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DE LA RECHERCHE À L'INDUSTRIE



INFLUENCE OF A PASSIVE LAYER ON THE KINETICS OF AN ELECTRON TRANSFER REACTION

17th ISE Topical Meeting |

Christian Bataillon² ; Marie Benoit¹ ; Benoît Gwinner¹ ;
Frédéric Miserque² ; Carlos Sanchez-Sanchez³ ;
Bernard Tribollet³ ; Vincent Vivier³.

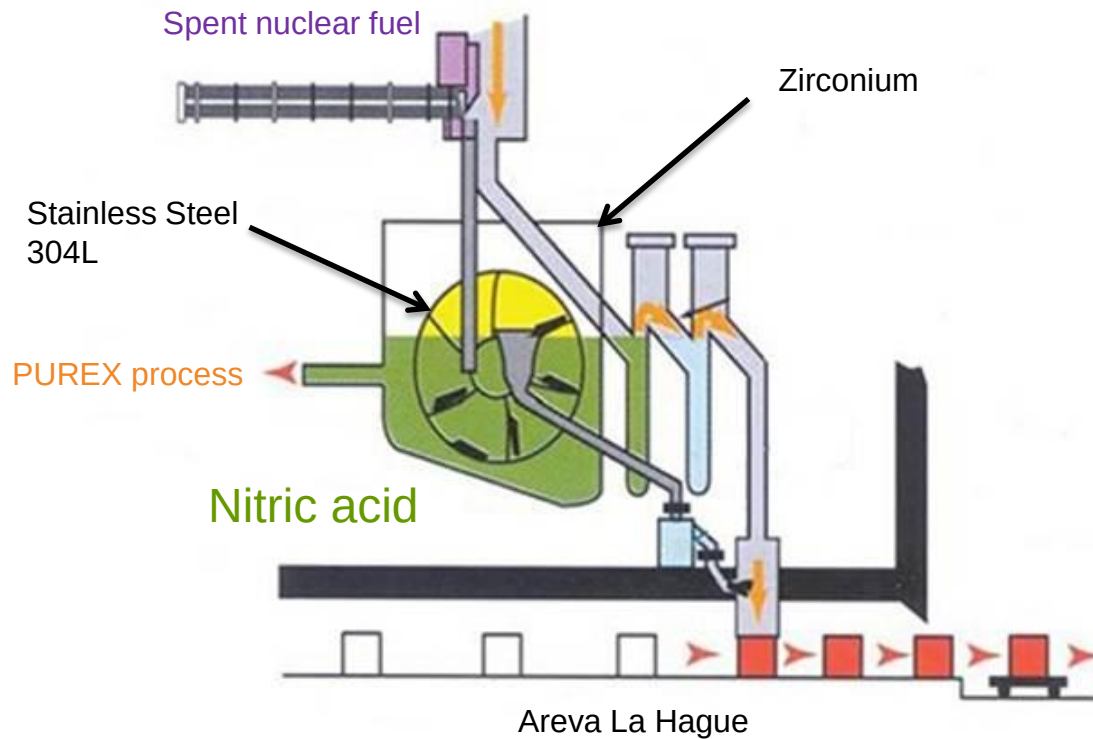
¹CEA, DEN, DANS, DPC, SCCME, Laboratoire d'Etude de la Corrosion Non Aqueuse,
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³CNRS - UPMC, UMR 8235, Laboratoire Interfaces et Systèmes Electrochimiques,
F-75252 Paris 05, France.

INDUSTRIAL CONTEXT

- Spent nuclear fuel reprocessing
 - Concentrated nitric acid environment
 - Use of stainless steel and zirconium as materials for containing concentrated nitric acid (passive materials with good corrosion/dissolution resistance in oxidizing media)



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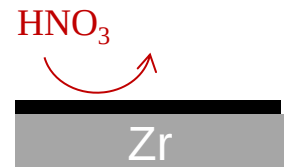
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- Objective: Kinetics modeling of the concentrated nitric acid reduction on passive materials



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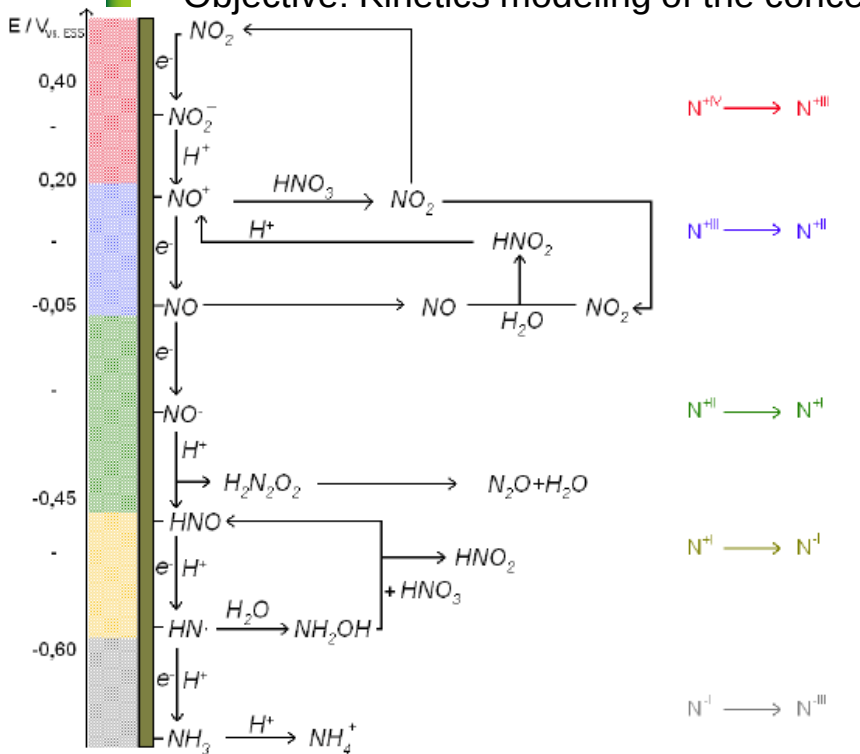
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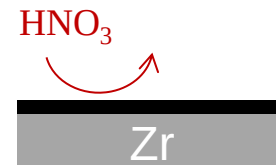
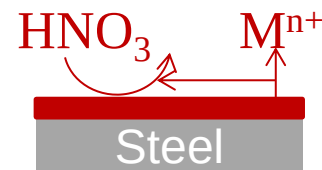
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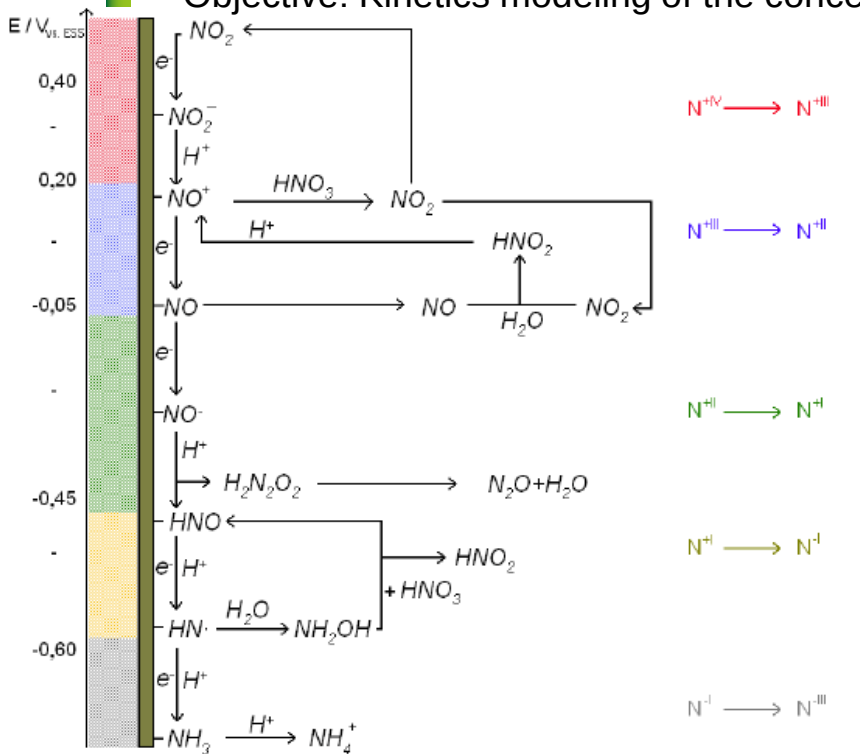
[R.Lange, Thesis 2012]



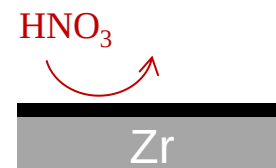
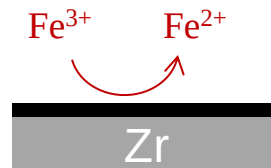
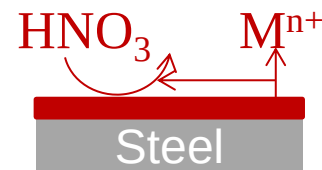
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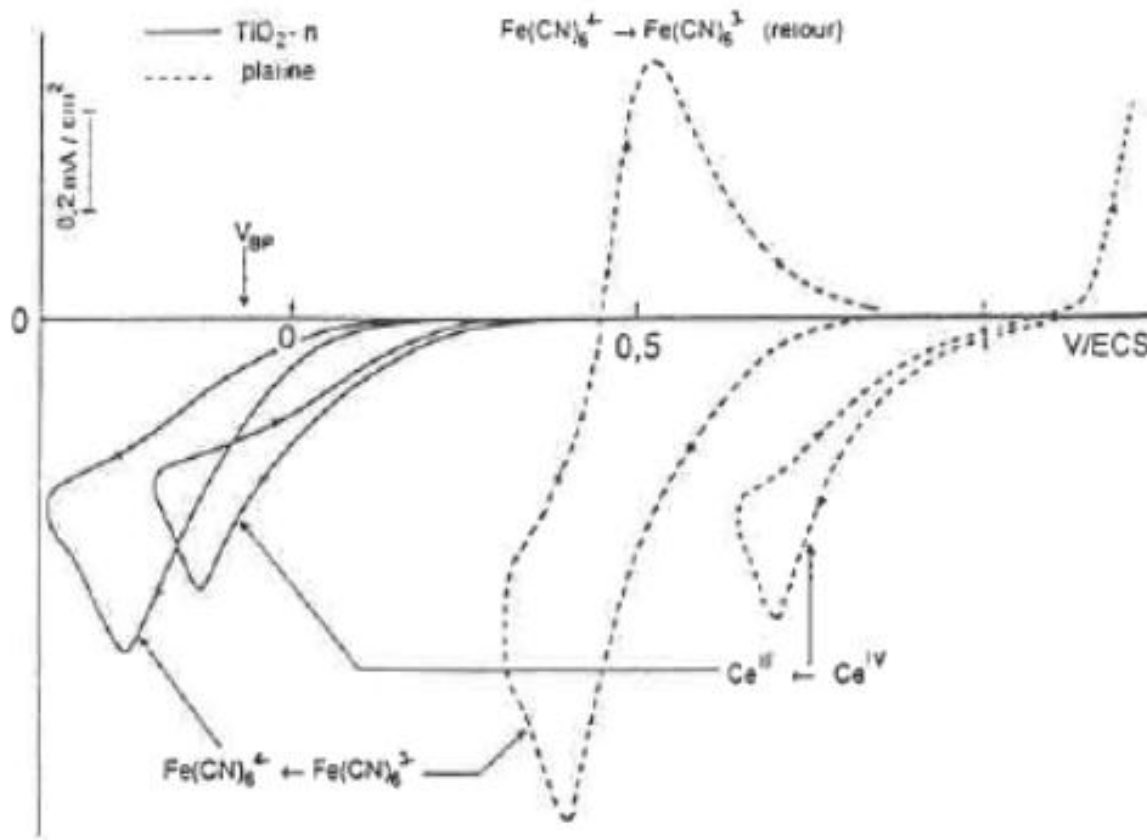
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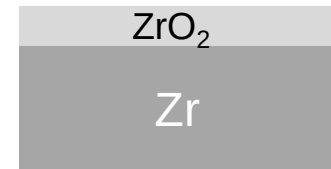
[Bard et al, J.Electrochem. Soc., 125 (1978), p246]

- The passive layer controls the flow of any electron exchange between the metal and an electrolyte
- Accordingly the charge transfer kinetics depends on passive layer properties

Objective: to study the role of the passive layer (ZrO_2) on the kinetics of reduction of Fe(III)/Fe(II) couple

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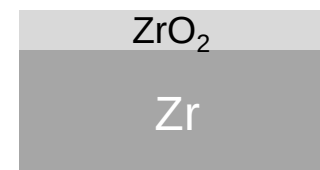
- Formation & characterization of passive layer with a controlled thickness
 - Formation of passive layer
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 - *Ex situ* method: XPS
 - *In situ* method: EIS
 - Results



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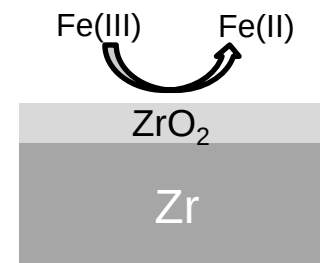
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■ Study of Fe(III) reduction kinetics by EIS on a nanometric passive film

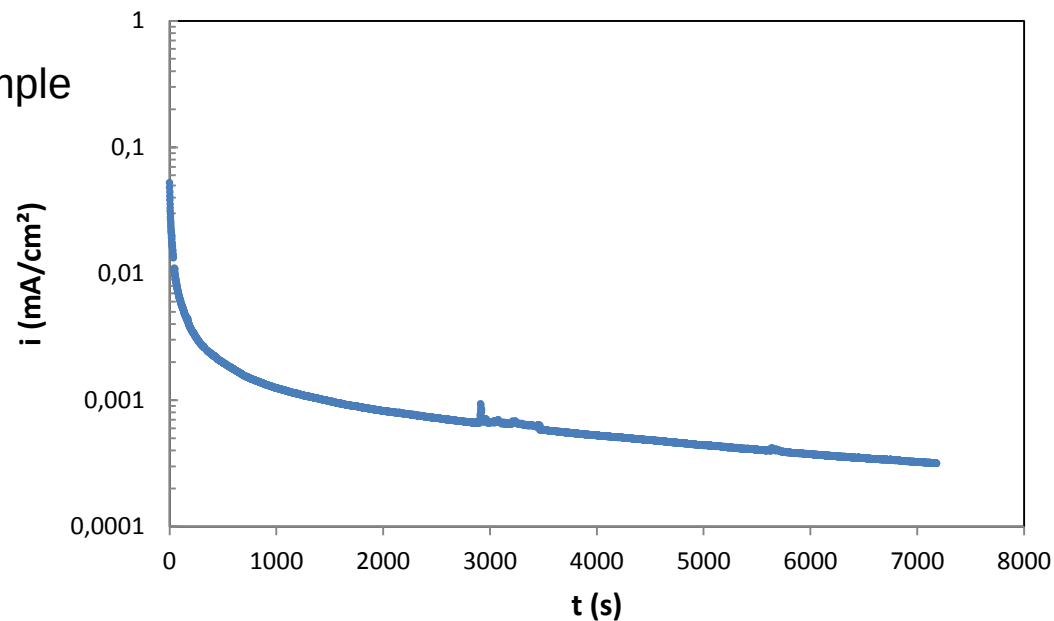
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■ Conclusion and outlook

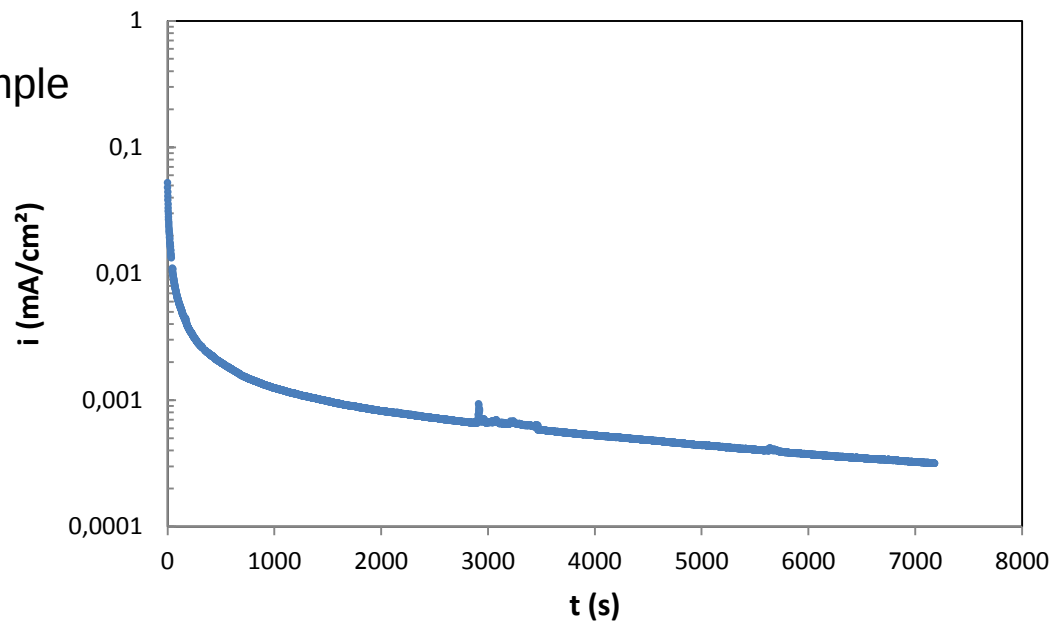
Formation of passive film

■ anodic potential polarization of the sample
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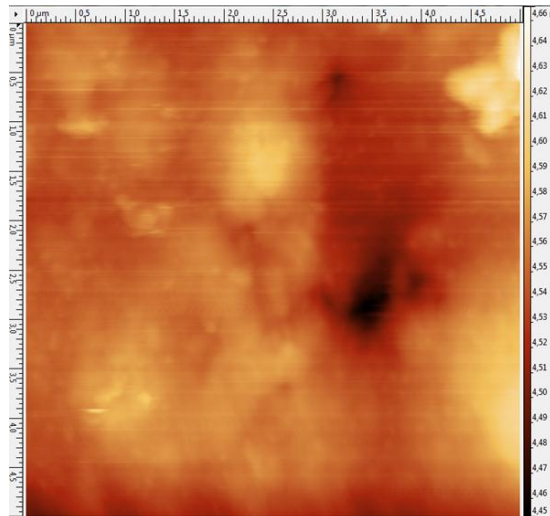
Sample	Potential of formation (V/ENH)	Time of polarization (s)
ZrM103	1,15	~940
ZrM104	Non-polarized	
ZrM105	1,15	~7200
ZrM106	1,5	~7200

Formation of passive film

■ anodic potential polarization of the sample in HNO₃ 4 mol/L 40°C:

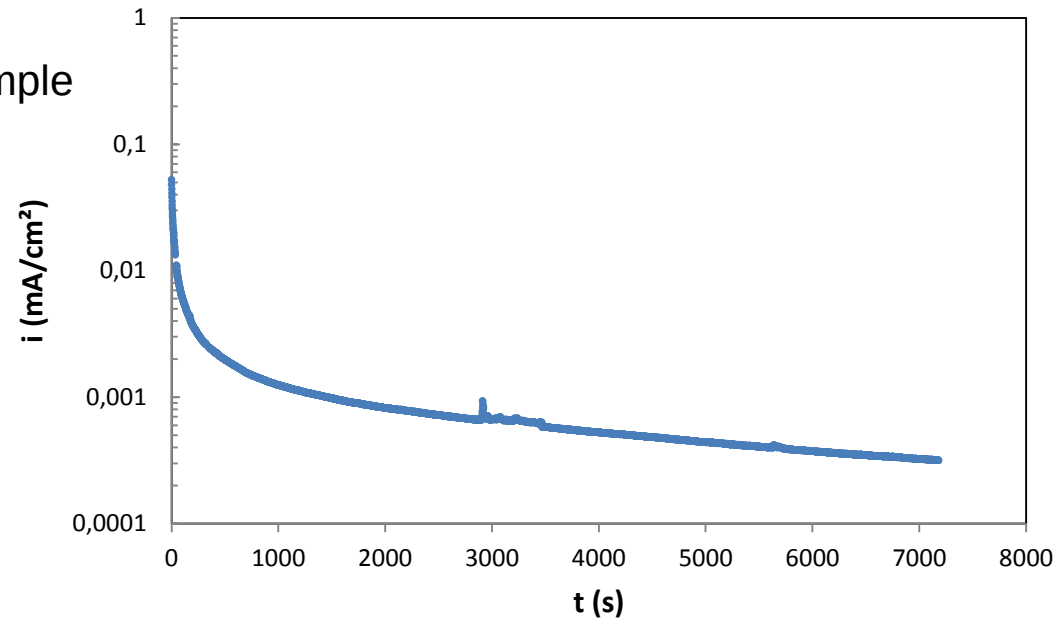
■ Characteristics of the passive film:

- chemically stable
- little rough (<200 nm)



AFM

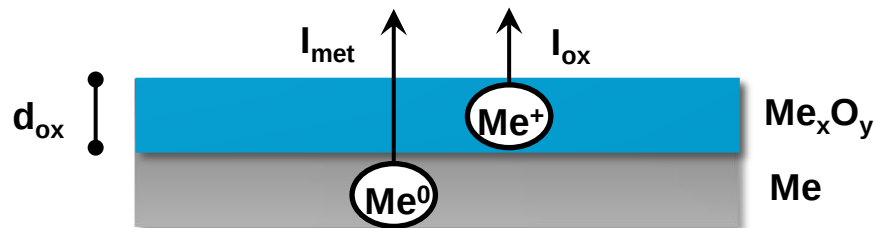
- Nanometric film thickness
 - *Ex situ*: XPS
 - *In situ*: EIS



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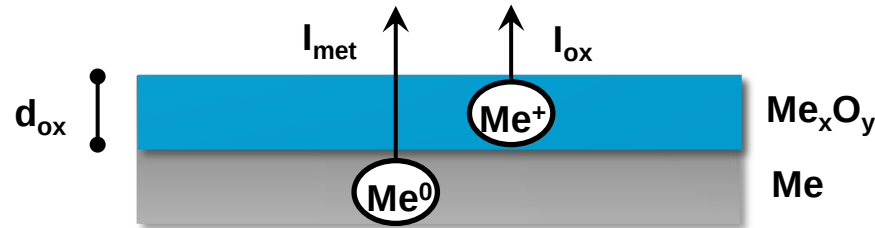
XPS: Principle and parameters

- **Oxide-layer model:** metallic surface coated with a uniform oxide layer (single element)



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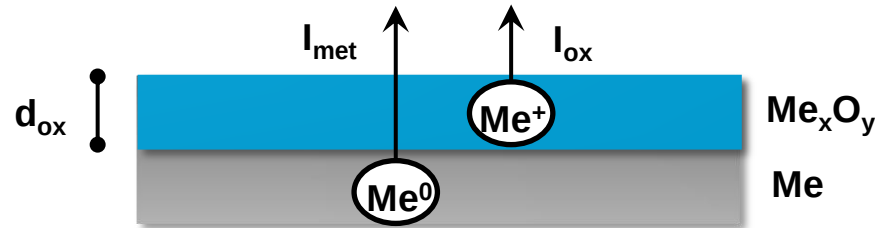


- The oxide thickness (d_{ox}) is estimated by:

$$d_{ox} = \lambda_{ox} \cos \theta \ln \left[\frac{N_{met}}{N_{ox}} \times \frac{\lambda_{met}}{\lambda_{ox}} \times \frac{I_{ox}}{I_{met}} + 1 \right]$$

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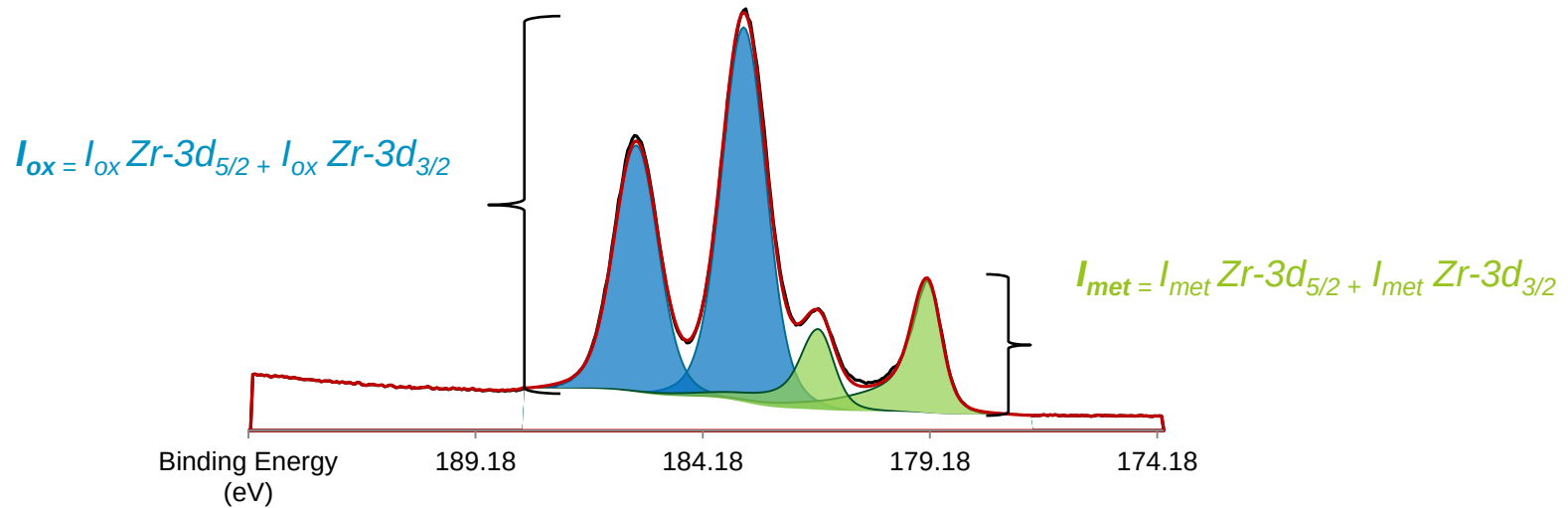
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- Intensities of electronic levels in metallic element (I_{met}) and oxide (I_{ox})
- Inelastic mean free path: average distance of an electron between two inelastic collisions in the metal (λ_{met}) and in the oxide (λ_{ox})
- Number of atoms per volume unit
- Angle between the sensor and the normal of the sample surface ($\cos \theta = 1$)

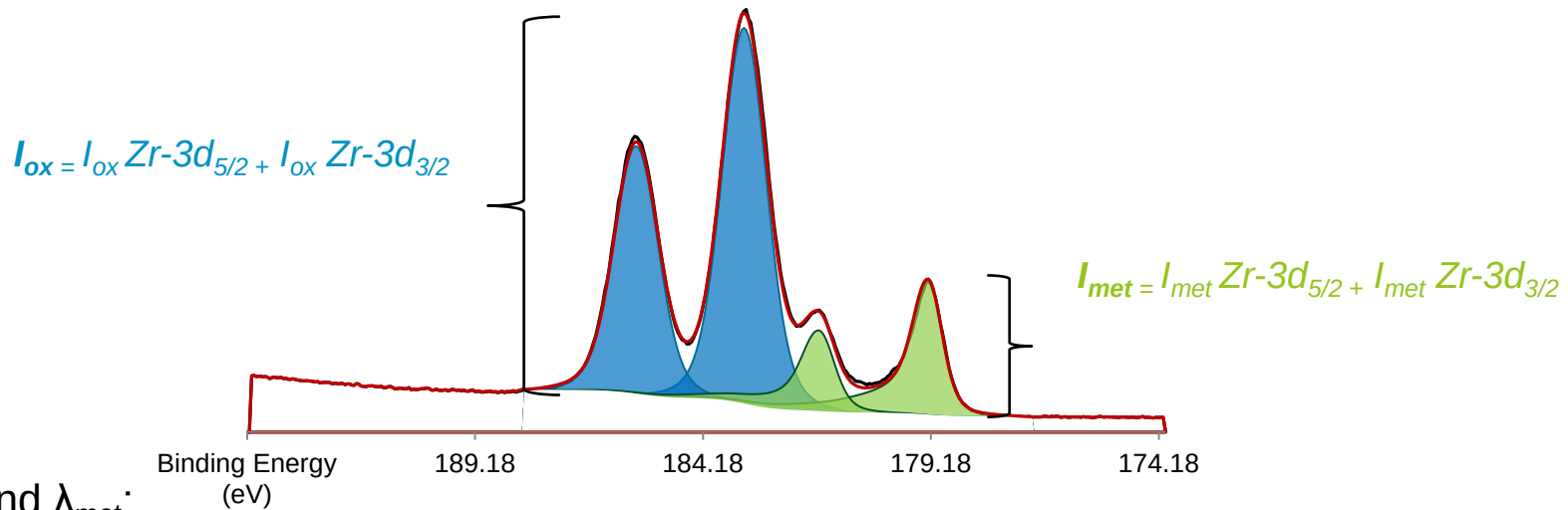
XPS: Parameters estimation

■ I_{ox} and I_{met} : Estimated by recomposing the spectra of Zr 3d levels



XPS: Parameters estimation

I_{ox} and I_{met} : Estimated by recomposing the spectra of Zr 3d levels



λ_{ox} and λ_{met} :

- Seah & Dench [1] (empirical)
- Tanuma, Powell et Penn (TPP-2M) [2] (*ab initio* calculus)
- Gries (G-1) [3] (*ab initio* calculus)

	λ_{met} (nm)	λ_{ox} (nm)
SD	2,3	4,9
TPP-2M	2,6*	2,3*
G-1	3,1*	2,4*

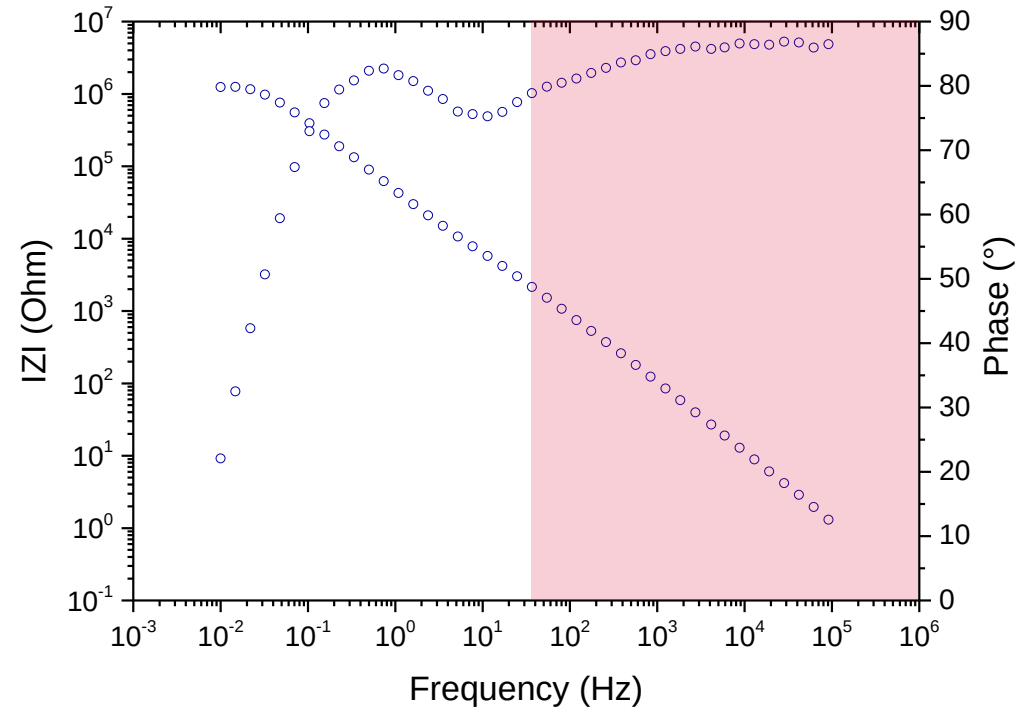
For Zirconium

[1] M.P. Seah and Dench Surf. Interface Anal. 1 (1979) 2
 [2] S. Tanuma, C.J. Powell, D.R. Penn, Surf. Interface Anal. 21 (1994) 165.
 [3] W.H Gries, Surf. Interface Anal. 24 (1996) 38
 * Selon NIST Standard Reference Database 71

EIS

- Complex capacitance representation

$$C(\omega) = \frac{1}{j \cdot \omega (Z(\omega) - R_e)}$$



EIS

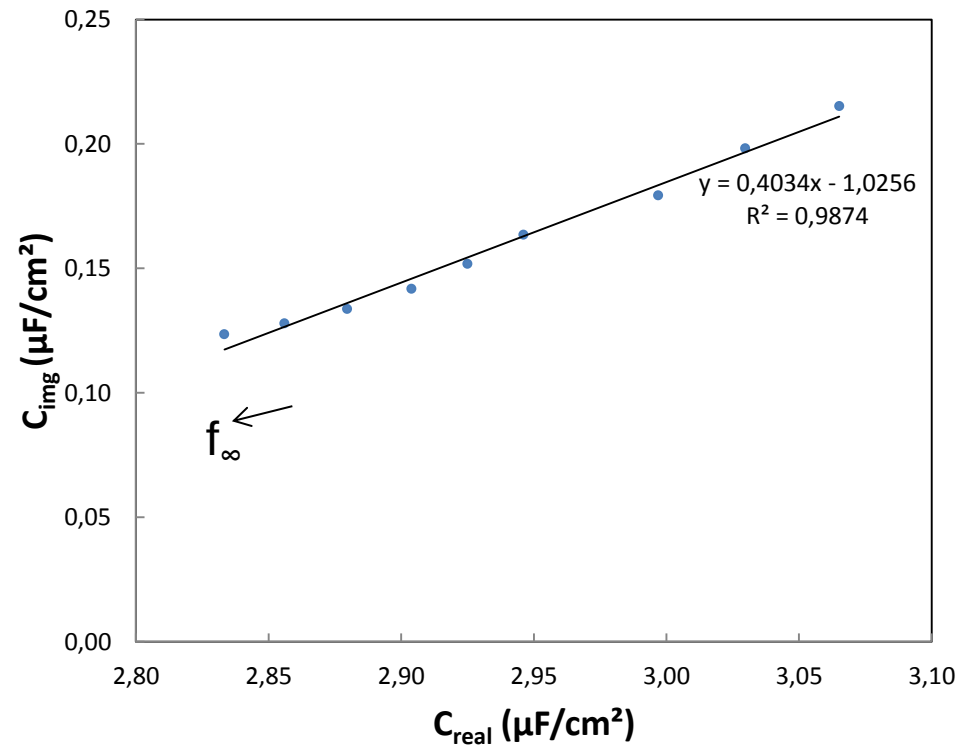
Complex capacitance representation

$$C(\omega) = \frac{1}{j \cdot \omega (Z(\omega) - R_e)}$$

Dielectric material behavior: Jonscher's Law^[1]

$$C(\omega) = C_\infty + \Delta C \cdot (j\omega)^{\alpha-1}$$

Avec $0 < \alpha < 1$



[1]Jonscher, A.K., A many-body universal approach to dielectric relaxation in solids. Physics of Dielectric Solids, 1980.

EIS

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Avec $0 < \alpha < 1$

With C_∞ : film thickness calculation:

$$d = \frac{\epsilon \epsilon_0}{C_\infty}$$

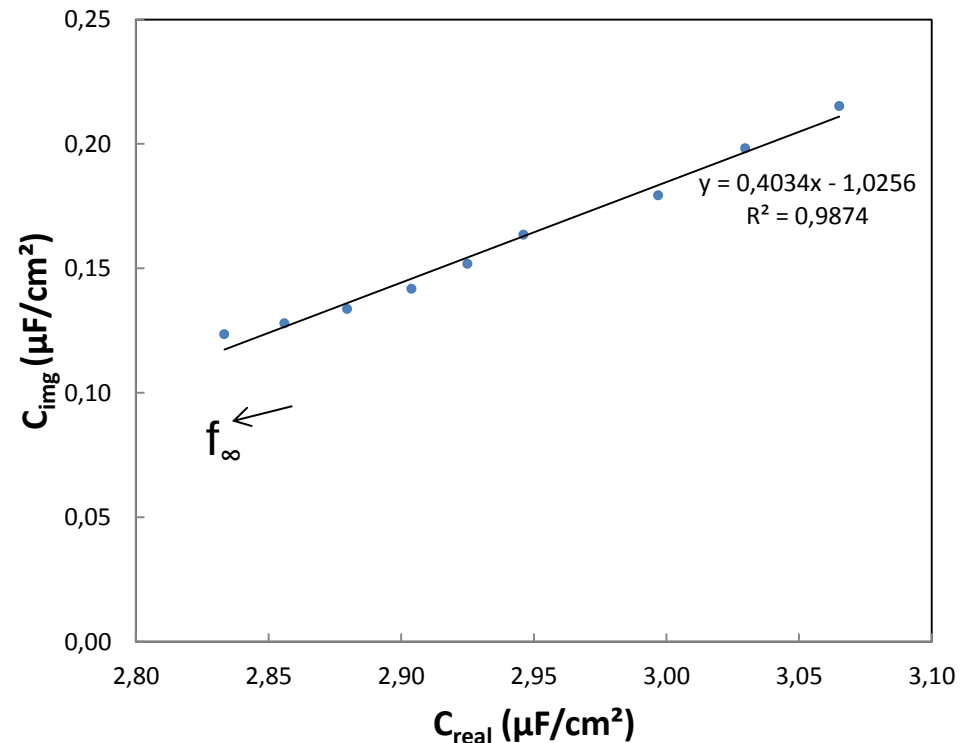
With: ϵ : dielectric constant of the material (22)

ϵ_0 : dielectric permittivity of vacuum ($8.85 \cdot 10^{-14}$ F/cm)

C_∞ : Infinite capacitance corresponding to the defectless oxide layer

(here, $2,56 \mu\text{F}/\text{cm}^2$)

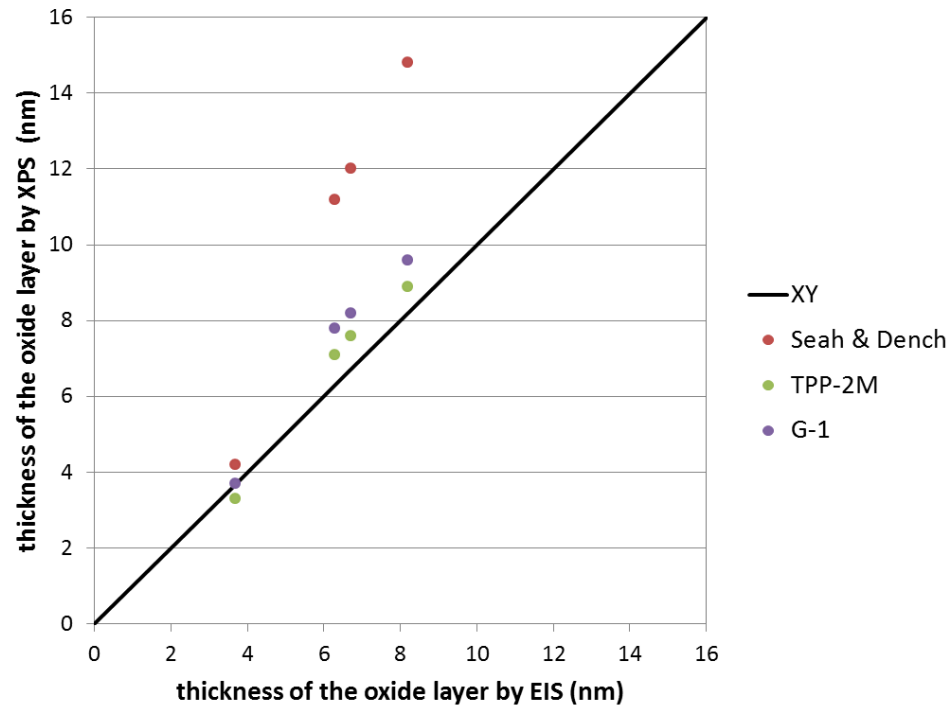
Another method to calculate the thickness, Power law's model ^[2] giving a similar result.



[1] Jonscher, A.K., A many-body universal approach to dielectric relaxation in solids. Physics of Dielectric Solids, 1980.

[2] B. Hirschorn, M. E. Orazem, B. Tribollet, V. Vivier, I. Frateur, and M. Musiani, *J. Electrochem. Soc.*, **157**, C458 2010.

■ Comparison of two techniques (XPS and EIS) for 4 samples



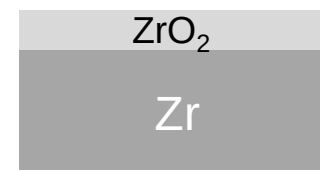
■ Discussion:

- consistent results
- TPP-2M method values seem closer to the EIS ones

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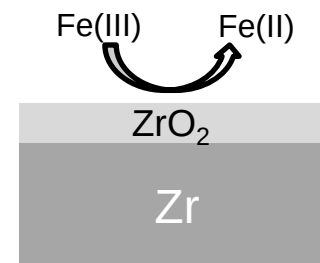
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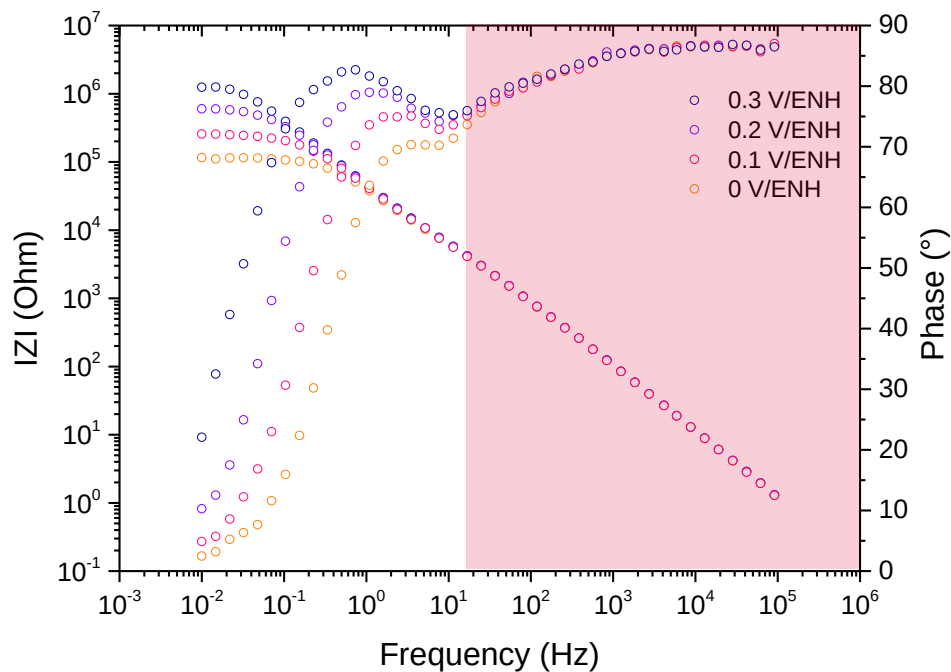
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■ Conclusion and outlook



Evolution of impedance spectra with potential

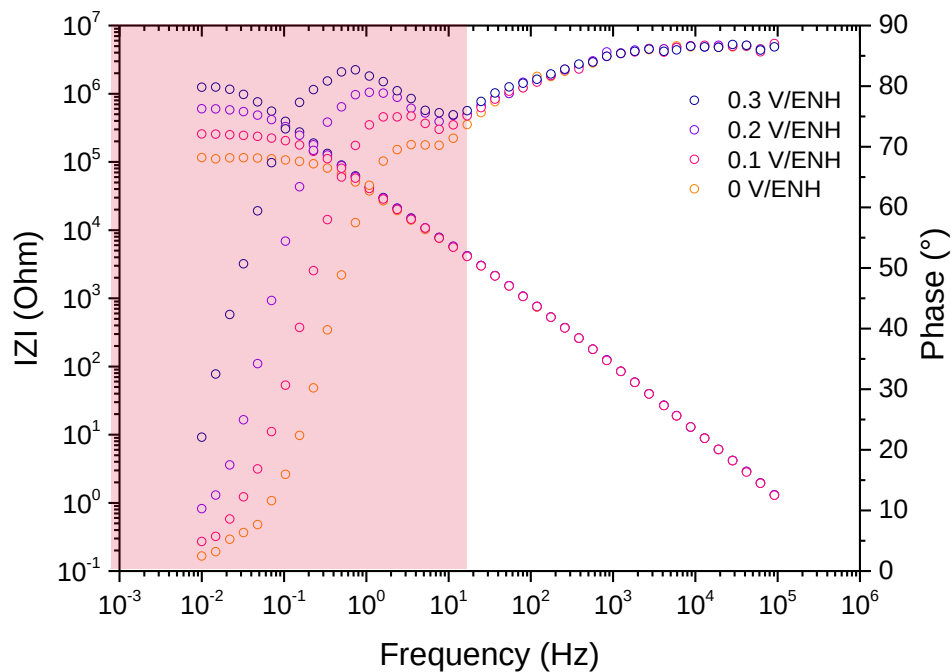


Bode Plot

ZrM106 (8.2 nm)
H₂SO₄ 0.5 M FeII/FeIII 0.1M
Room temperature



Evolution of impedance spectra with potential

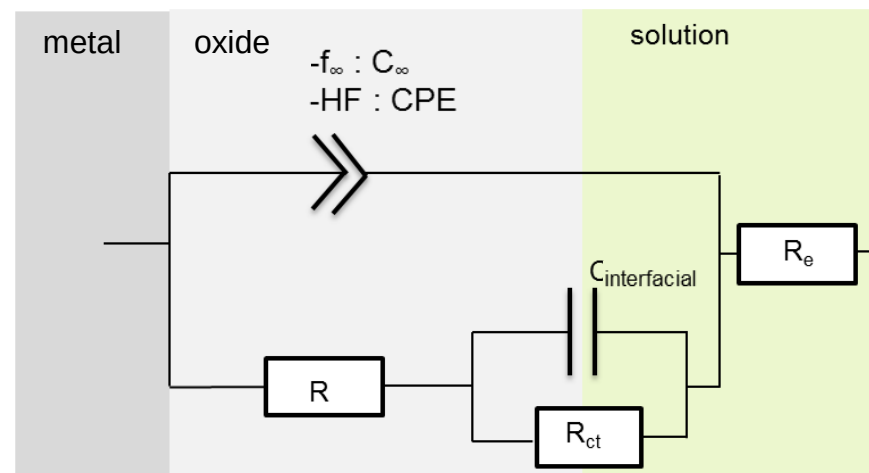


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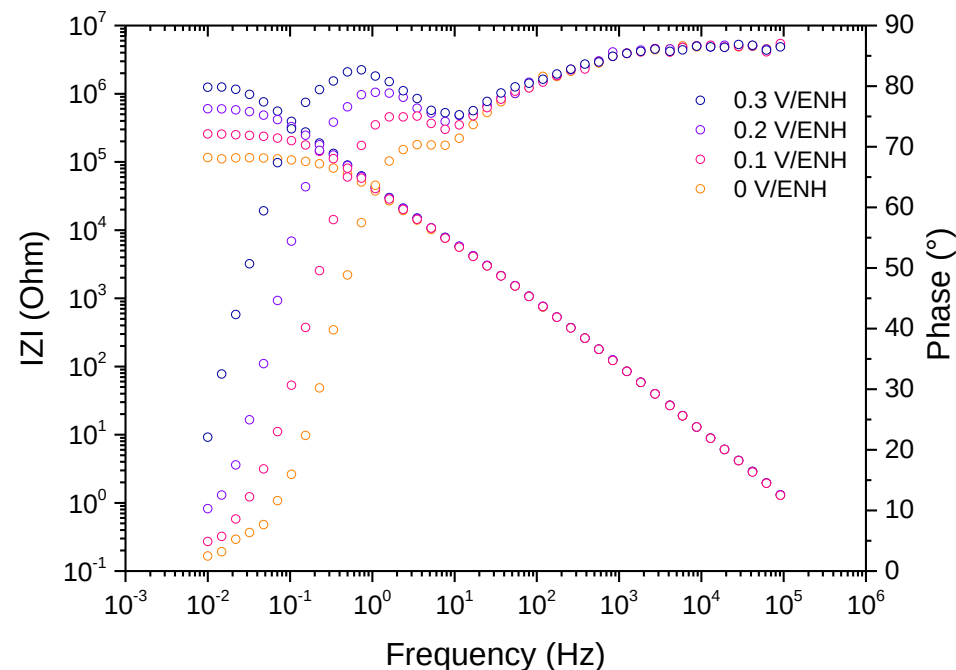
Evolution of impedance spectra with potential

Proposed equivalent circuit:



With:

- R_e : Electrolyte resistance
- C_∞ (at f_∞) & CPE: defectless capacitance representing film and the dielectric losses in the film
- $C_{interfacial}$: Space charge capacitance and double layer capacitance
- R_{ct} : charge transfer resistance
- R : its physical meaning is open to interpretation.



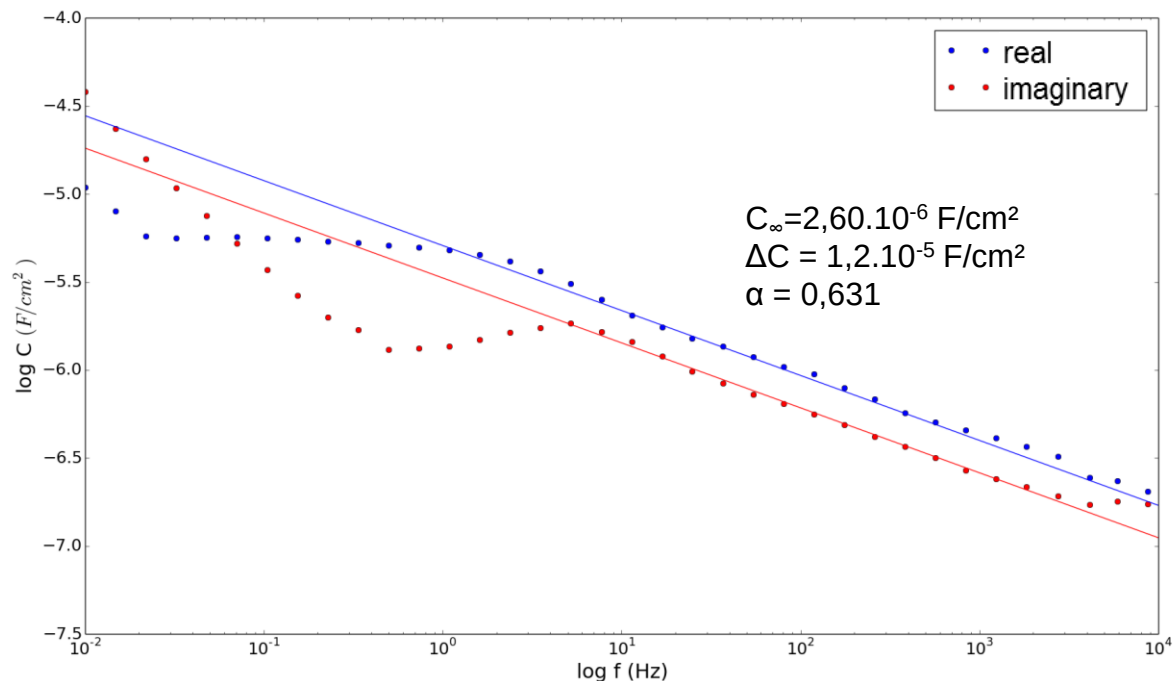
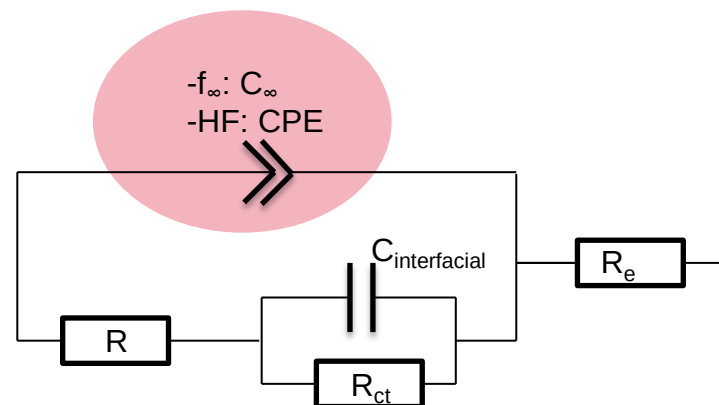
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Justification of the equivalent circuit

As before the high frequency part is attributed to the dielectric properties of the film (Jonscher's Law)

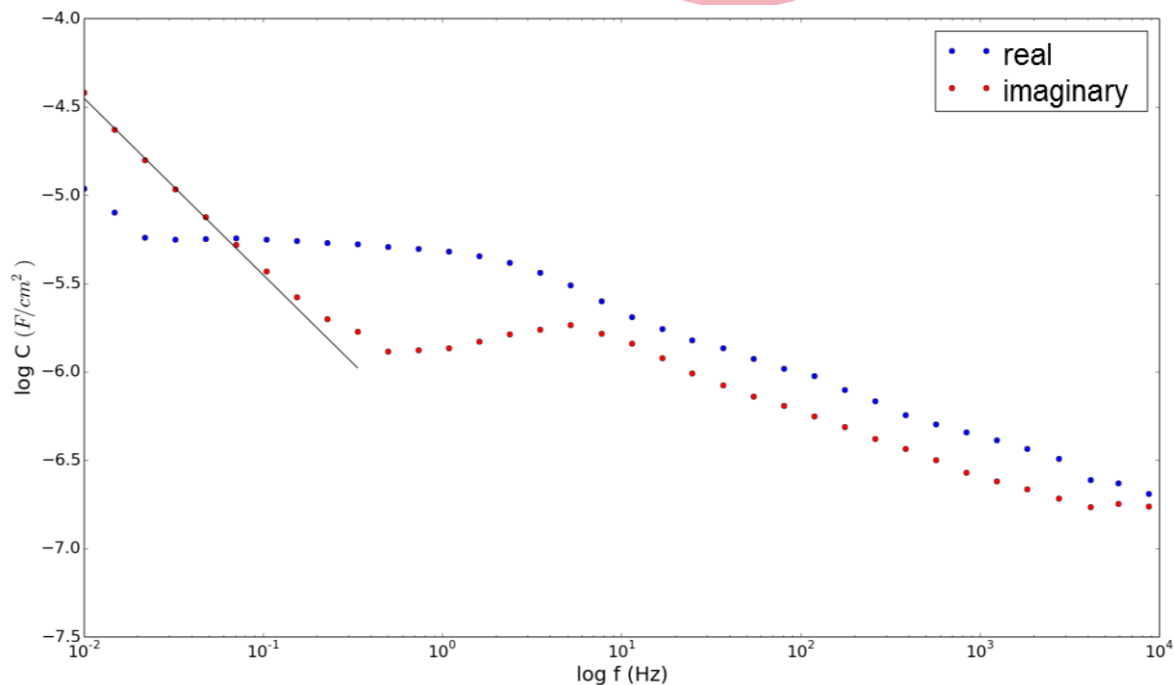
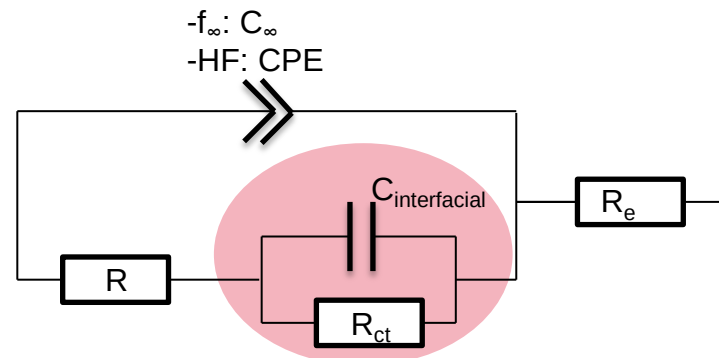




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■ Low frequency part: R_{ct} & $C_{interfacial}$



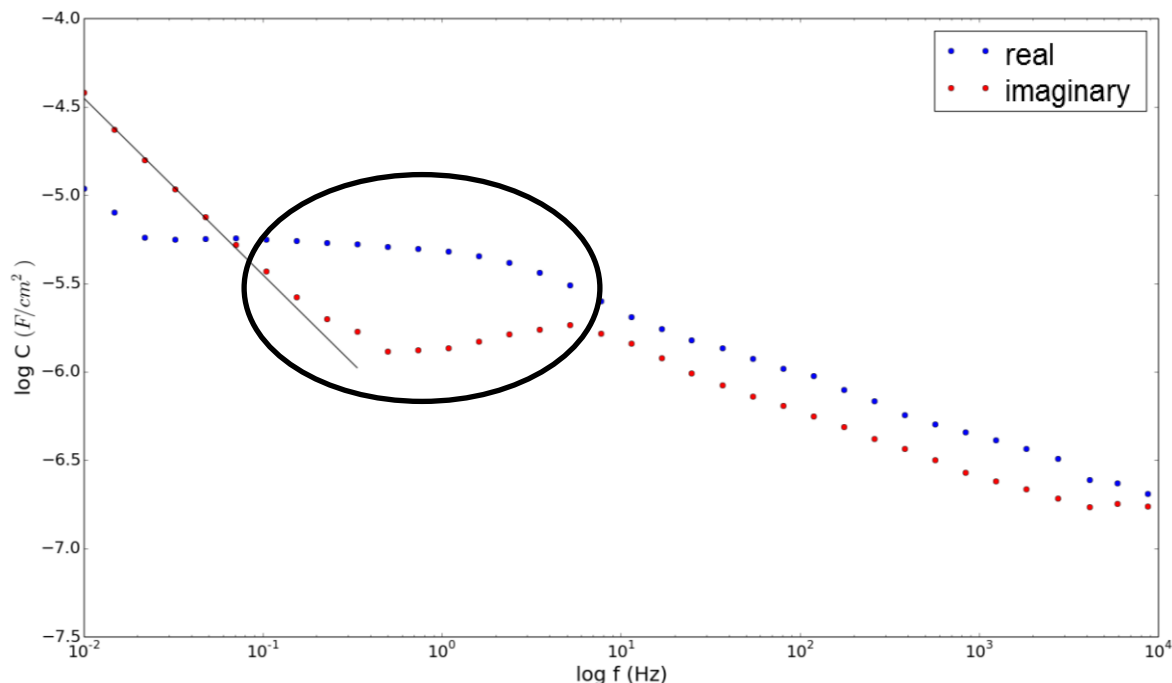
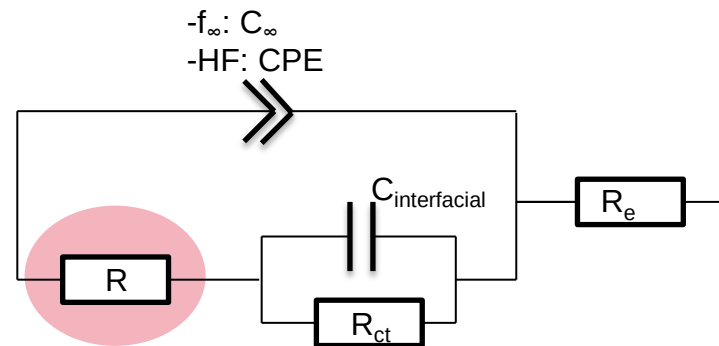


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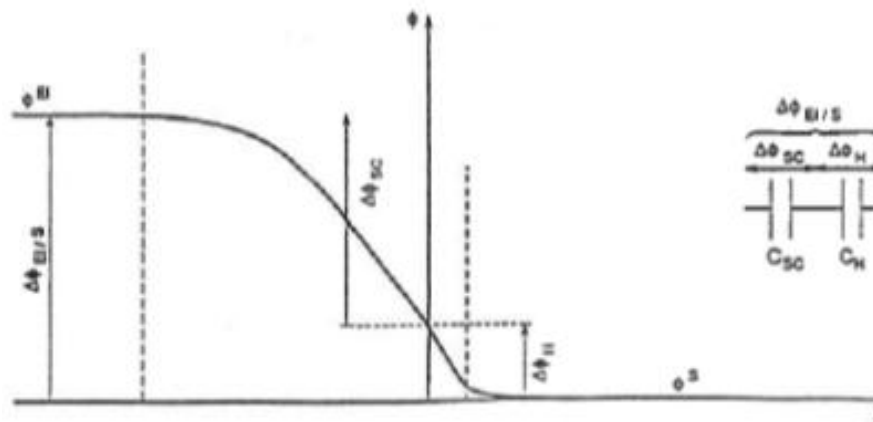
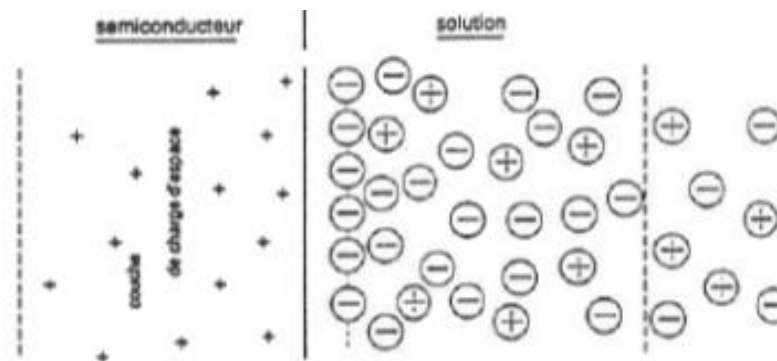
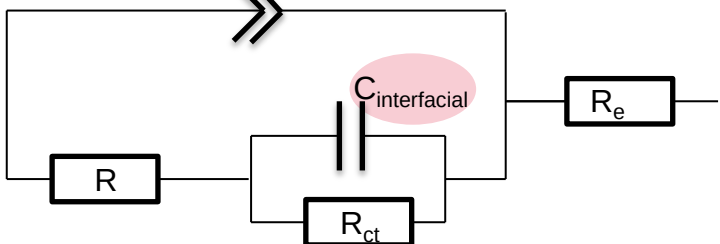
Low frequency part: R_{ct} & $C_{interfacial}$

Intermediate frequency part: R



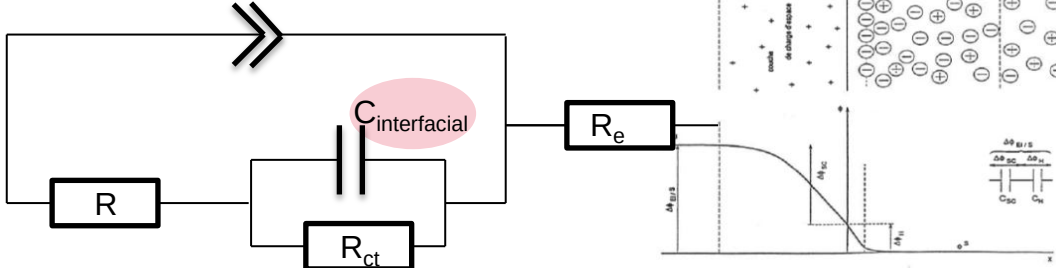
Semiconducting properties of the film

-f_∞: C_∞
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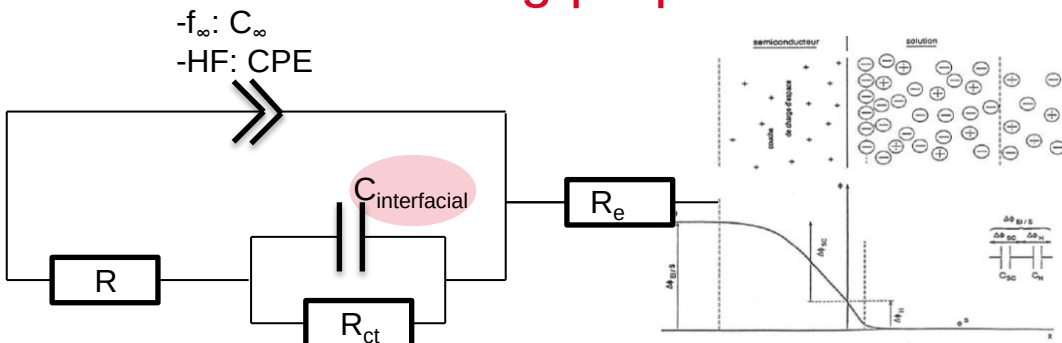
■ Verification of the Mott-Schottky's law:

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon \epsilon_0 q_e N_0} \left(E - E_{bp} - \frac{k_B T}{q_e} \right)$$

With: ϵ : dielectric constant of the material
 ϵ_0 : dielectric permittivity of vacuum: $8,85 \cdot 10^{-14} \text{ F/cm}^2$
 q_e : elementary charge of the electron
 N_0 : charge carriers number
 k_B : Boltzmann's constant
 E_{BP} : flat band potential



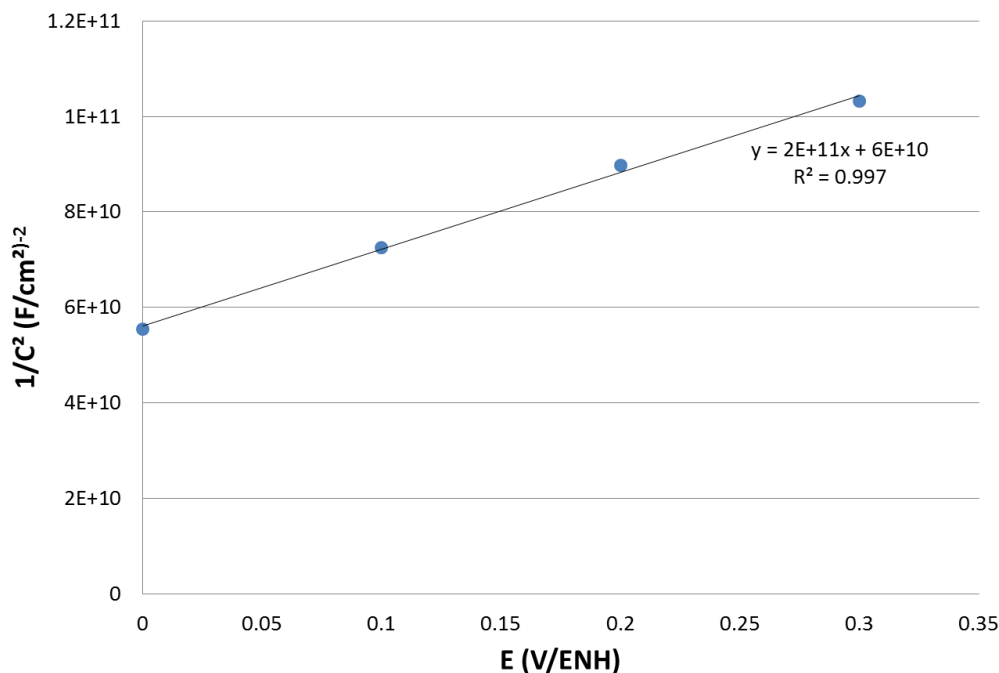
Semiconducting properties of the film



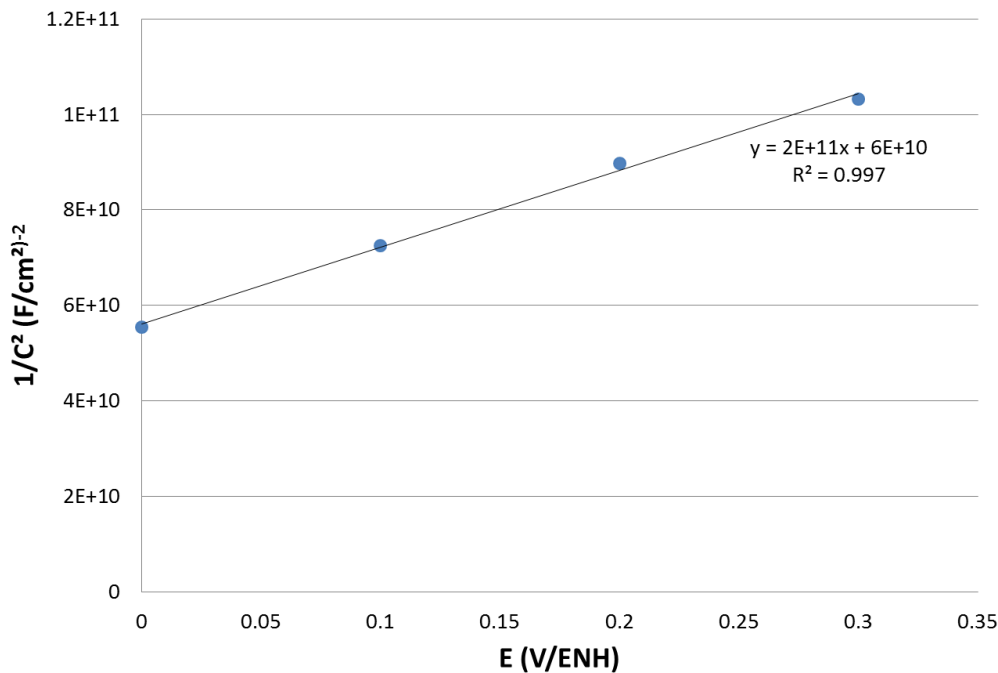
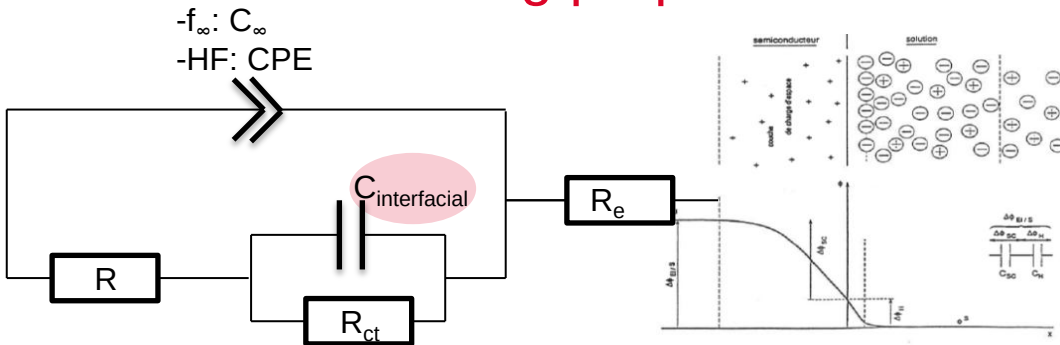
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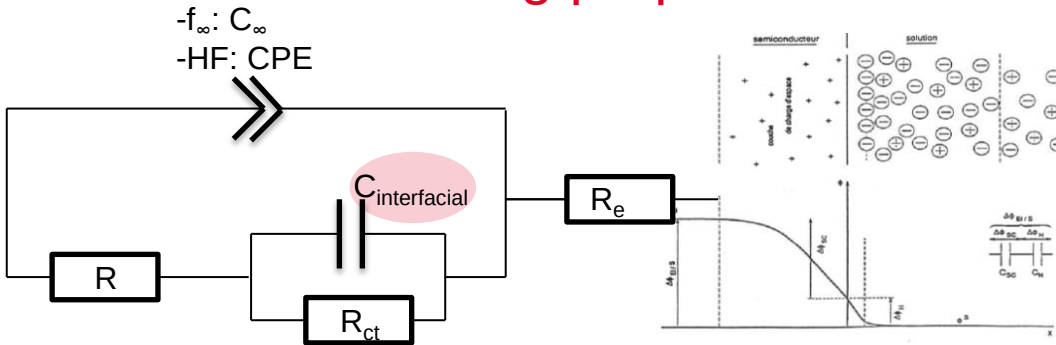
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■ Results:

- Positive slope: ZrO₂ n-type semiconductor
- Determination of the charge number carriers N_0

Semiconducting properties of the film



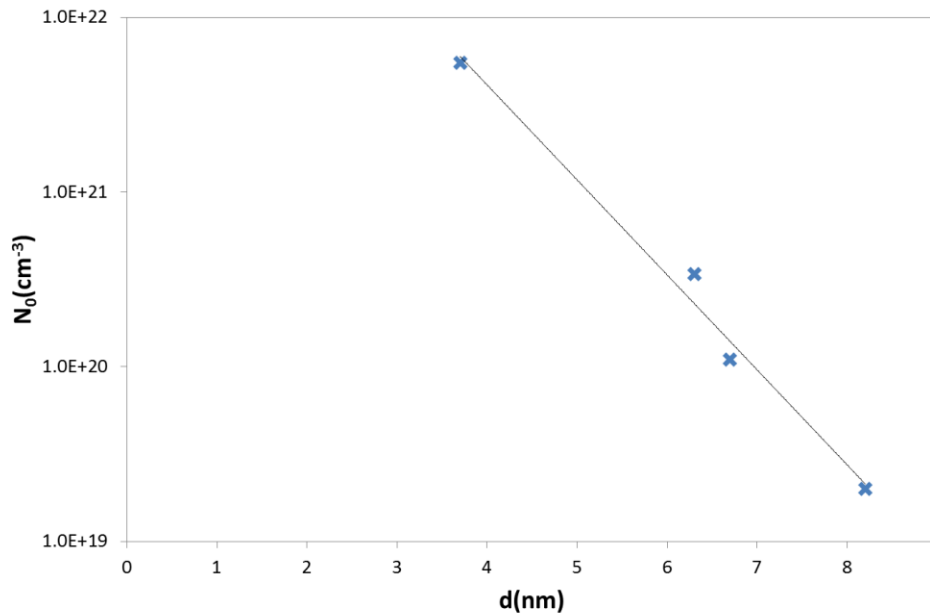
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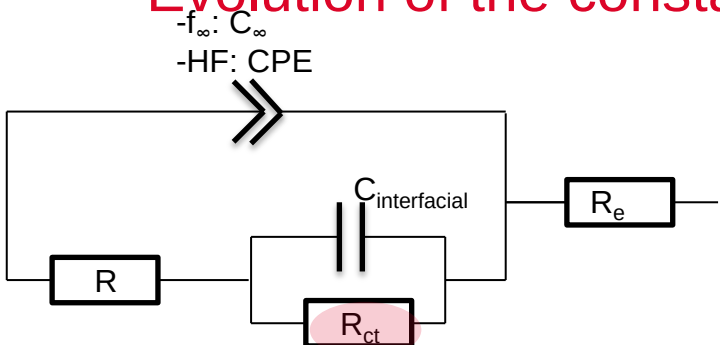
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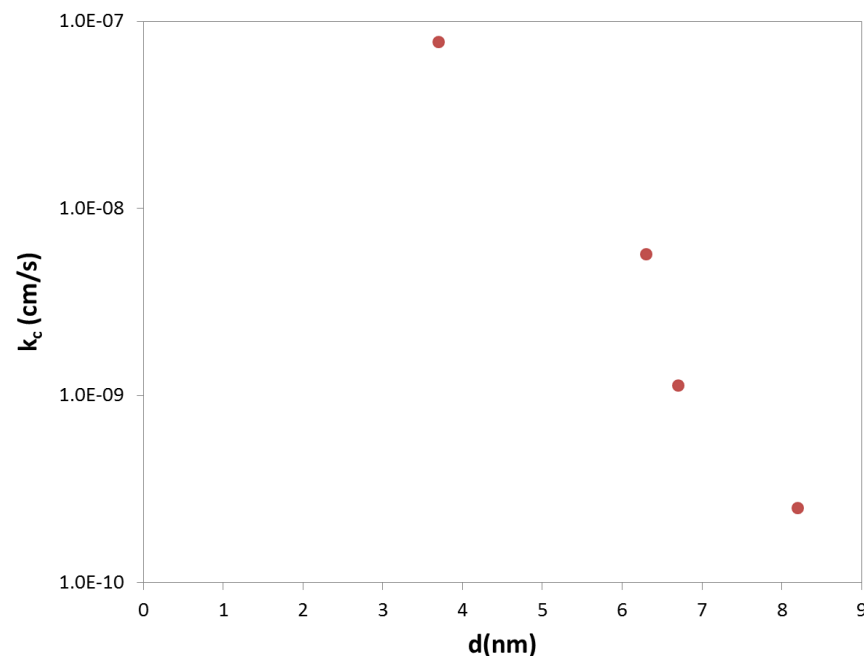
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- Determination of the charge number carriers N_0



Evolution of the constant rate k_c according to thickness



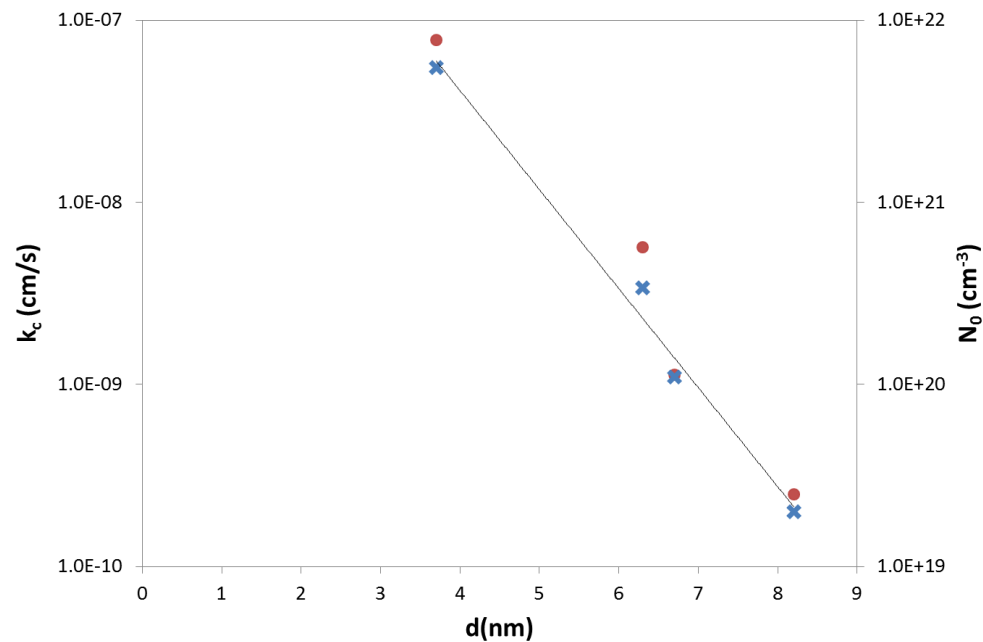
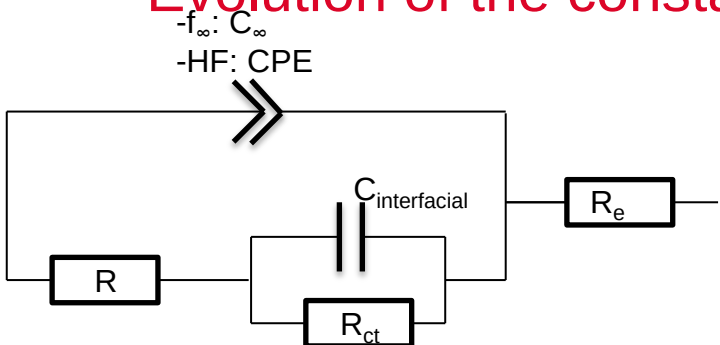
$$R_{ct} = \frac{RT}{\alpha n^2 F^2 S \left(k_c \overline{C_{ox}}(0) e^{\frac{-\alpha n F}{RT}(E-E^0)} \right)}$$



- k_c (determined from R_{ct}) decreases as the thickness increases



Evolution of the constant rate k_c according to thickness



- k_c (determined from R_{ct}) decreases as the thickness increases
- k_c follows the same trend as N_0

The evolution of k_c is linked to the semiconducting properties of ZrO₂

Conclusions

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CONCLUSION & OUTLOOK

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Outlook

- Extension of the approach to other systems
 - Stainless steel
 - $\text{HNO}_3/\text{HNO}_2$



Reprocessing plant of La Hague

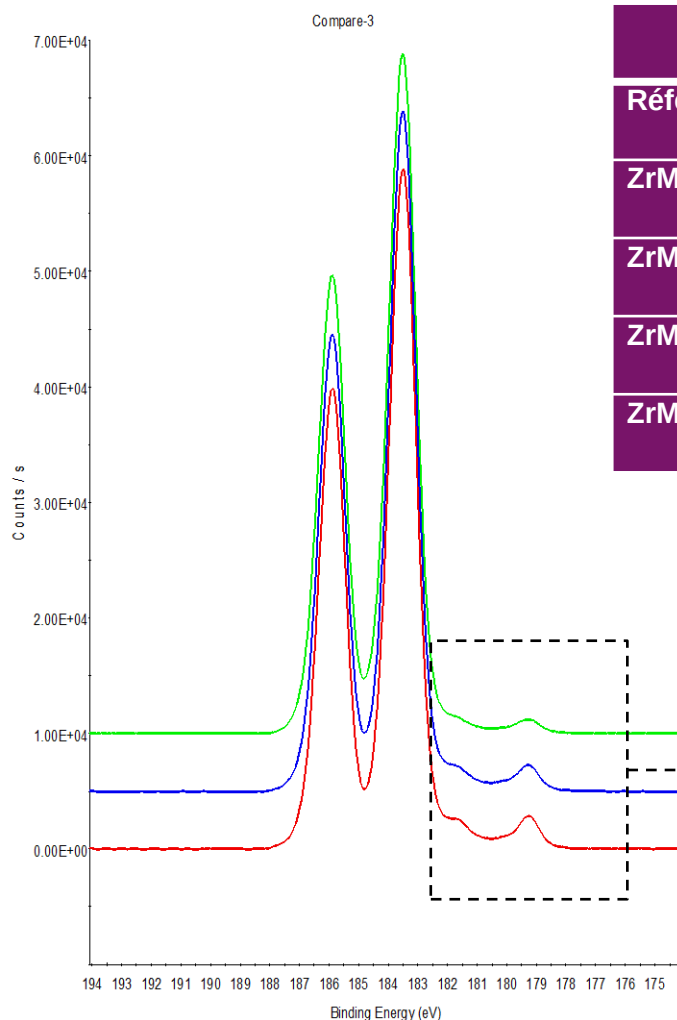
Acknowledgments:



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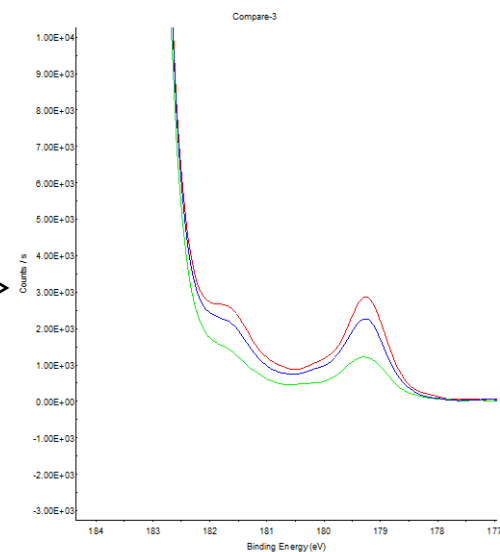
ELABORATION D'UN FILM PASSIF CONTRÔLÉ - DÉTERMINATION ÉPAISSEUR

Comparaison des valeurs d'épaisseur du film passif: XPS/EIS

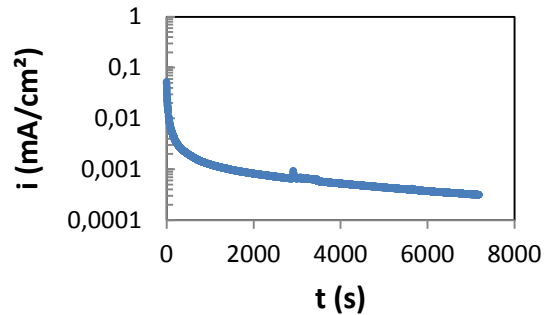


	EIS	XPS		
Référence	$d_{\min}$ (EIS) (nm)	d_{SD} (nm)	d_{TPP-2M} (nm)	d_{G-1} (nm)
ZrM103	5,6	11,2	7,1	7,8
ZrM104	/	4,2	3,3	3,7
ZrM105	6,3	12,0	7,6	8,2
ZrM106	7,7	14,8	8,9	9,6

Comparaison des spectres Zr-3d normalisés sur le niveau $Zr_{ox}-3d_{5/2}$



CROISSANCE DU FILM PASSIF



Caractéristiques du film passif:

- de faible épaisseur
- stable
- non poreuse

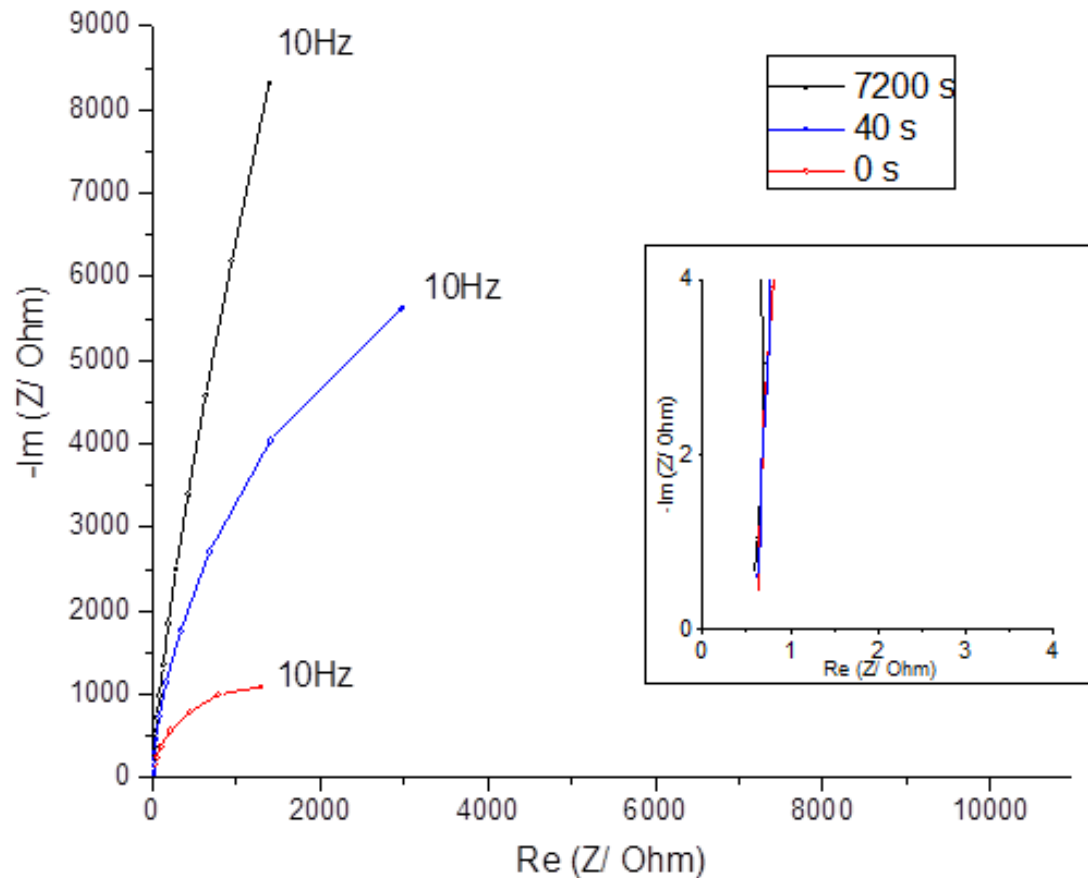
■ Boucle capacitive:
processus se déroulant en parallèle

■ Représentation de Nyquist pas
adaptée

■ Représentation de type capacité
complexe adaptée à ce type de processus

$$C(\omega) = \frac{1}{j \cdot \omega(Z(\omega) - R_e)}$$

Suivi EIS de la croissance du film



Représentation de Nyquist