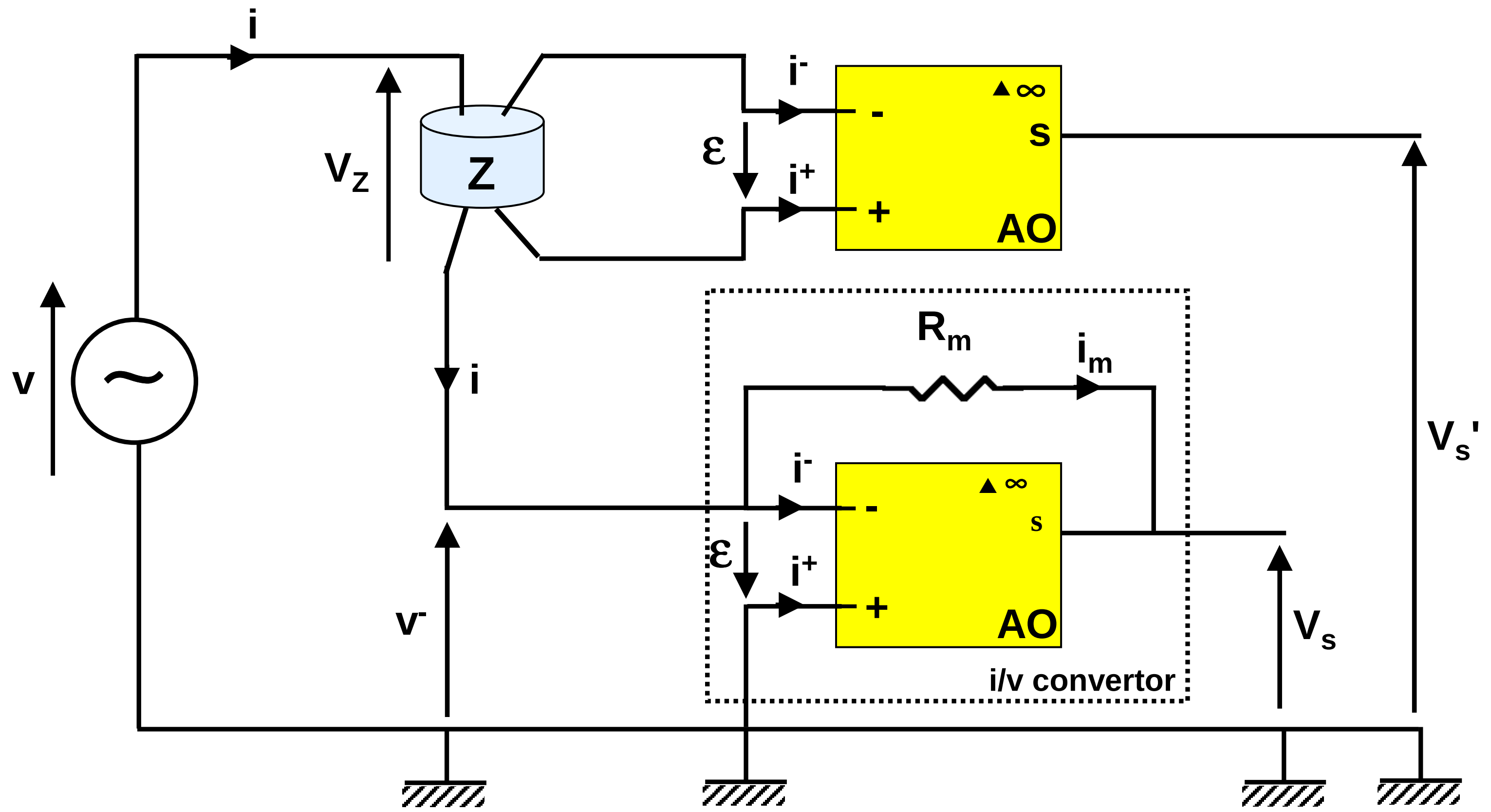
- Theoretical equations are proposed for each frequency zones of the $\alpha_\theta = f(\log(f))$ and $\lambda_\theta = f(\alpha_\theta)$ representations, giving relationships between the electrical parameters studied

- All the parameters R_i, C_i, f_i (i = b, gb) of these processes can be extracted
  - from this representation and using equations or
  - in combination with the classical ones

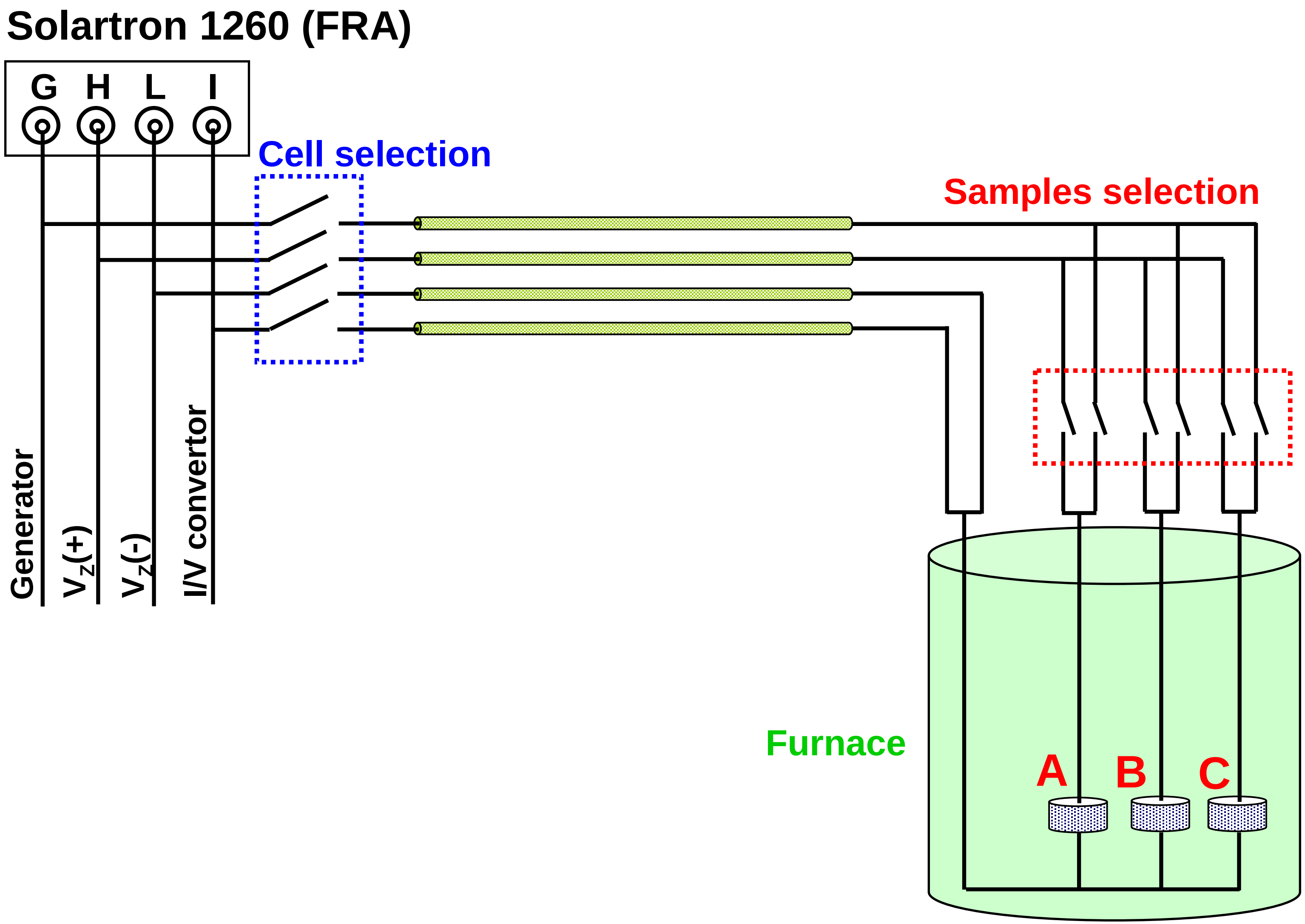
- These parameters can be used as starting parameters for NLLS fitting of impedance spectra

- Equations can be implemented in NLLS fitting software to limit the possible range of variation of the parameters studied

Annex 1



Annex 2


Solartron 1260 (FRA)
G H L I
Cell selection
Samples selection
Generator
V_Z(+)
V_Z(-)
I/V convertor
Furnace
A B C