Influence of a passive layer on the kinetics of nitric acid reduction

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INFLUENCE OF A PASSIVE LAYER ON THE KINETICS OF NITRIC ACID REDUCTION

Marie Benoit[1*], Christian Bataillon[2], Benoît Gwinner[1] ; Frédéric Miserque[2], Carlos M. Sanchez-Sanchez[3], Bernard Tribollet[3], Vincent Vivier[3**]

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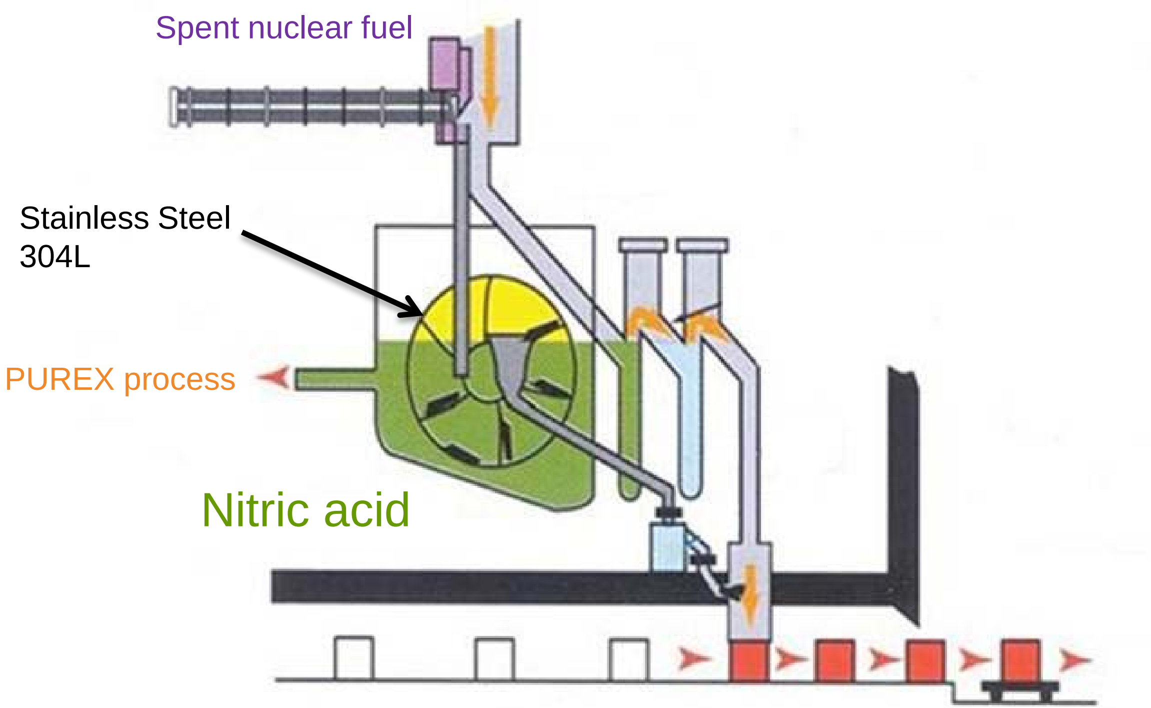
[3]Sorbonne Universités, UPMC Univ Paris 06, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques, 4 place Jussieu, F-75005, France.

***vincent.vivier@upmc.fr*

EIS 2016

INDUSTRIAL CONTEXT

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



Areva La Hague

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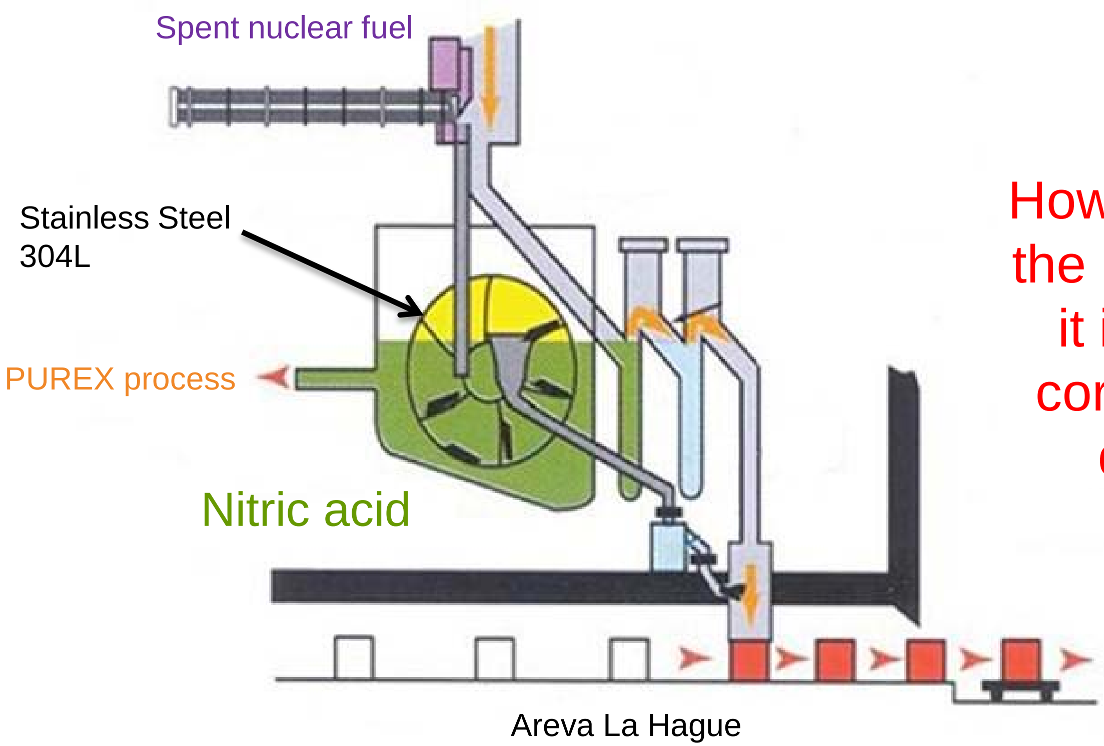
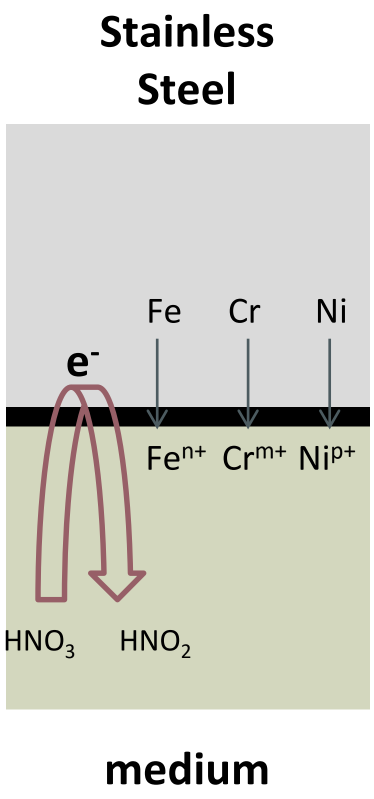


However, for the prediction of the lifetime of the equipment, it is essential to know the corrosion mechanisms and quantify their kinetics.

Why do we need to understand cathodic processes in nitric acid solution?

- **Anodic process**: oxidation of material
- **Cathodic process**: medium reduction



4 to 8 M HNO_3 → highly concentrated acidic solution
→ oxidizing media

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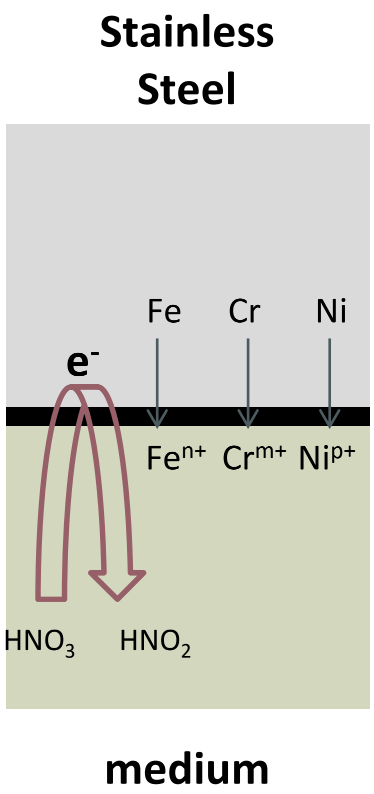

The kinetics of these two processes can be characterized by their current density

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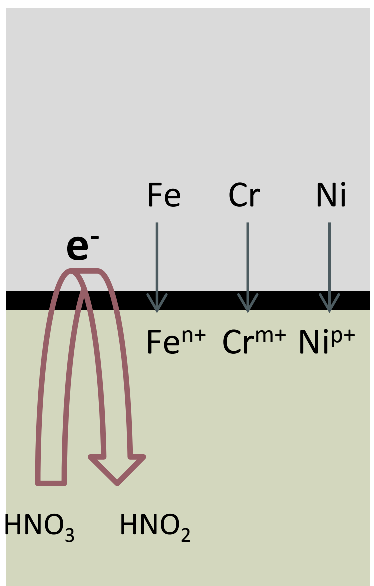
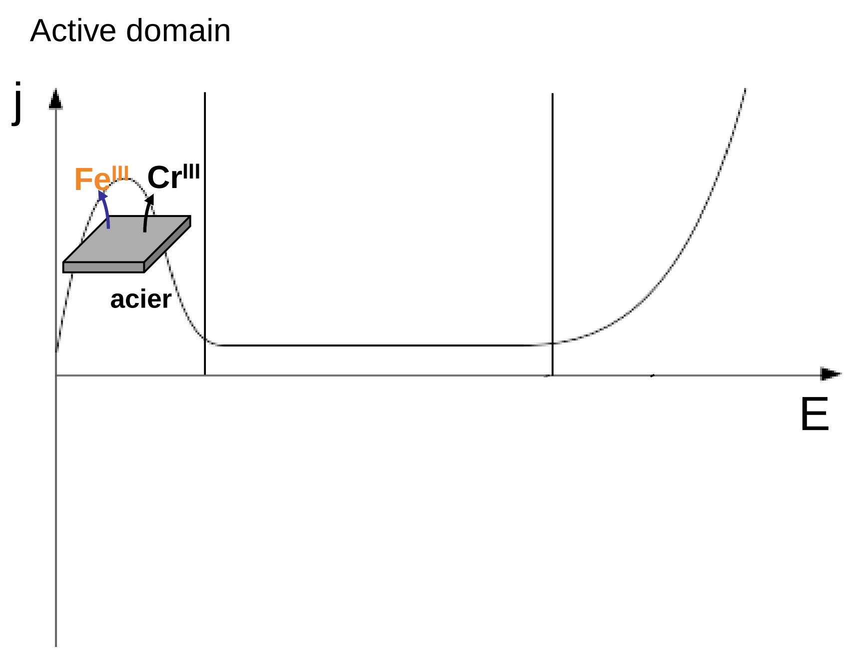
Stainless Steel



medium



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[E. Tcharkhtchi et al., Corrosion Science, 2016]

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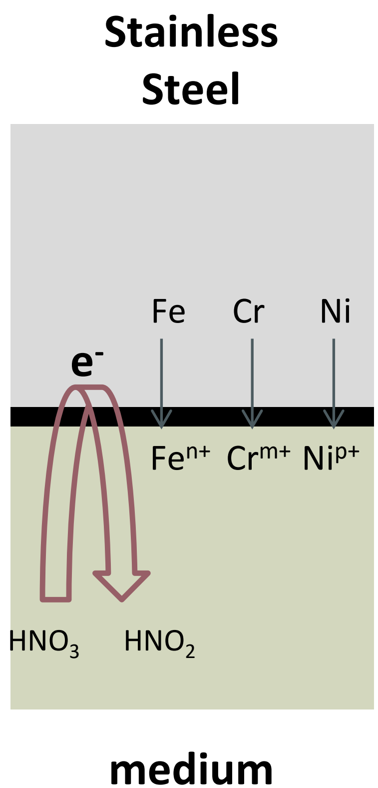

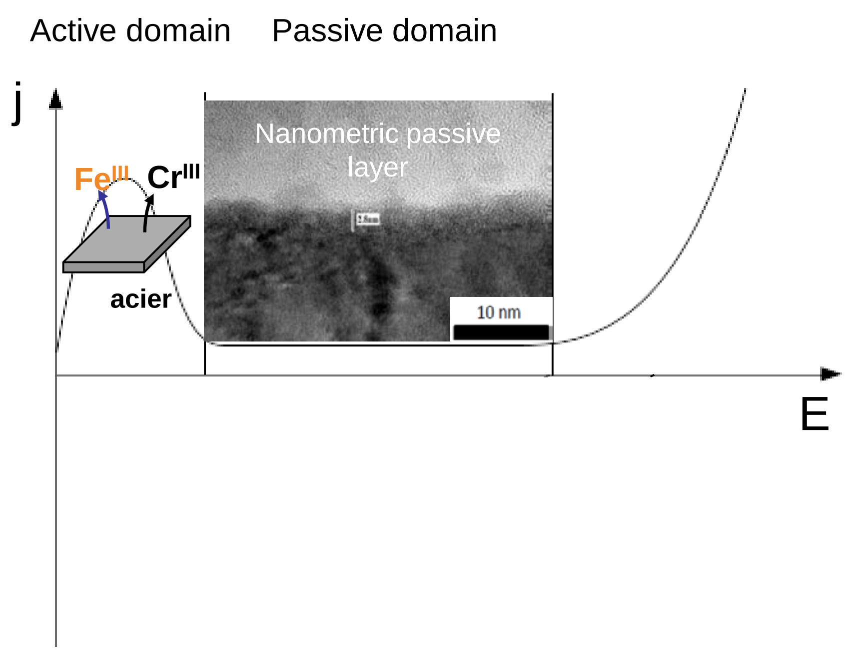

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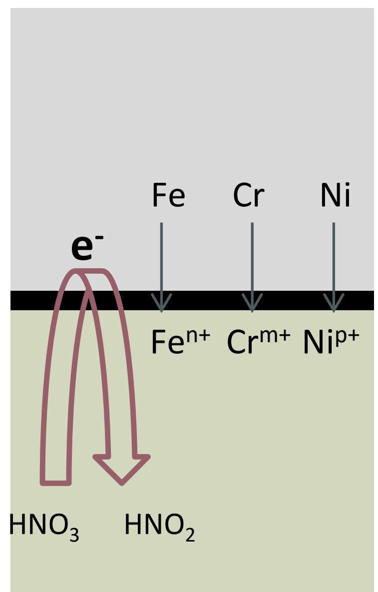

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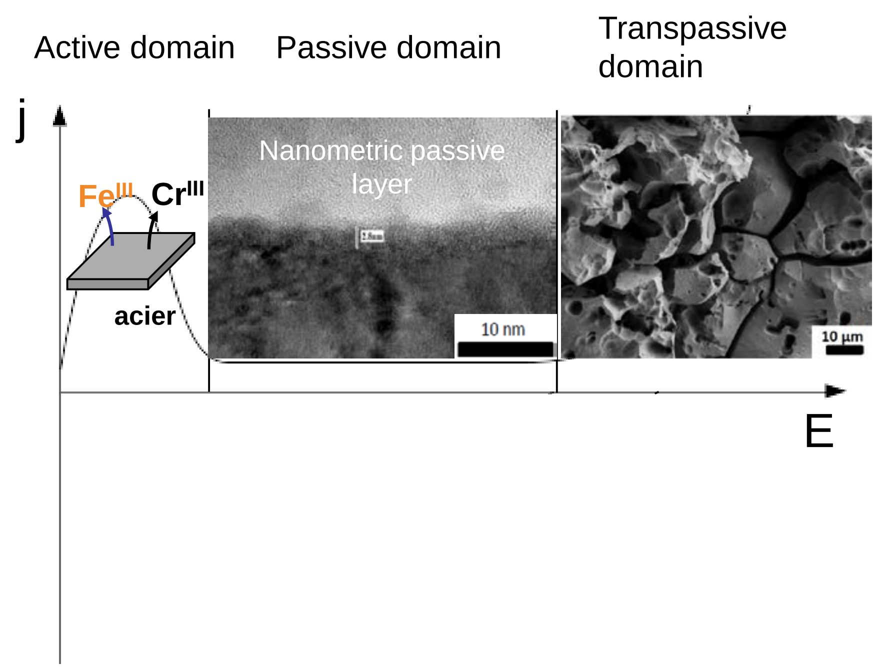

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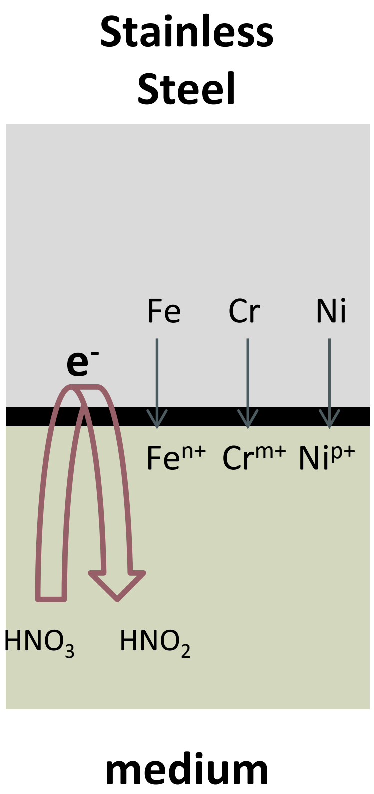

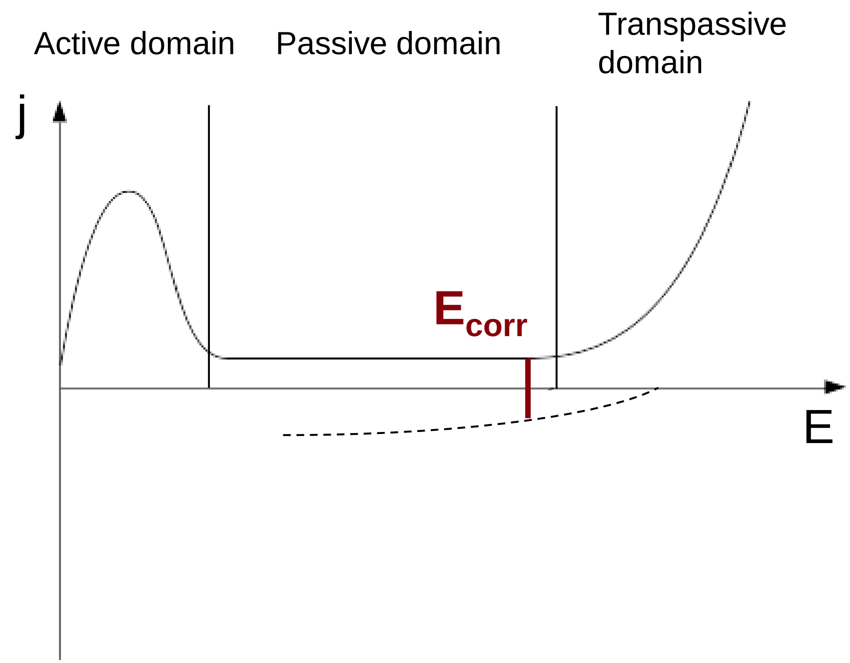

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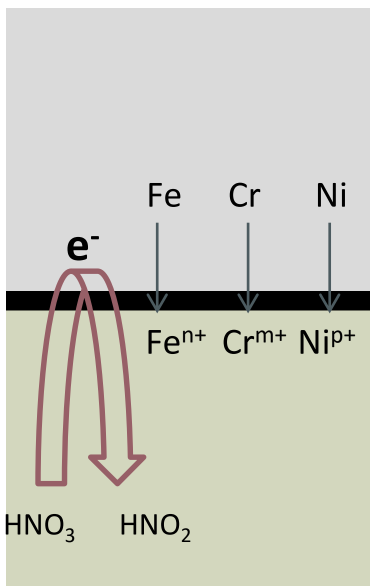

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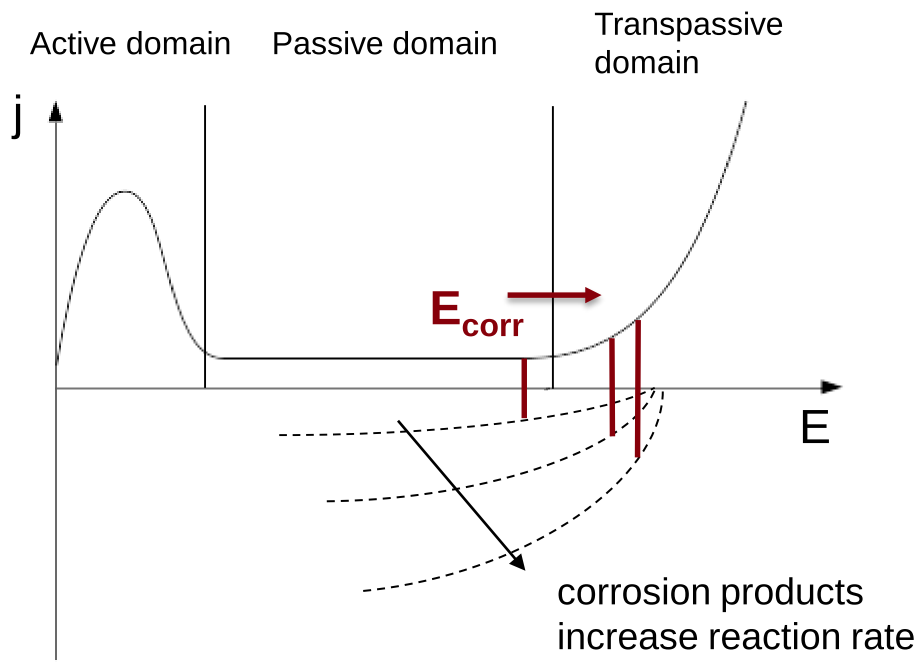

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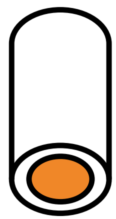
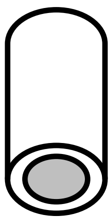
OUTLINE

Mechanisms of nitric reduction:



gold

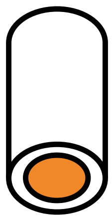
[D. Sicsic et al., Eur. J. Inorg. Chem., 2014]



stainless steel

[R. Lange et al., Electrochem. Com. 2013]
[F. Balbaud et al., Eur. J. Inorg. Chem.,2000]

Kinetics of nitric reduction:



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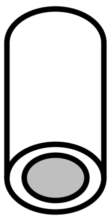

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MECHANISMS OF NITRIC ACID REDUCTION

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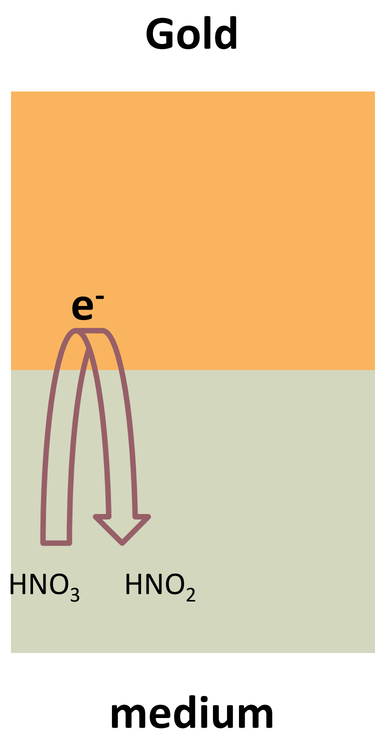

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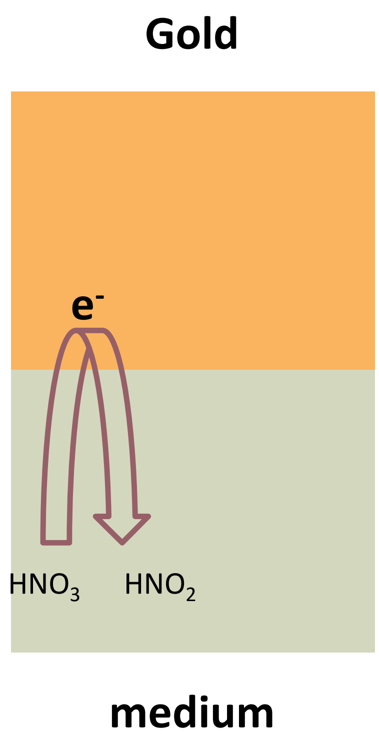

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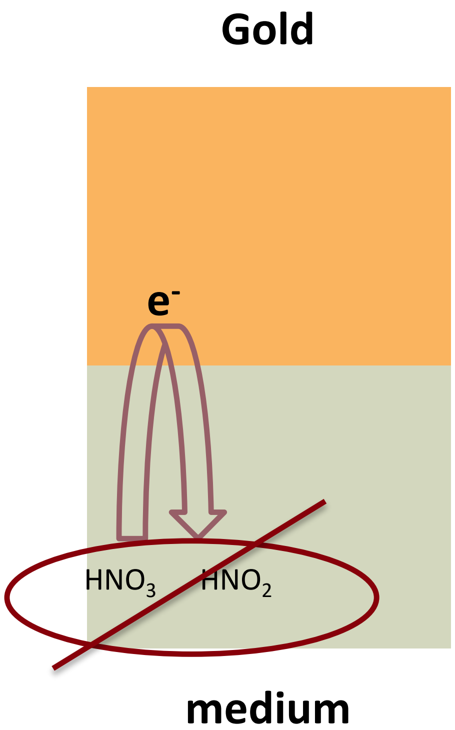

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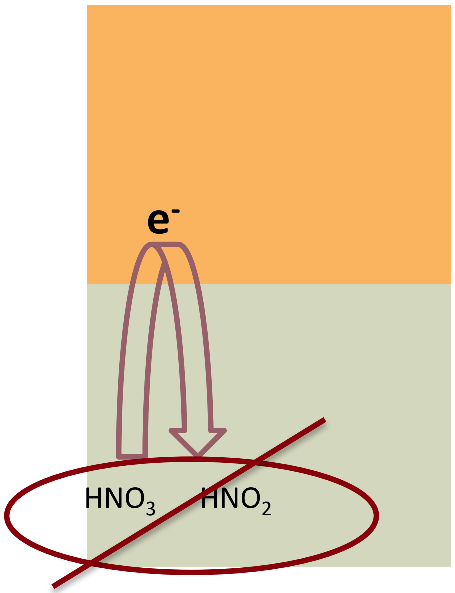
Gold



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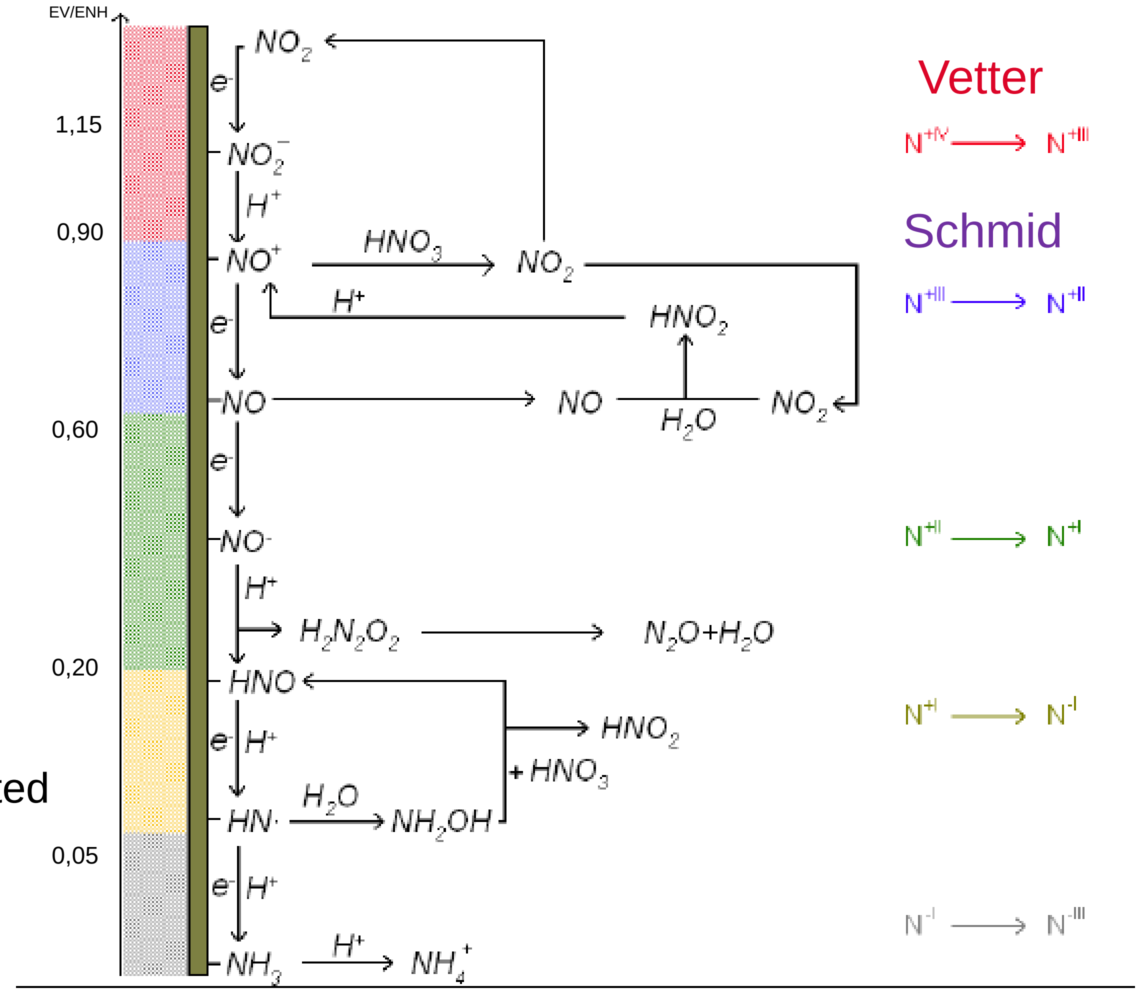

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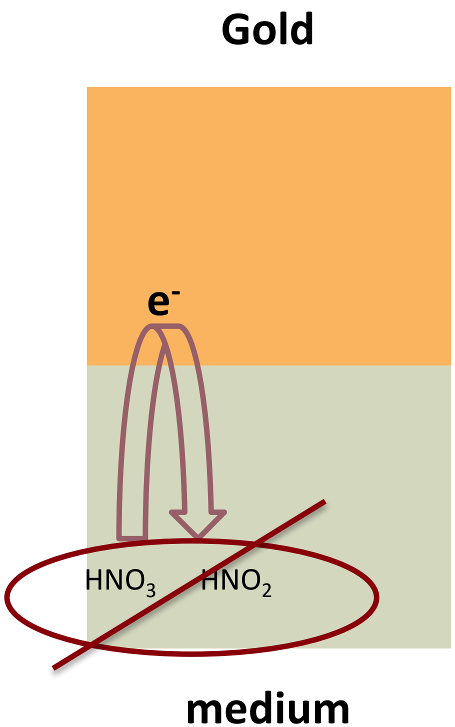

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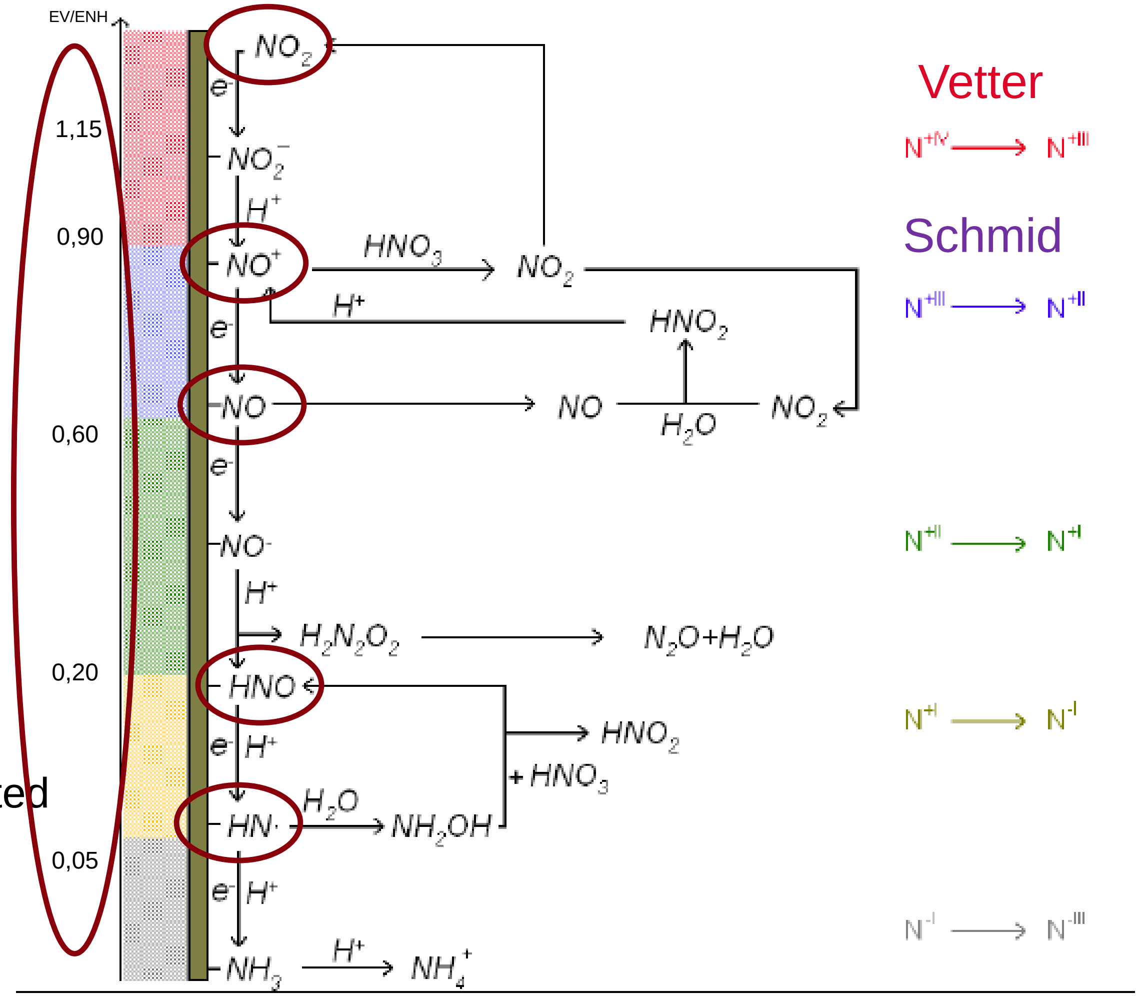

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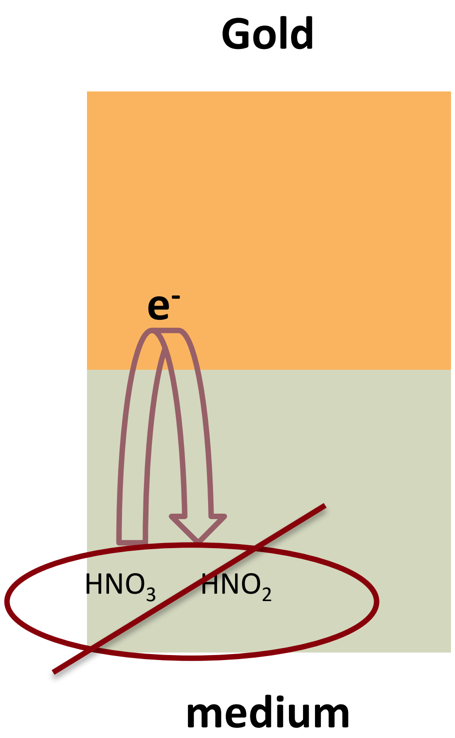

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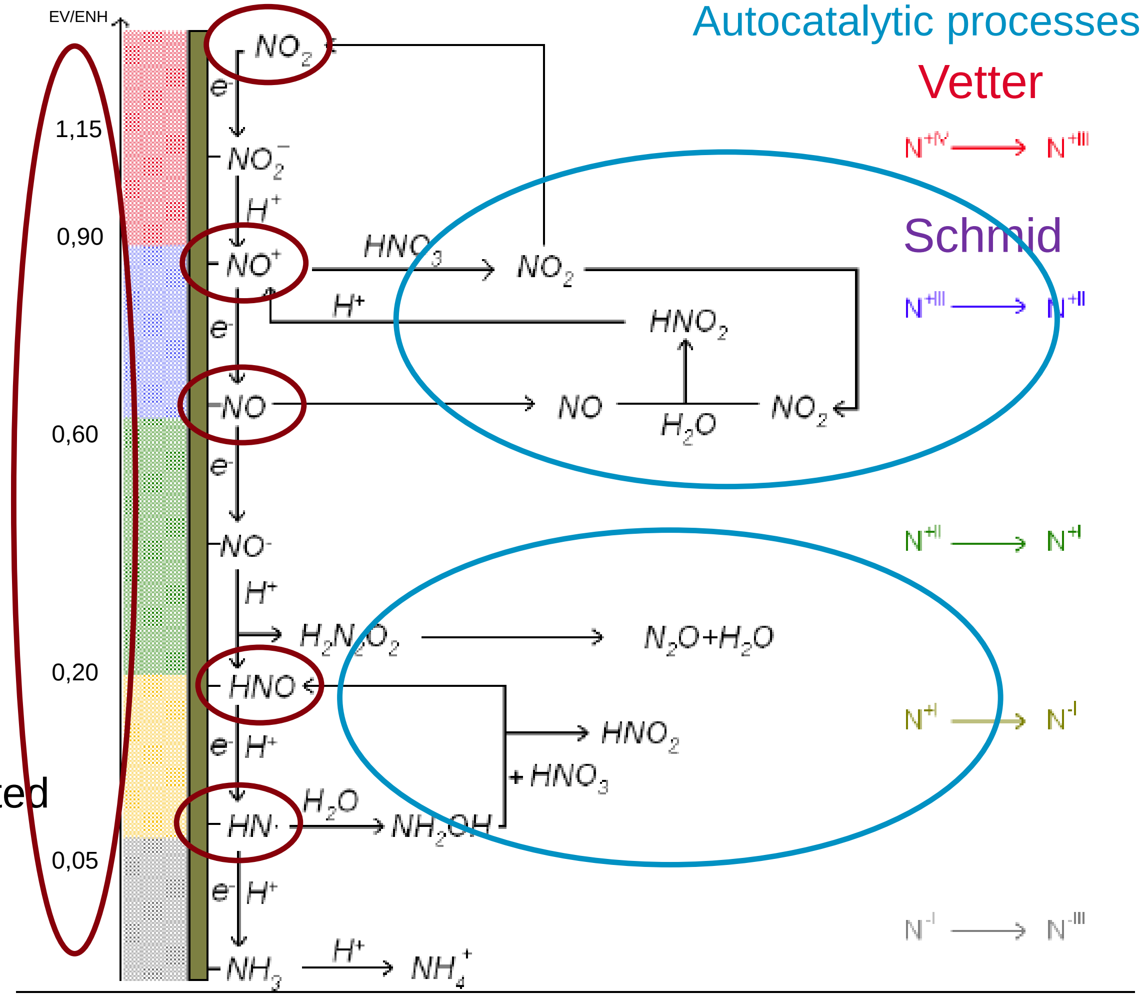

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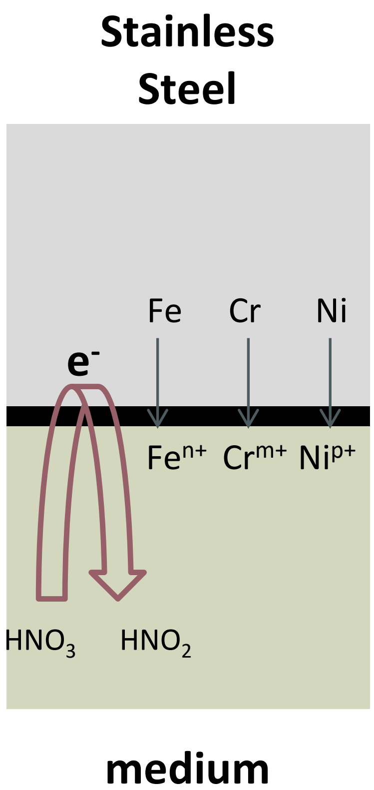

V. Razygraev [1] + F. Balbaud [2]:
Mechanisms in competition on stainless steel

R. Lange [3]: Schmid dominates on stainless steel

Schmid's mechanisms:

$$HNO_{2,sol} \rightarrow HNO_{2,ads}$$

$$HNO_{2,ads} + e^- + H^+ \rightarrow NO_{ads} + H_2O$$

$$NO_{ads} + \frac{1}{2}H^+ + \frac{1}{2}NO_3^- + \frac{1}{2}H_2O \rightarrow \frac{3}{2}HNO_{2,sol}$$

[1] [Razygraev et al.,Zashchita Mettalov, 1990]
[2] [F. Balbaud et al., Eur. J. Inorg. Chem.,2000]
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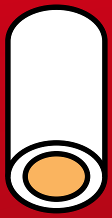
KINETICS OF NITRIC ACID REDUCTION ON GOLD



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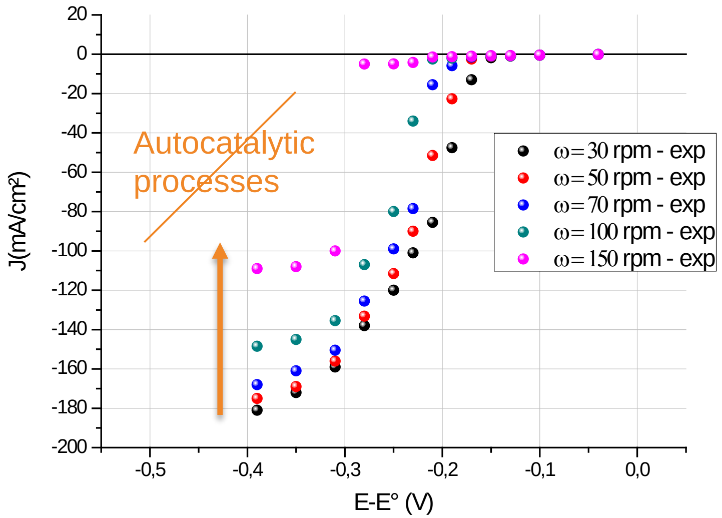
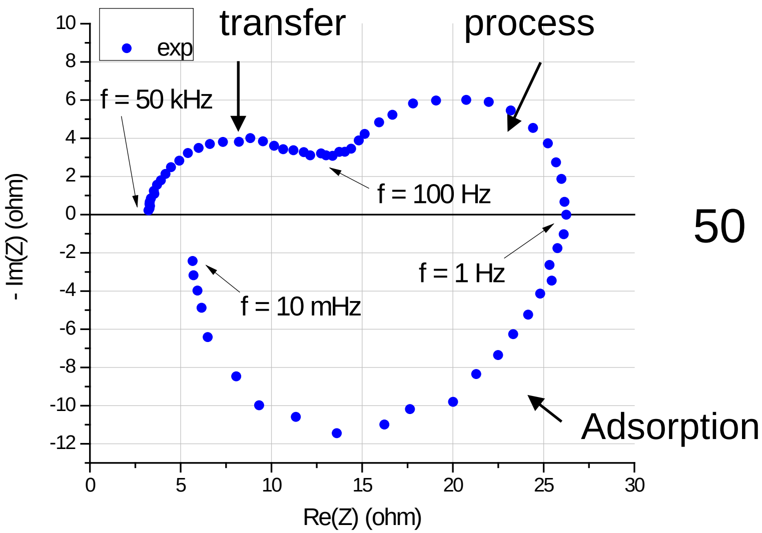
KINETICS OF NITRIC REDUCTION ON GOLD

RDE results



EIS results



50 rpm

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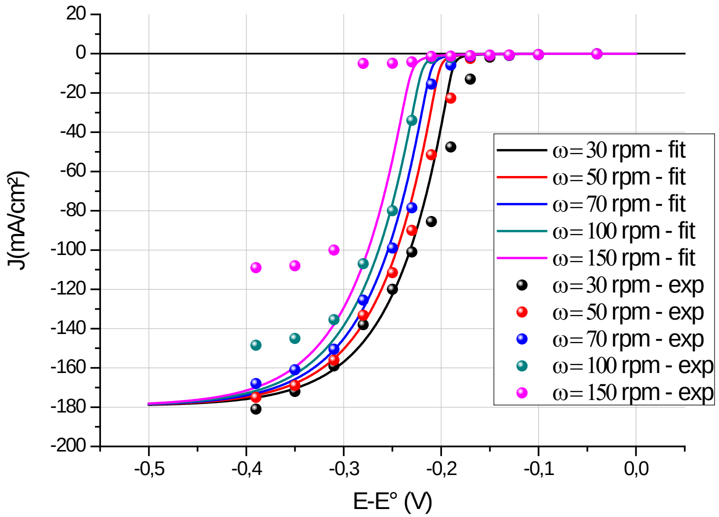
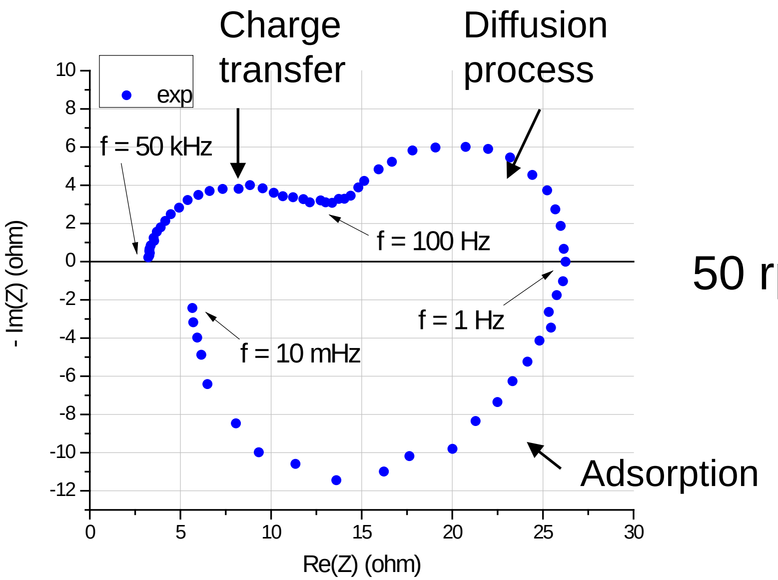
KINETICS OF NITRIC REDUCTION ON GOLD

Modelling of current and EIS





50 rpm

$$i_S = \frac{1}{2k'_2\delta}\left(FS(2C^*Dk'_2 + 2\beta Dk'_3 - \beta k'_2 k'_3) - \sqrt{8F^2S^2\beta C^*Dk'^2_2 k'_3\delta + \left(FS(\beta k'_2 k'_3\delta - 2C^*Dk'_3 - 2\beta Dk'_2)\right)^2}\right)$$

Good fit for low speed

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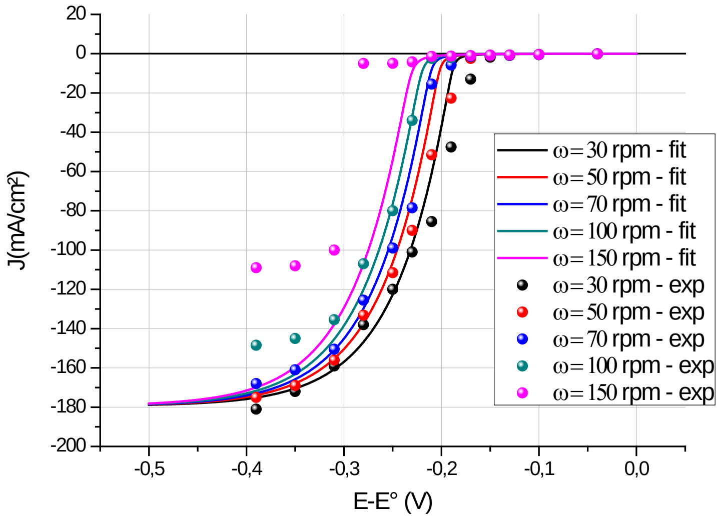

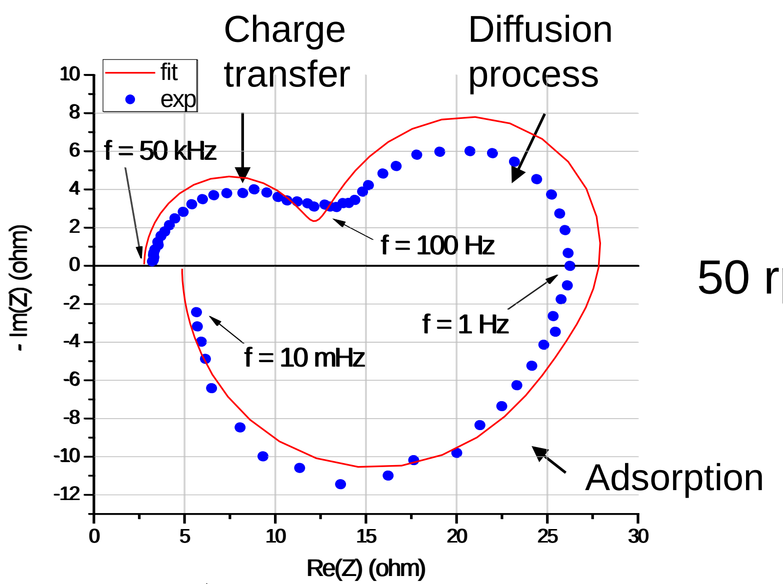

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$$\frac{1}{Z_f} = -FS\left(k'_2.C^0_S.b_2(1-\theta_S) - k'_2.C^0_S.\frac{\Delta\theta}{\Delta E} + k'_2(1-\theta_S)\frac{\Delta C^0}{\Delta E}\right)$$

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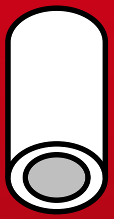
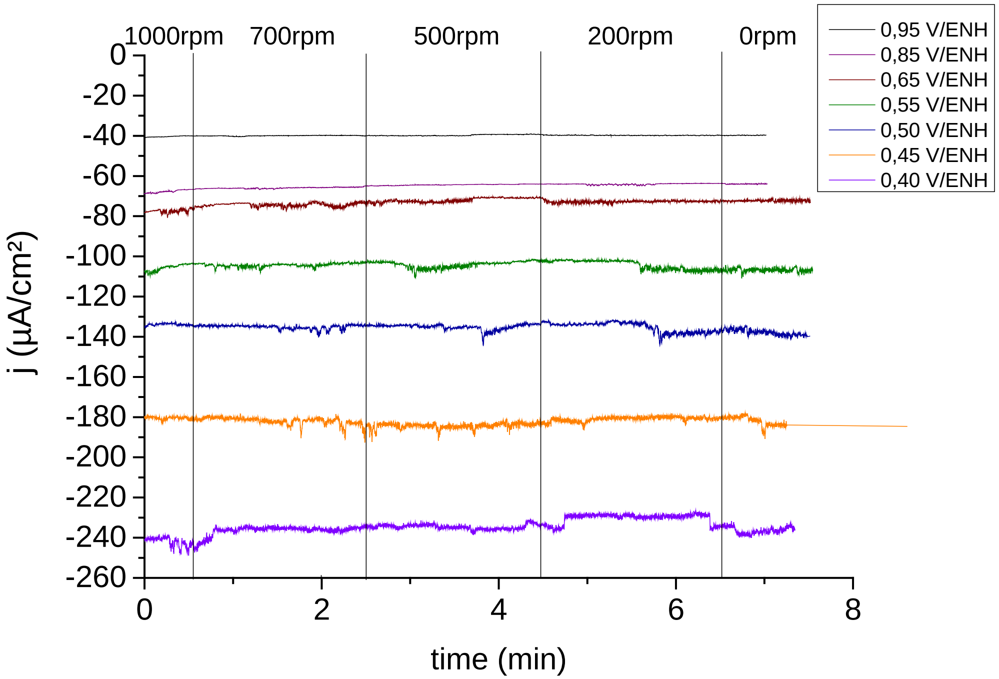
KINETICS OF NITRIC ACID REDUCTION ON STAINLESS STEEL



KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L

Which is the limiting step on stainless steel?



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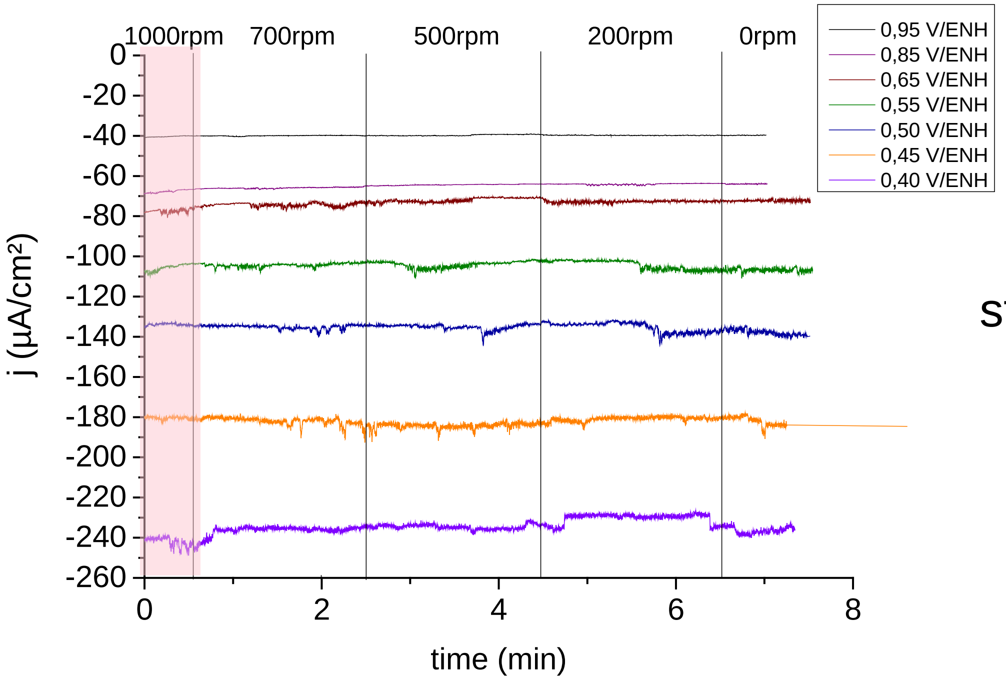

No influence of rotation speed on stainless steel (from 4M 40°C – to 8M 100°C)

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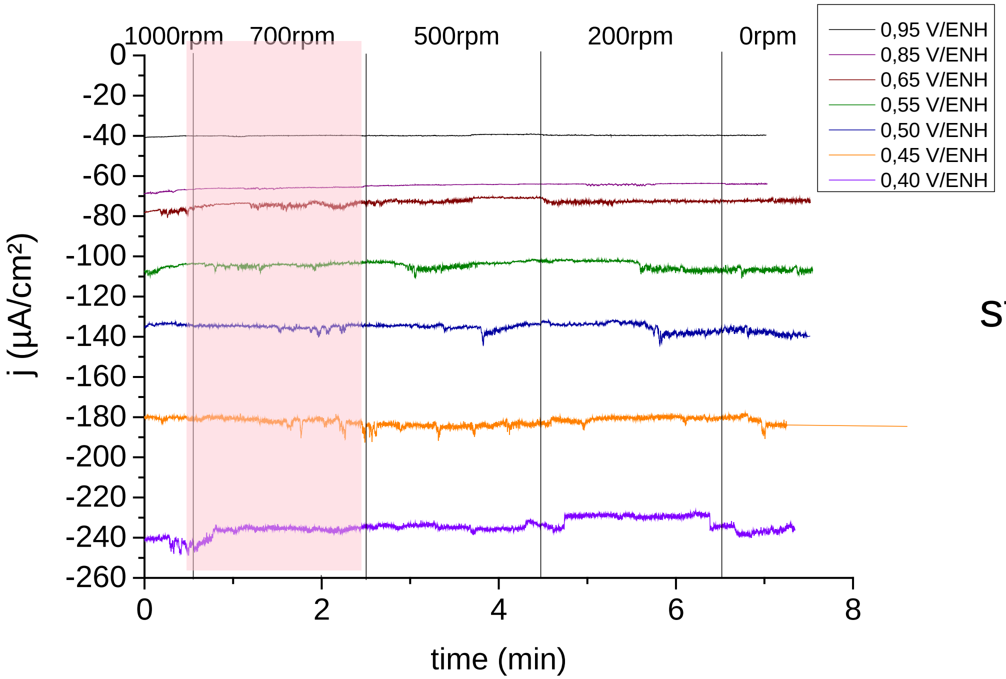

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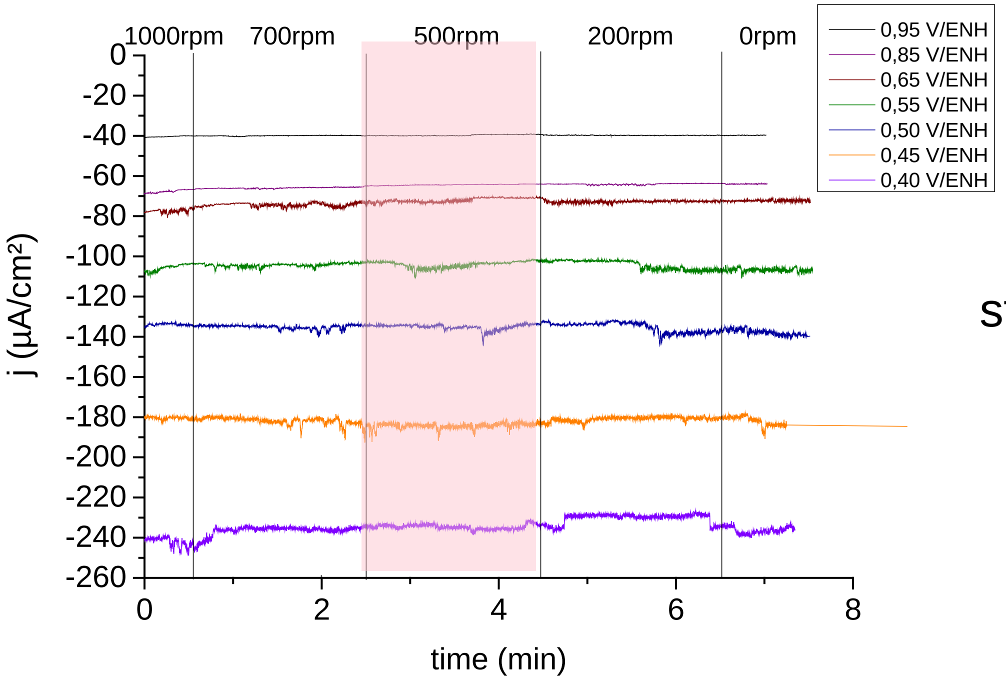

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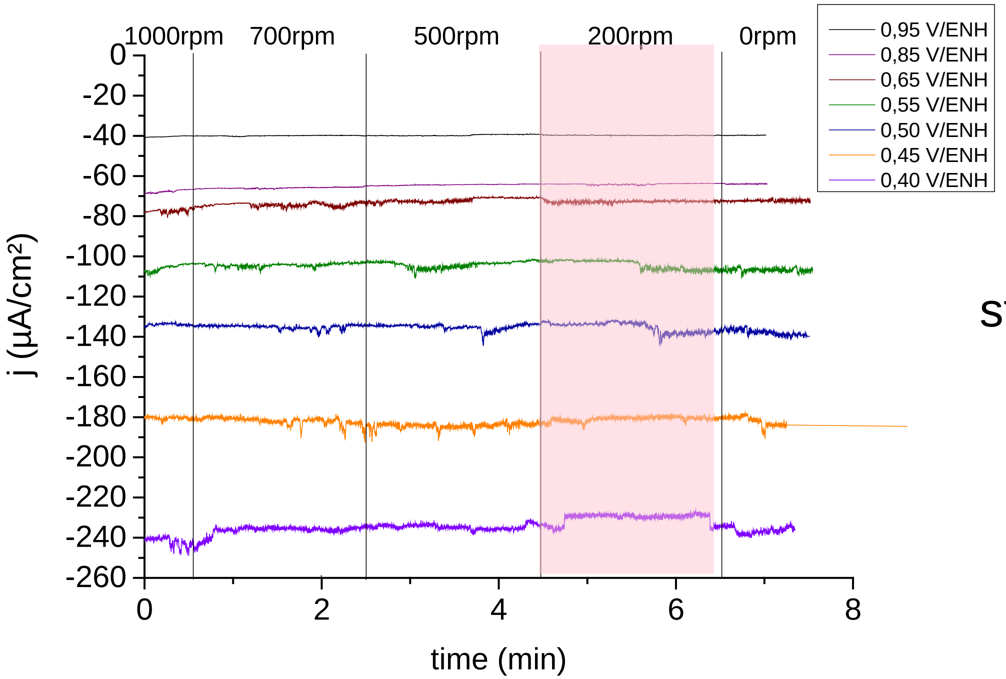

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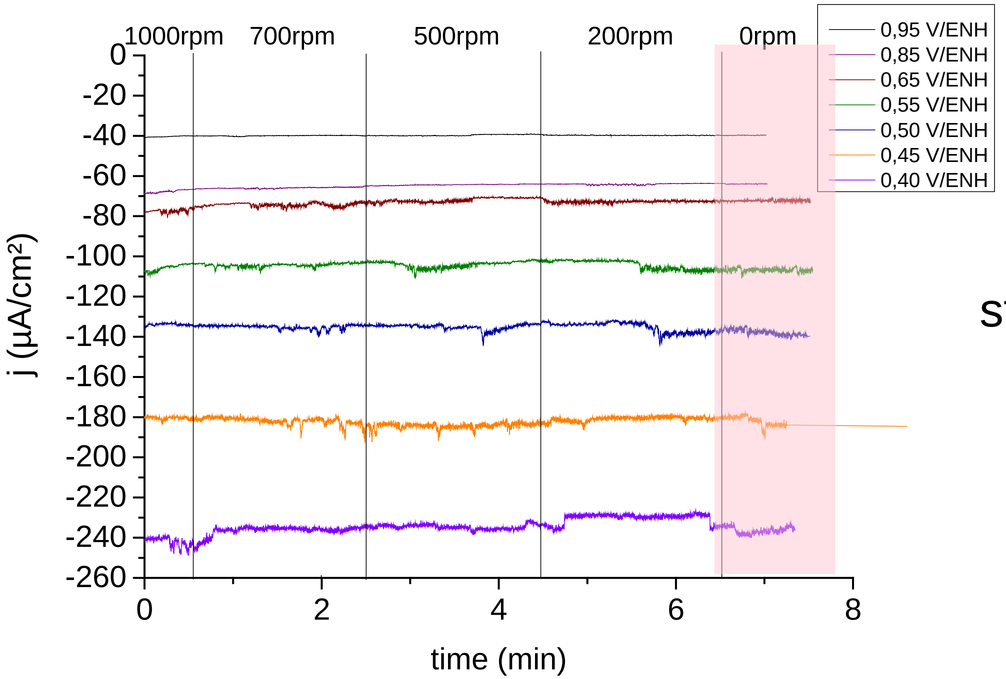

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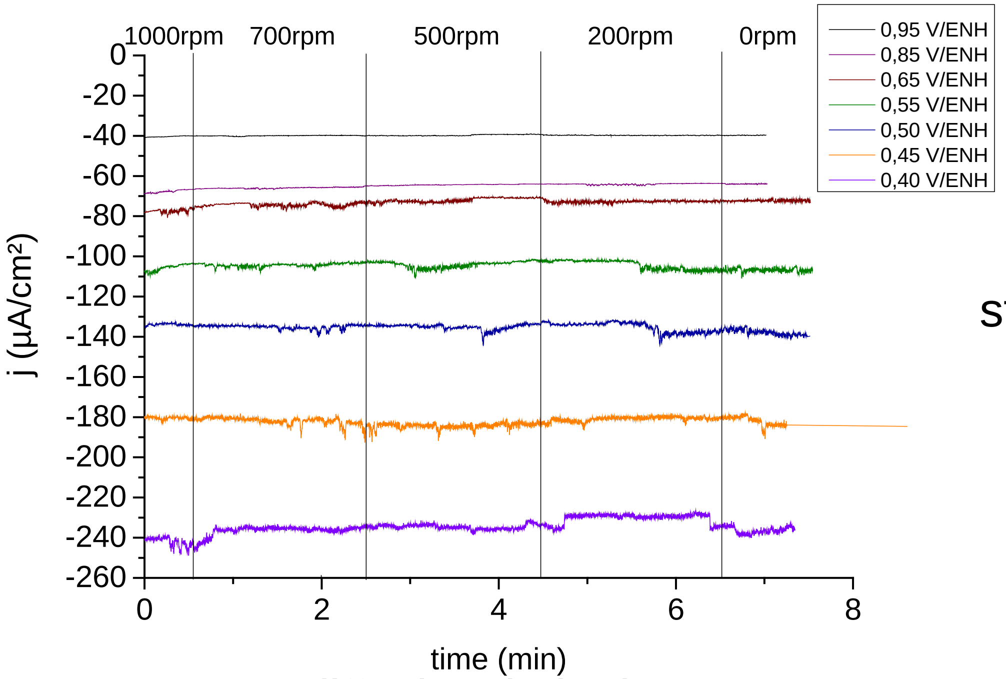

No influence of rotation speed on stainless steel (from 4M 40°C – to 8M 100°C)

→ No diffusion limitation

Charge transfer and adsorption are limited steps on stainless steel

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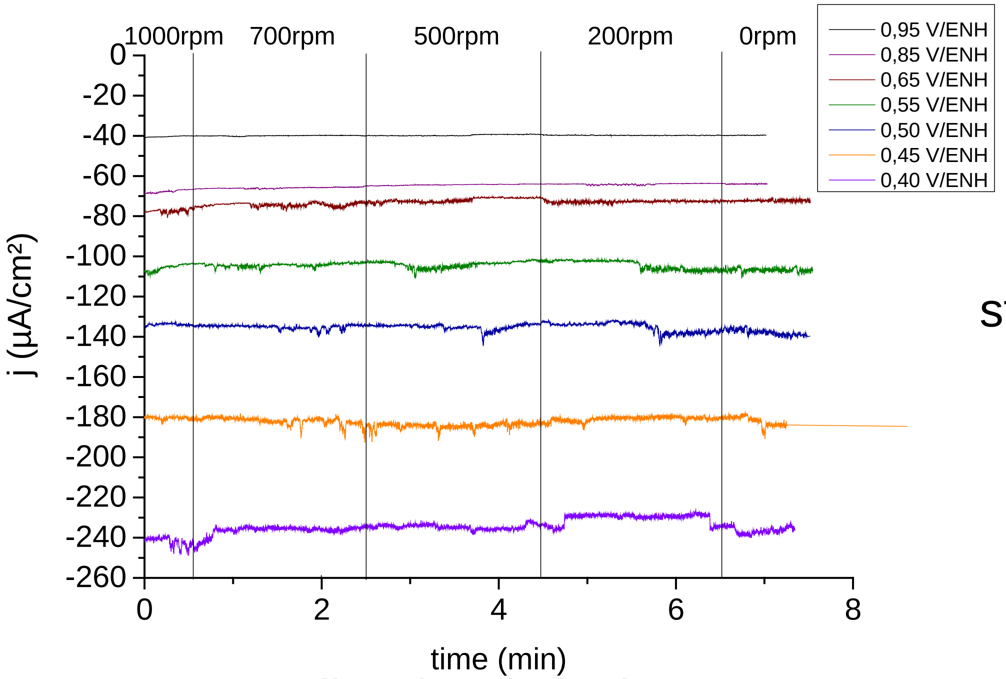

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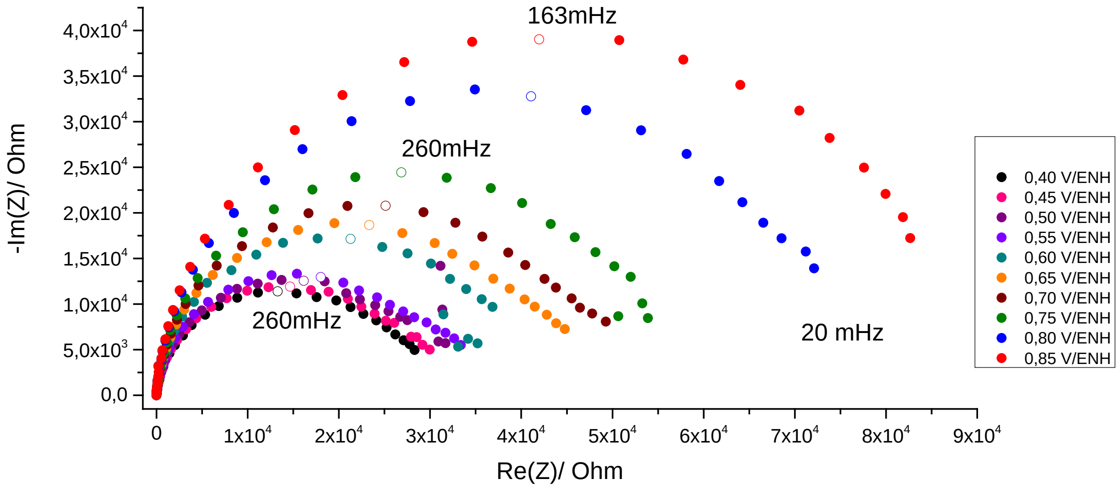
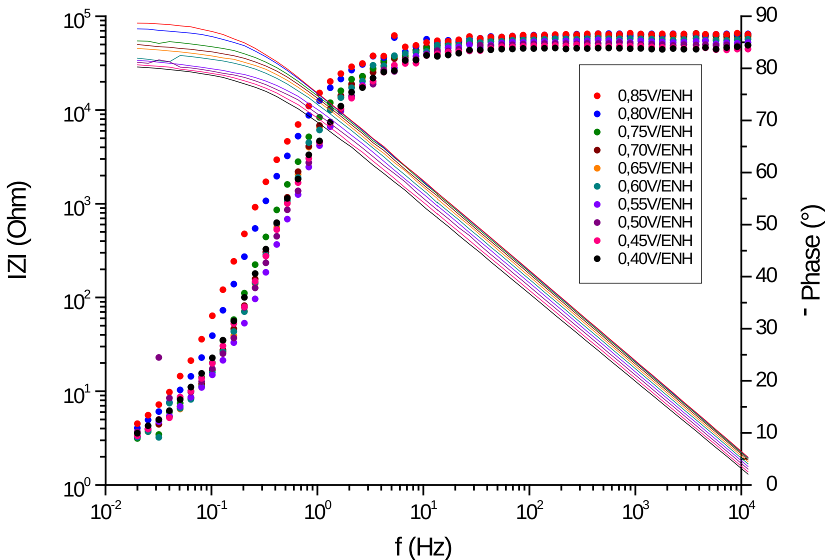
Charge transfer and adsorption are limited steps on stainless steel

Conversely to gold electrode, the autocatalytic processes play a minor role on stainless steel

KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L: EIS

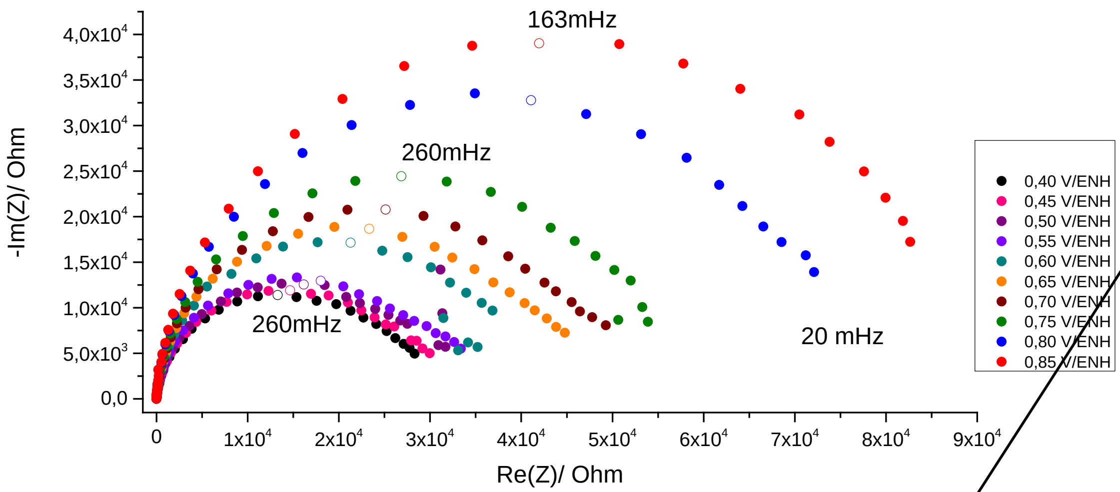
Experimental results at 4M 40°C on passivated stainless steel 0.5 cm²

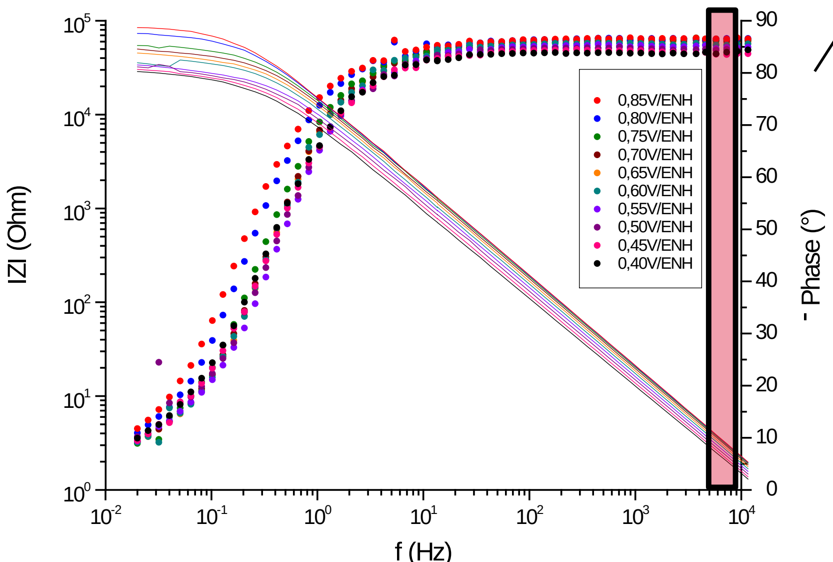




KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L: EIS

Experimental results at 4M 40°C on passivated stainless steel 0.5 cm²

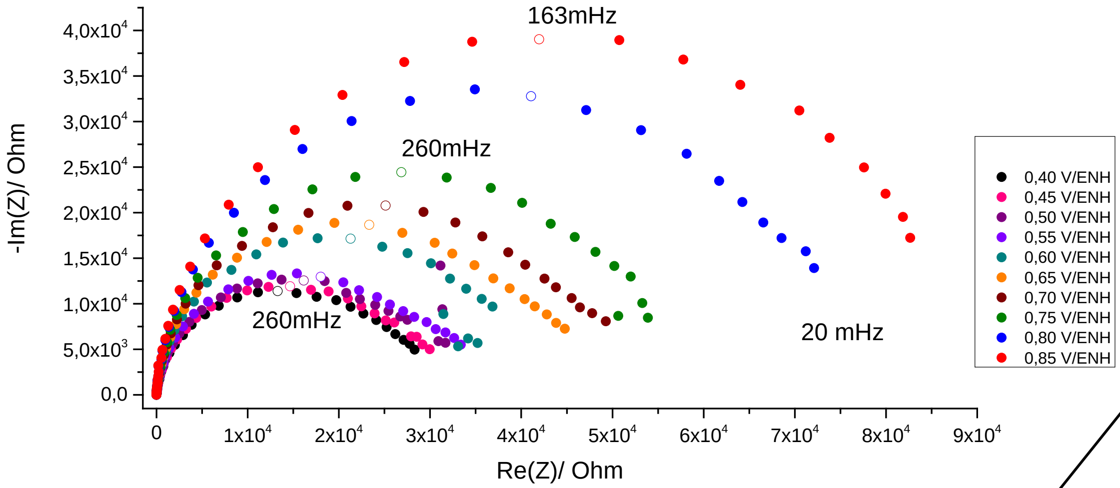


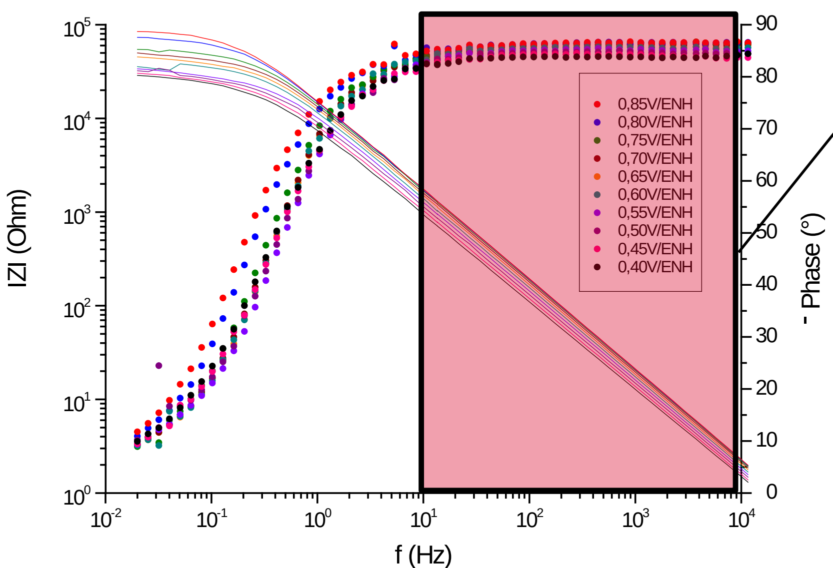


HF domain:
Oxide layer thickness

KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L: EIS

Experimental results at 4M 40°C on passivated stainless steel 0.5 cm²



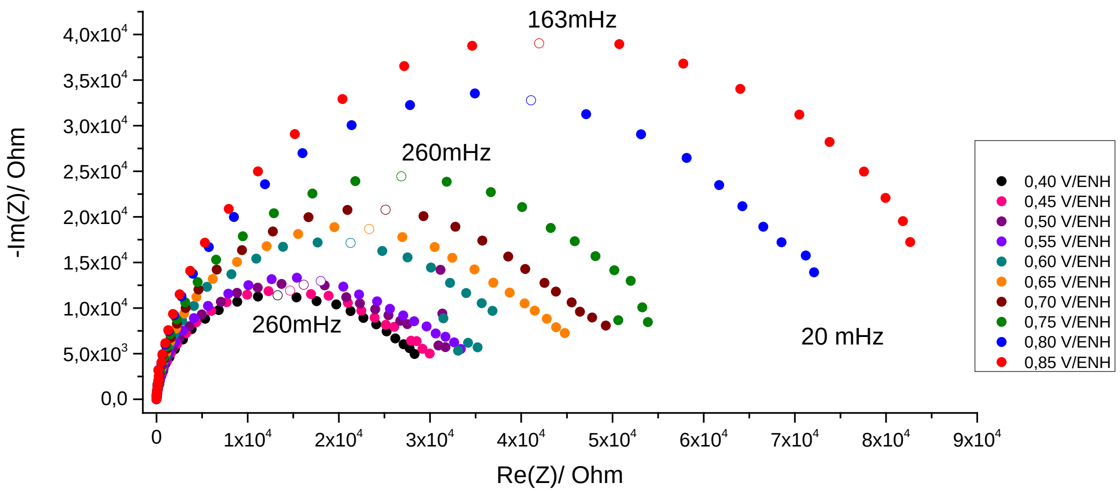


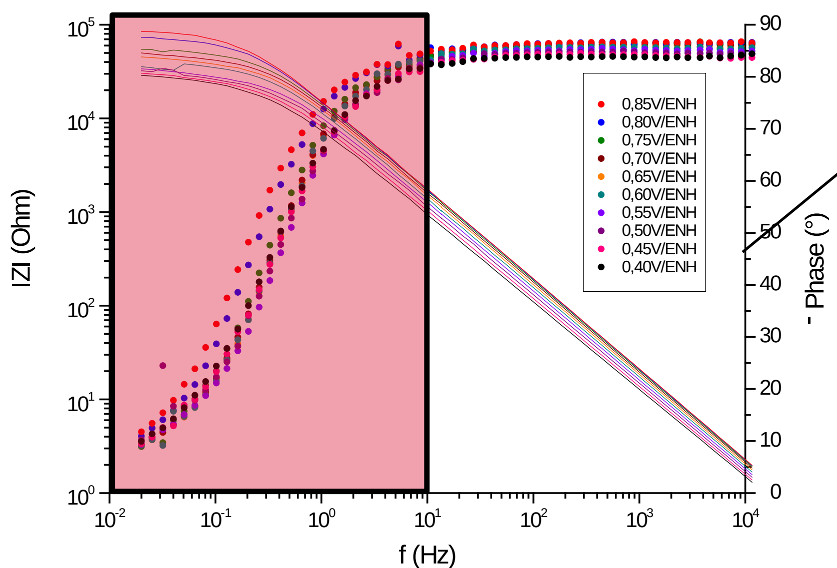
HF domain:
Oxide layer thickness

Constant Phase Element:
Dielectric properties of the oxide layer

KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L: EIS

Experimental results at 4M 40°C on passivated stainless steel 0.5 cm²





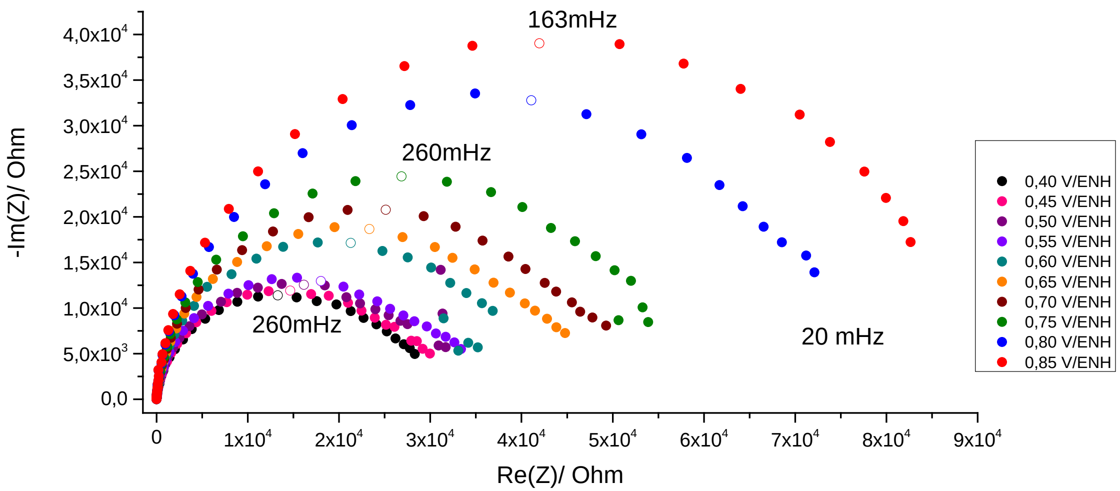
HF domain:
Oxide layer thickness

Constant Phase Element:
Dielectric properties of the oxide layer

Faradaic processes

KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L: EIS

Experimental results at 4M 40°C on passivated stainless steel 0.5 cm²



HF domain:
Oxide layer thickness

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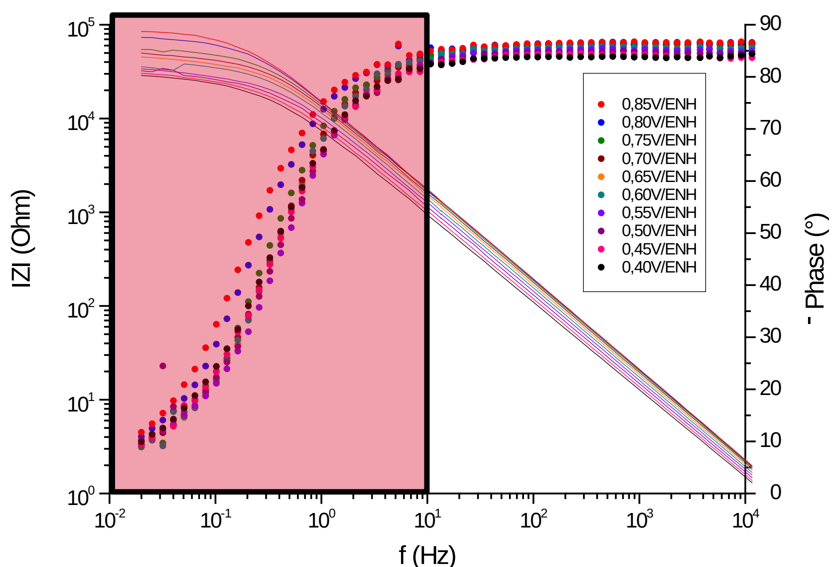
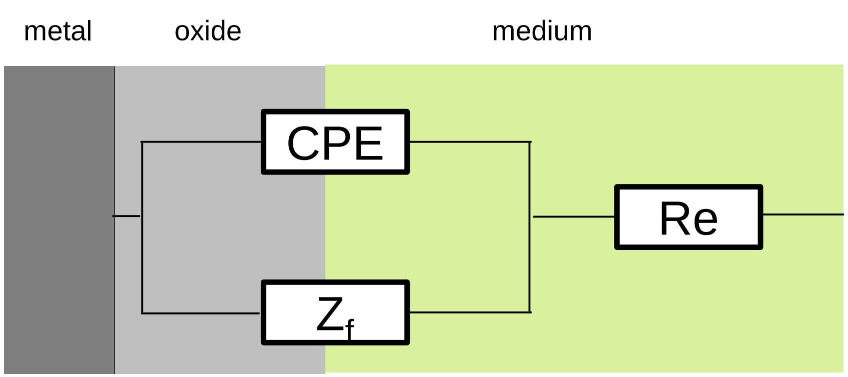
Faradaic processes

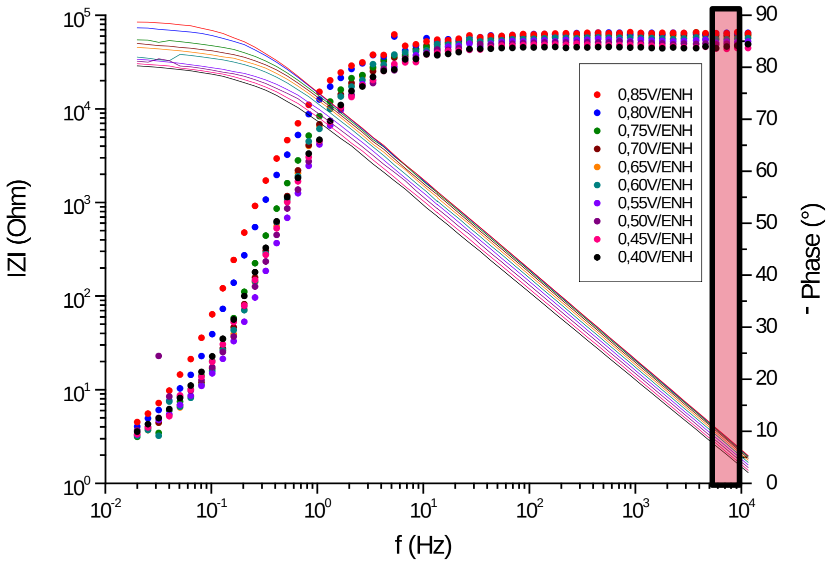


Equivalent circuit used:

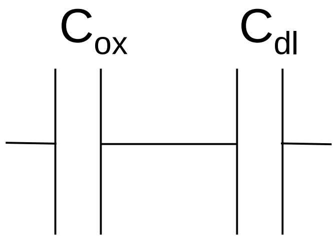


KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L: HF DOMAIN

Bode representation:

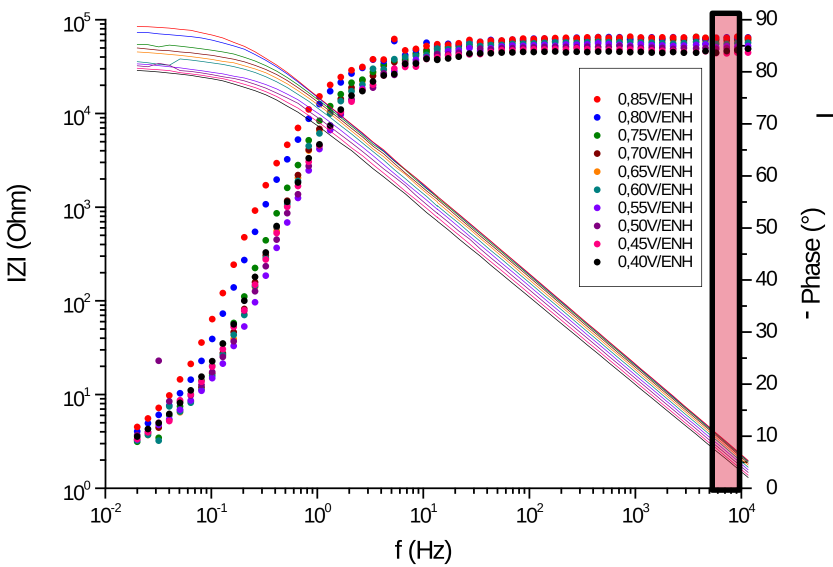


At infinite frequencies:

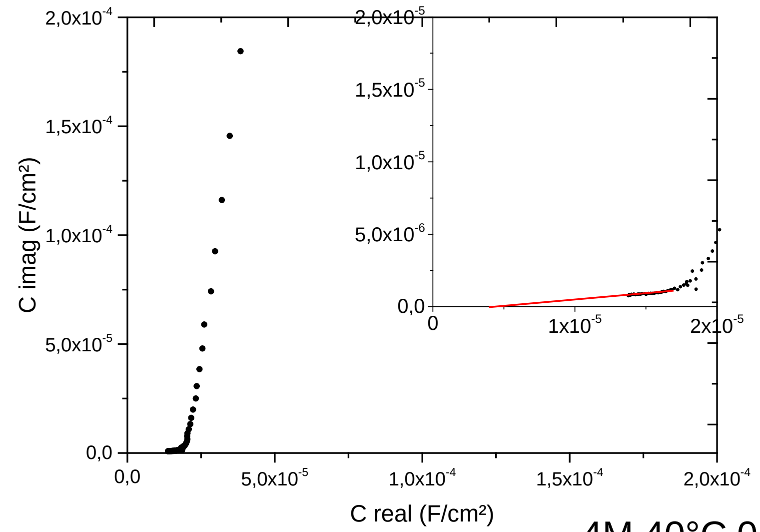


KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L: HF DOMAIN

Bode representation:

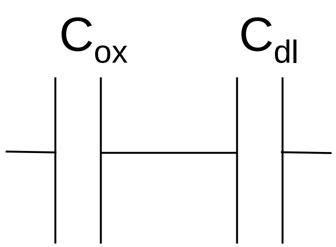


Cole & Cole representation:



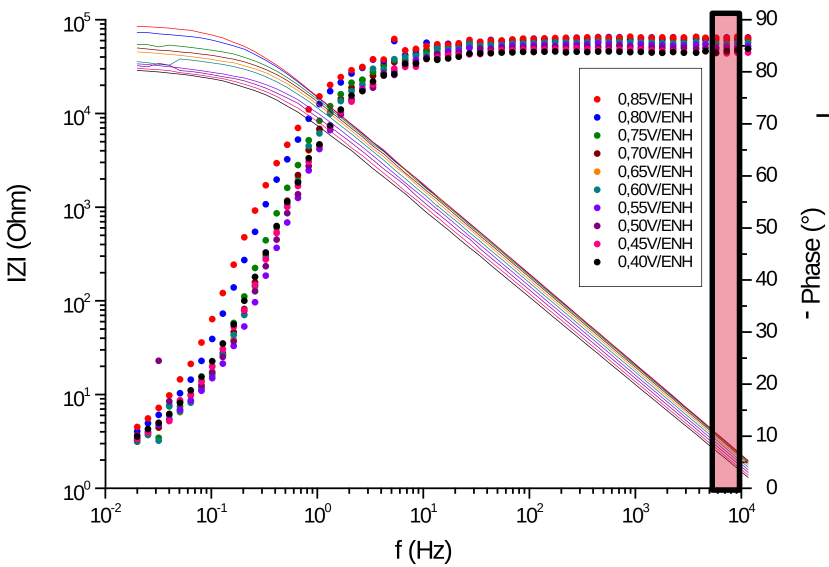
4M 40°C 0.85 V/ENH

At infinite frequencies:



KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L: HF DOMAIN

Bode representation:



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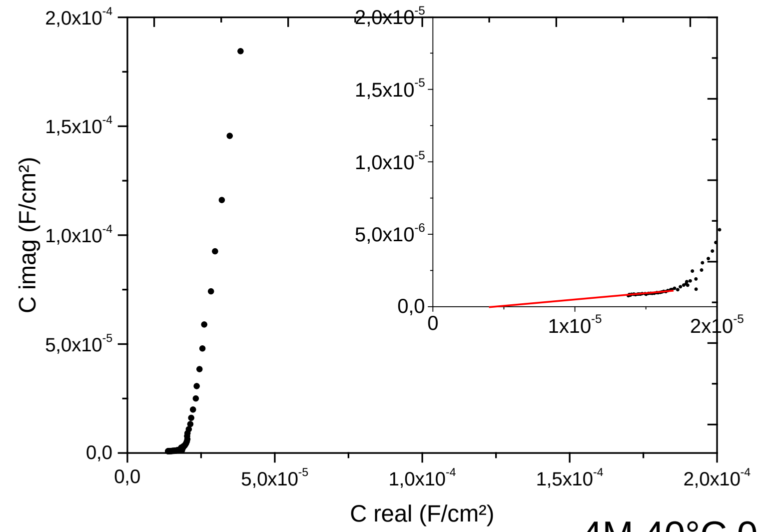
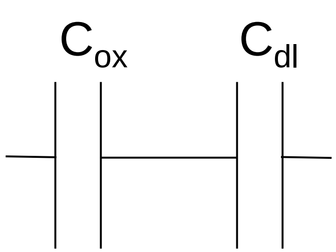


4M 40°C 0.85 V/ENH

At infinite frequencies:

By extrapolation: $C_\infty = 4.1\ 10^{-6}\ F.cm^{-2}$



If we consider this value as the capacitance of the oxide we can calculate its thickness:

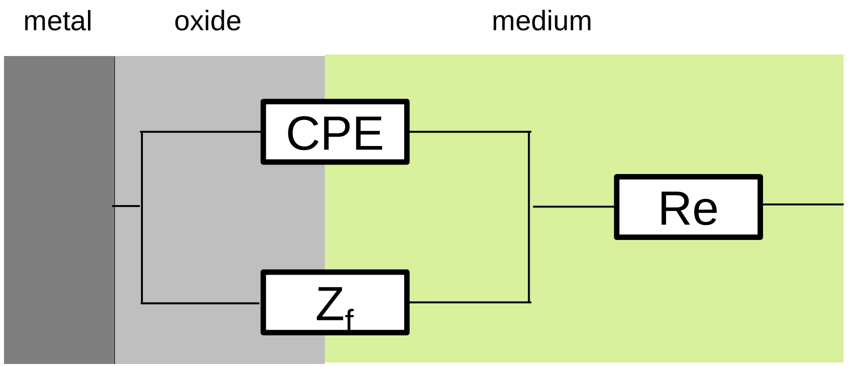
$$d = \frac{\varepsilon\varepsilon_0}{C_\infty} = 2.6\ \text{nm}$$

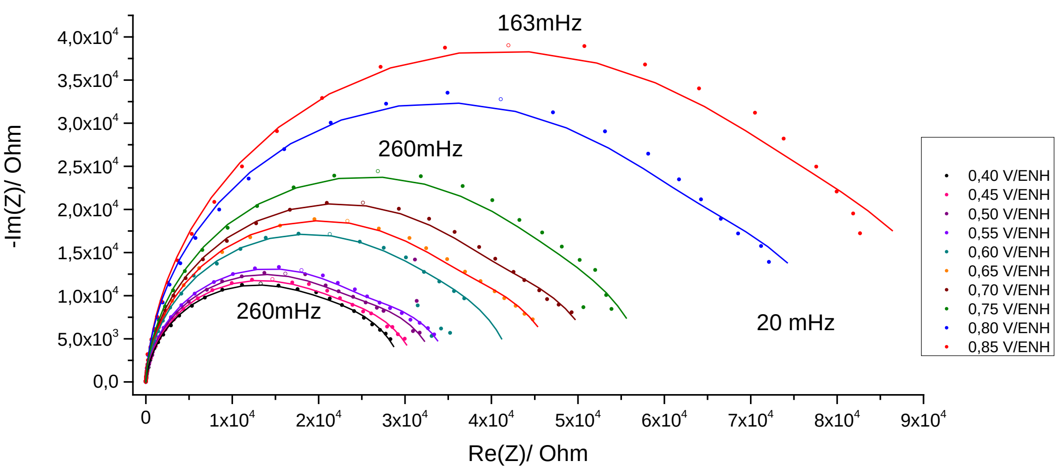
By XPS: d = 3 nm

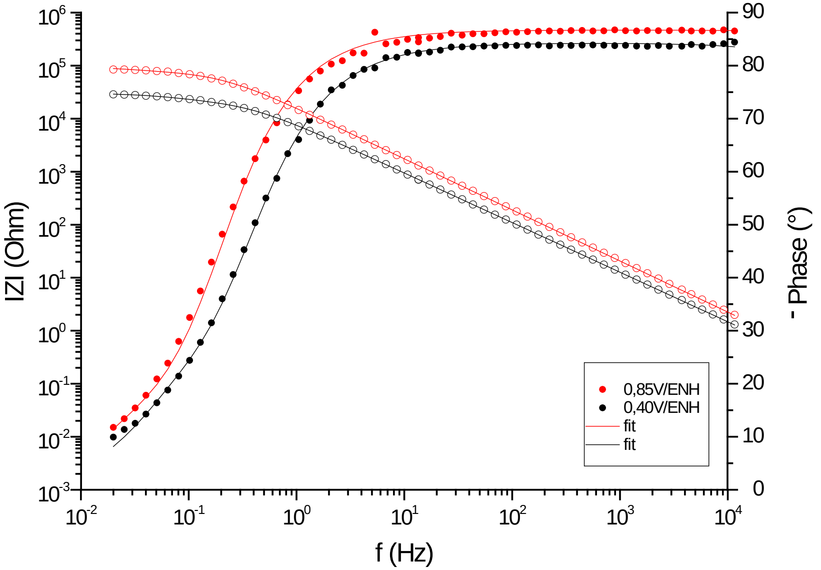
Assuming C_{dl} 30 µF.cm⁻², d = 2.2 nm

[M.Benoit et al., Electrochemica Acta, 201, 2016]

KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L: CIRCUIT EQUIVALENT PARAMETERS

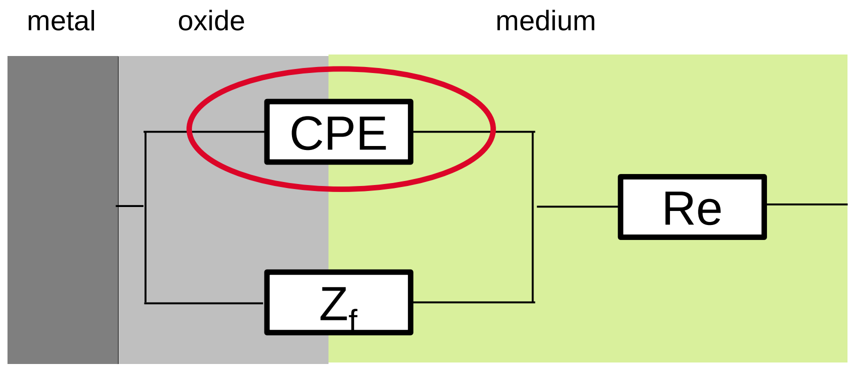


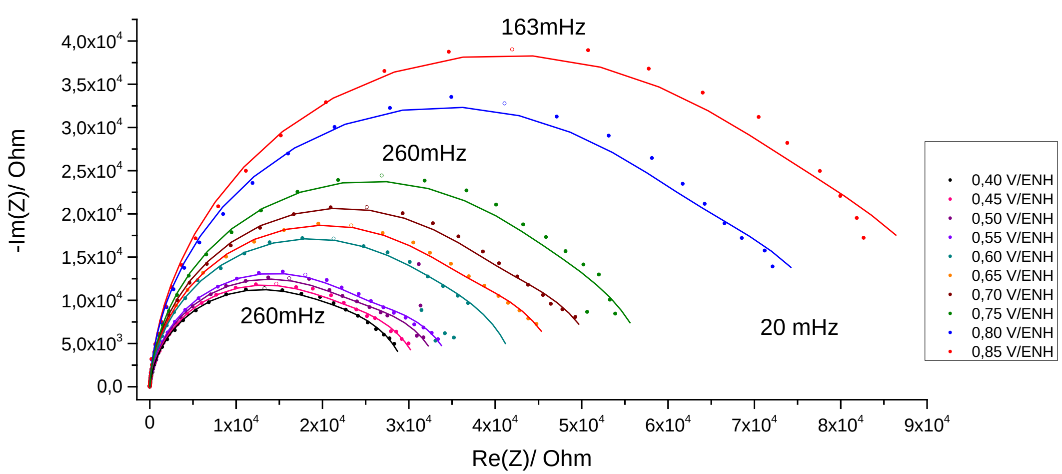


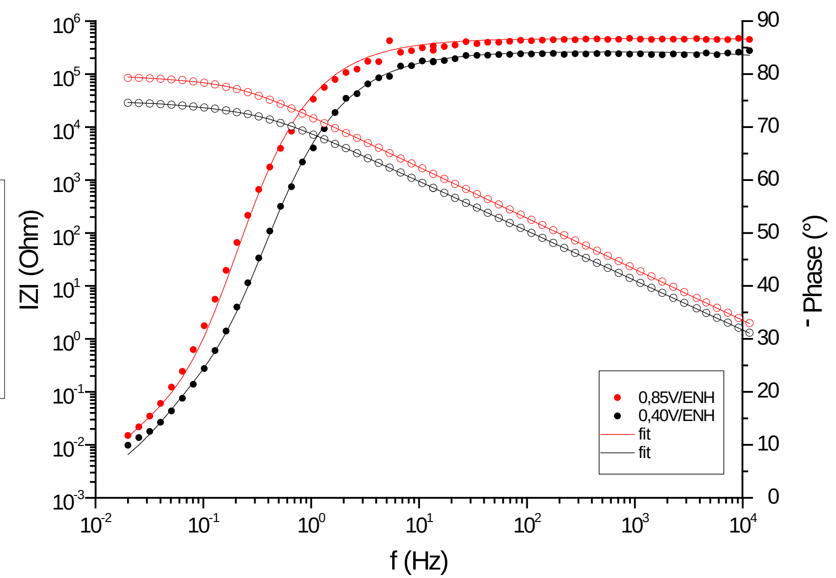


→ Good fit for all potentials

KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L: CIRCUIT EQUIVALENT PARAMETERS





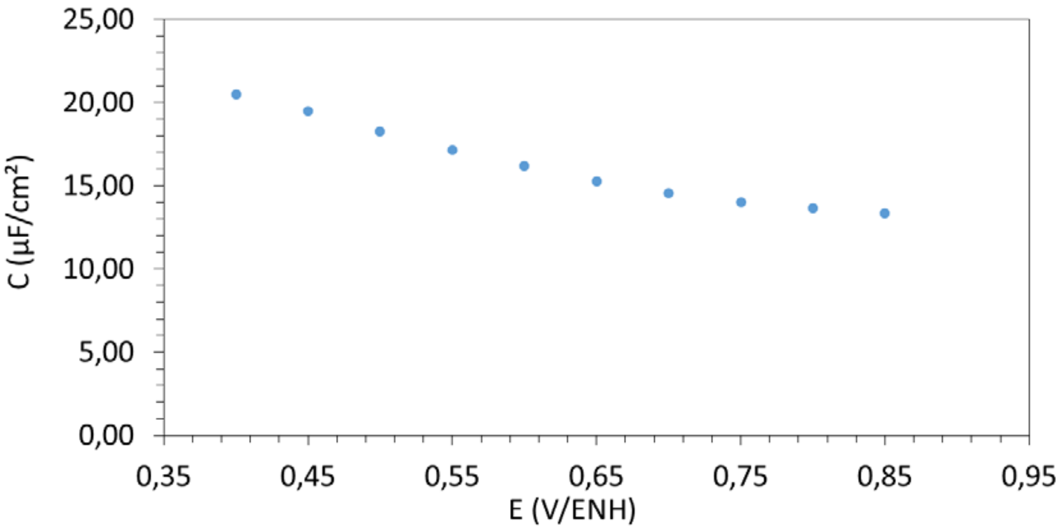


→ Good fit for all potentials

KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L: CPE

For CPE parameters we used Brugg's formula to obtain capacitance values:

$$C_{eff} = Q^{1/\alpha} R_e^{(1-\alpha)/\alpha}$$



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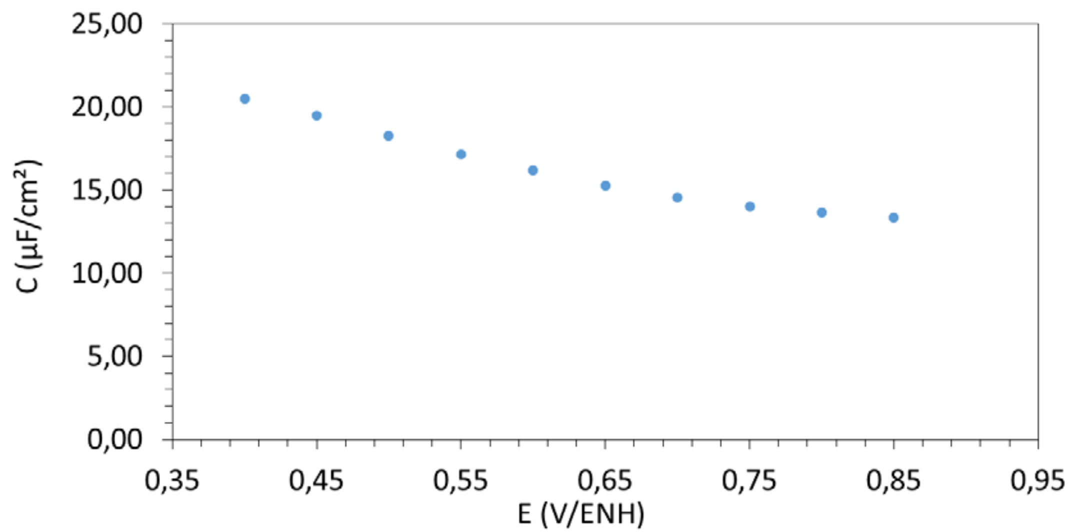
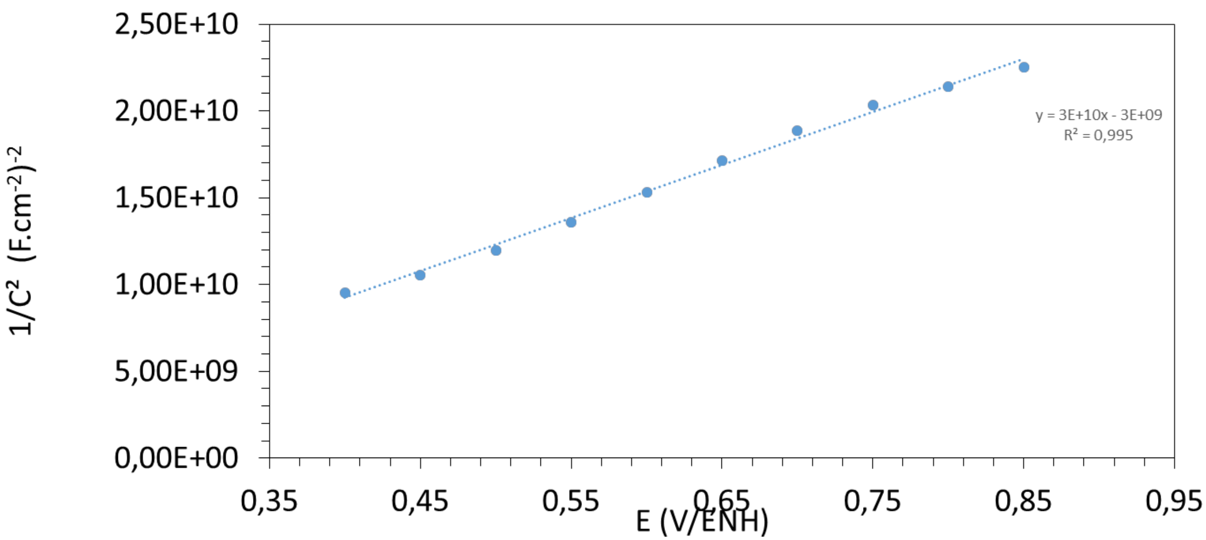


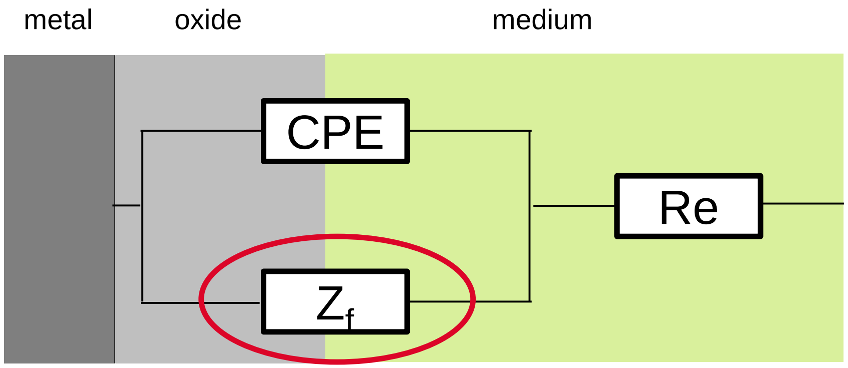
→ Verification of Mott Schottky's law



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

N_0=1,5.10^{21} cm^{-3}

KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L: FARADAIC PROCESSES



$$HNO_{2,sol} \xrightarrow{k_1} HNO_{2,ads} \qquad k'_1 = k_1[HNO_2]$$

$$HNO_{2,ads} + e^- + H^+ \xrightarrow{k°_2} NO_{ads} + H_2O \qquad k'_2 = k^{\circ}_2 a_H e^{(b_2(E-E°))}$$

$$NO_{ads} + \frac{1}{2}H^+ + \frac{1}{2}NO_3^- + \frac{1}{2}H_2O \xrightarrow{k_3} \frac{3}{2}HNO_2 \qquad k'_3 = k_3\sqrt{a_N a_e a_H}$$

Stationary solutions:

$$\theta_{1S} = \frac{k'_1}{k'_1 + \dfrac{k'_2.k'_1}{k'_3} + k'_2.\beta} \qquad \theta_{2S} = \frac{k'_2}{k'_3}\theta_{1S}$$

Non stationary solutions:

$$\frac{\Delta\theta_1}{\Delta E} = \frac{-k'_2.b_2.\beta.\theta_{1S} - \left(\dfrac{k'_1.k'_2.b_2.\theta_{1S}}{j\omega + k'_3}\right)}{j\omega\beta + k'_1 + k'_2.\beta + \dfrac{k'_2.k'_1}{j\omega + k'_3}} \qquad \frac{\Delta\theta_2}{\Delta E} = \frac{k'_2.b_2.\theta_{1S} + k'_2.\dfrac{\Delta\theta_1}{\Delta E}}{j\omega + k'_3}$$

Impedance:

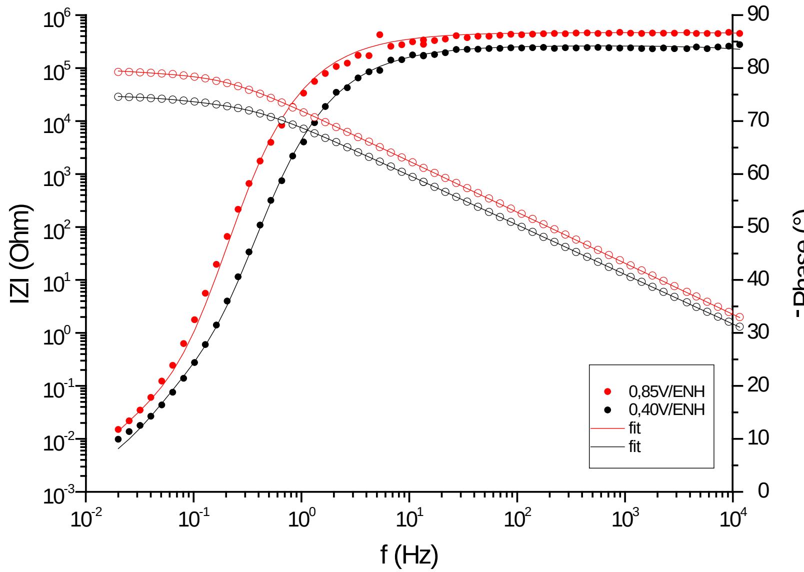
$$\frac{1}{Z_f} = -FS\left(k'_2.\beta.\frac{\Delta\theta_1}{\Delta E} + k'_2.b_2.\beta.\theta_{1S}\right)$$

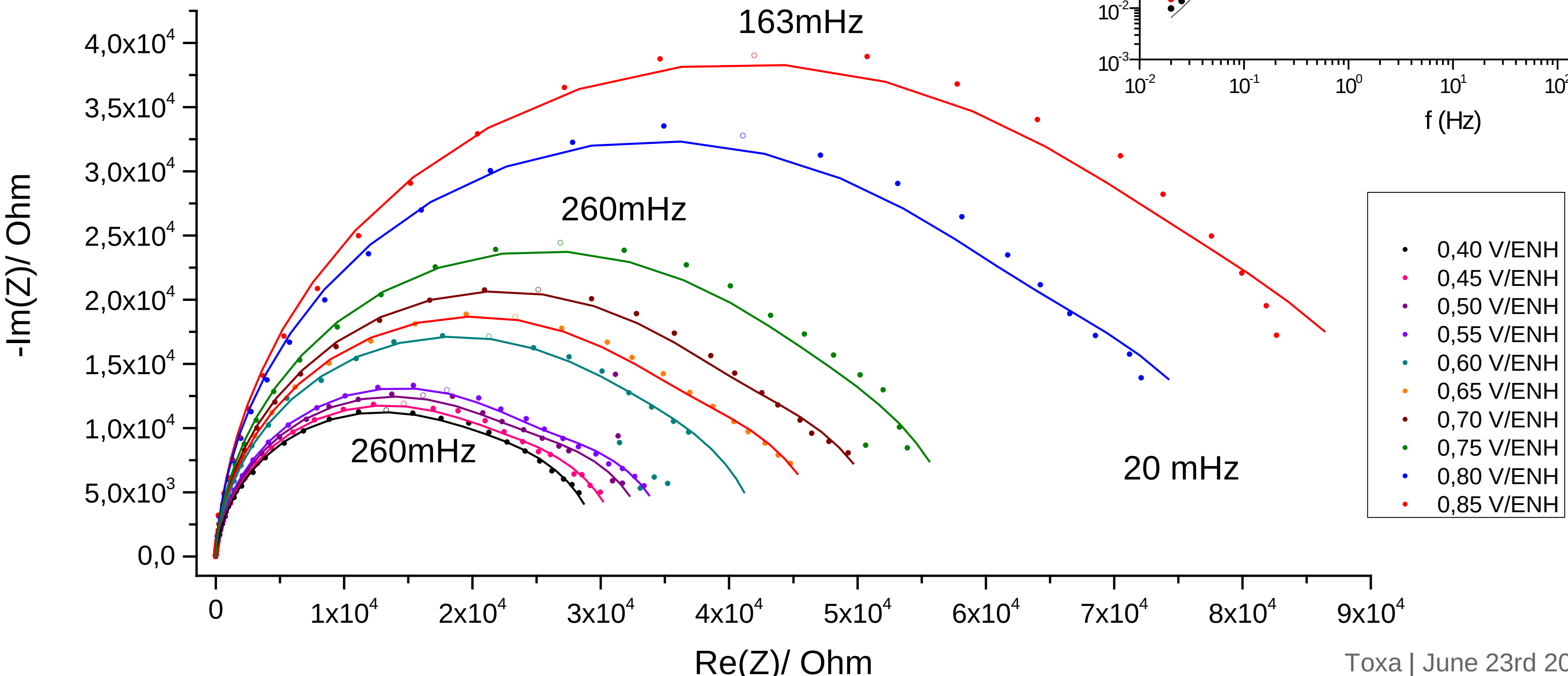
KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L: FARADAIC PROCESSES

→ Fitted kinetic constants:

$k_1 = 0.03 \pm 0.02\ cm.s^{-1}$
$k°_2 = 6.10^{-4} \pm 2\ 10^{-4}\ s^{-1}$
$[k_3 = 2\ 10^{7}\ s^{-1}]$

On Gold [3] : $k_1 = 1.10^{3}\ cm.s^{-1}$
$k°_2 = 1.10^{5}\ s^{-1}$
$k_3 = 1.10^{7}\ s^{-1}$



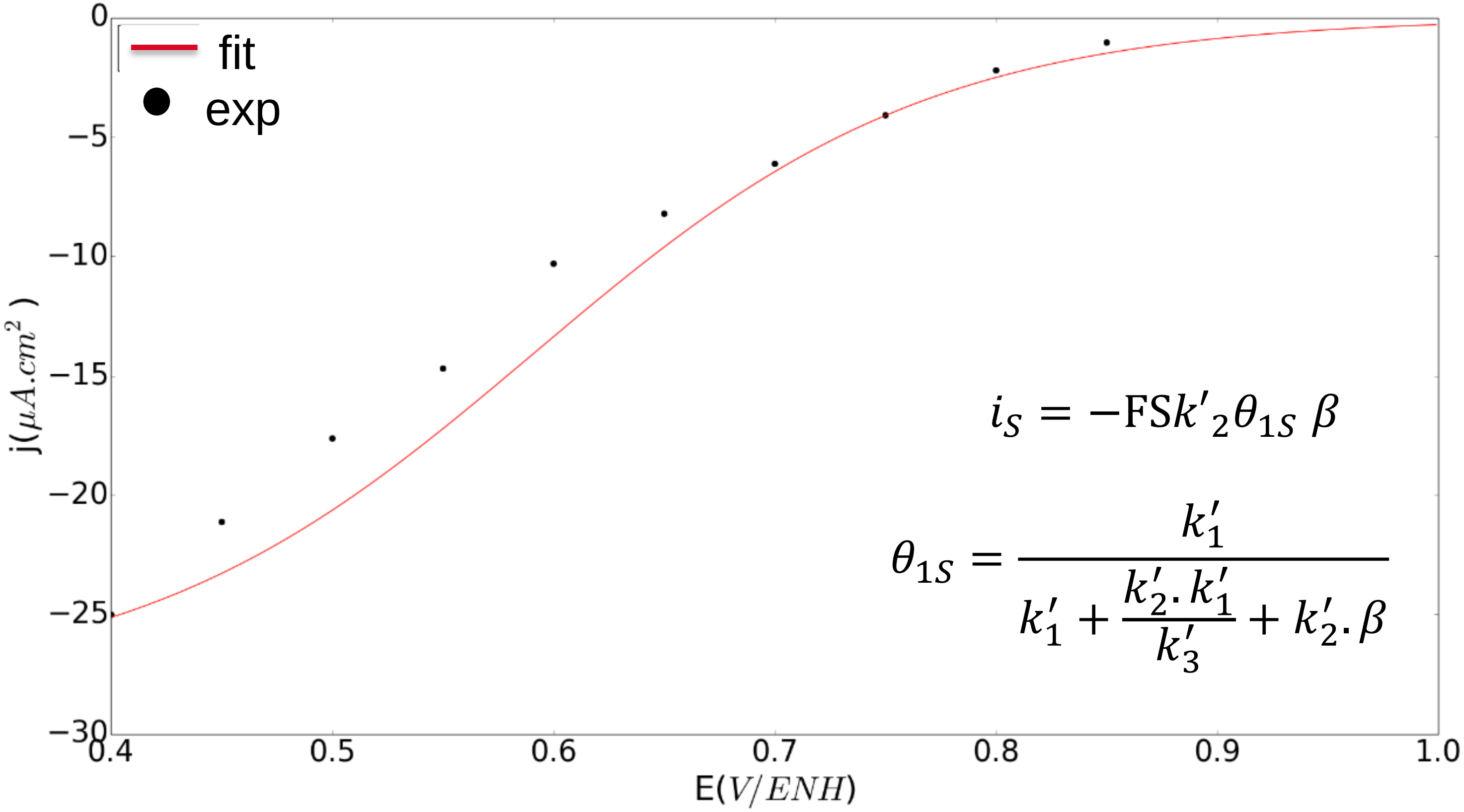


[3] [R. Lange et al., Electrochem. Com. 2013]

KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L

Kinetic constants validated by stationary current (4M 40°C):

Constants used:
k_1= 0,03 cm.s^{-1}
$k°_2$= 6.10^{-4} s^{-1}
k_3= 2.10^6 s^{-1}



$$i_S = -\mathrm{FS}k'_2\theta_{1S}\ \beta$$

$$\theta_{1S} = \frac{k'_1}{k'_1 + \frac{k'_2.k'_1}{k'_3} + k'_2.\beta}$$

DE LA RECHERCHE À L'INDUSTRIE

CONCLUSIONS & OUTLOOK

- On stainless steel:
  - Same mechanism as on gold
  - Conversely to gold electrode, the autocatalytic processes play a minor role
  - Oxide layer slows down kinetics reduction
  - Oxide layer properties can be obtained by EIS (thickness & dielectrics properties)
  - Kinetic constants have been determined and verified by modelling of stationary current
- To go further: fitting in progress for other experimental conditions

Thank you for your attention

Acknowledgments

AREVA

J. Agullo, C. Bataillon, M. Bigot, N. Brijou-Mokrani, N. Cavaliere, C-A, Deblonde, P. Fauvet, O. Geneve, N. Gruet, S. Heurtault, P. Laghoutaris, B. Laurent, F. Miserque, B. Puga Nieto, M. Rivollier, R. Robin, C.M. Sanchez-Sanchez, P. Suegama, B. Tribollet.

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KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L : 8M 100°C

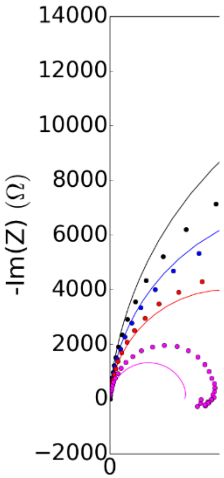
$$HNO_{2,sol} \xrightarrow{k_1} HNO_{2,ads}$$

$$HNO_{2,sol} + e^- + H^+ \xrightarrow{k°_2} NO_{ads} + H_2O$$

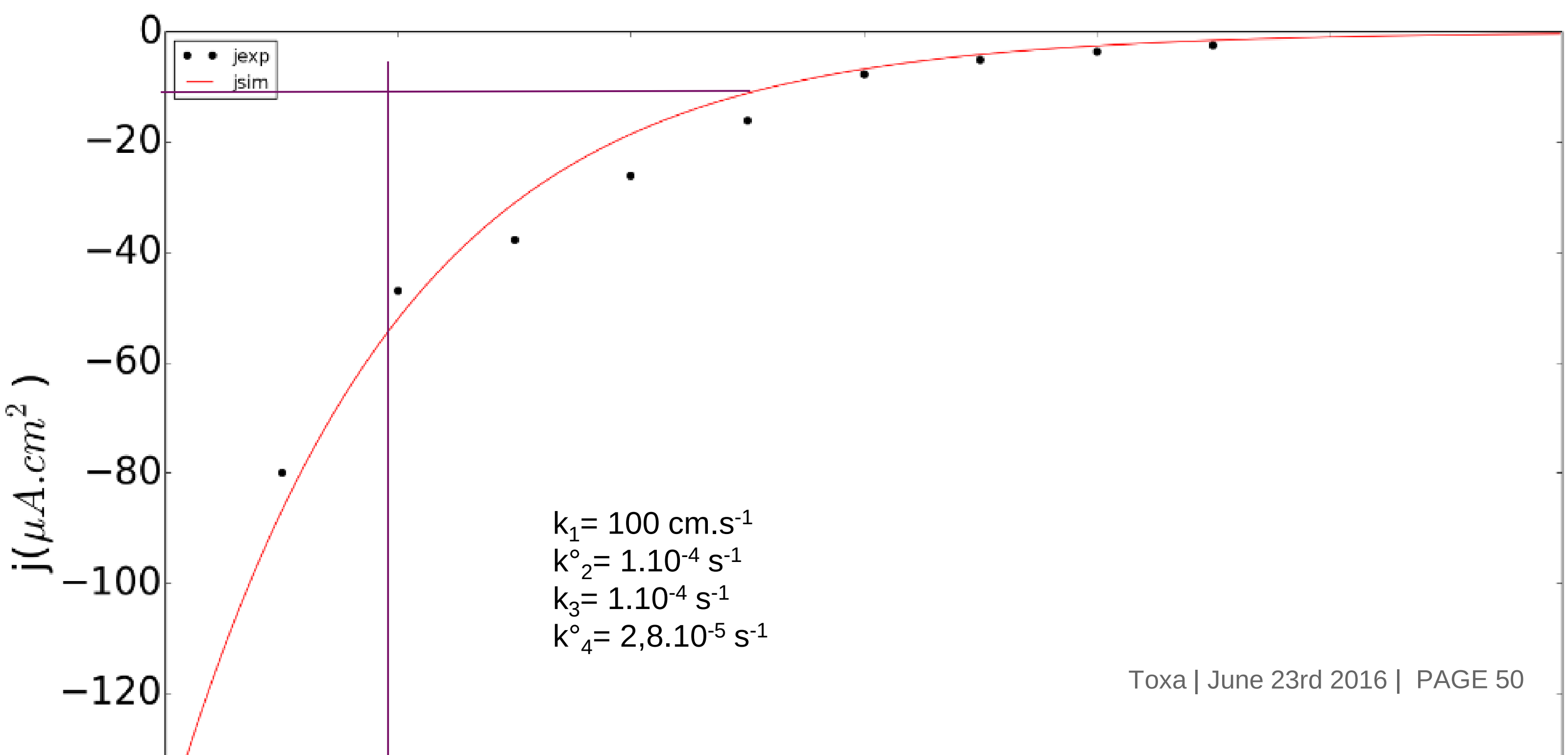
$$NO_{ads} + \frac{1}{2}H^+ + \frac{1}{2}NO_3^- + \frac{1}{2}H_2O \xrightarrow{k_3} \frac{3}{2}HNO_2$$

$$NO_{ads} + e^- \xrightarrow{k°_4} NO^-_{sol}$$

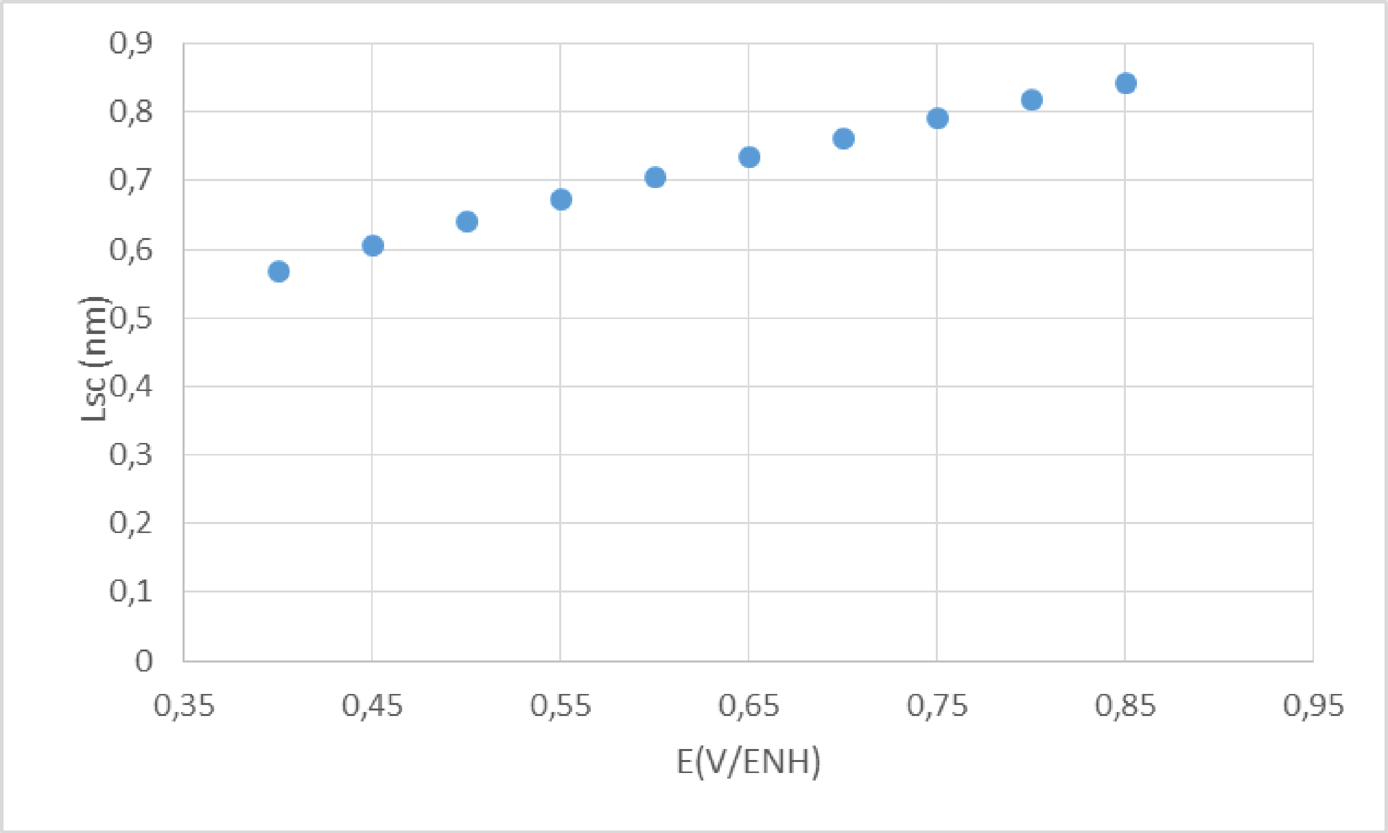
EIS Simulations :

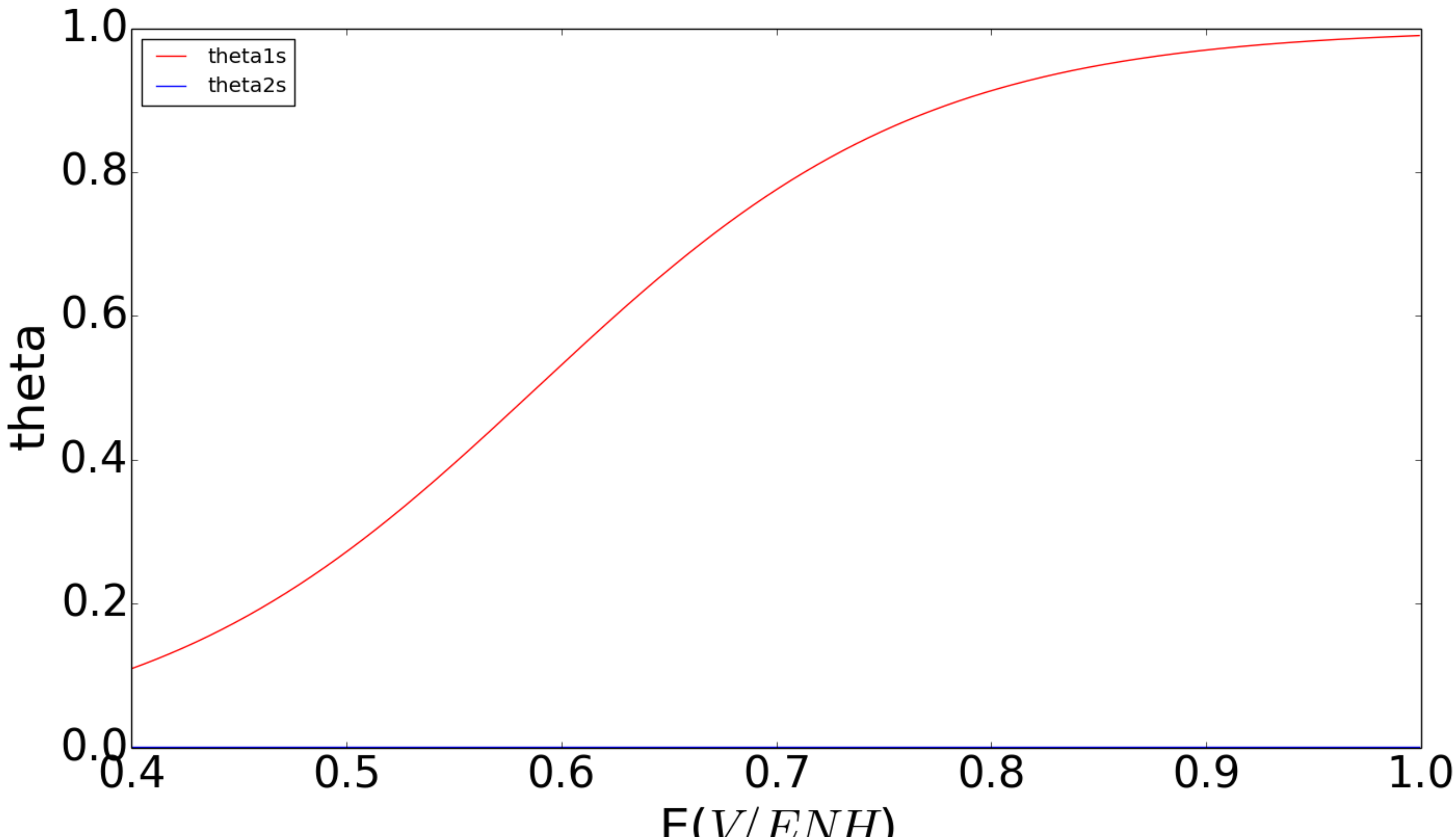


Stationary current simulation :



E_{FB}=0,09 V/ENH


0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Lsc (nm)
0,35
0,45
0,55
0,65
0,75
0,85
0,95
E(V/ENH)


theta1s
theta2s
1.0
0.8
0.6
0.4
0.2
0.0
theta
0.4
0.5
0.6
0.7
0.8
0.9
1.0

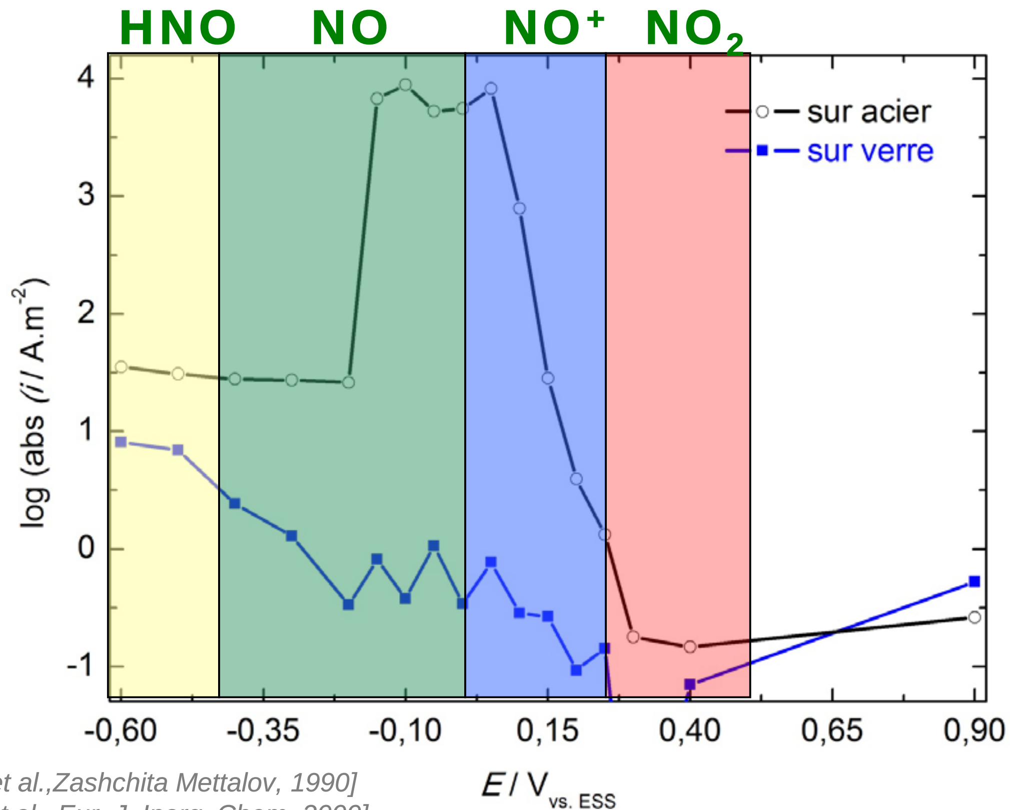
MECHANISMS ON STAINLESS STEEL

V. Razygraev [1] + F. Balbaud [2]:

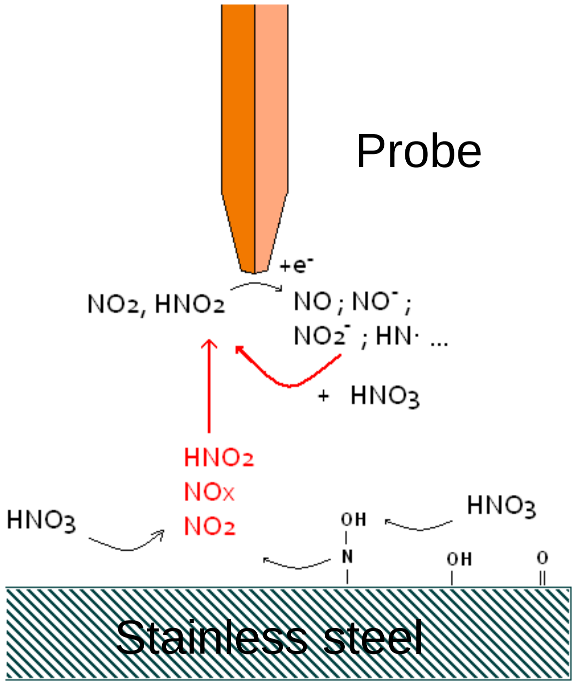
Successive mechanisms (Vetter and Schmid) on gold

Mechanisms in competition on stainless steel

R. Lange [3]: Schmid dominates on stainless steel

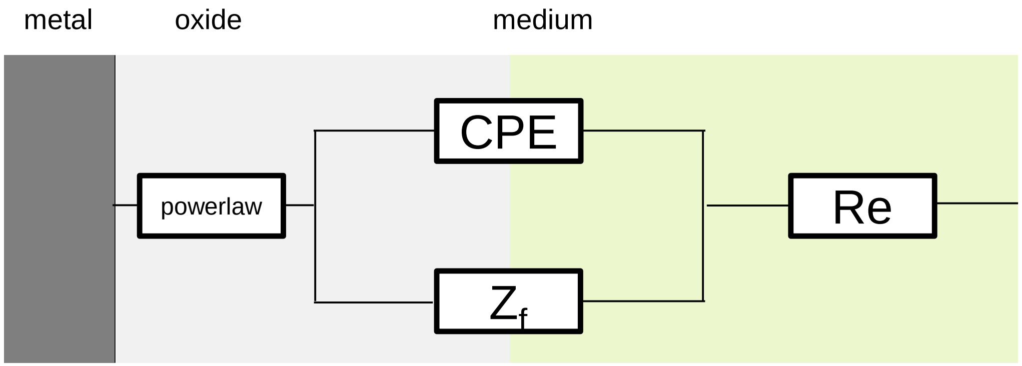


Chronoamperometry
µ-electrode Pt (∅ 25 µm)
I_{stat} after 400 s ;
d_{S-S} = 2 µm, HNO_3 8 mol/L à Tamb.



[1] [Razygraev et al.,Zashchita Mettalov, 1990]
[2] [F. Balbaud et al., Eur. J. Inorg. Chem.,2000]
[3] [R. Lange et al., Electrochem. Com. 2013]

KINETICS OF NITRIC REDUCTION ON STAINLESS STEEL 304L : 8M 100°C



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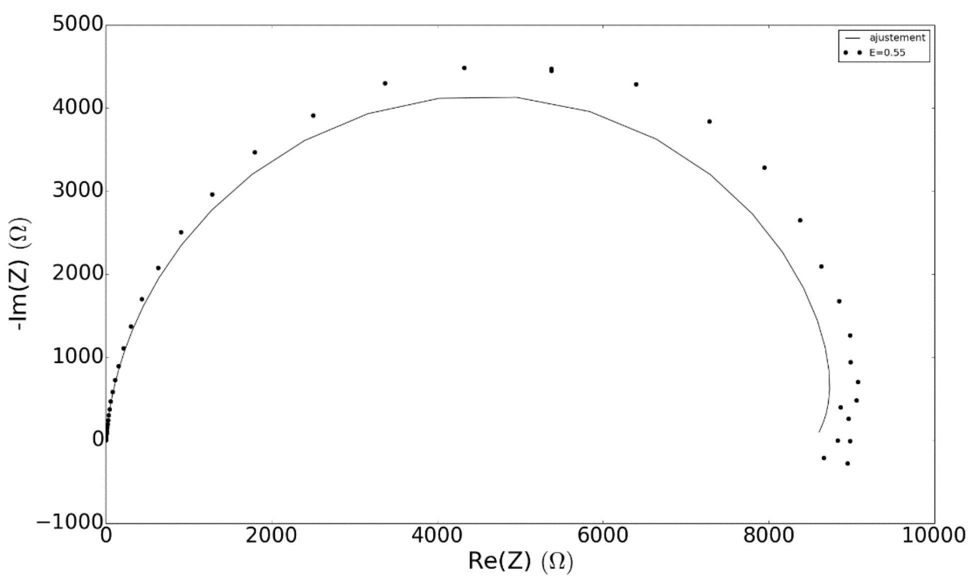
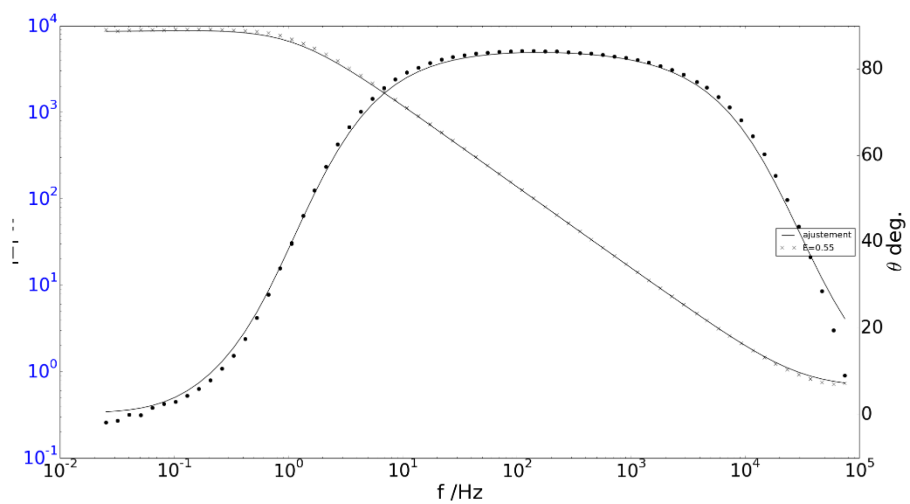
$$NO_{ads} + \frac{1}{2}H^+ + \frac{1}{2}NO_3^- + \frac{1}{2}H_2O \xrightarrow{k_3} \frac{3}{2}HNO_2$$

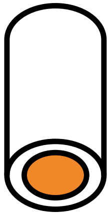
$$NO_{ads} + e^- \xrightarrow{k^\circ_4} NO^-_{sol}$$

Simulation for 0,55 V/ENH (Q_{dl} & α_{dl} fitted for this potential):





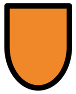
Etude du système HNO_3/HNO_2



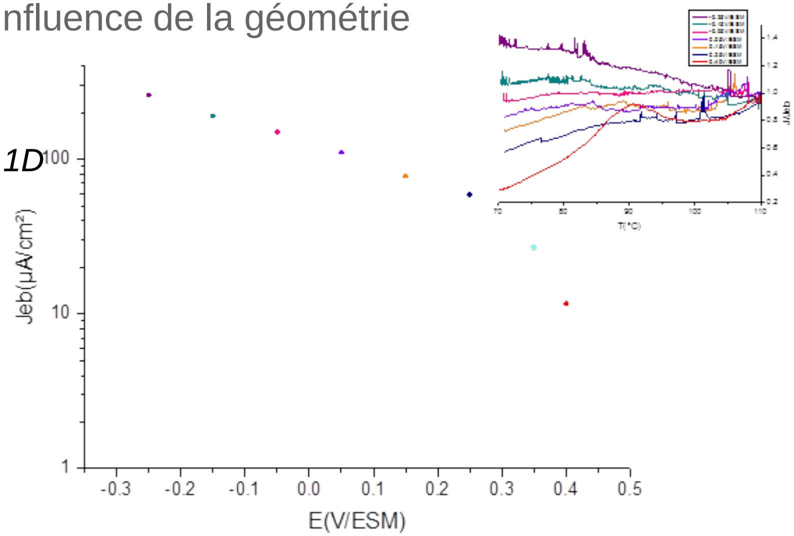
Identification du mécanisme sur Acier *[Razygraev, 2014]*

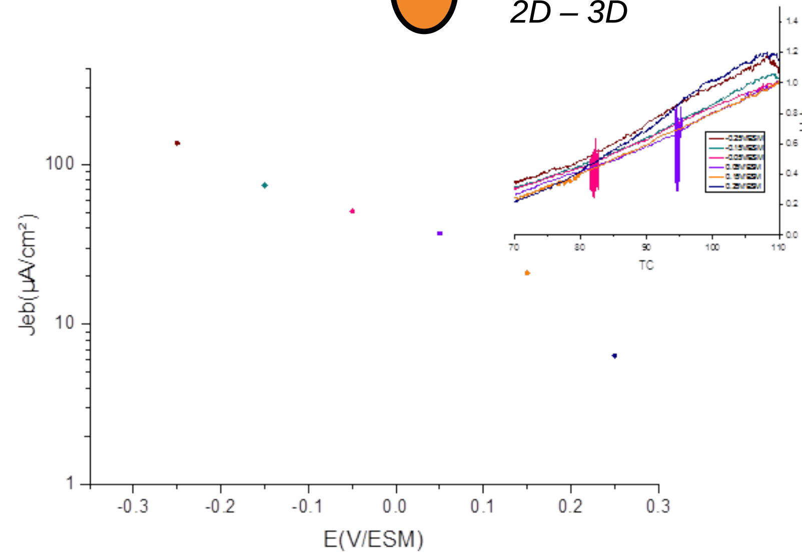
Influence de la géométrie

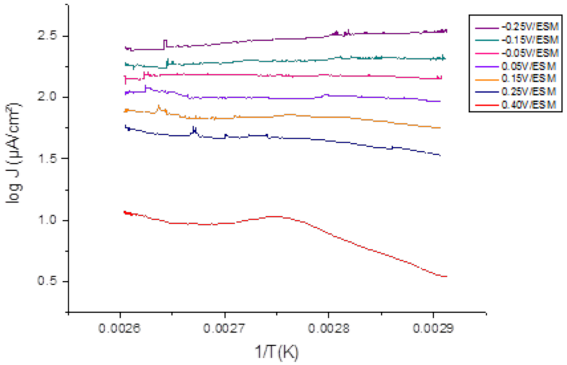
Diffusion 1D

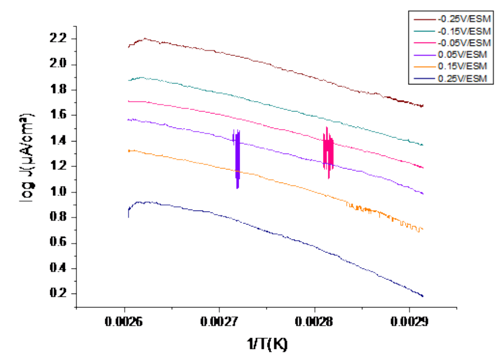


Diffusion 2D – 3D









Arrhenius → ~ mécanisme multiple (homogène)

Arrhenius → ~ mécanisme simple (hétérogène)