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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.

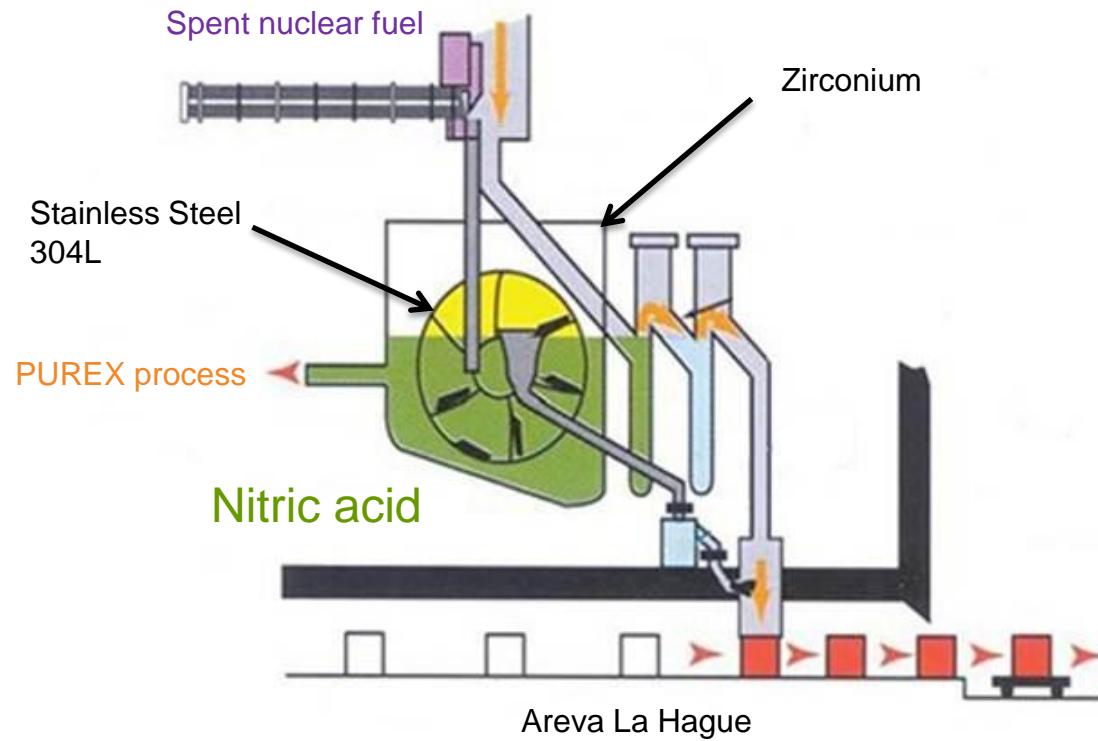
¹CEA, DEN, DANS, DPC, SCCME, Laboratoire d'Etude de la Corrosion Non Aqueuse,
F-91191 Gif-sur-Yvette, France.

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³CNRS - UPMC, UMR 8235, Laboratoire Interfaces et Systèmes Electrochimiques,
F-75252 Paris 05, France.

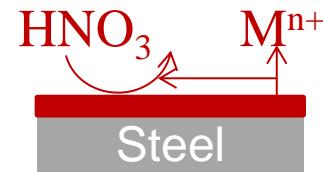
INDUSTRIAL CONTEXT

- 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)



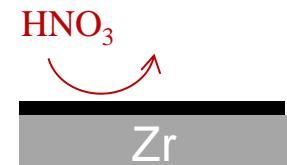
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- Objective: Kinetics modeling of the concentrated nitric acid reduction on passive materials



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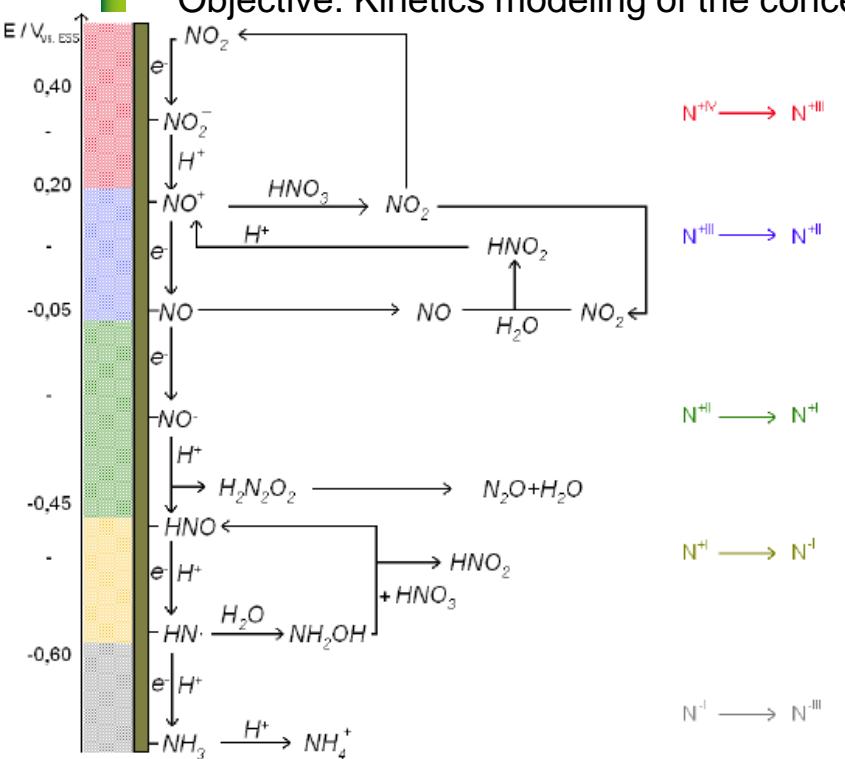
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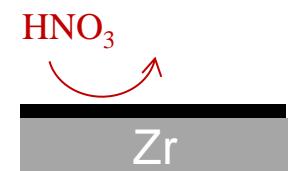
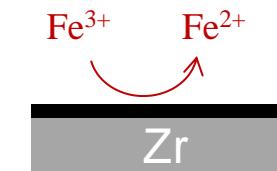
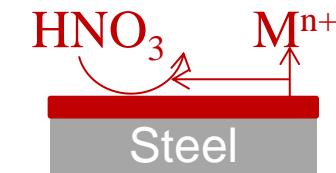
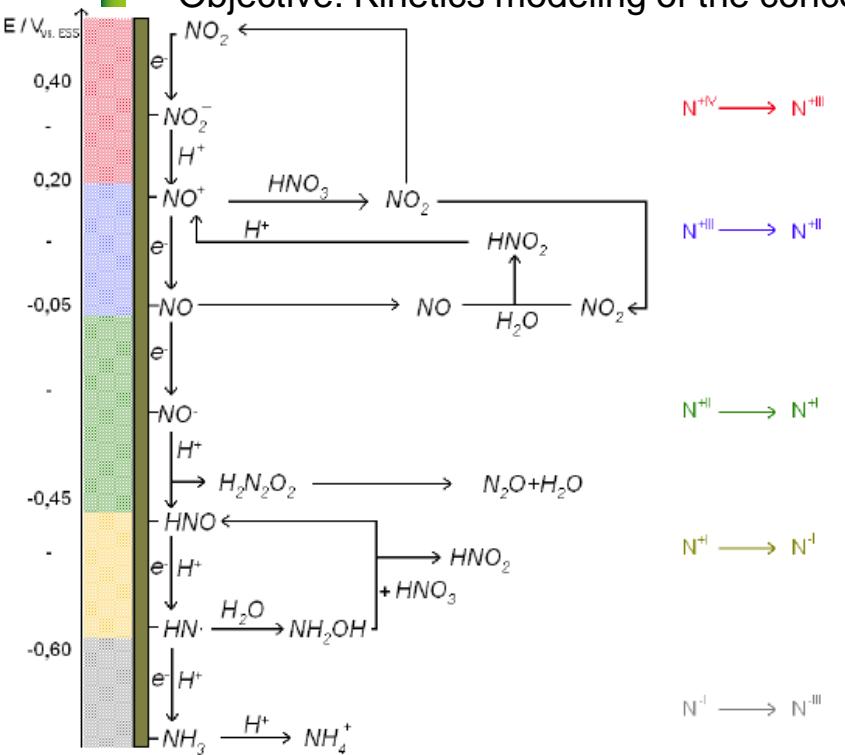
[R.Lange, Thesis 2012]



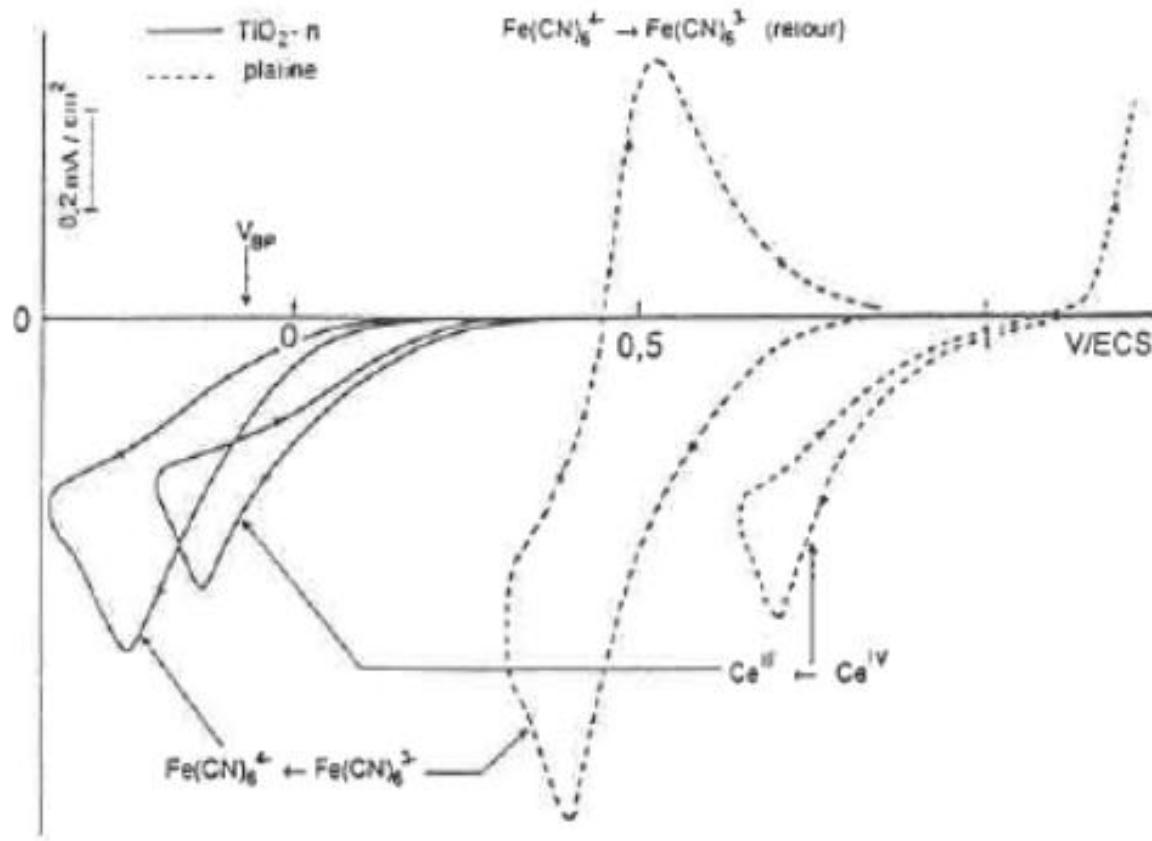
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LITERATURE



[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

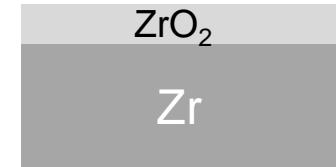
OUTLINE

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

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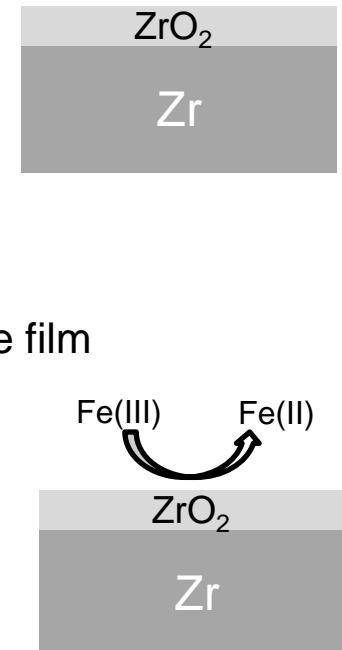
- Formation & characterization of passive layer with a controlled thickness
 - Formation of passive layer
 - Monitoring the (nanometric scaled) thickness
 - *Ex situ* method: XPS
 - *In situ* method: EIS
 - Results



OUTLINE

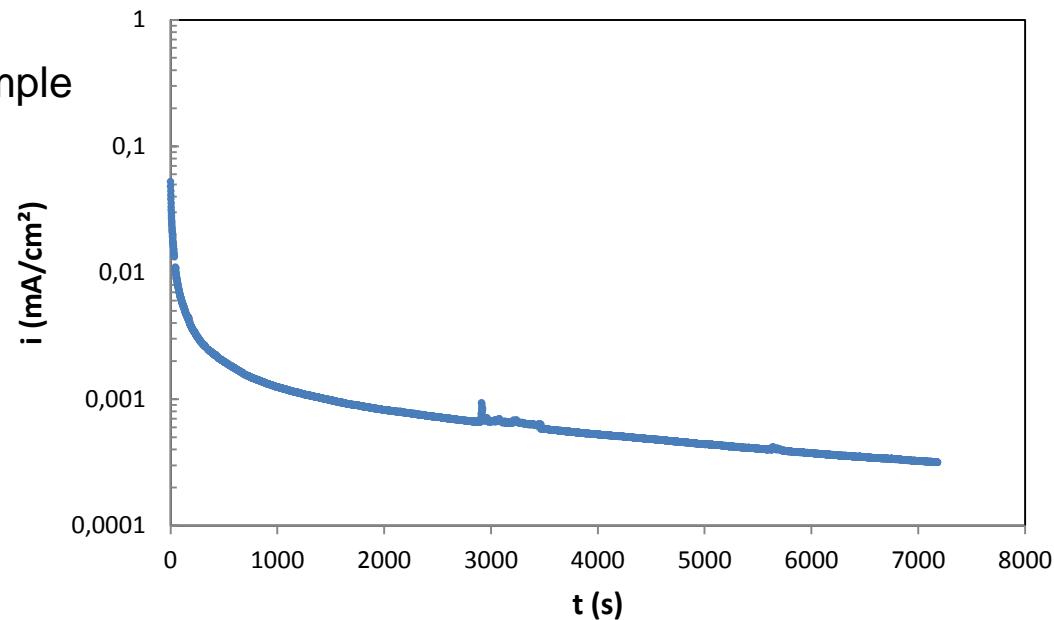
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- Study of Fe(III) reduction kinetics by EIS on a nanometric passive film
 - EIS analysis
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- Conclusion and outlook



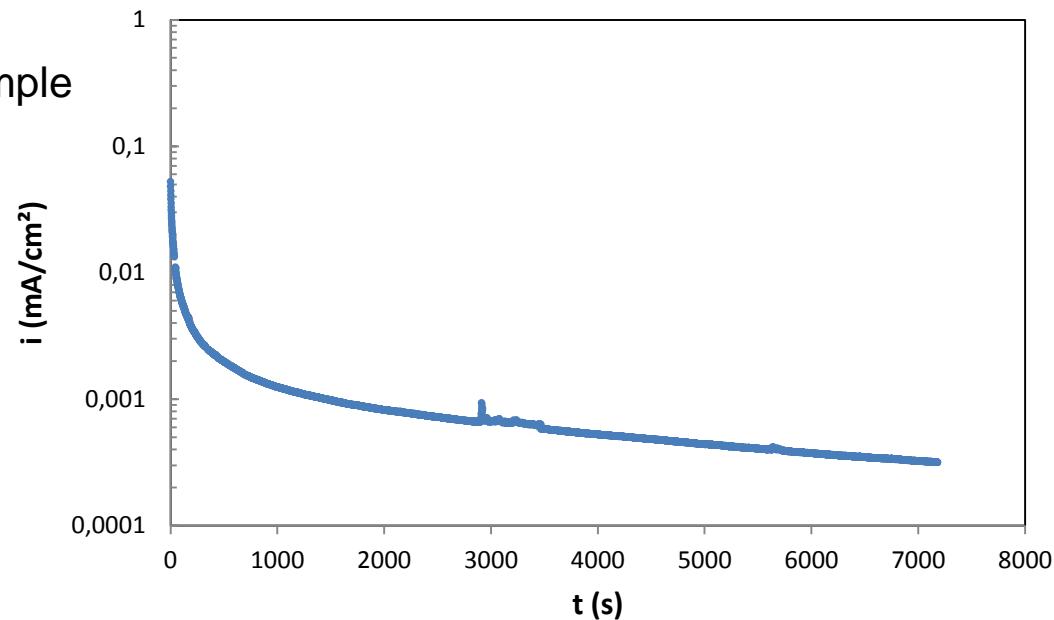
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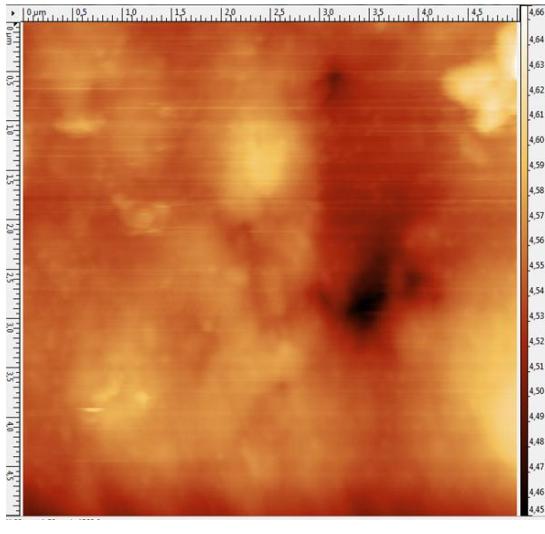


Sample	Potential of formation (V/ENH)	Time of polarization (s)
ZrM103	1,15	~940
ZrM104	Non-polarized	
ZrM105	1,15	~7200
ZrM106	1,5	~7200

Formation of passive film

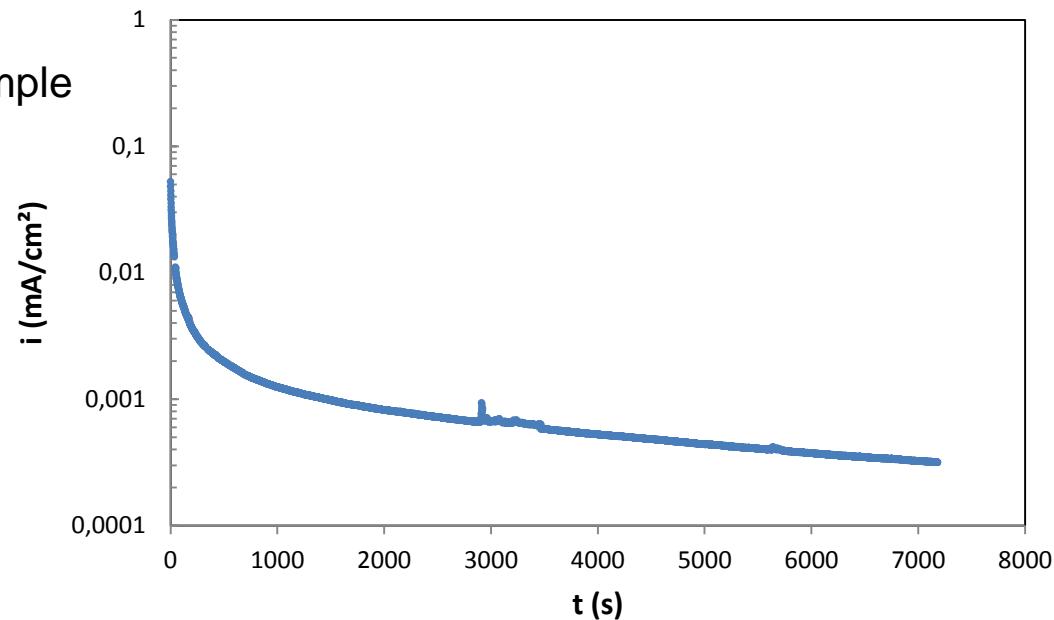
- anodic potential polarization of the sample in HNO_3 4 mol/L 40°C:

- Characteristics of the passive film:
 - chemically stable
 - little rough (<200 nm)



AFM

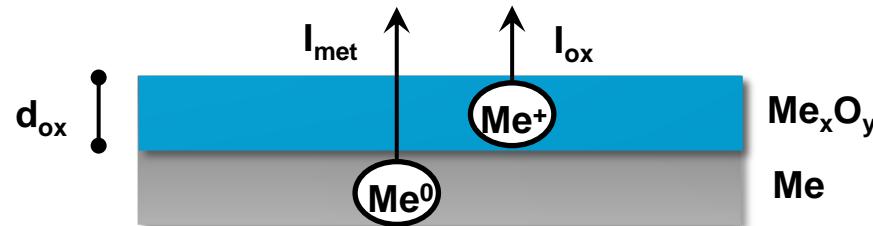
- Nanometric film thickness
 - *Ex situ*: XPS
 - *In situ*: EIS



Sample	Potential of formation (V/ENH)	Time of polarization (s)
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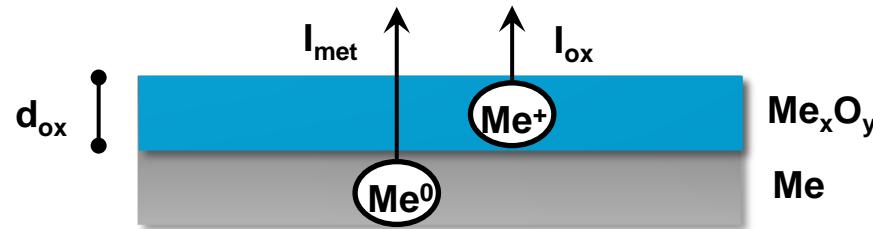
XPS: Principle and parameters

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



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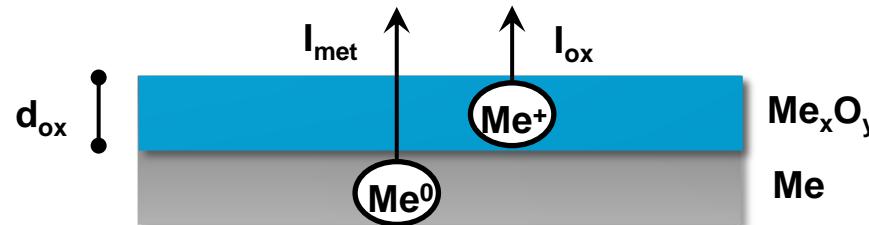


- The oxide thickness (d_{ox}) is estimated by:

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

XPS: Principle and parameters

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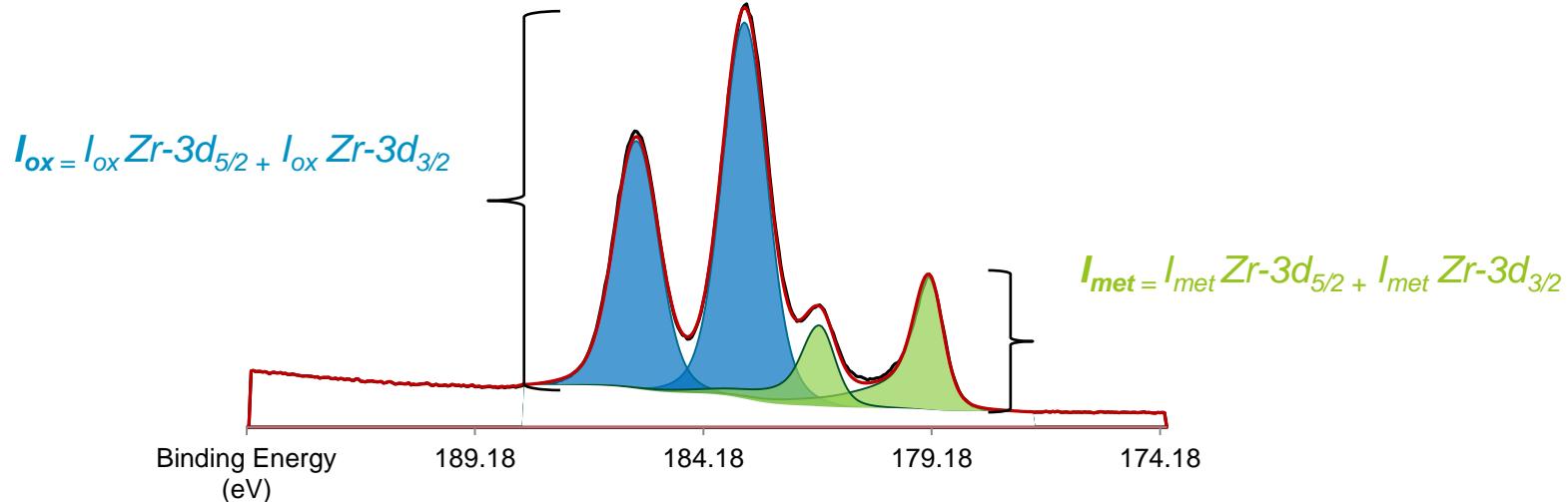
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- Intensities of electronic levels in metallic element (I_{met}) and oxide (I_{ox})
- Inelastic mean free path: average distance of an electron between two inelastic collisions in the metal (λ_{met}) and in the oxide (λ_{ox})
- Number of atoms per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

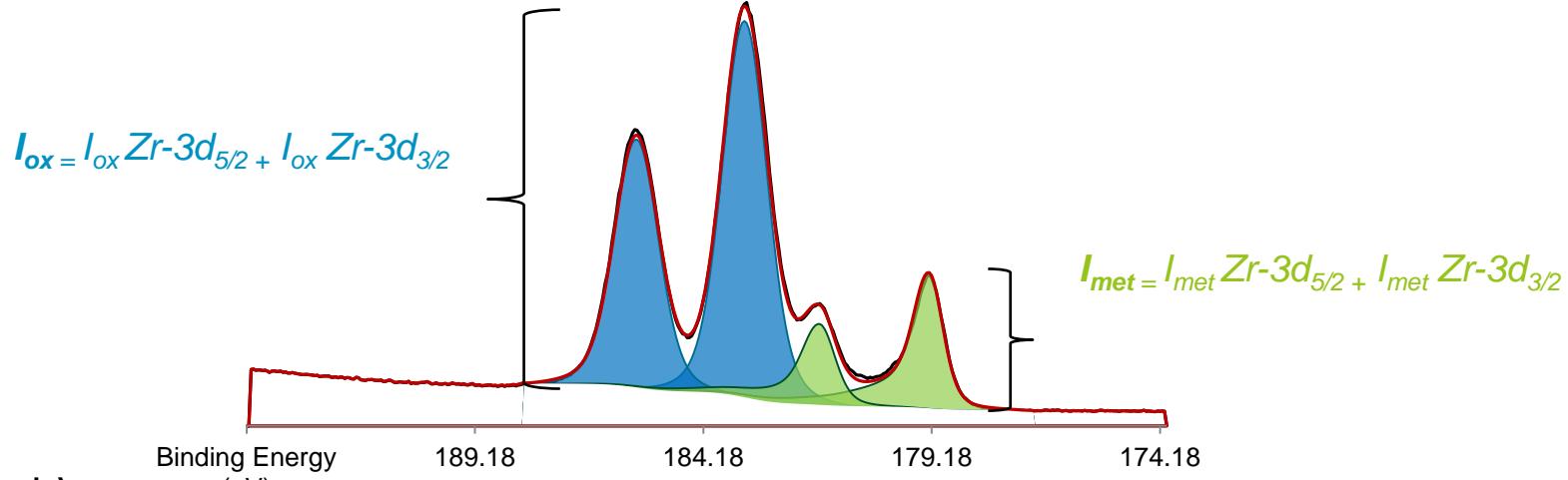
XPS: Parameters estimation

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



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- 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)

	$\lambda_{\text{met}} (\text{nm})$	$\lambda_{\text{ox}} (\text{nm})$
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

CHARACTERIZATION OF A PASSIVE LAYER WITH A CONTROLLED THICKNESS - MONITORING THE NANOMETRIC THICKNESS

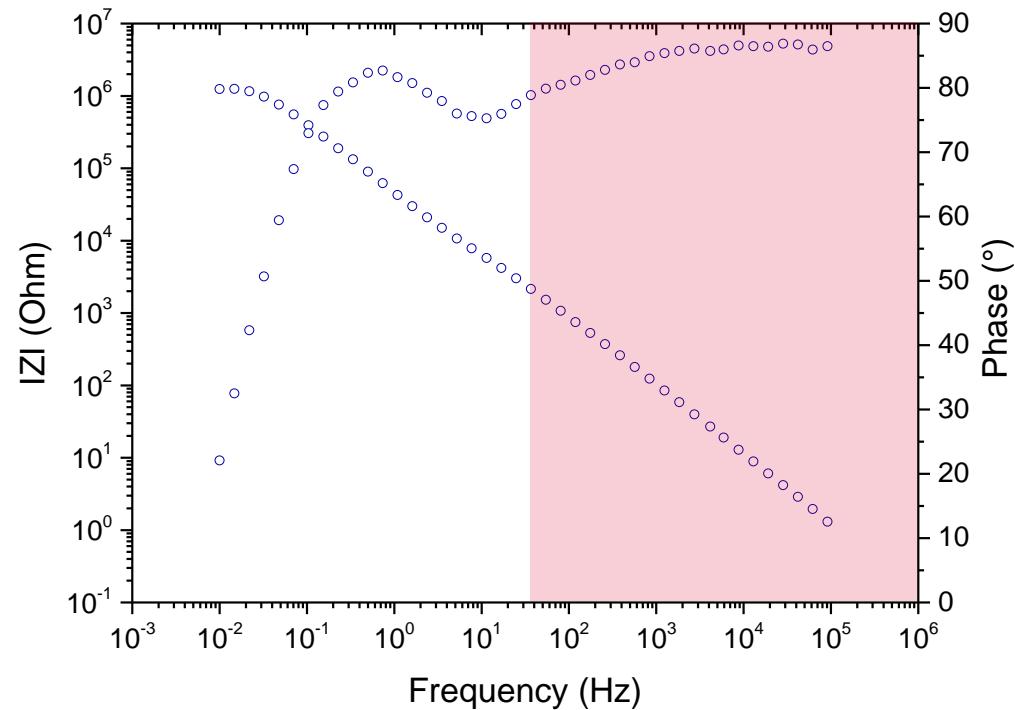
 ZrO_2

Zr

EIS

- Complex capacitance representation

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



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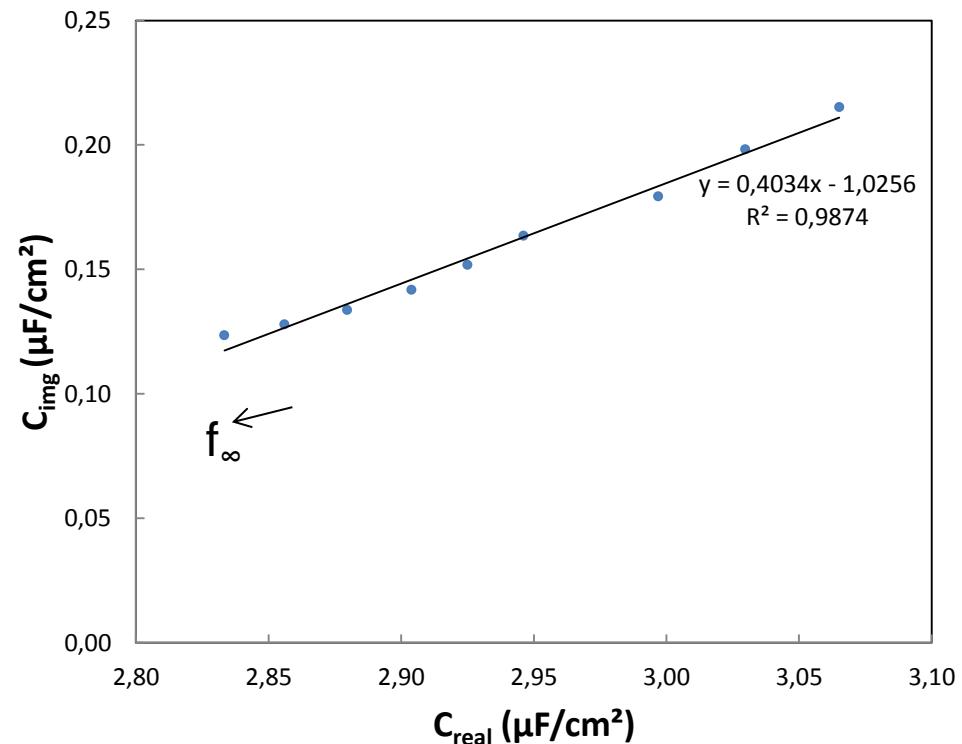
- Complex capacitance representation

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

- 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.

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- With C_∞ : film thickness calculation:

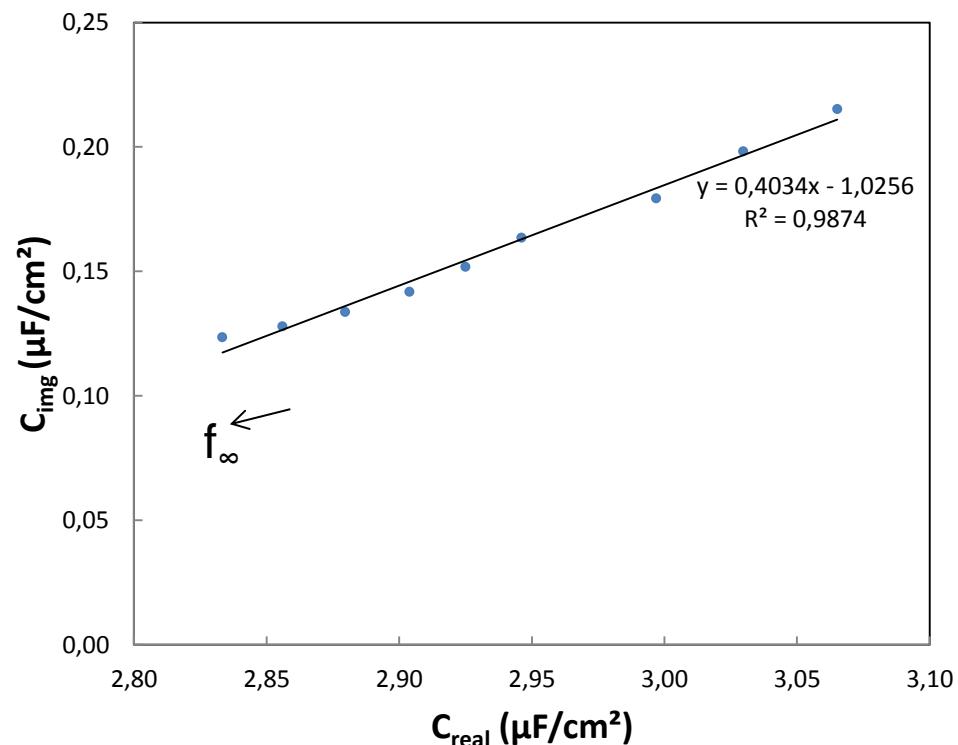
$$d = \frac{\epsilon \epsilon_0}{C_\infty}$$

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

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

C_∞ : Infinite capacitance corresponding to the defectless oxide layer

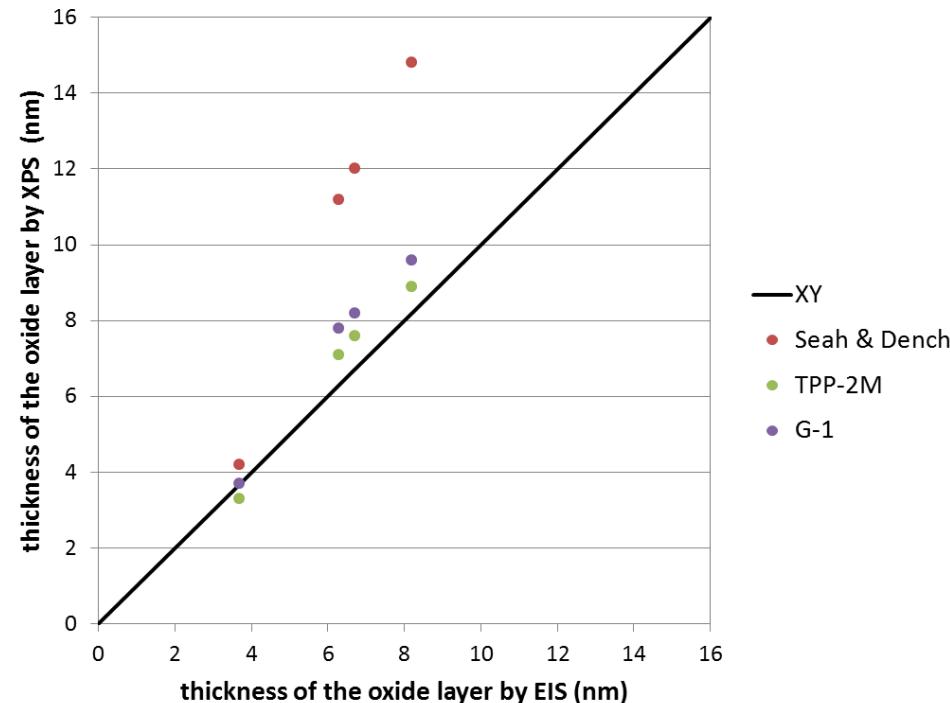
(here, $2,56 \mu\text{F}/\text{cm}^2$)



- 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:**

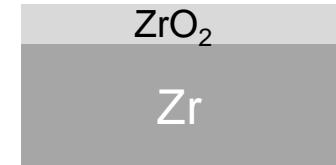
- consistent results
- TPP-2M method values seem closer to the EIS ones

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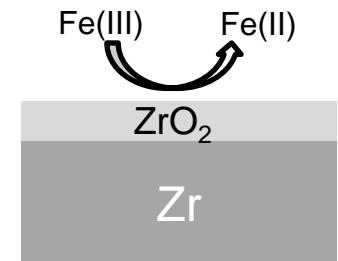
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■ Study of Fe(III) reduction kinetics by EIS on a nanometric passive film

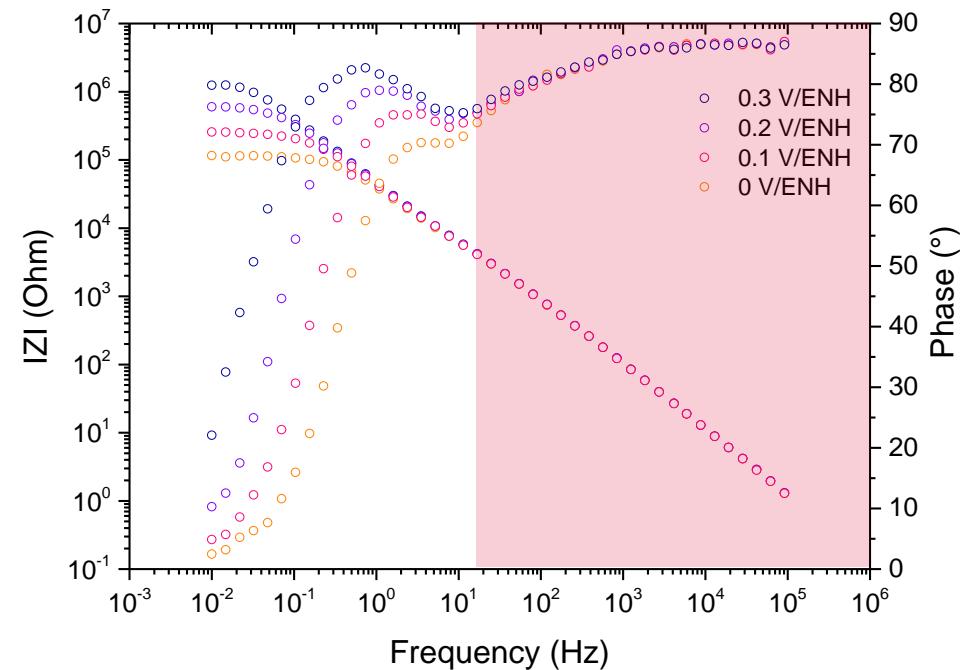
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■ Conclusion and outlook



KINETICS OF FE(III) REDUCTION BY EIS

Evolution of impedance spectra with potential



Bode Plot

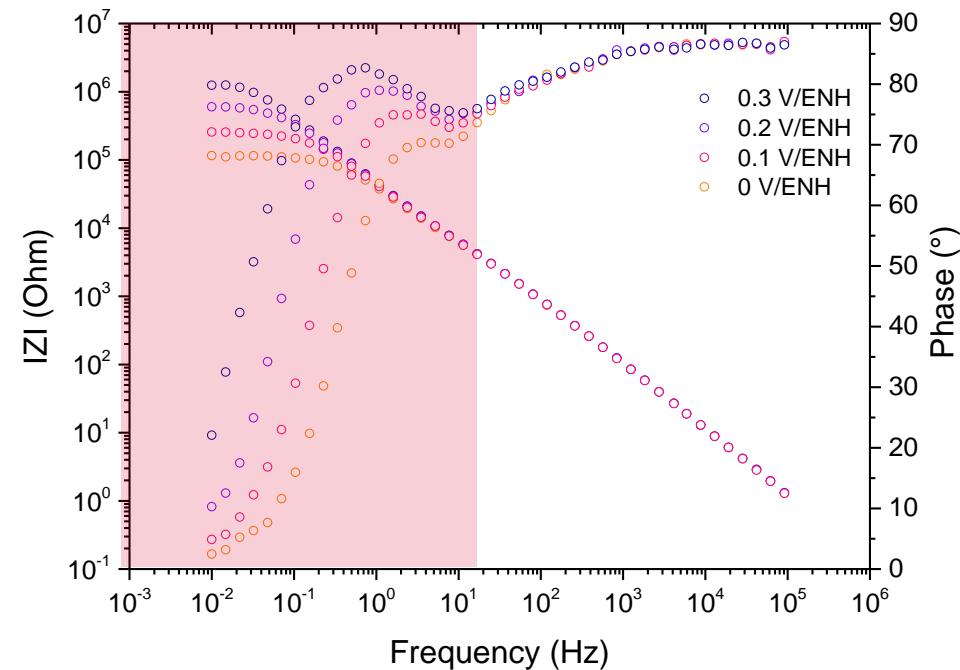
ZrM106 (8.2 nm)

H_2SO_4 0.5 M FeIII/FeIII 0.1M

Room temperature

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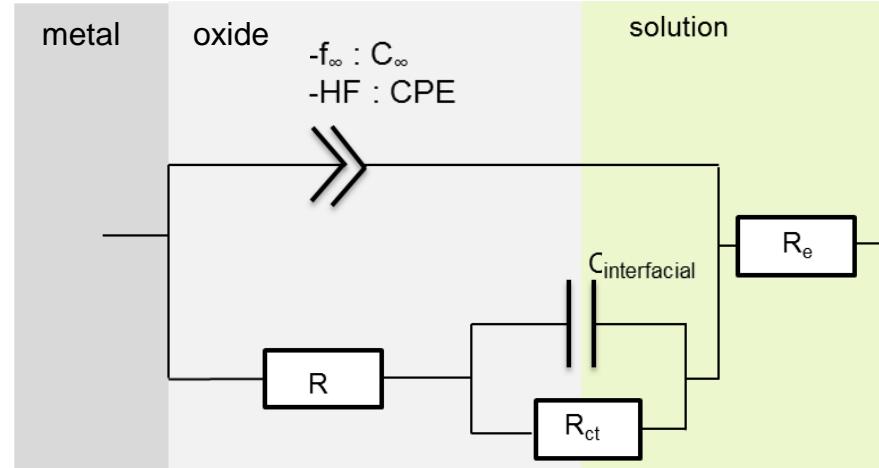
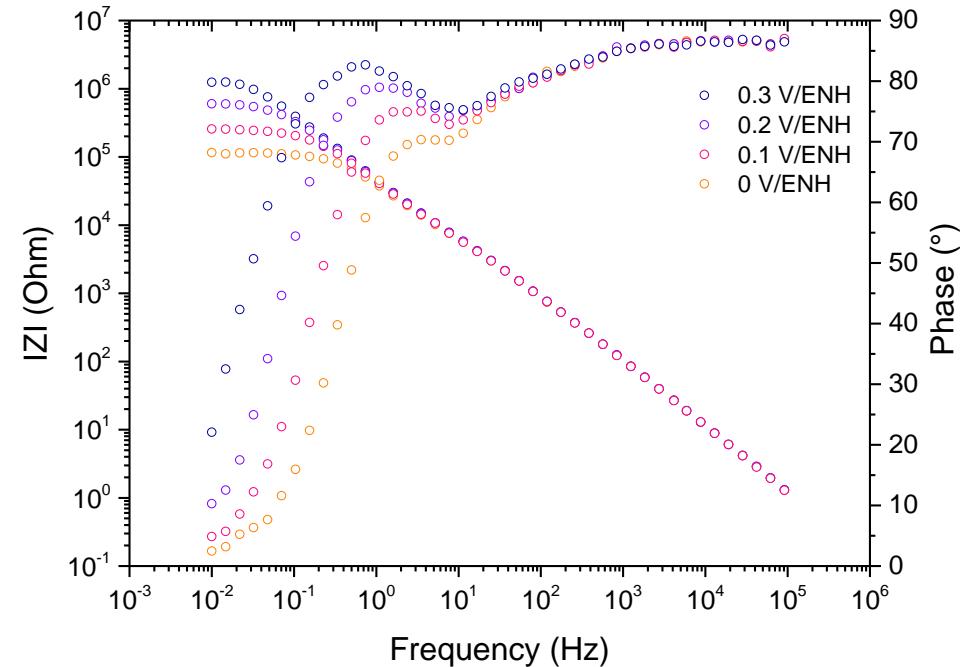
H_2SO_4 0.5 M FeIII/FeIII 0.1M

Room temperature

KINETICS OF FE(III) REDUCTION BY EIS

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
- $C_{\text{interfacial}}$: Space charge capacitance and double layer capacitance
- R_{ct} : charge transfer resistance
- R : its physical meaning is open to interpretation.

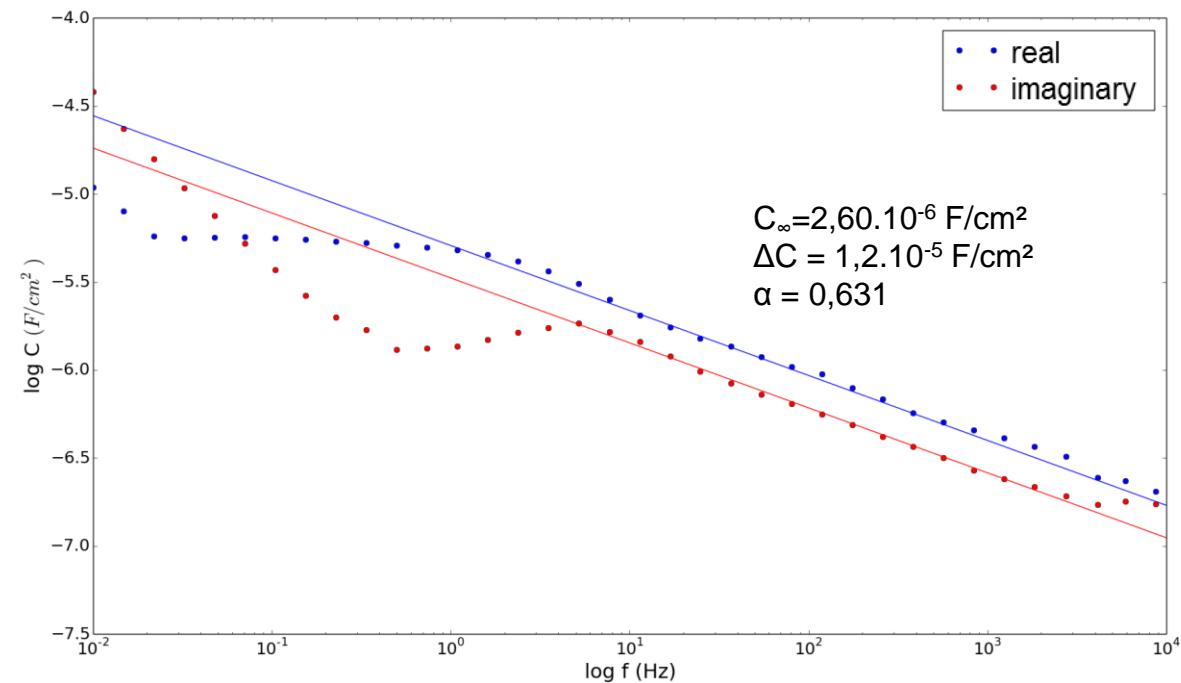
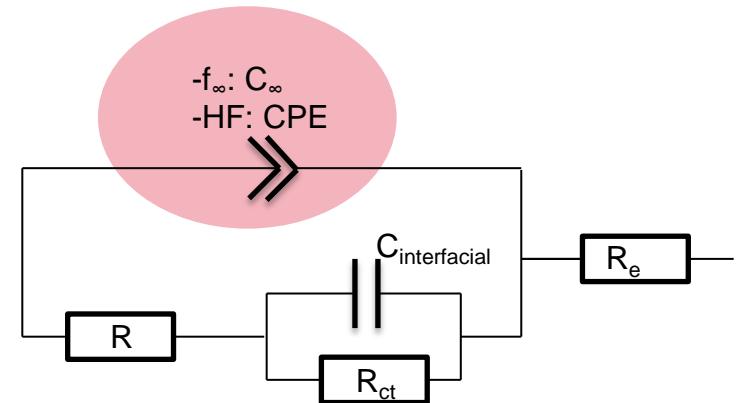
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KINETICS OF FE(III) REDUCTION BY EIS



Justification of the equivalent circuit

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

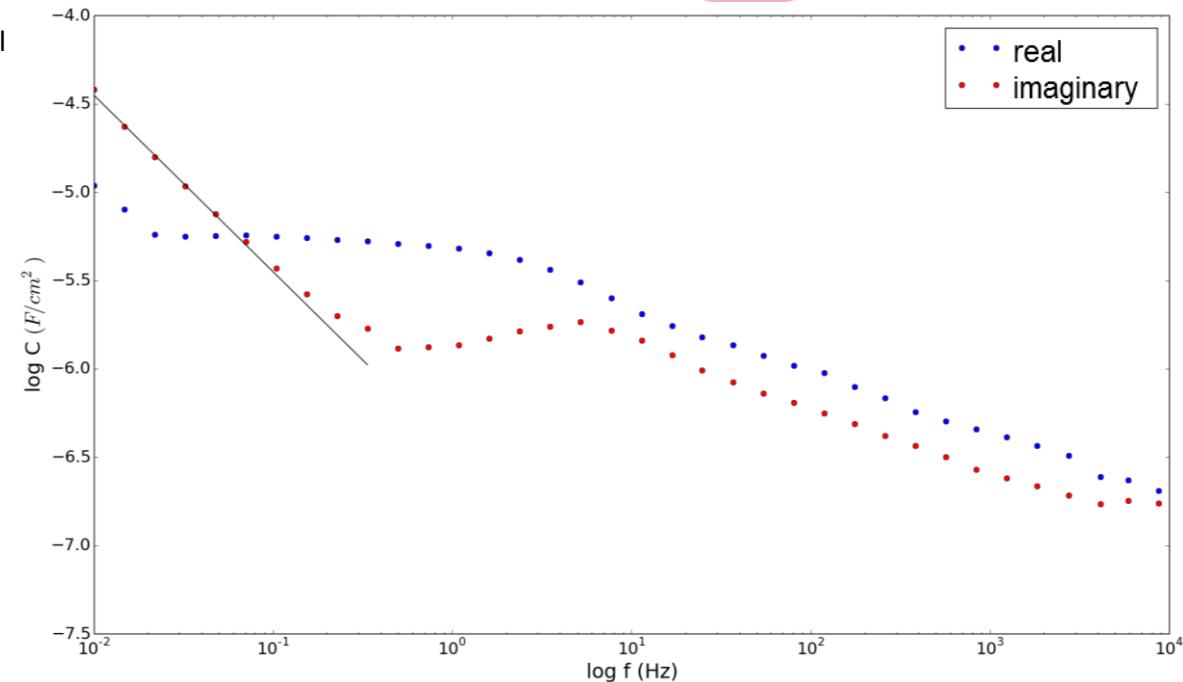
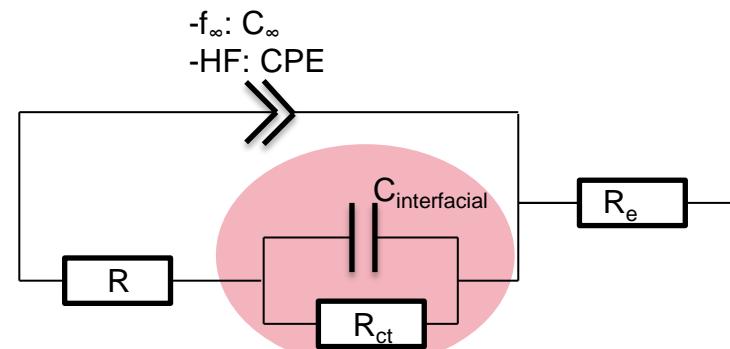


KINETICS OF FE(III) REDUCTION BY EIS



Justification of the equivalent circuit

- As before the high frequency part is attributed to the dielectric properties of the film (Jonscher's Law)
- Low frequency part: R_{ct} & $C_{\text{interfacial}}$

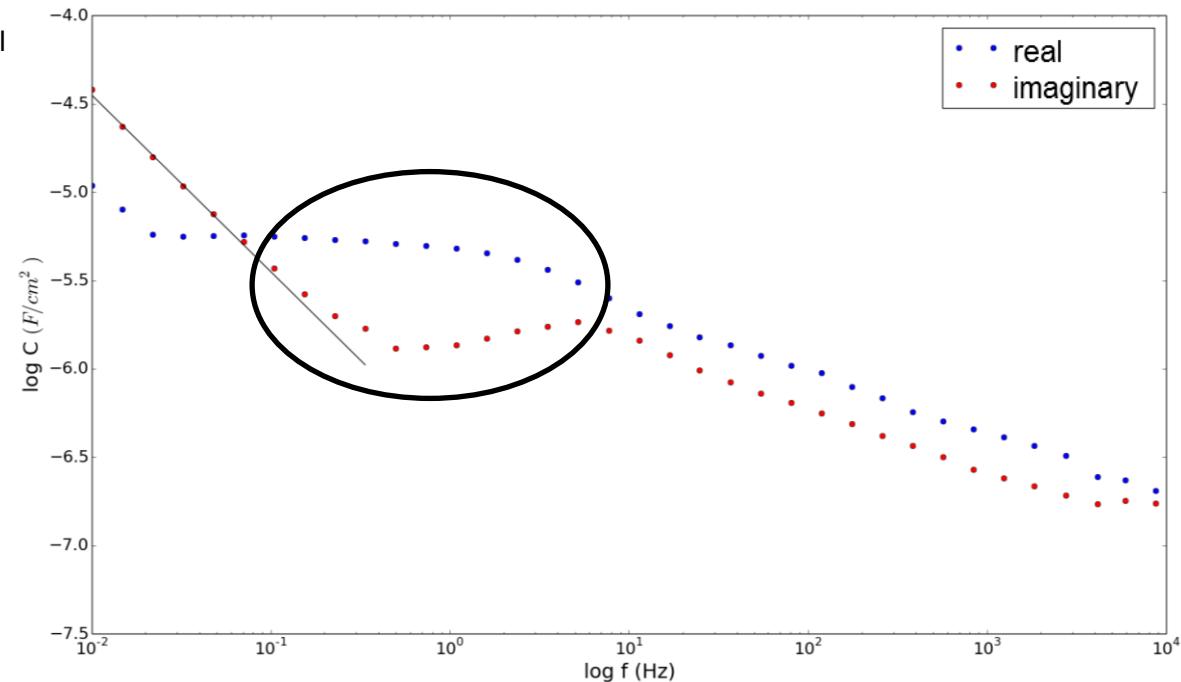
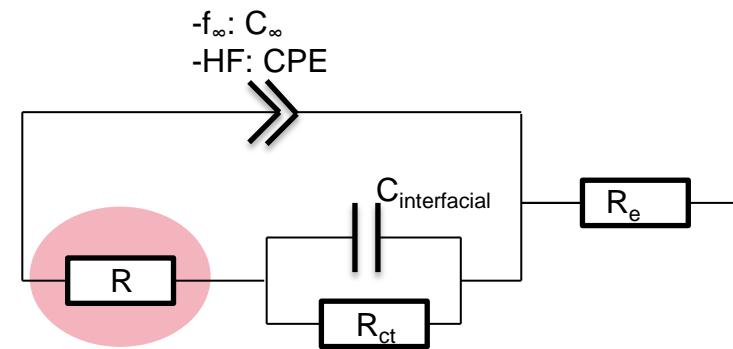


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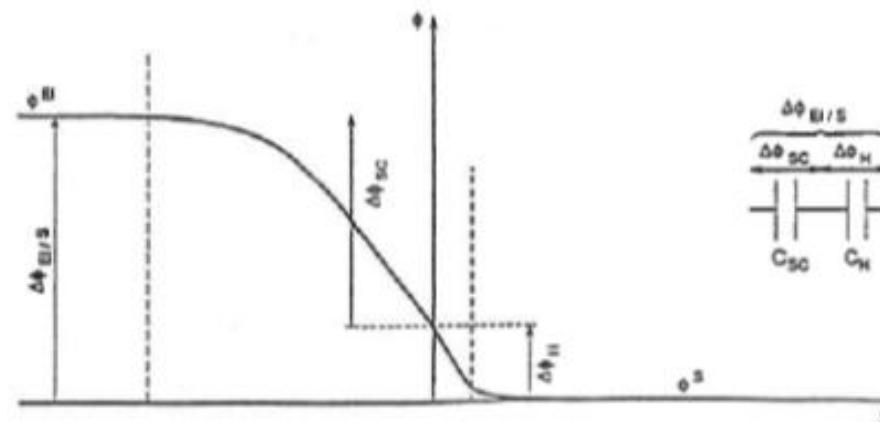
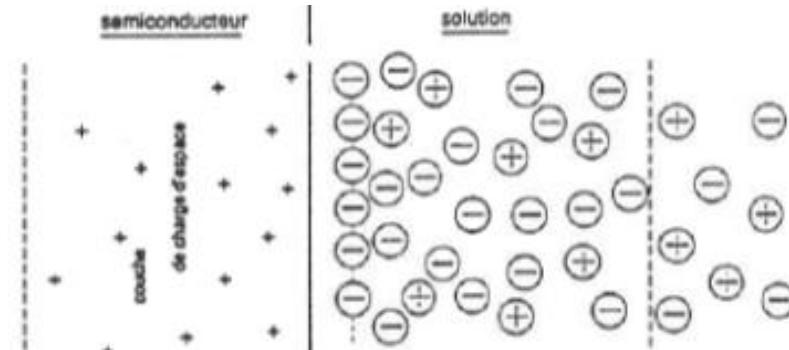
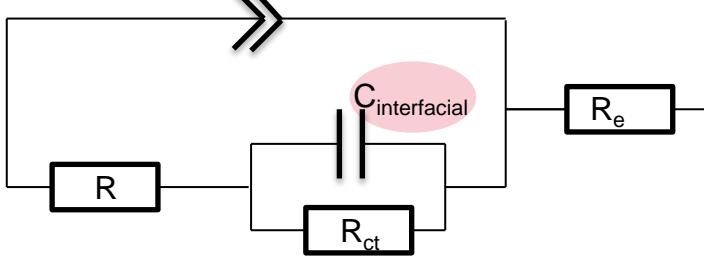
- As before the high frequency part is attributed to the dielectric properties of the film (Jonscher's Law)
- Low frequency part: R_{ct} & $C_{interfacial}$
- Intermediate frequency part: R



KINETICS OF FE(III) REDUCTION BY EIS

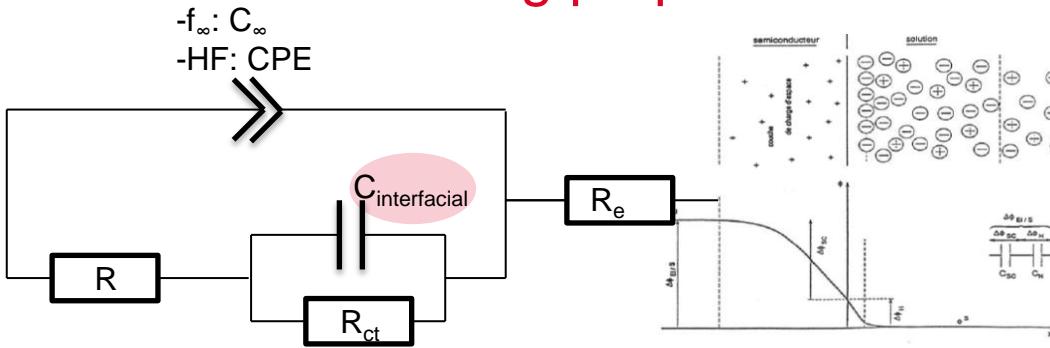
Semiconducting properties of the film

-f_∞: C_∞
-HF: CPE



KINETICS OF FE(III) REDUCTION BY EIS

Semiconducting properties of the film



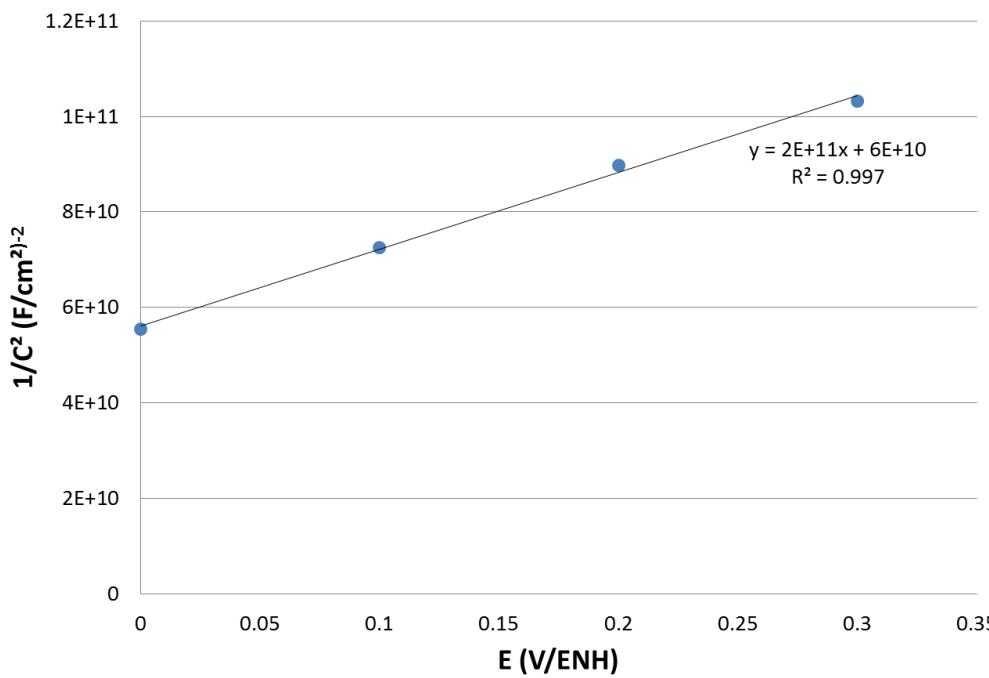
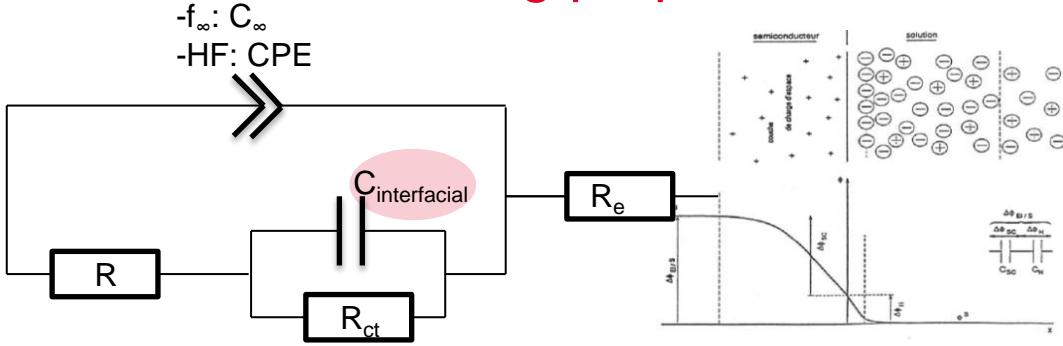
■ Verification of the Mott-Schottky's law:

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

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

KINETICS OF FE(III) REDUCTION BY EIS

Semiconducting properties of the film



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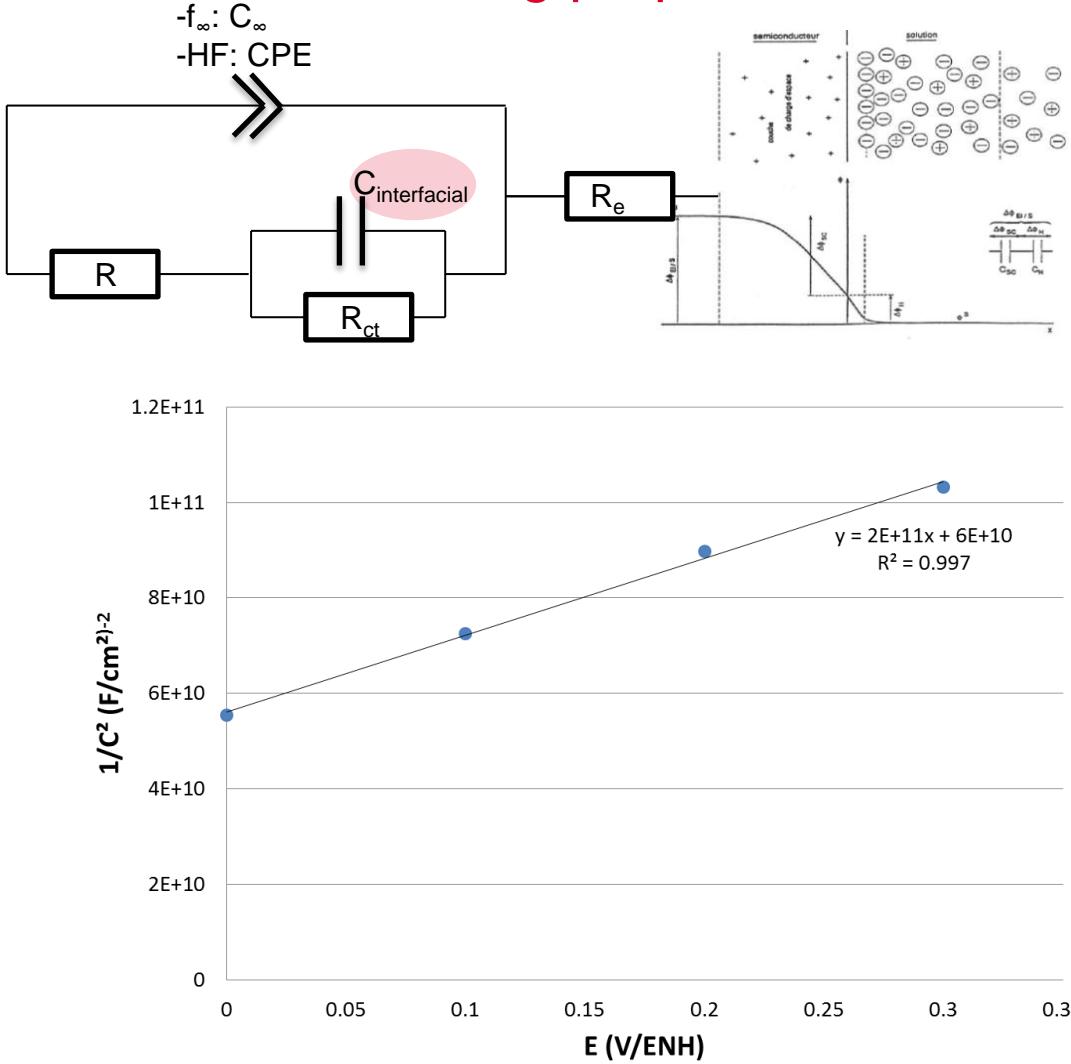
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Semiconducting properties of the film



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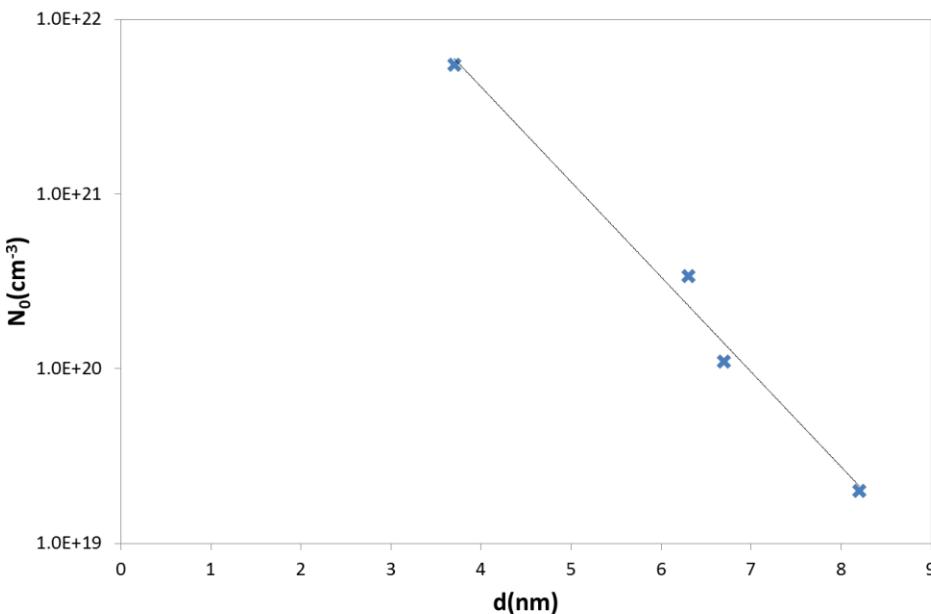
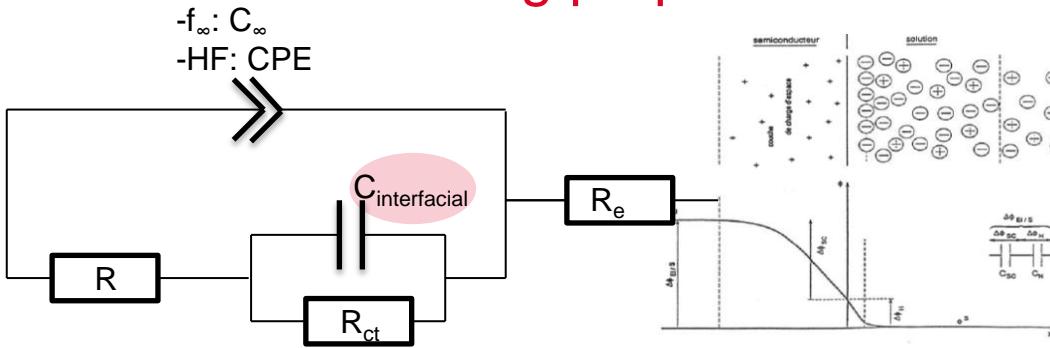
Results:

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

KINETICS OF FE(III) REDUCTION BY EIS



Semiconducting properties of the film



- Verification of the Mott-Schottky's law:

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

With:
 ϵ : dielectric constant of the material
 ϵ_0 : dielectric permittivity of vacuum: $8.85 \cdot 10^{-14}$ F/cm²
 q_e : elementary charge of the electron
 N_0 : charge carriers number
 k_B : Boltzmann's constant
 E_{BP} : flat band potential

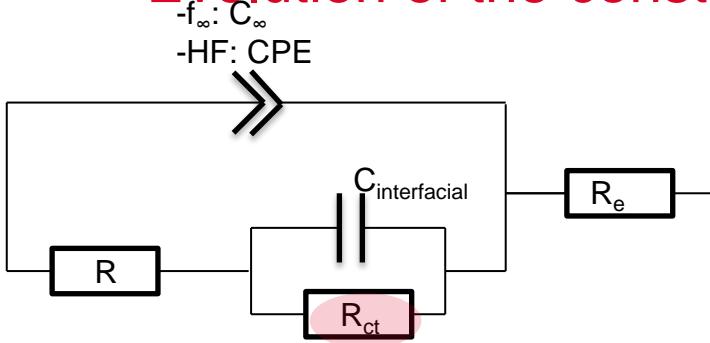
Results:

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

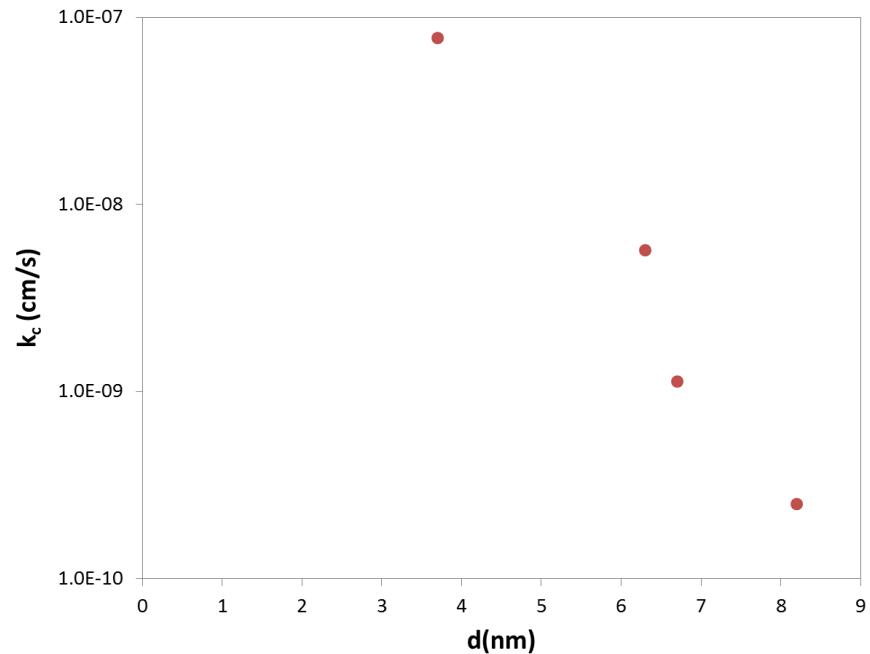
KINETICS OF FE(III) REDUCTION BY EIS



Evolution of the constant rate k_c according to thickness



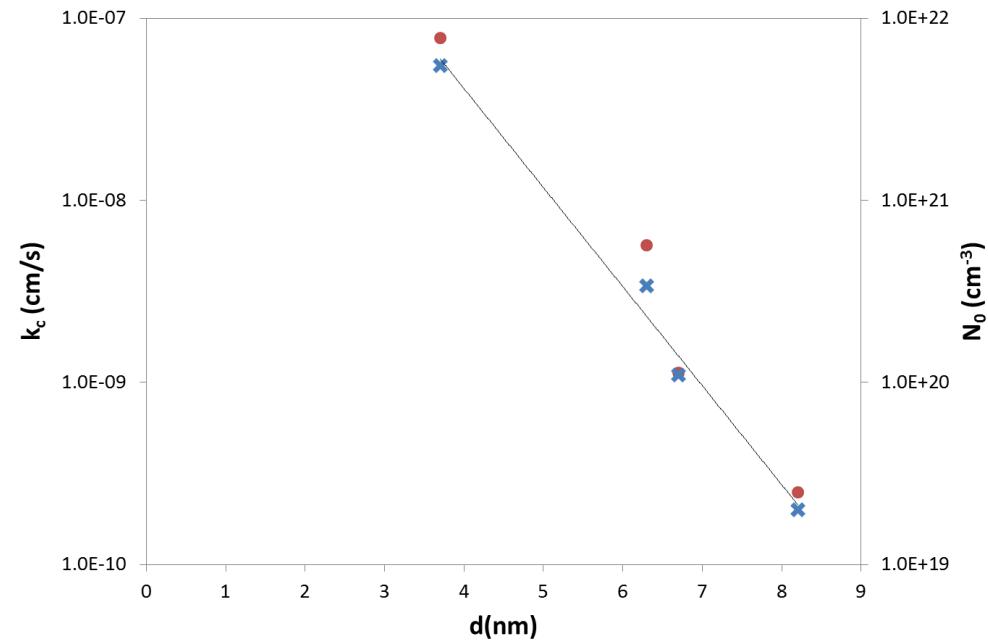
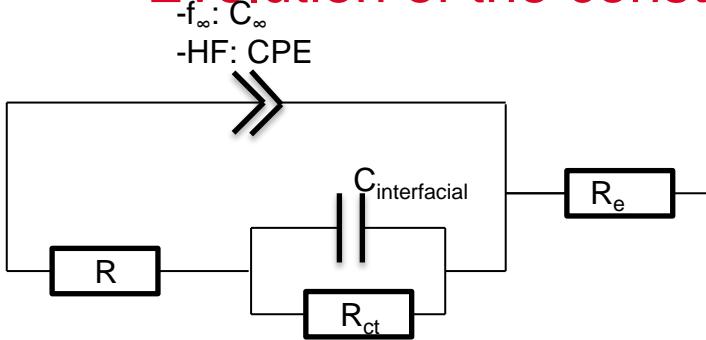
$$R_{ct} = \frac{RT}{\alpha n^2 F^2 S \left(k_c \overline{C}_{ox}(0) e^{\frac{-\alpha n F}{RT}(E - E^0)} \right)}$$



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

KINETICS OF FE(III) REDUCTION BY EIS

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 ZrO_2

CONCLUSION & OUTLOOK

Conclusions

- Formation of ZrO₂ layers:
 - Formation of 4 layers of different thicknesses
 - Comparison of 2 experimental techniques for the thickness measurement

CONCLUSION & OUTLOOK

Conclusions

- Formation of ZrO_2 layers:
 - Formation of 4 layers of different thicknesses
 - Comparison of 2 experimental techniques for the thickness measurement
- Kinetics of Fe(III) reduction
 - Advanced understanding of EIS spectra
 - Properties of ZrO_2 layer: C_∞ (d), C_{sc} (N_0)
 - Kinetics of Fe(III) reduction: R_{ct} (k_c)
 - Constant k_c :
 - decreases with d
 - Linked to N_0

CONCLUSION & OUTLOOK

Conclusions

- Formation of ZrO_2 layers:
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Outlook

- Extension of the approach to other systems
 - Stainless steel
 - HNO_3/HNO_2



Reprocessing plant of La Hague

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ELABORATION D'UN FILM PASSIF CONTRÔLÉ - DÉTERMINATION ÉPAISSEUR

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

7.00E+04

Compare-3

6.00E+04

5.00E+04

4.00E+04

3.00E+04

2.00E+04

1.00E+04

0.00E+00

Counts / s

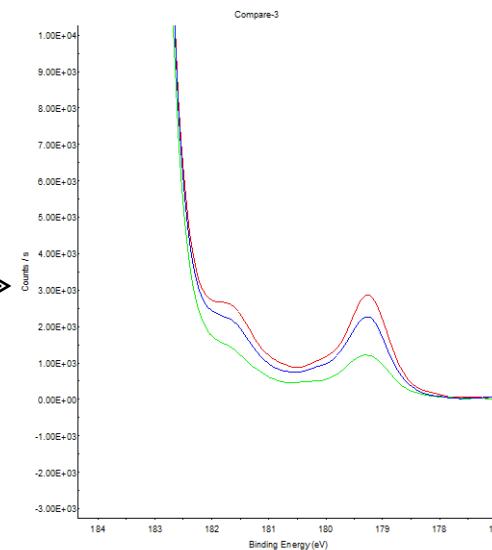
194 193 192 191 190 189 188 187 186 185 184 183 182 181 180 179 178 177 176 175

Binding Energy (eV)

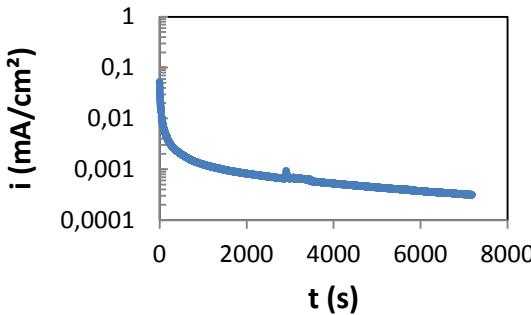
Référence	EIS				XPS			
	d_{\min} (EIS) (nm)	d_{SD} (nm)	d_{TPP-2M} (nm)	d_{G-1} (nm)				
ZrM103	5,6	11,2	7,1	7,8				
ZrM104	/	4,2	3,3	3,7				
ZrM105	6,3	12,0	7,6	8,2				
ZrM106	7,7	14,8	8,9	9,6				

Zrm106
Zrm105
Zrm103

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:

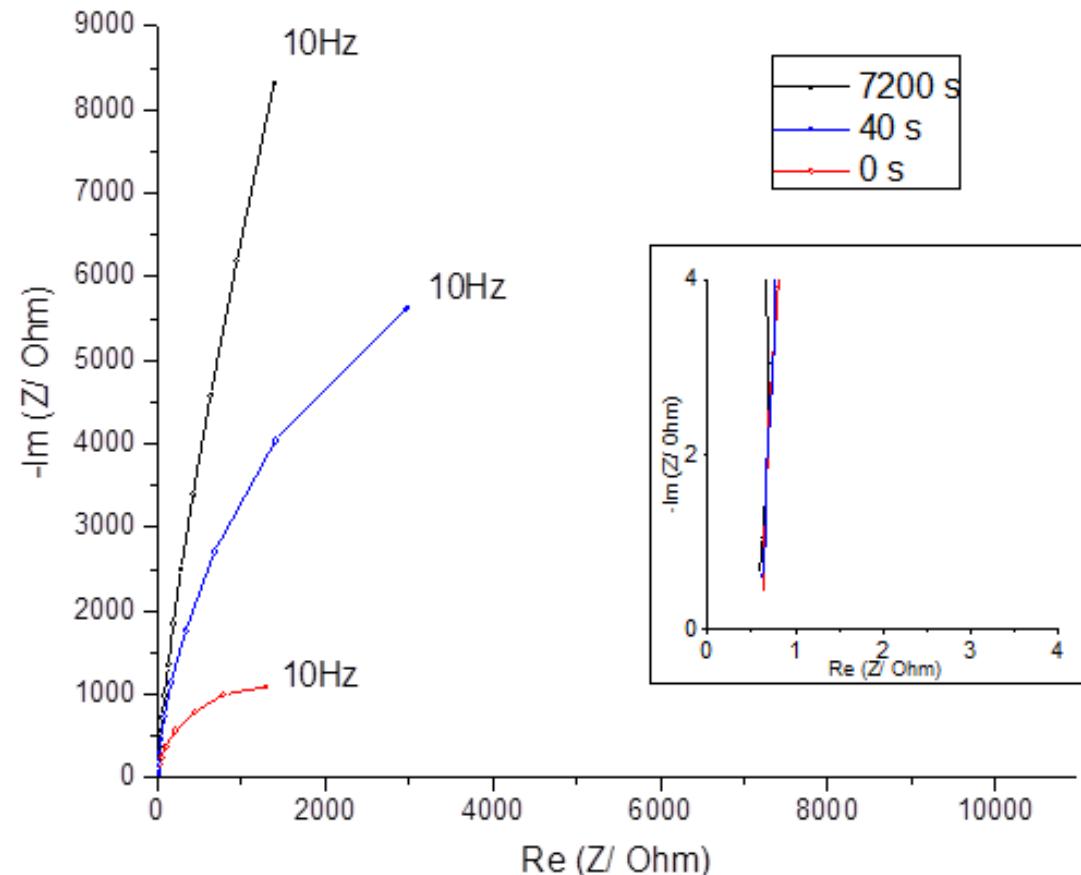
processus se déroulant en parallèle

■ 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