DE LA RECHERCHE À L'INDUSTRIE

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

17th ISE Topical Meeting

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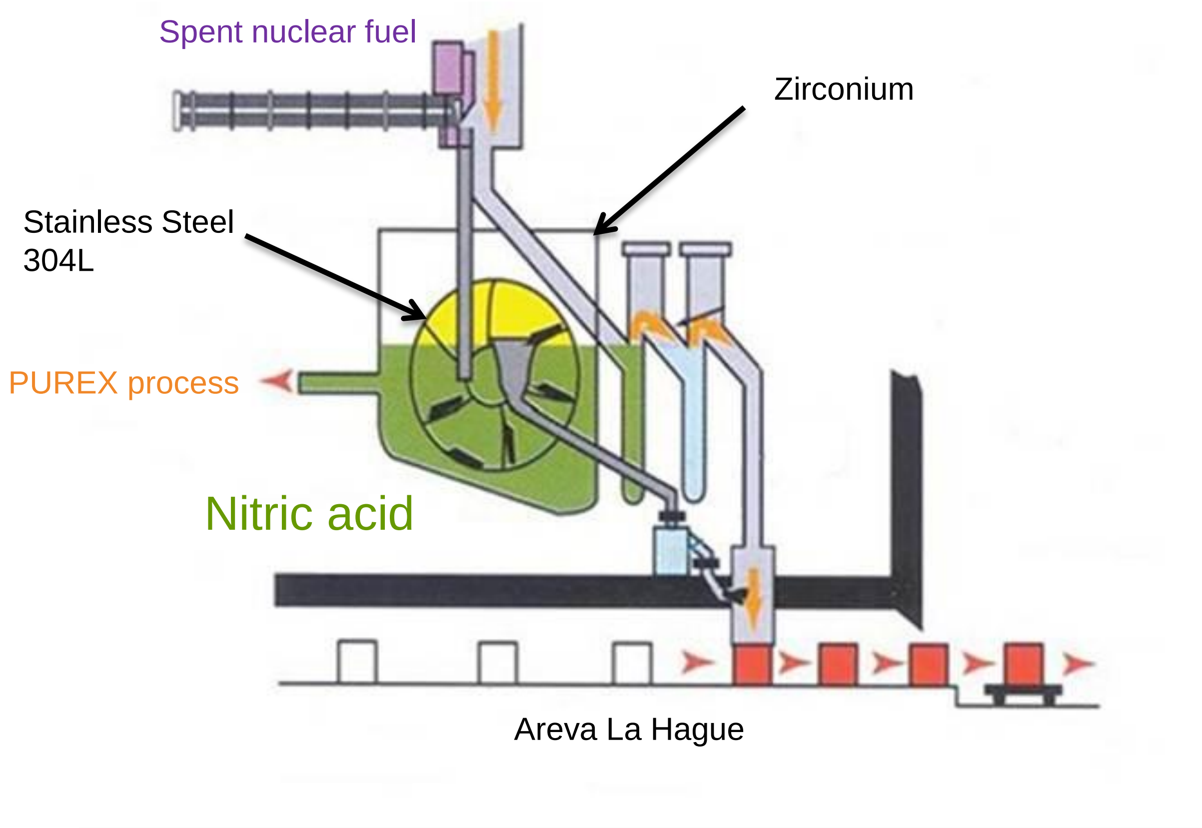
[3]CNRS - UPMC, UMR 8235, Laboratoire Interfaces et Systèmes Electrochimiques, F-75252 Paris 05, France.

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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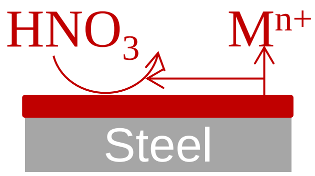

[R.Lange, Thesis 2012]

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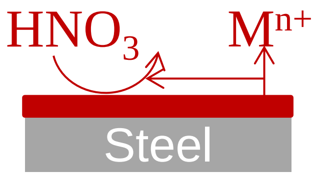

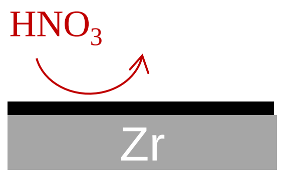

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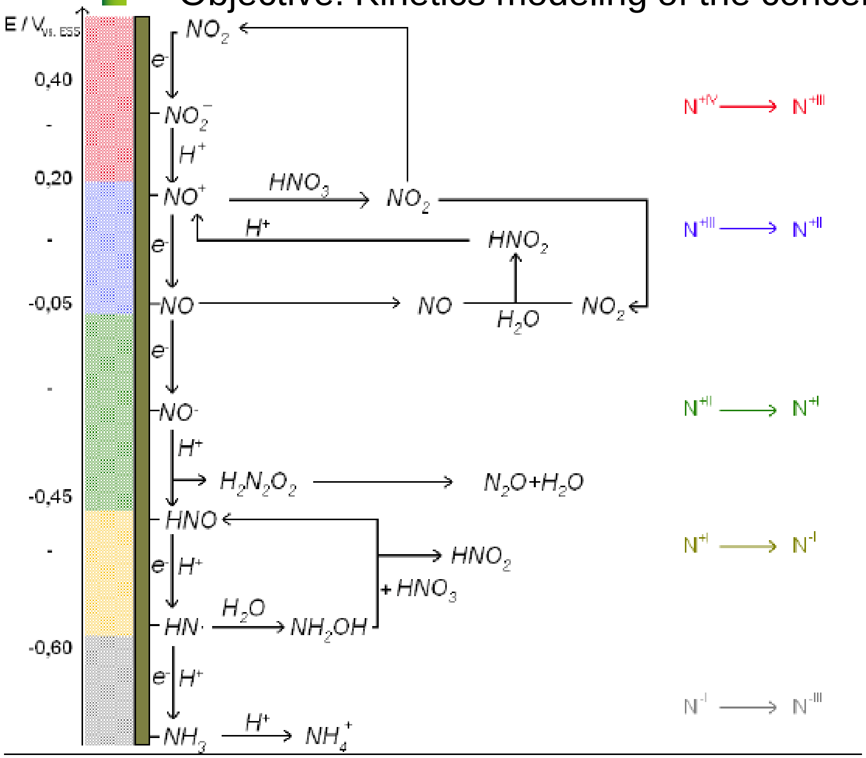

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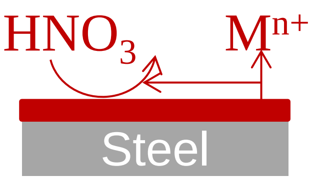

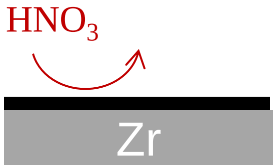

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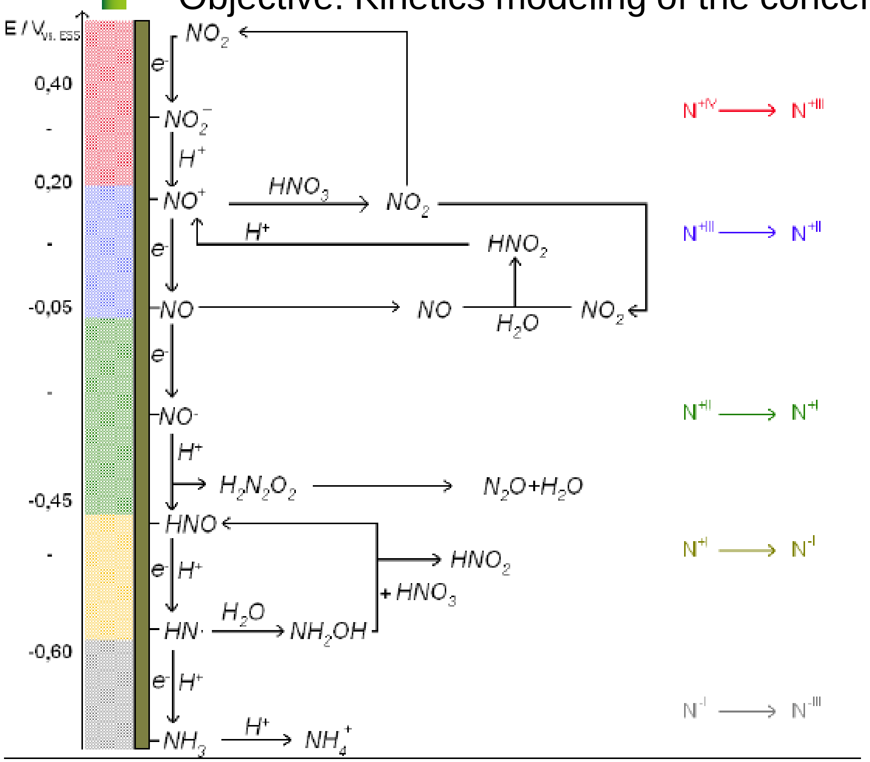

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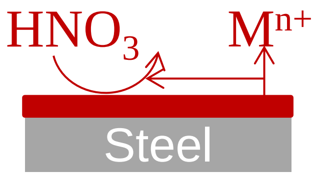
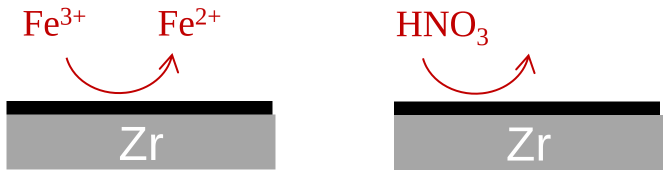
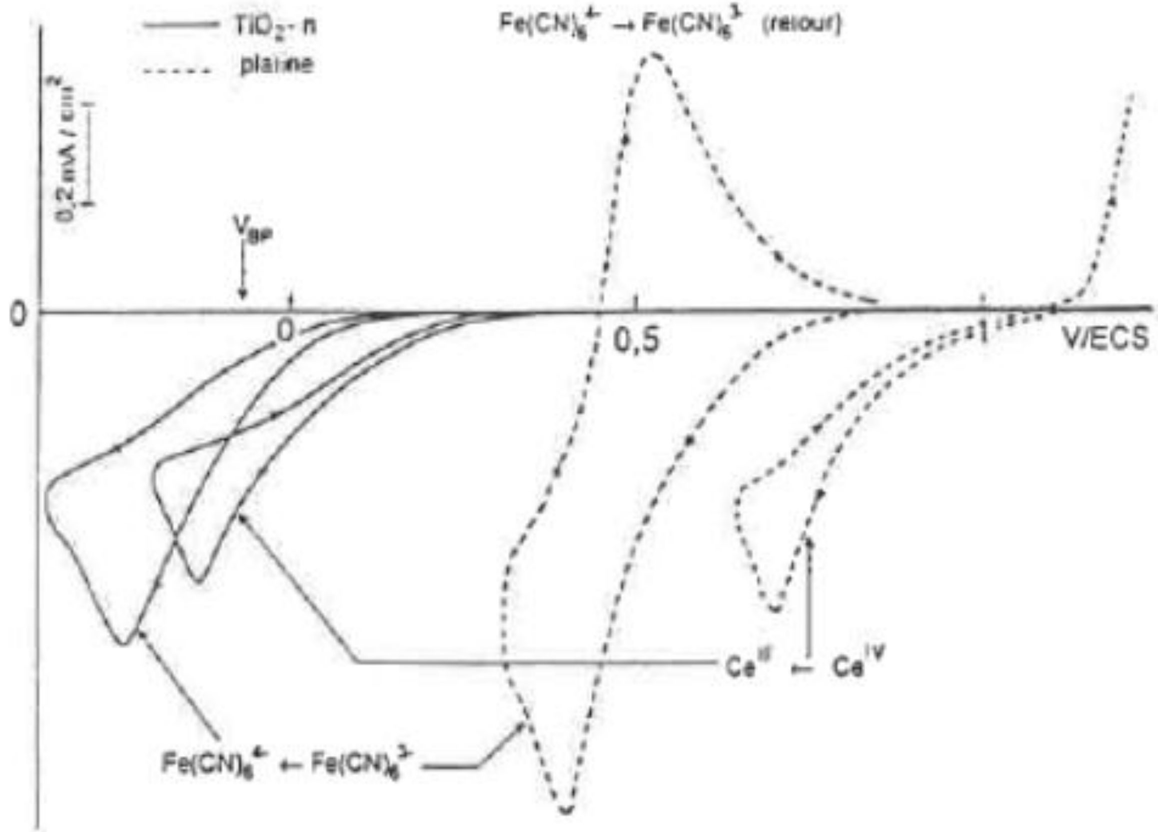




LITERATURE



[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 Fe(III)/Fe(II) couple

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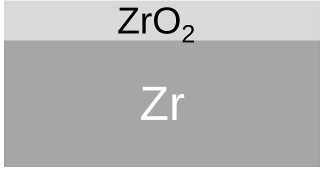
  - Monitoring the (nanometric scaled) thickness
    - \- *Ex situ* method: XPS
    - \- *In situ* method: EIS
  - Results



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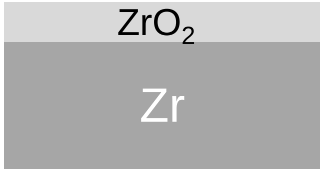
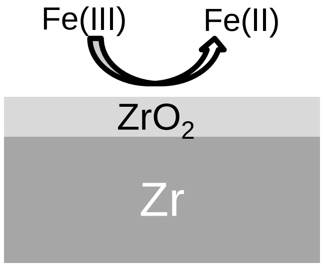


- Study of Fe(III) reduction kinetics by EIS on a nanometric passive film
  - EIS analysis
  - Results



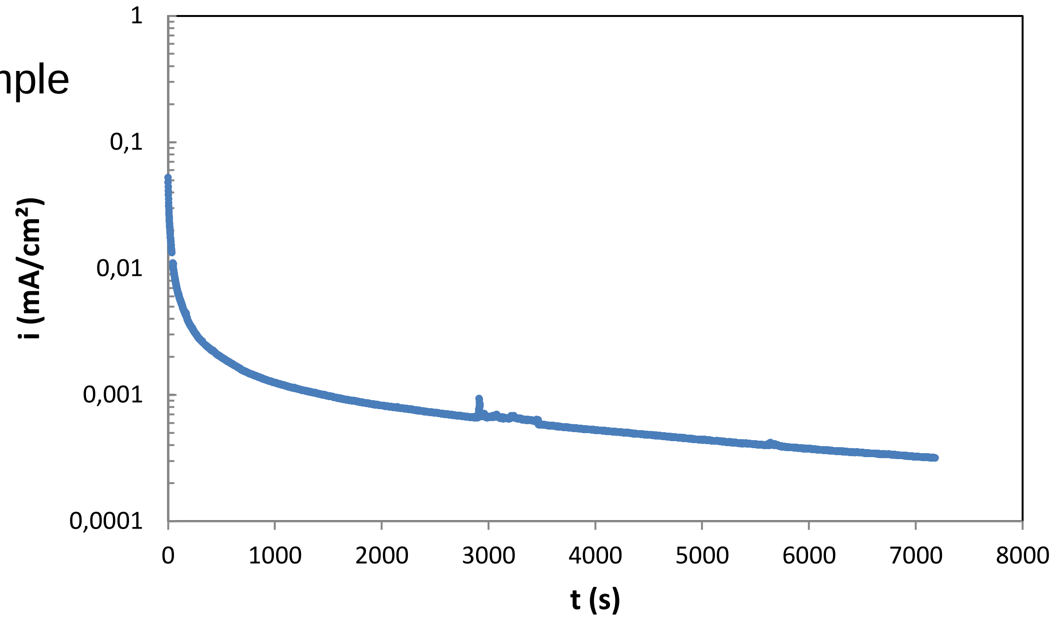
- Conclusion and outlook

FORMATION OF A PASSIVE LAYER WITH A CONTROLLED THICKNESS - EXPERIMENTAL METHOD

ZrO_2
Zr

Formation of passive film

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



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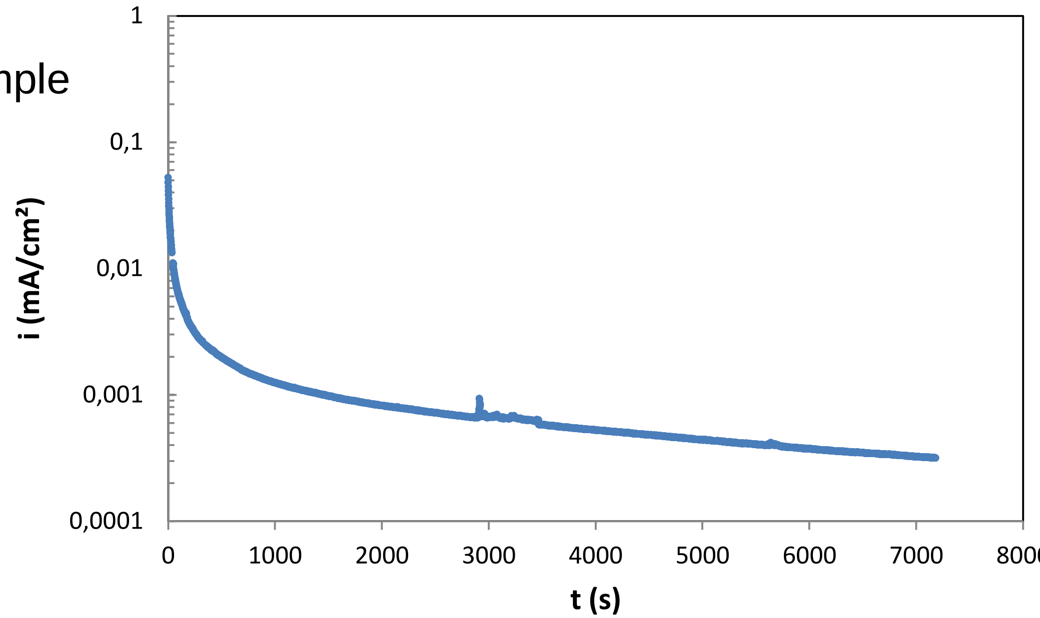
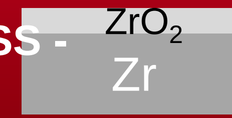


Sample	Potential of formation (V/ENH)	Time of polarization (s)
ZrM103	1,15	~940
ZrM104	Non-polarized	
ZrM105	1,15	~7200
ZrM106	1,5	~7200



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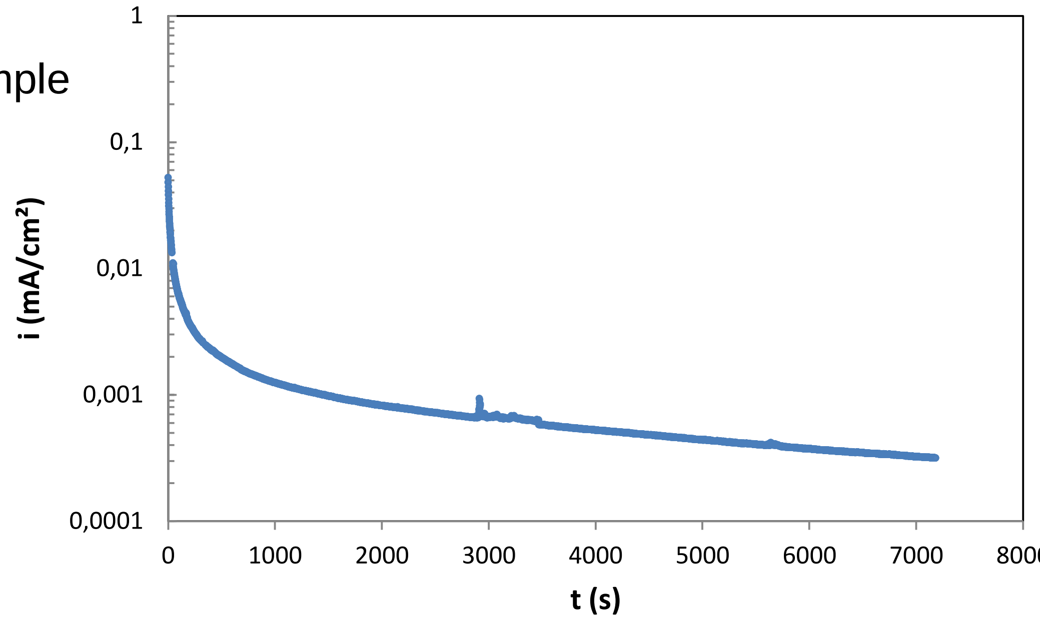

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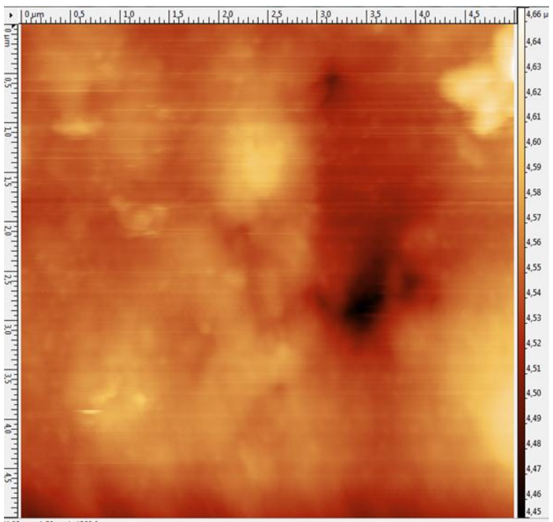
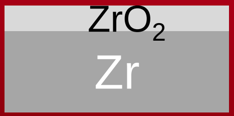
- Characteristics of the passive film:
  - chemically stable
  - little rough (<200 nm)



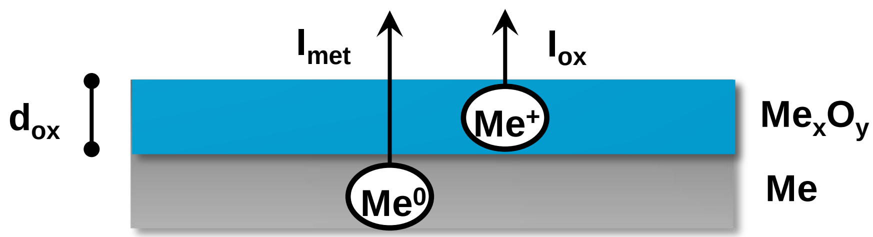
AFM

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



XPS: Principle and parameters

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



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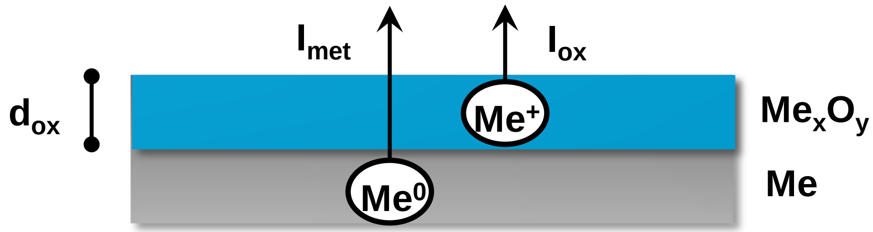

- The oxide thickness (d_{ox}) is estimated by:

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

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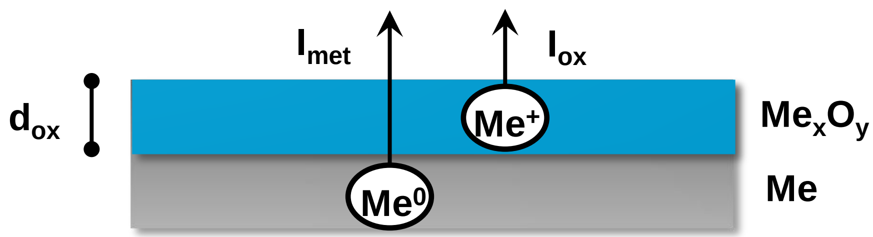

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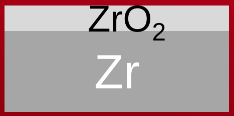
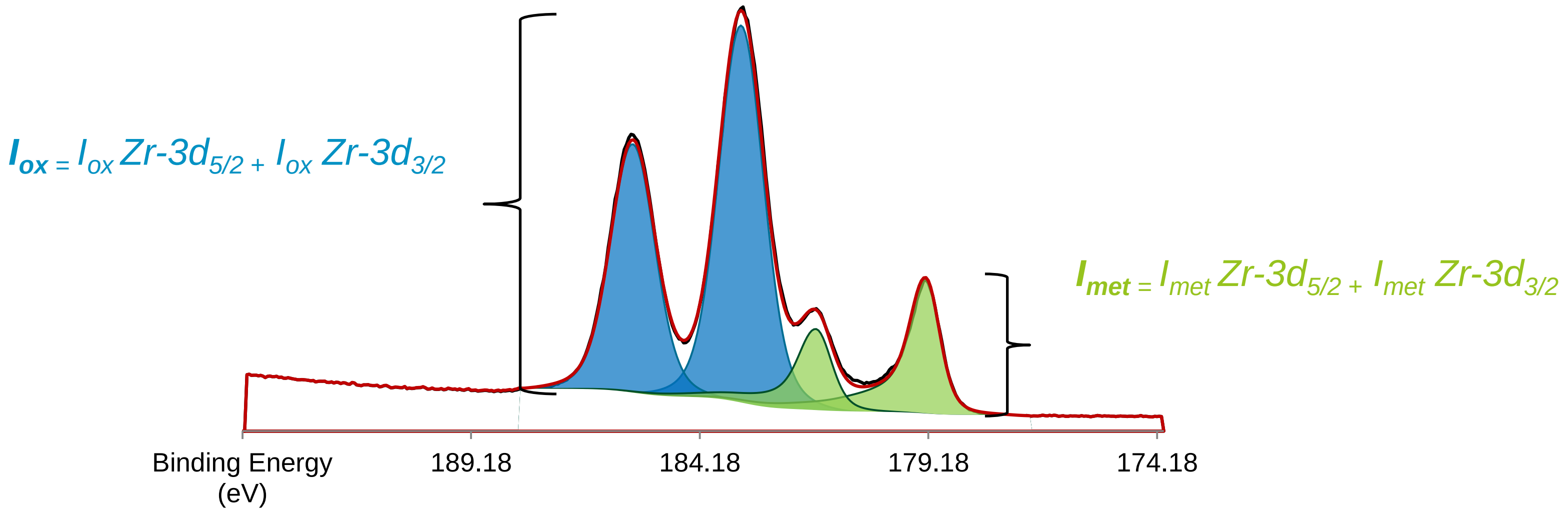
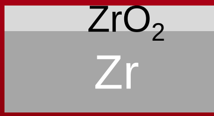
- Intensities of electronic levels in metallic element (I_{met}) and oxide (I_{ox})
- Inelastic mean free path: average distance of an electron between two inelastic collisions in the metal (λ_{met}) and in the oxide (λ_{ox})
- Number of atoms per volume unit
- Angle between the sensor and the normal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



XPS: Parameters estimation

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





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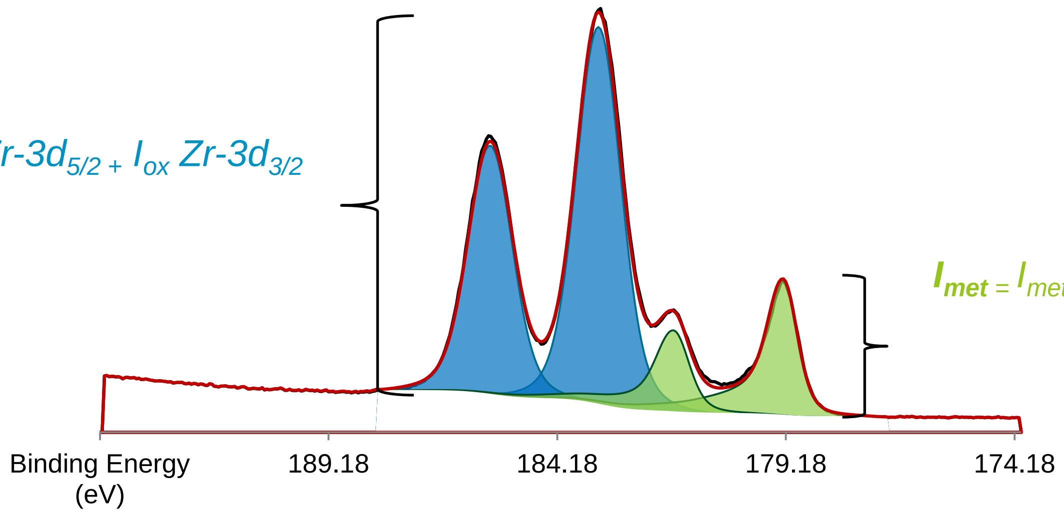
$I_{ox} = I_{ox}\,Zr\text{-}3d_{5/2} + I_{ox}\,Zr\text{-}3d_{3/2}$



$I_{met} = I_{met}\,Zr\text{-}3d_{5/2} + I_{met}\,Zr\text{-}3d_{3/2}$

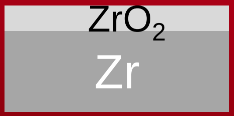
- λ_{ox} and λ_{met}:
  - Seah & Dench [1] (empirical)
  - Tanuma, Powell et Penn (TPP-2M) [2] (*ab initio* calculus)
  - Gries (G-1) [3] (*ab initio* calculus)

	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

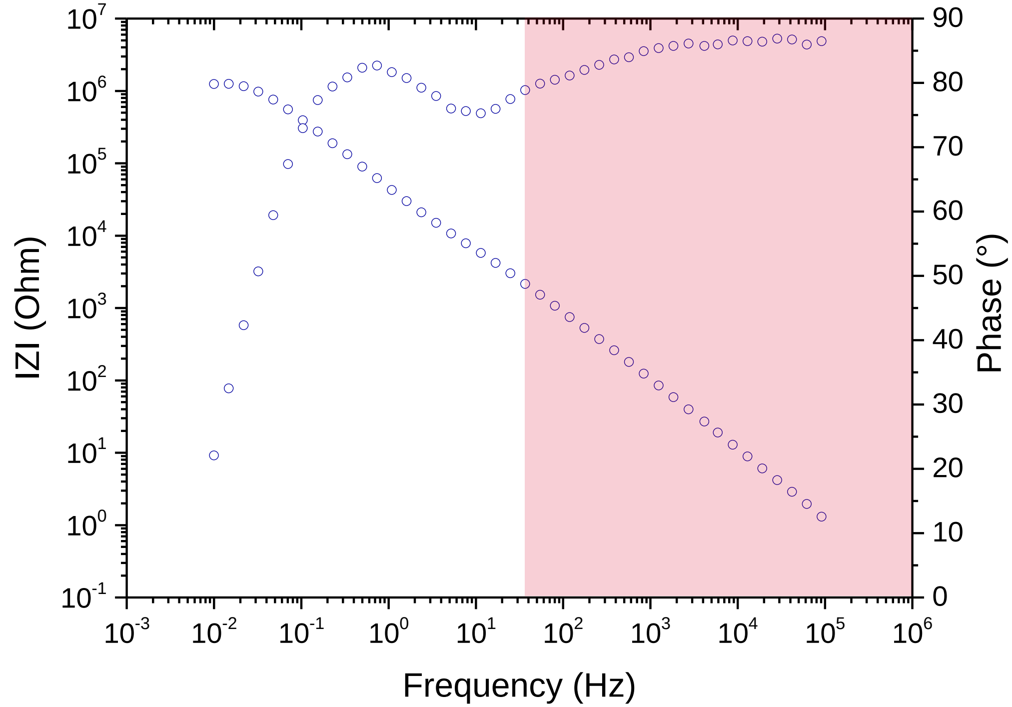
CHARACTERIZATION OF A PASSIVE LAYER WITH A CONTROLLED THICKNESS - MONITORING THE NANOMETRIC THICKNESS



EIS

- Complex capacitance representation

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



ZrO_2
Zr

EIS

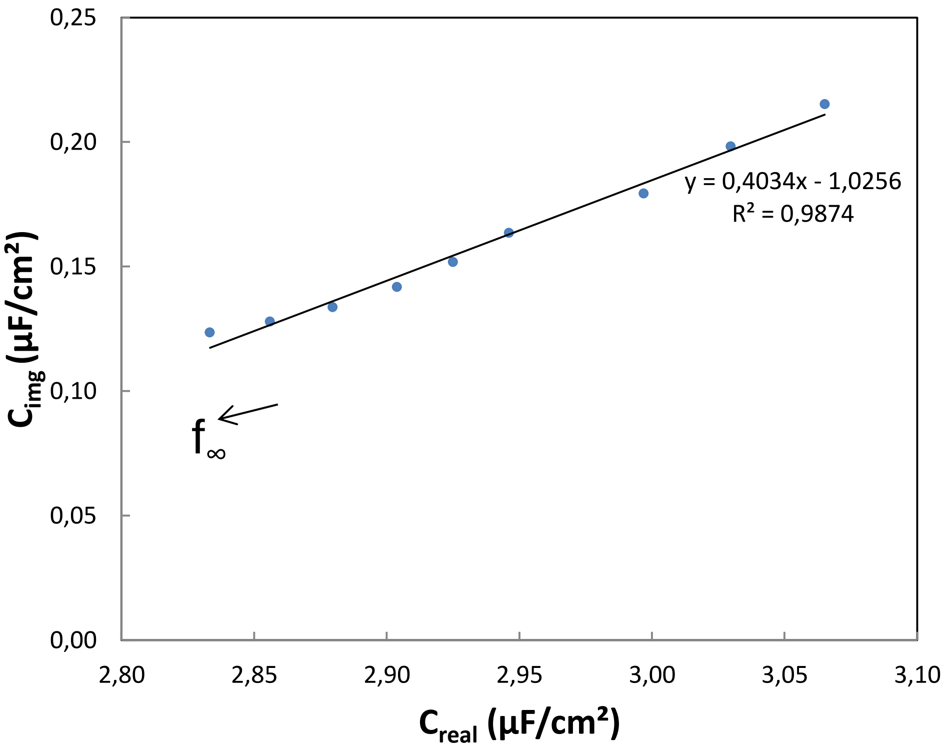
- Complex capacitance representation

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

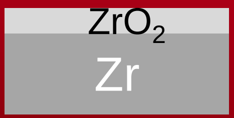
- Dielectric material behavior: Jonscher's Law[1]

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

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

Avec $0<\alpha<1$

- With C_∞: film thickness calculation:

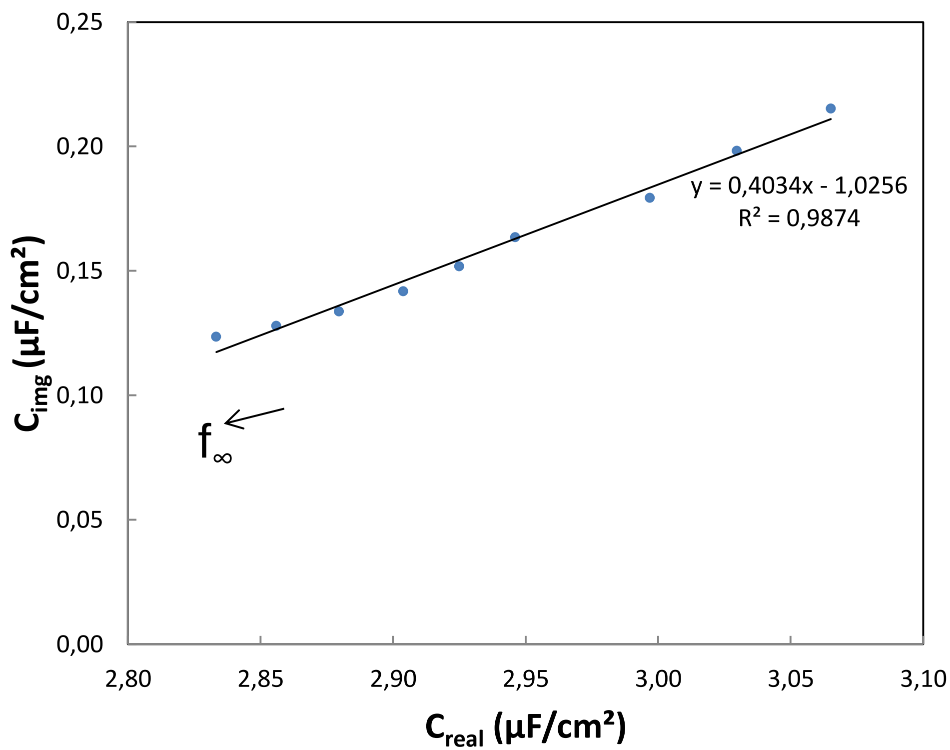
$$d = \frac{\varepsilon\varepsilon_0}{C_\infty}$$

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

ε_0: dielectric permittivity of vacuum ($8.85.10^{-14}$ F/cm)

C_∞: Infinite capacitance corresponding to the defectless oxide layer

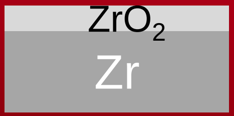
(here, 2,56µF/cm²)



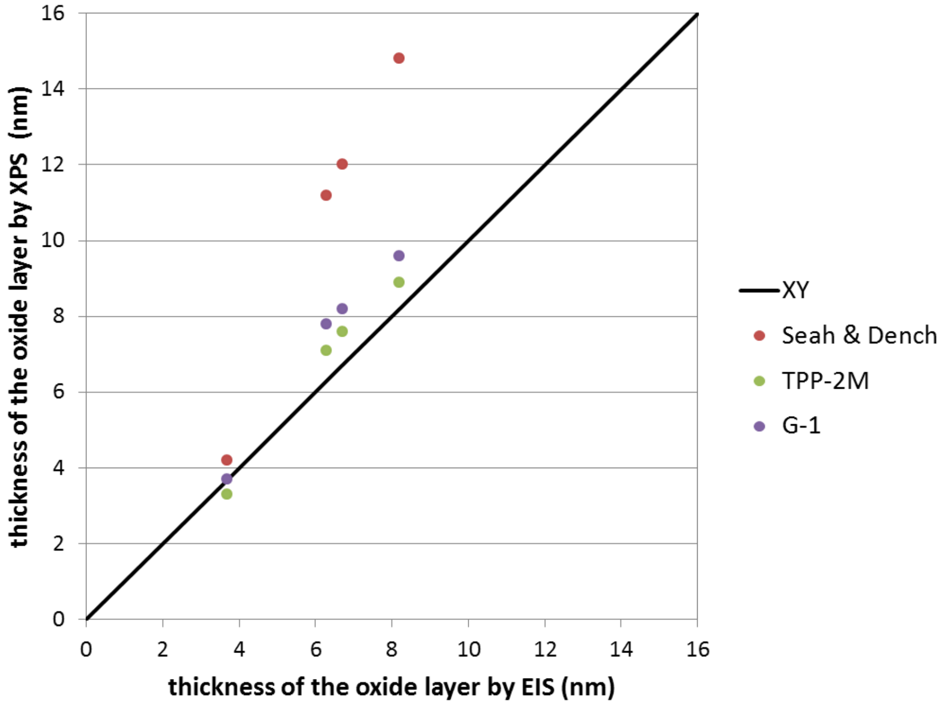
- Another method to calculate the thickness, Power law's model [2] giving a similar result.

[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.

CHARACTERIZATION OF PASSIVE LAYERS WITH A CONTROLLED THICKNESS - RESULTS



- 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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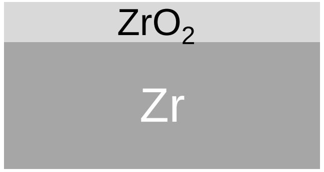

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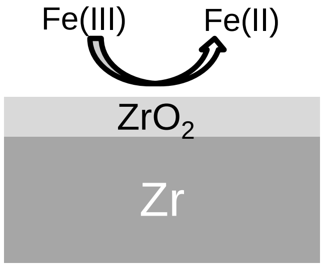
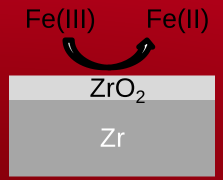
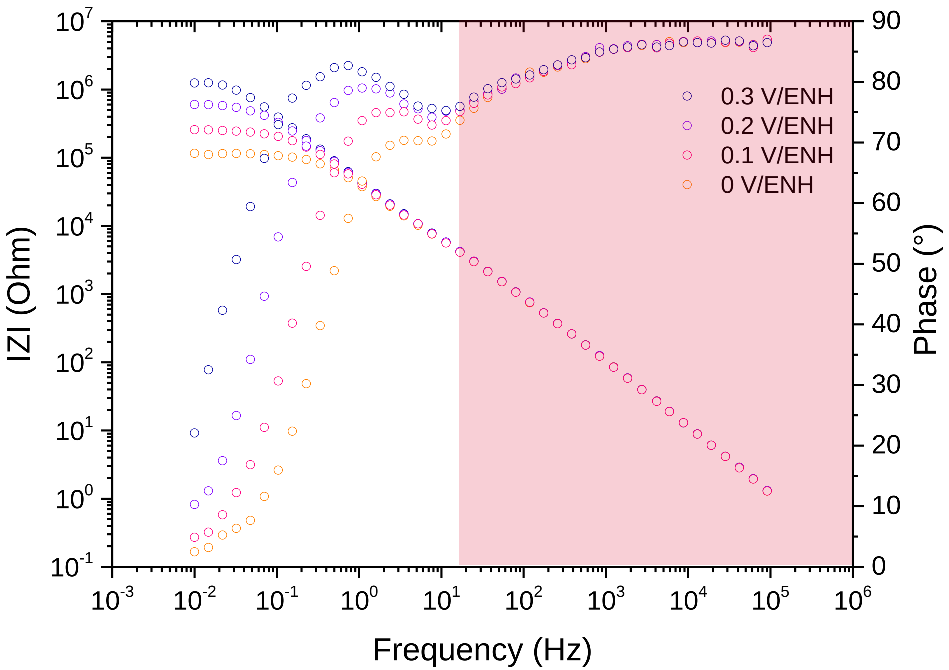


- Conclusion and outlook

KINETICS OF FE(III) REDUCTION BY EIS



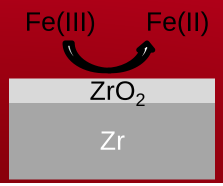
Evolution of impedance spectra with potential



Bode Plot

ZrM106 (8.2 nm)
H_2SO_4 0.5 M FeII/FeIII 0.1M
Room temperature

KINETICS OF FE(III) REDUCTION BY EIS



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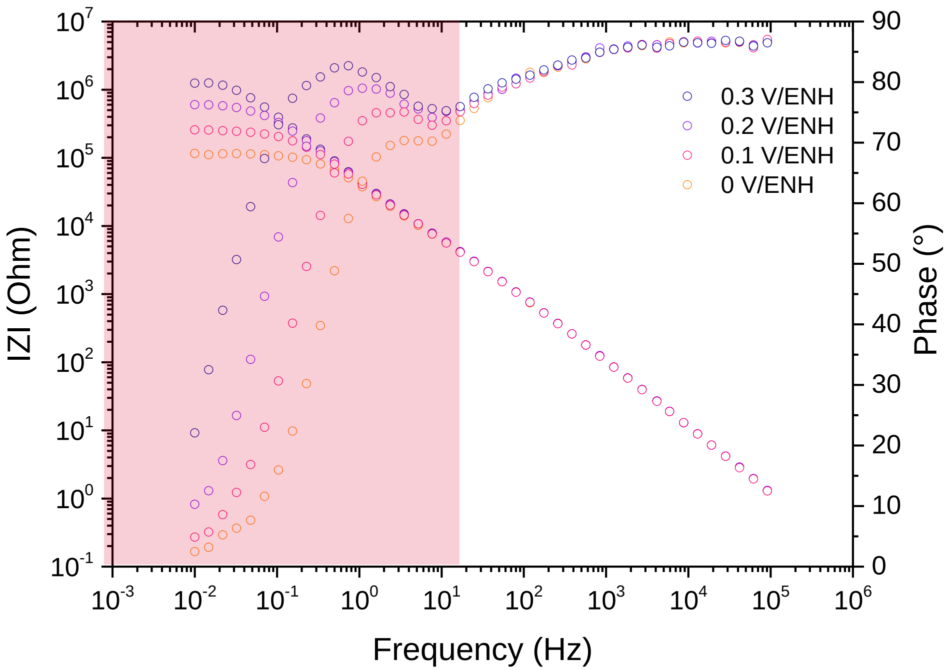

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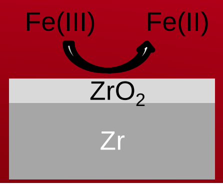

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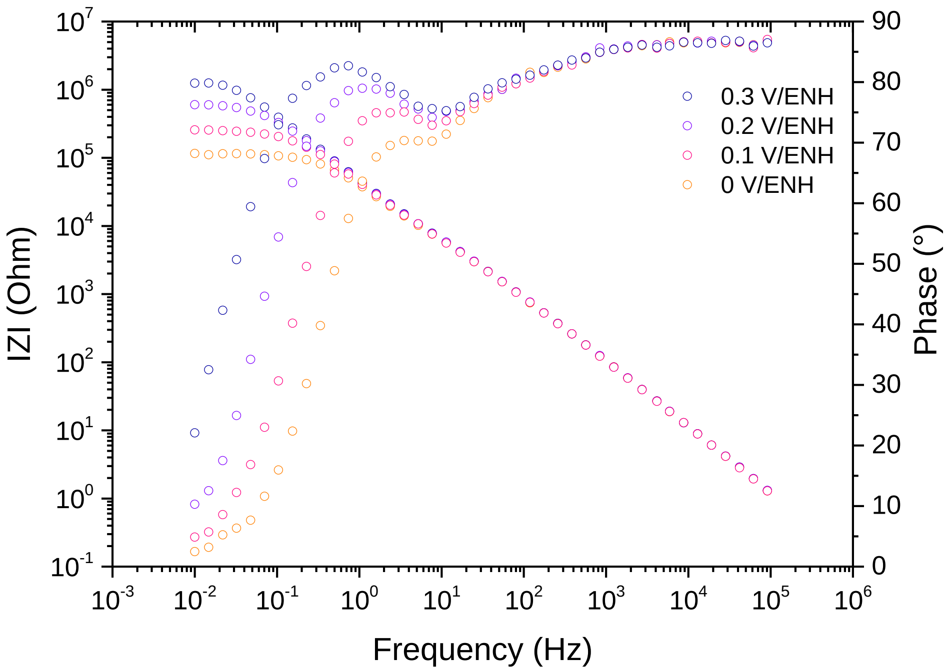

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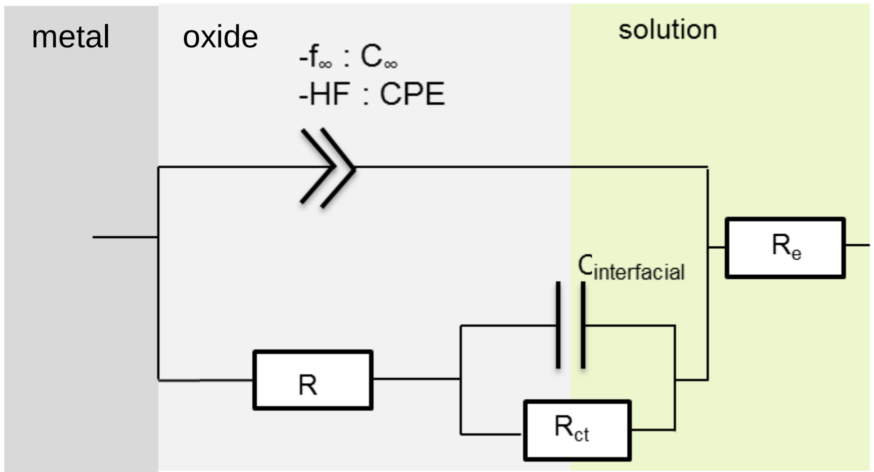
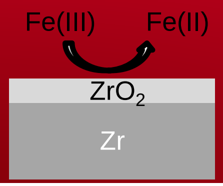
- Proposed equivalent circuit:



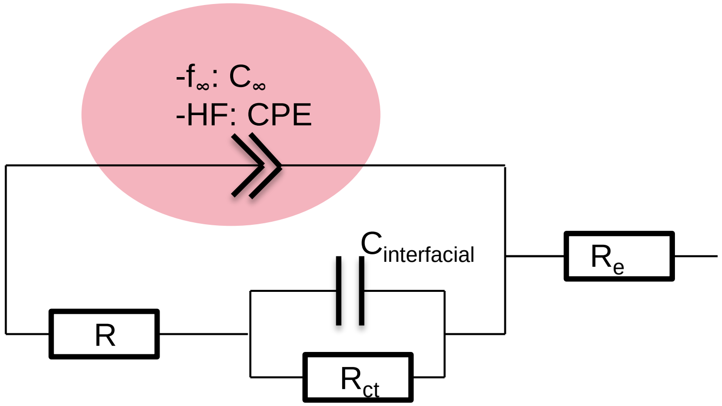
- With:
  - R_e: Electrolyte resistance
  - C_∞ (at f_∞) & CPE: defectless capacitance representing film and the dielectric losses in the film
  - $C_{interfacial}$: Space charge capacitance and double layer capacitance
  - R_{ct}: charge transfer resistance
  - R: its physical meaning is open to interpretation.

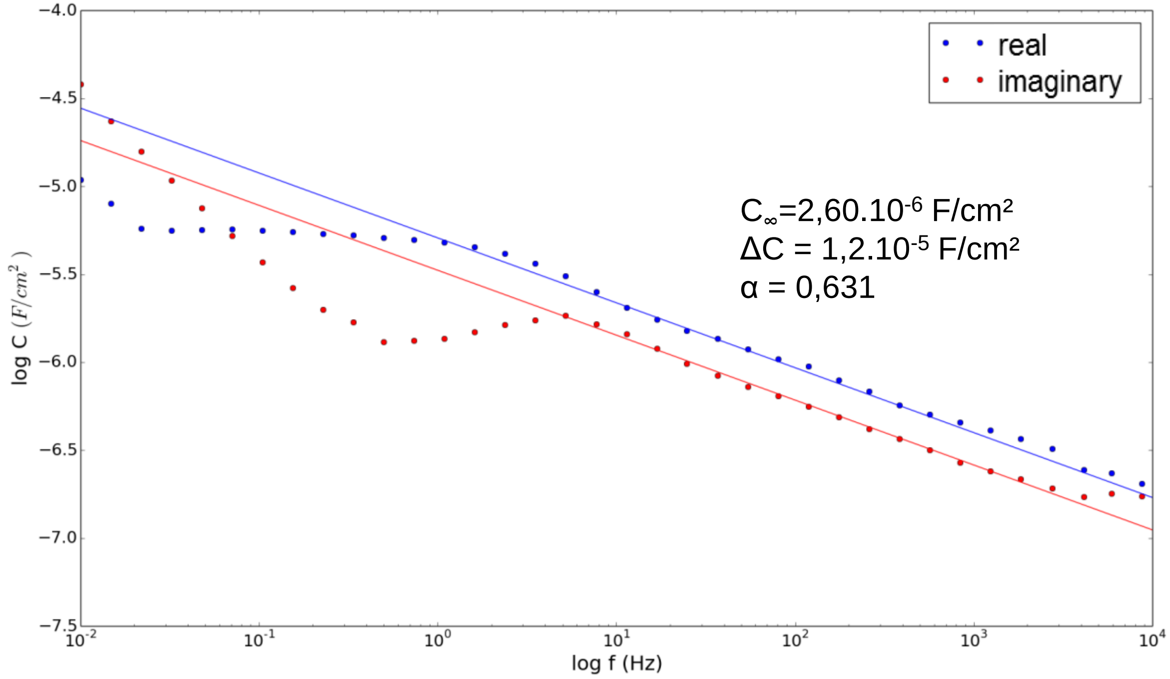
KINETICS OF FE(III) REDUCTION BY EIS



Justification of the equivalent circuit

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





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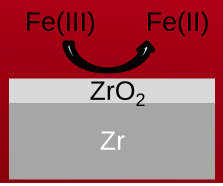
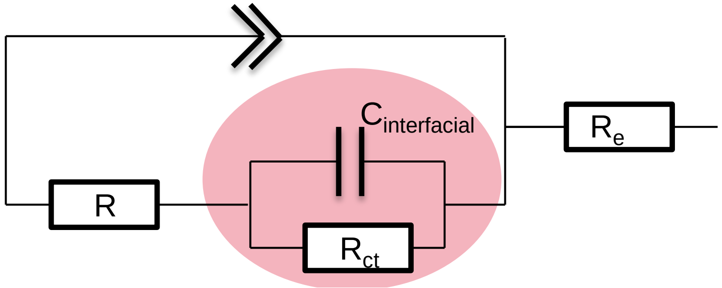
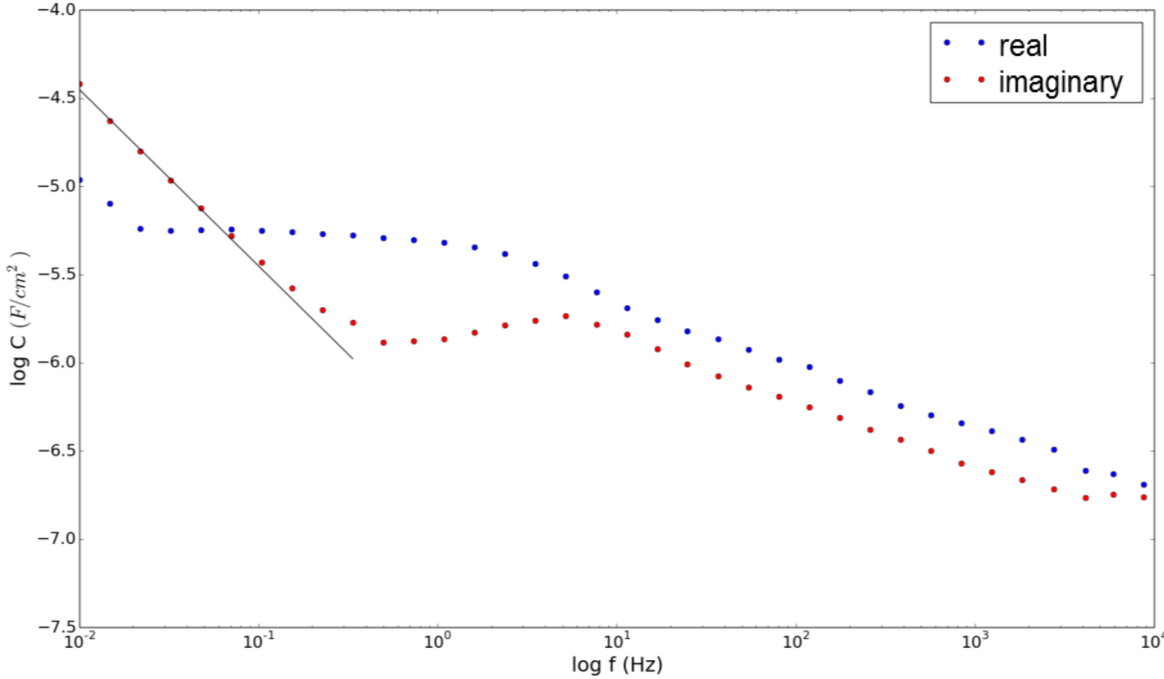


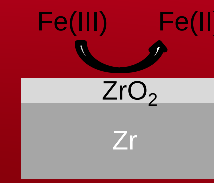
Justification of the equivalent circuit



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



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)
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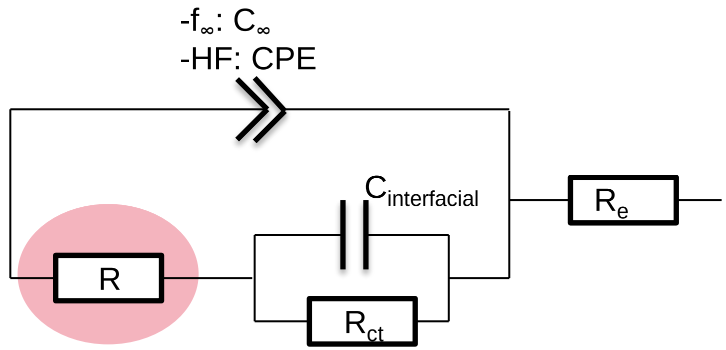
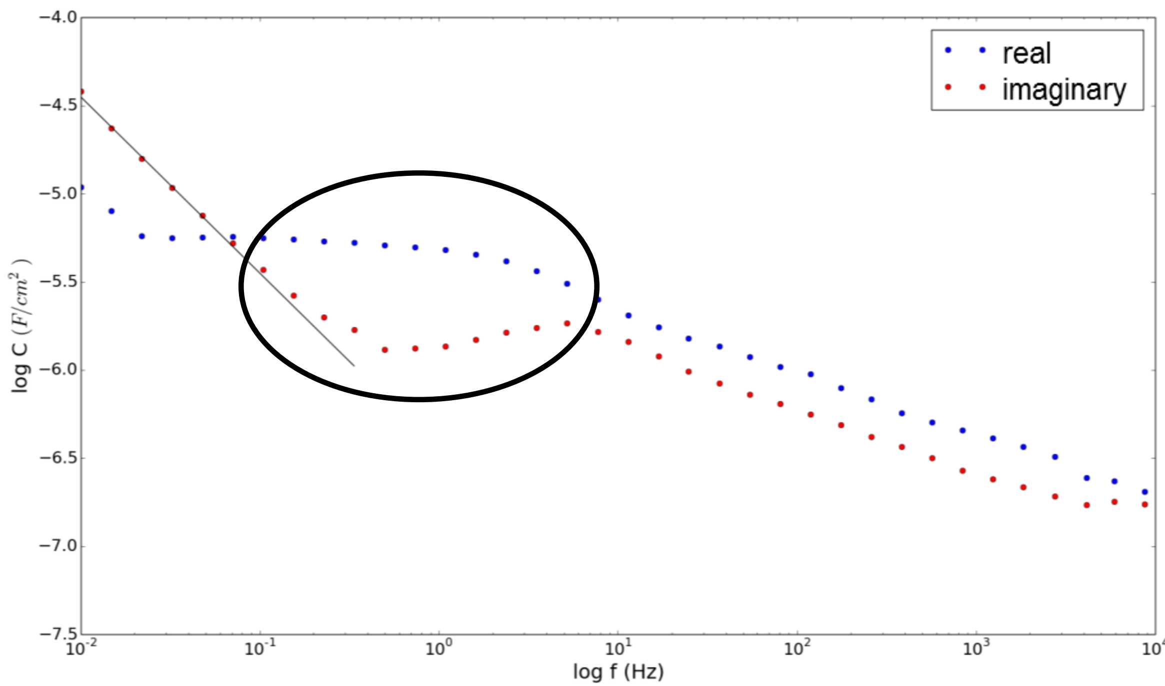
- Intermediate frequency part: R





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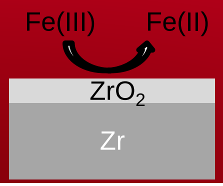
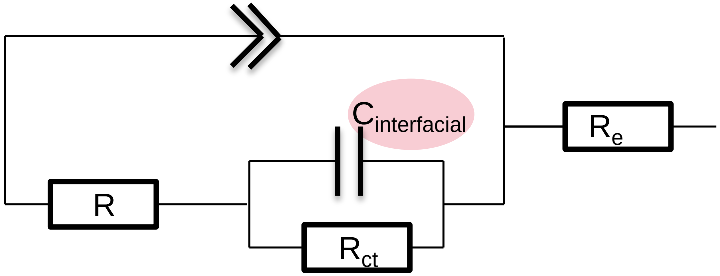
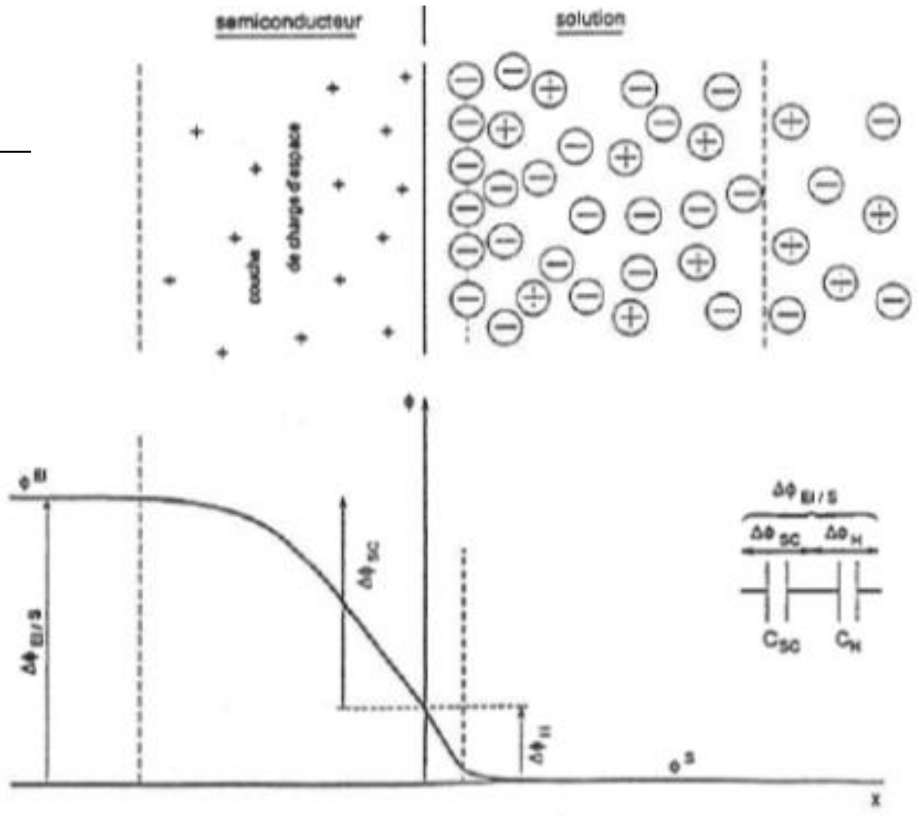


Semiconducting properties of the film

- f_∞: C_∞
- HF: CPE





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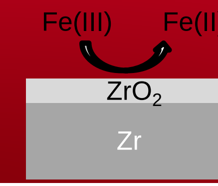

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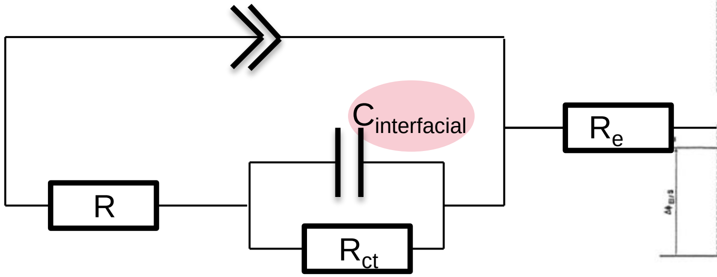

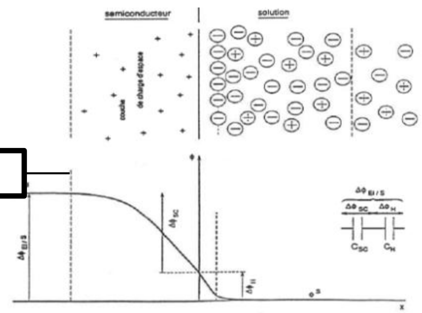

- Verification of the Mott-Schottky's law:

$$\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon \varepsilon_0 q_e N_0}\left(E - E_{bp} - \frac{k_B T}{q_e}\right)$$

With: ε: dielectric constant of the material
ε_0: dielectric permittivity of vacuum: $8{,}85.10^{-14}$ F/cm²
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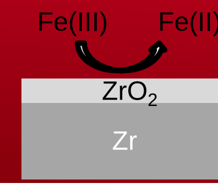

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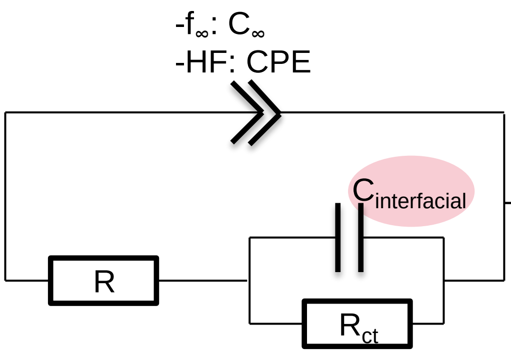

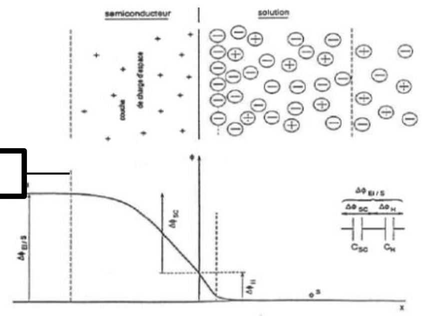

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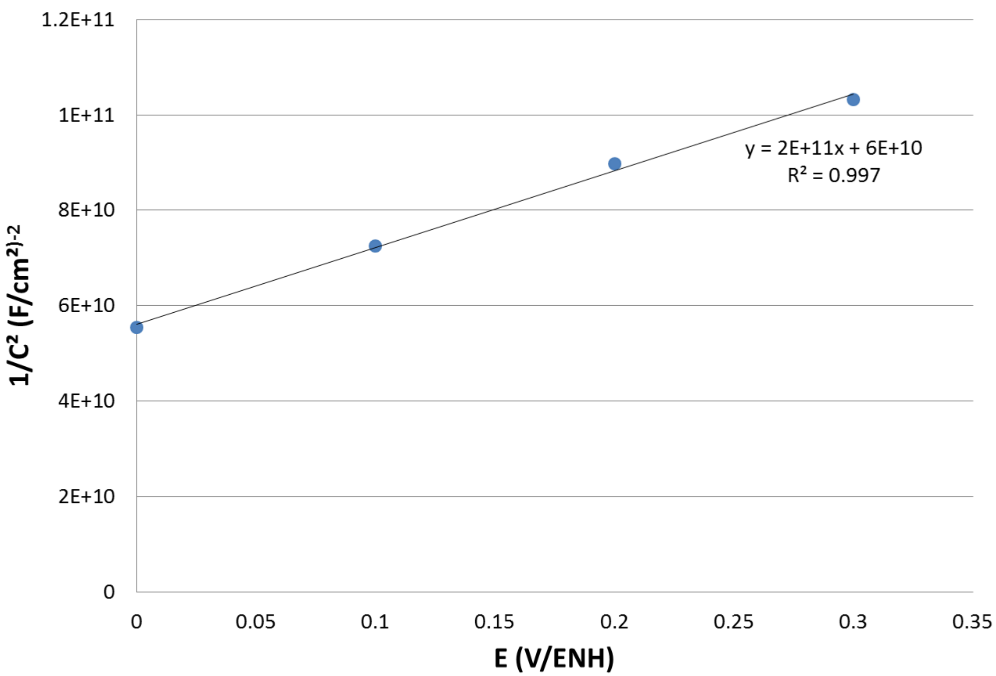

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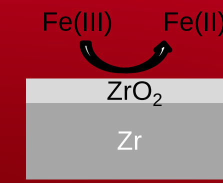

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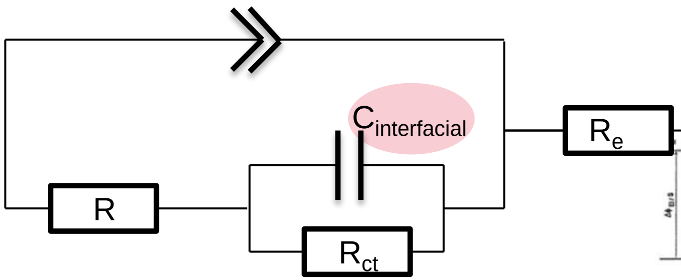

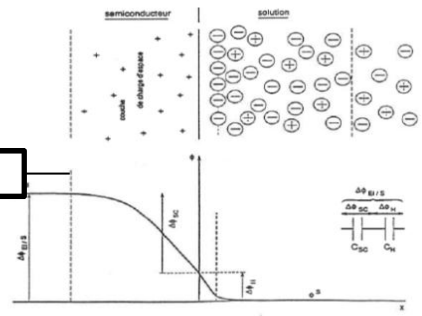

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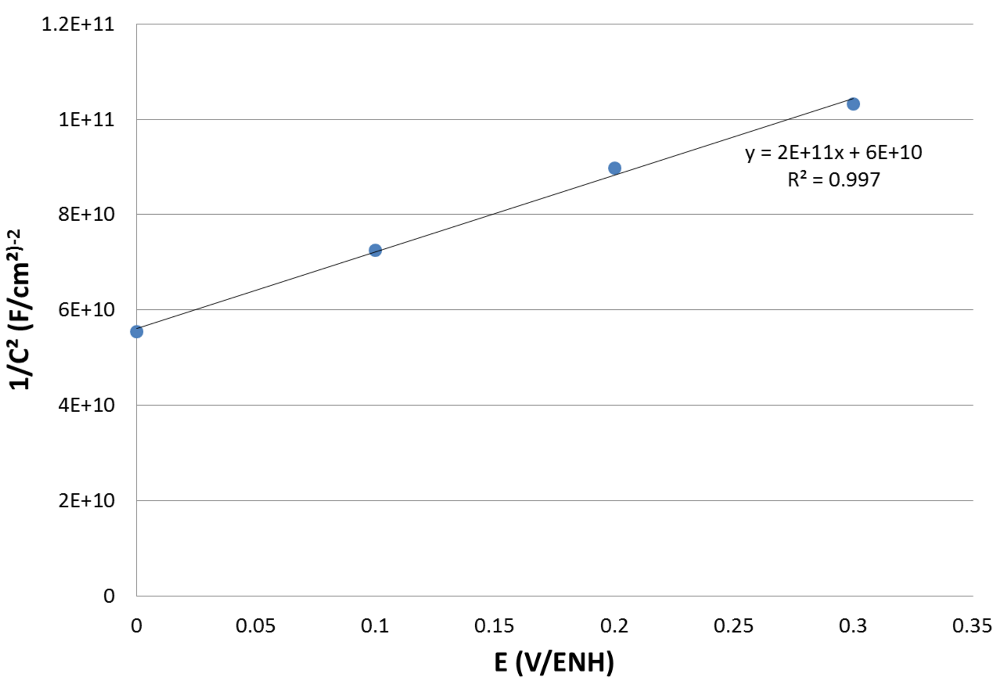

- Results:
  - Positive slope: ZrO_2 n-type semiconductor
  - Determination of the charge number carriers N_0

KINETICS OF FE(III) REDUCTION BY EIS

Semiconducting properties of the film

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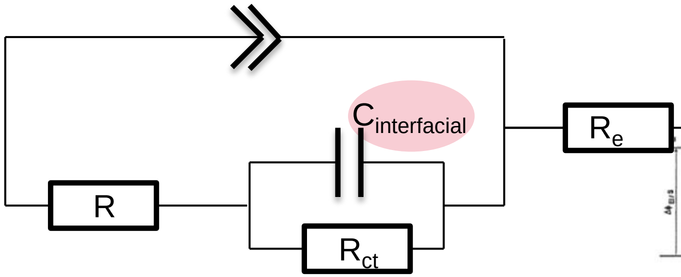

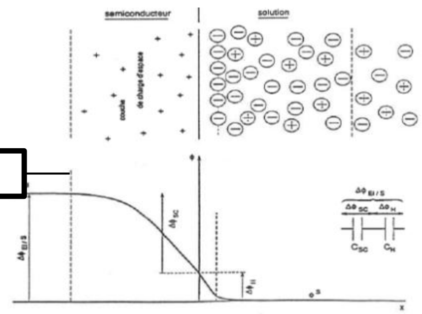

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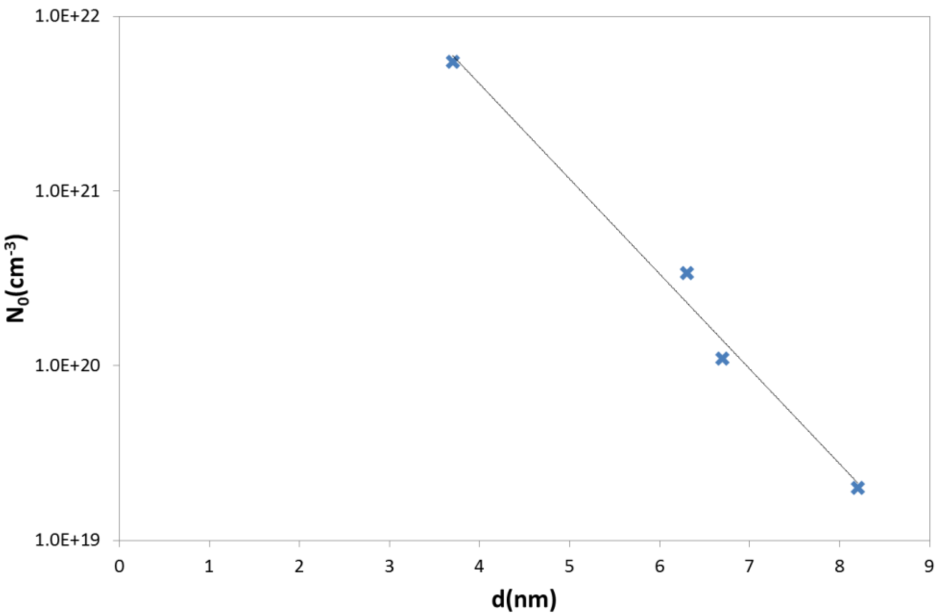

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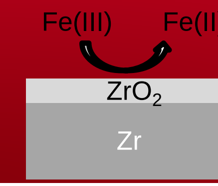
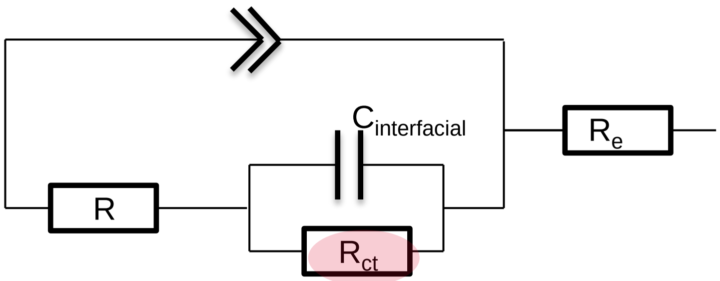
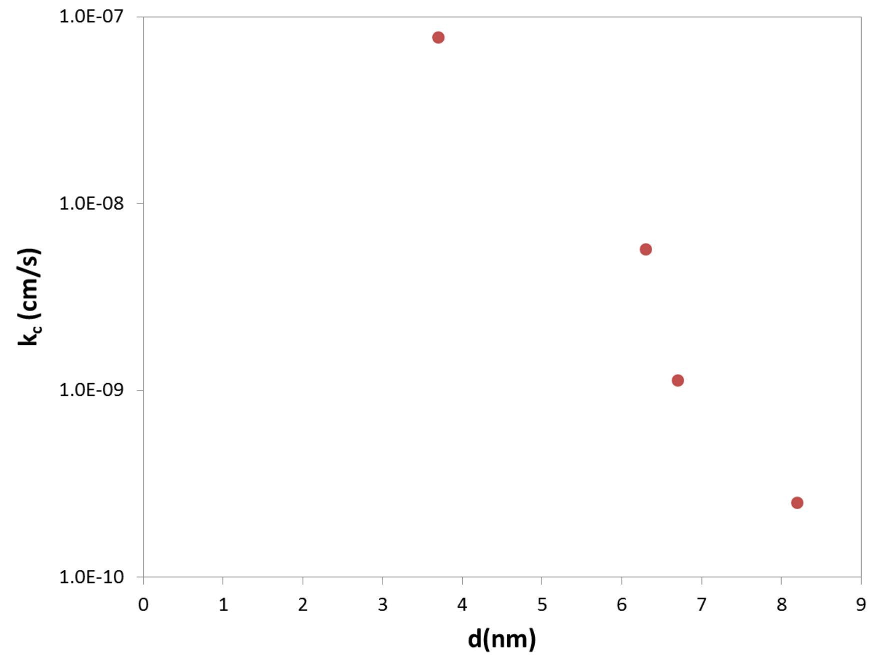


Evolution of the constant rate k_c according to thickness

-f_∞: C_∞
-HF: CPE



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



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

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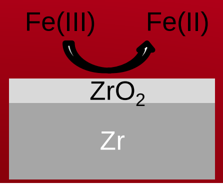

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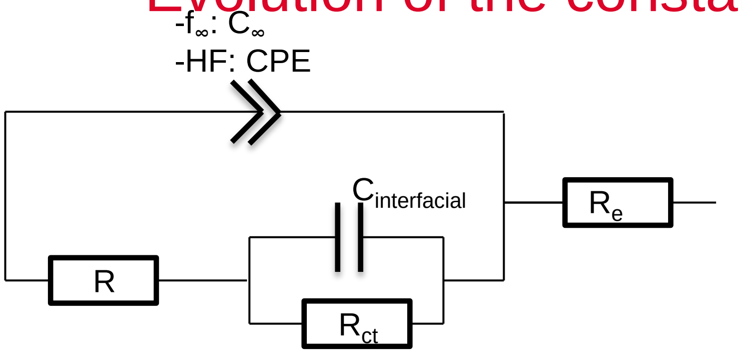

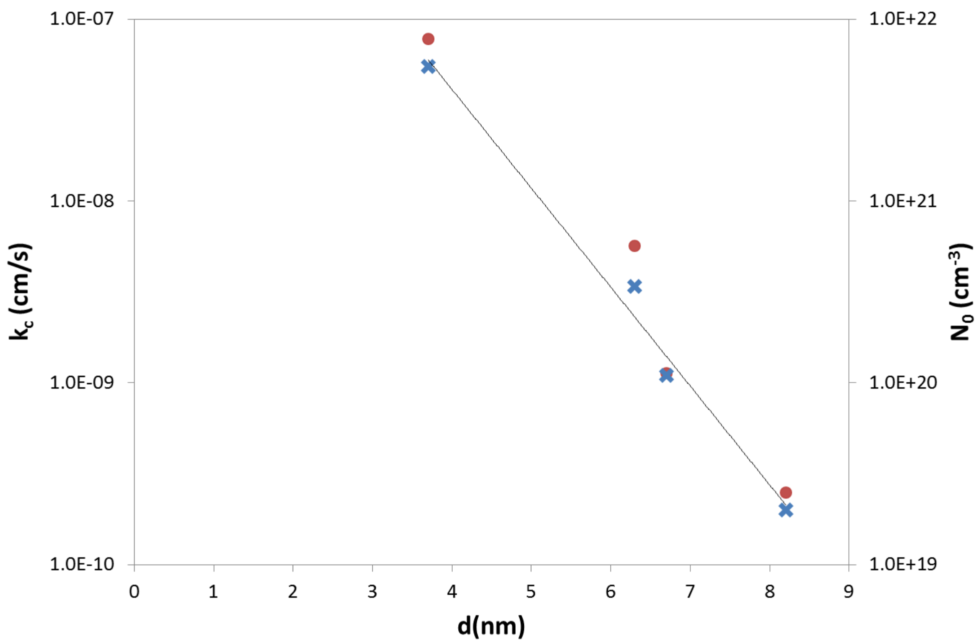

- k_c (determined from R_{ct}) decreases as the thickness increases
- k_c follows the same trend as N_0

The evolution of k_c is linked to the semiconducting properties of ZrO_2

CONCLUSION & OUTLOOK

Conclusions

- Formation of ZrO_2 layers:
  - Formation of 4 layers of different thicknesses
  - Comparison of 2 experimental techniques for the thickness measurement

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  - Advanced understanding of EIS spectra
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    - decreases with d
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CONCLUSION & OUTLOOK

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Outlook

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

Reprocessing plant of La Hague

Acknowledgments:

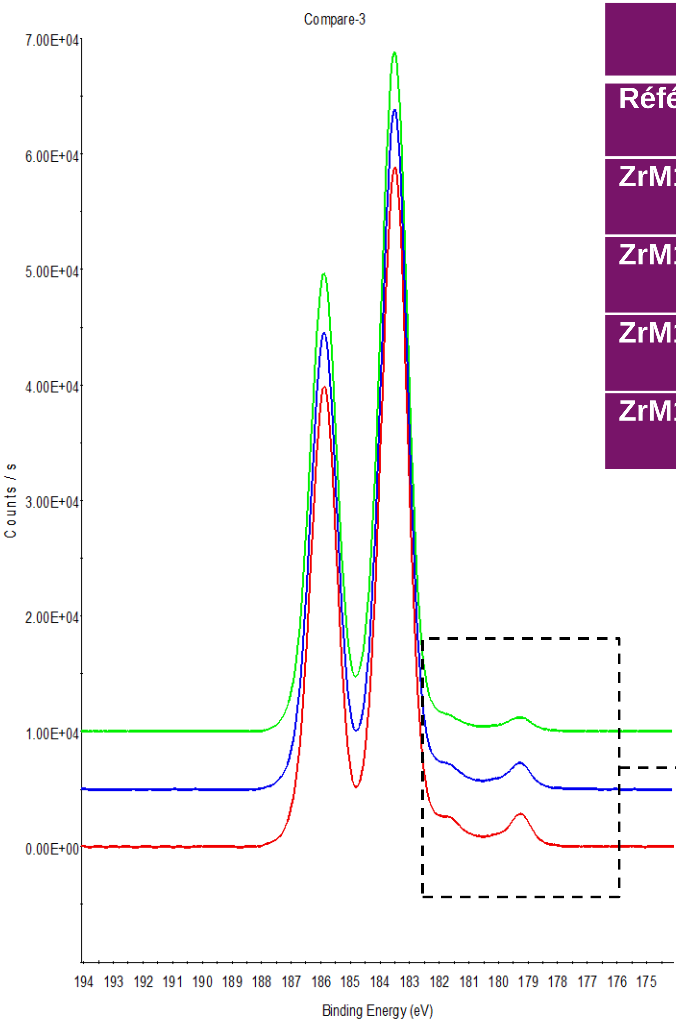
AREVA

M. Bigot, N. Brijou-Mokrani, N. Cavaliere, C-A. Decoupigny, A. Fallet, P. Fauvet, O. Geneve, N. Gruet, S. Heurtault, P. Laghoutaris, B. Laurent, F. Martin, S. Pasquier-Tilliette, B. Puga, M. Rivollier, R. Robin, V. Soulié.

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

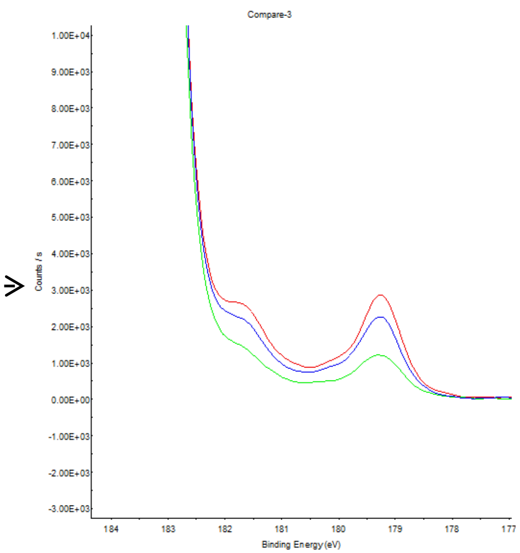


Zrm106

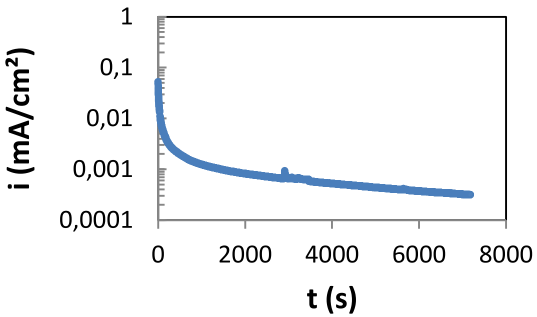
Zrm105

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

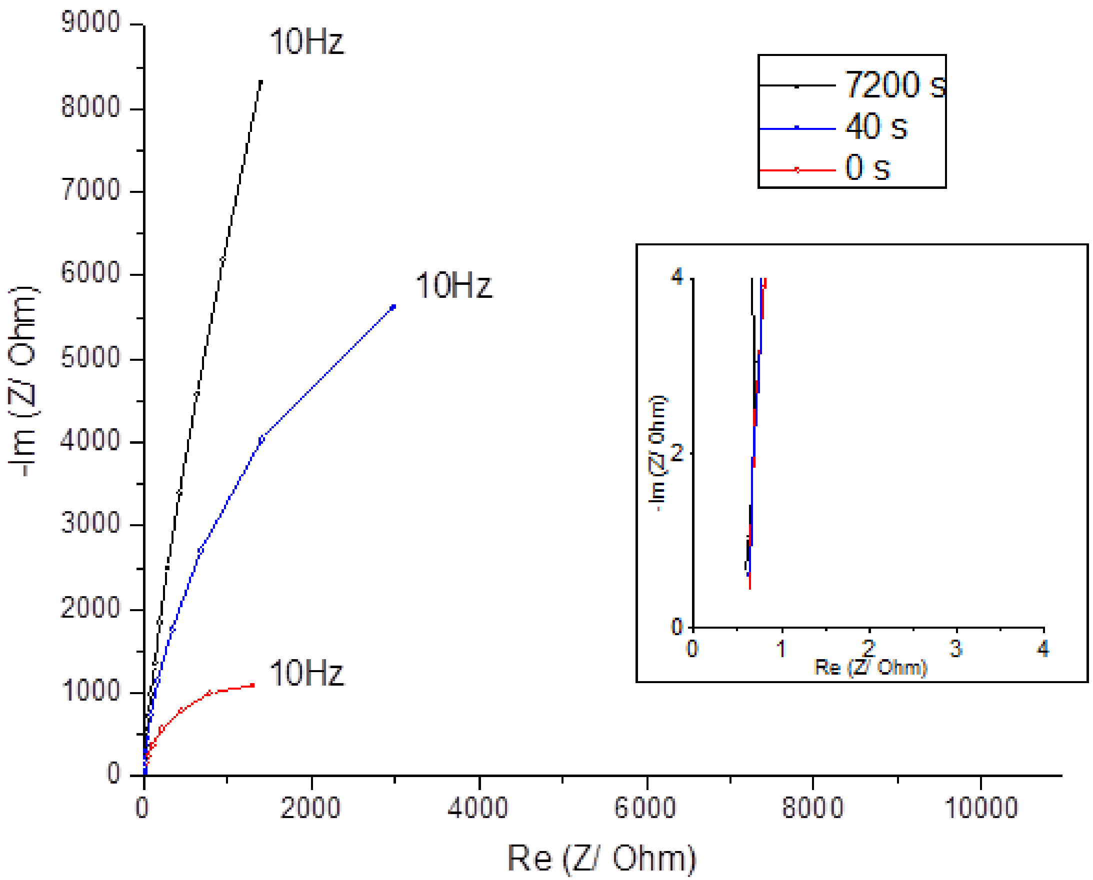
- Boucle capacitive:
processus se déroulant en parallèle

- Représentation de Nyquist pas adaptée

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

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

Suivi EIS de la croissance du film



Représentation de Nyquist