Physical Multiscale Modelling of the Electrochemical Dynamics in a PEFC

An infinite dimensional Bond Graph approach

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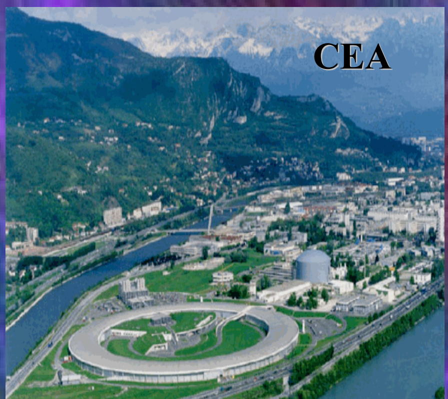
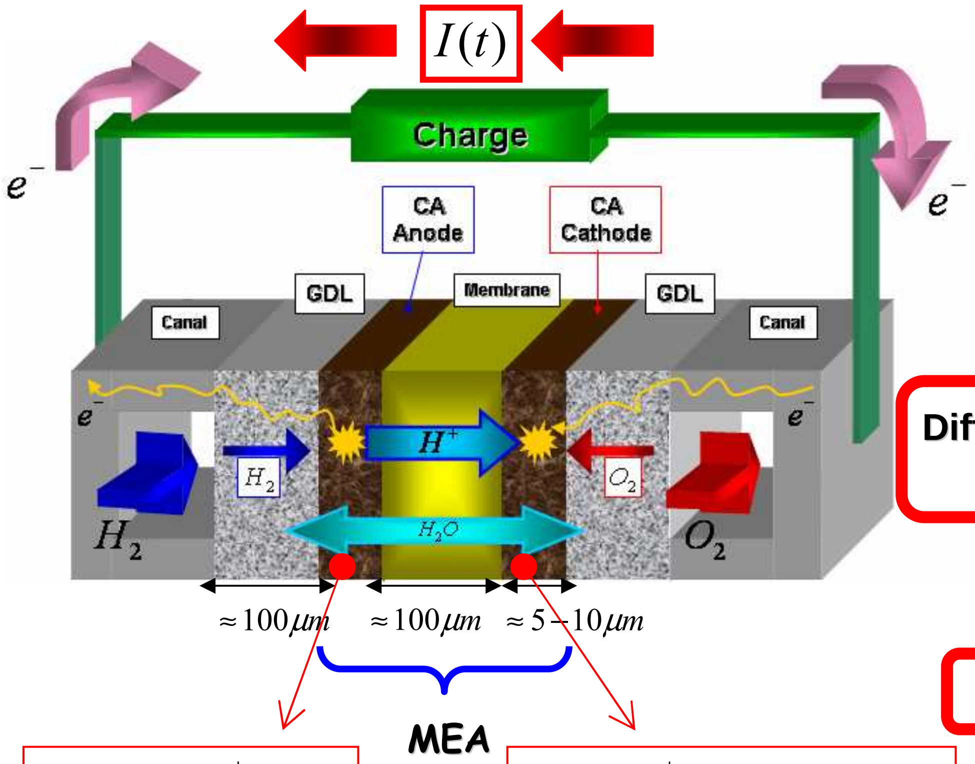


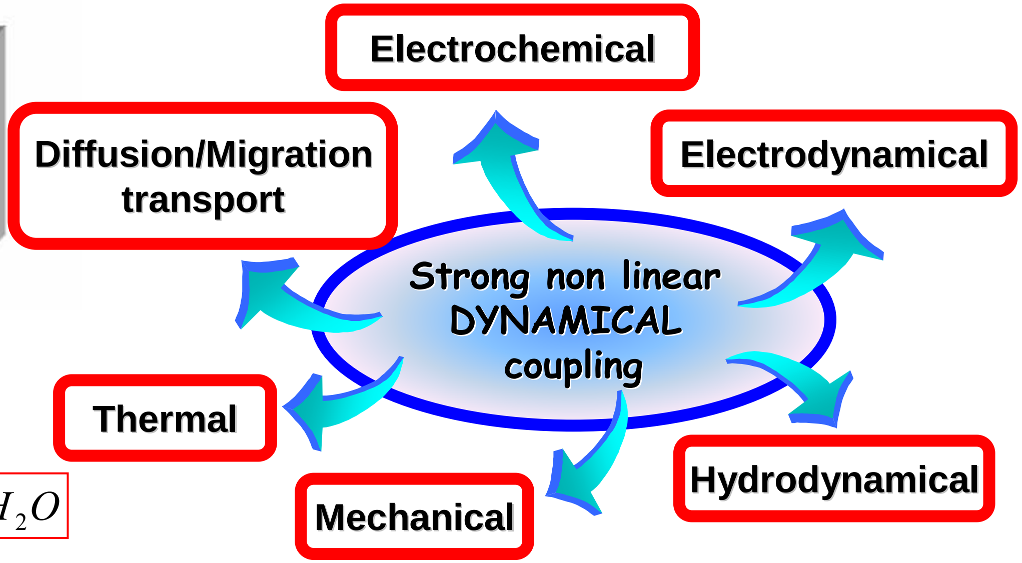
When PEFC design meets Theory



$$2H_2 \Rightarrow 4H^+ + 4e^-$$

$$O_2 + 4H^+ + 4e^- \Rightarrow 2H_2O$$

MEA
- **Platine** (reactions activations…)
- **Nafion®** (proton transport…)
- **Carbone** (electron transport…)



Optimization problem in an space of several tens of parameters, with merit function being power density obtained at given cost and lifetime.

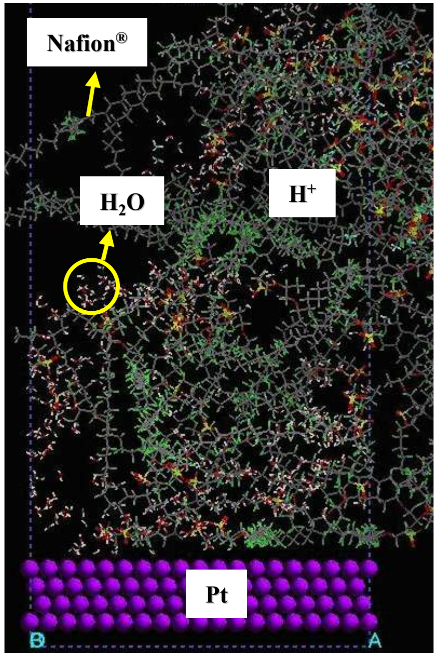
Accurate models are crucial in order to identify the origin of the performance losses of fuel cell electrodes and to evaluate their theoretical limits. Such models can help in the improvement of the electrodes (optimisation of Pt loading, diminution of fabrication costs).

Two kinds of PEFC modelling

Enhanced design of materials, membrane and electrodes

Highly resolved structural models and reliable ex-situ diagnostics

- **H. Pitsch (Stanford):** electrochemical reactions by Monte Carlo
- **E. Spohr (Juelich):** Proton and water transport by Molecular Dynamics
- **T. Jacob (Max Planck):** electrochemical reactions by Molecular Dynamics
- **S. Paddison (Los Alamos):** proton transport by Statistical Mechanics
- **V. Zhdanov (Göterborg)** (Monte Carlo)



Performance modelling at the systems level: how do we build the best PEFC with existing materials?

Information on in-situ performance and help to envisage how changes to the architecture of key materials could affect PEFC performance.

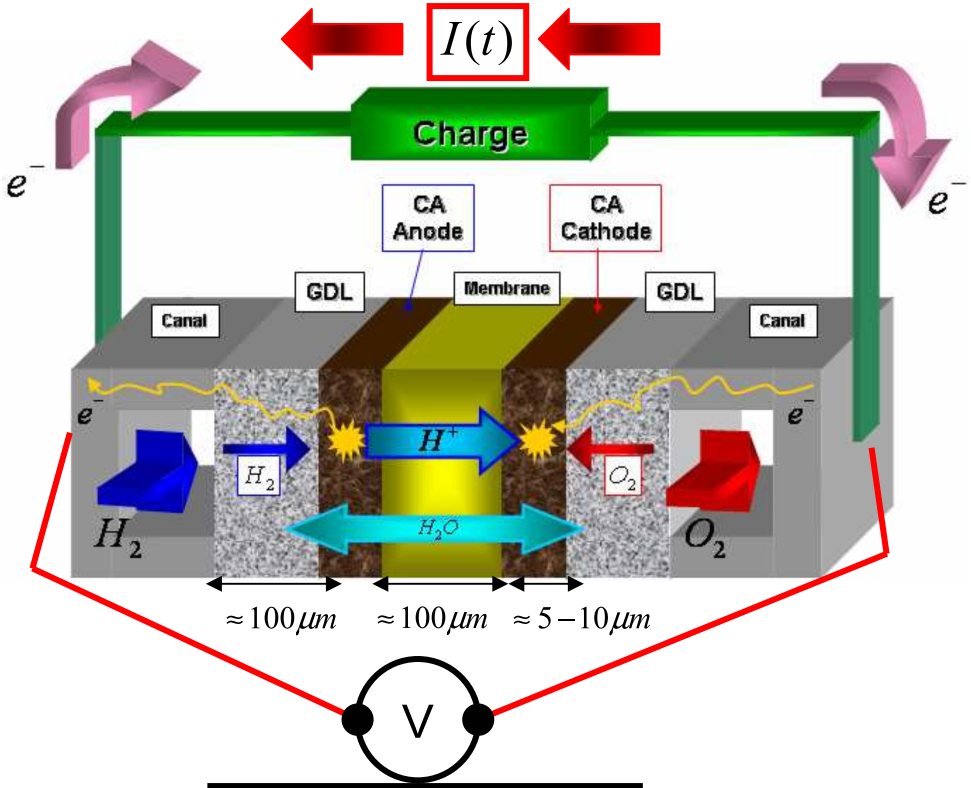
- **T. Springer (Los Alamos):** macrohomogeneous models
- **Y. Wang (Pennsylvania):** water transport
- **M. Eikerling (Simon Fraser)**
- **A. Kulikovsky (Juelich):** Reactant transport and electrochemistry

- **A. Kornyshev (Imperial College)**
- 2D and 3D CFD models (thermal, fluidics)
- **J-P. Diard, Y. Bultel (ENSEEG):** electrochemistry (electrical impedances)
- **G. Dauphin-Tanguy (Lille):** 0D-Bond Graph FC/system interaction modelling

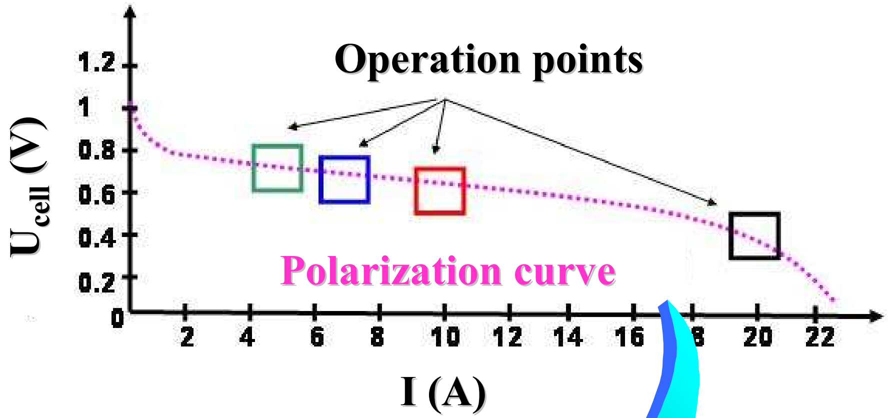
PEFC characterisation in the laboratory

Strong behaviour sensitivity to:

- $I \quad T \quad P_{H_2} \quad P_{O_2}$
- Composition and structure (C/Pt loading, etc)
- Time



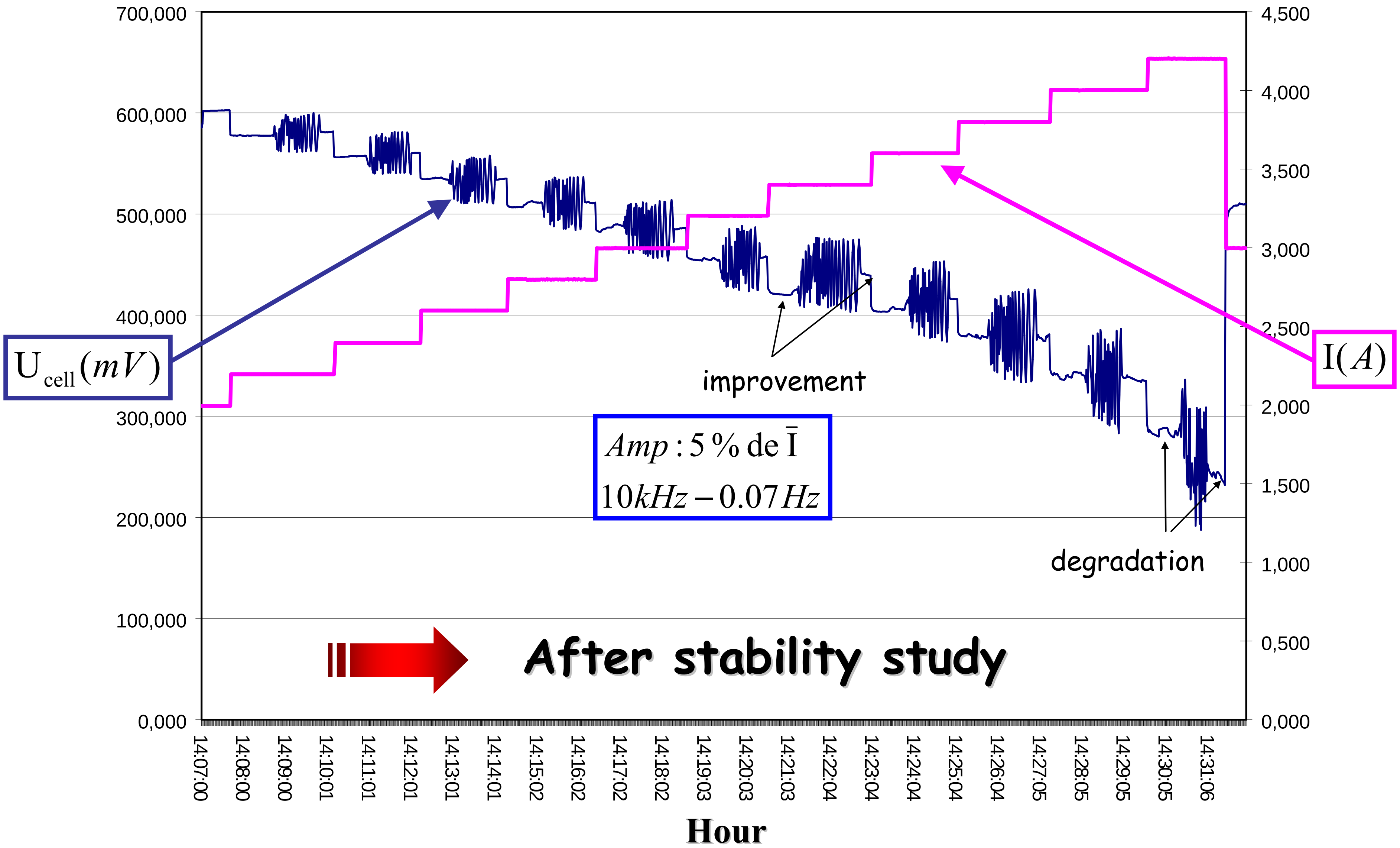
$$U_{cell}(t) = U_C(t) - U_A(t)$$



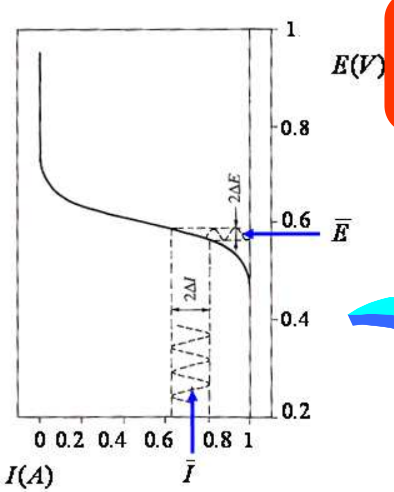
In order to give more insight

Transient techniques: cyclic voltametry, Lissajous, current steps, Non Linear and <u>Linear Electrochemical Impedance Spectroscopy (EIS)</u>…

Electrochemical Impedance Spectroscopy (1/2)



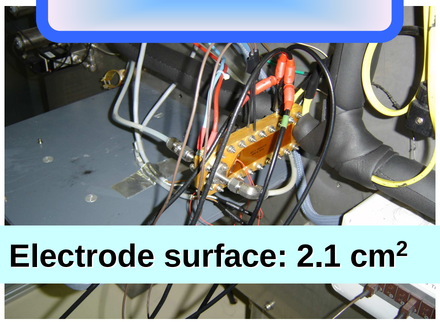
Electrochemical Impedance Spectroscopy (2/2)



$Amp: 5\,\%\ \text{de}\ \bar{I}$

$10kHz - 0.07Hz$

PAC-Maille Cell



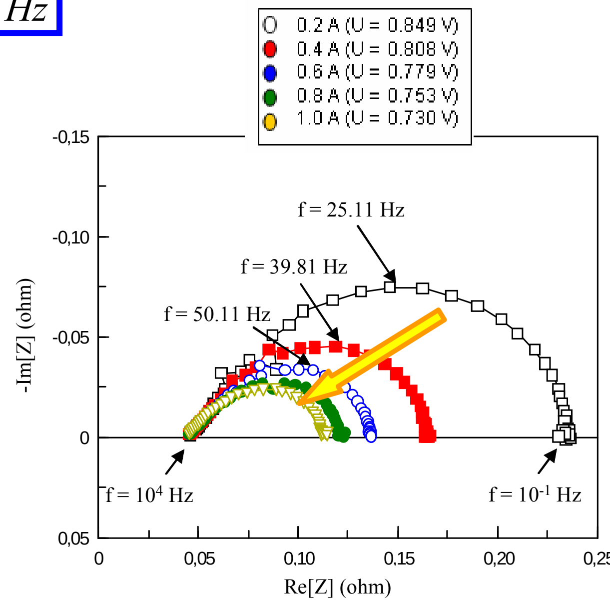
Electrode surface: 2.1 cm²

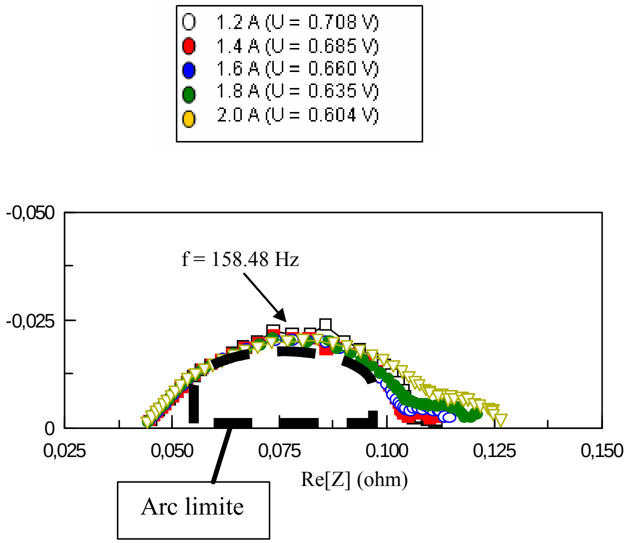
$EME\ 40\%$

$T = 353\ K$

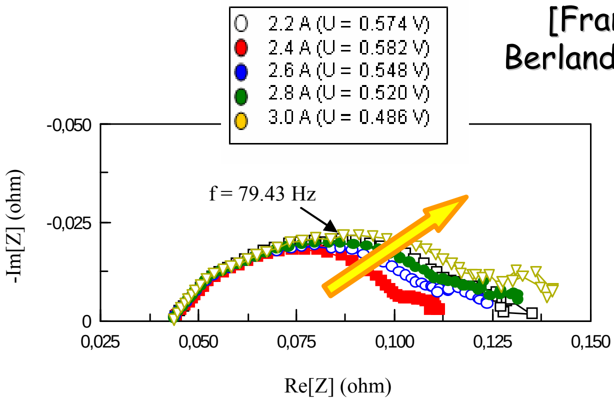
$P_{H_2} = P_{O_2} = 1.5\ bar$

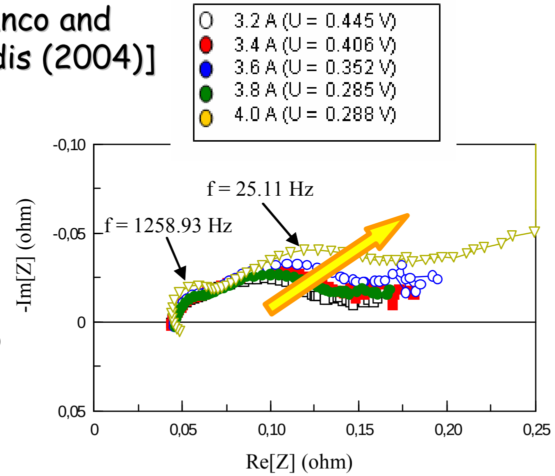
Ex. EIS sensitivity to nominal current



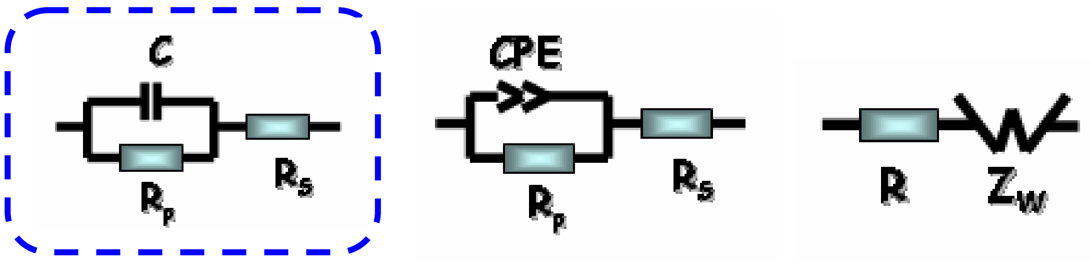


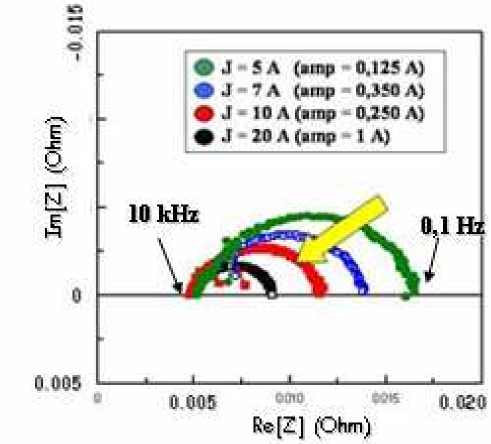
[Franco and Berlandis (2004)]



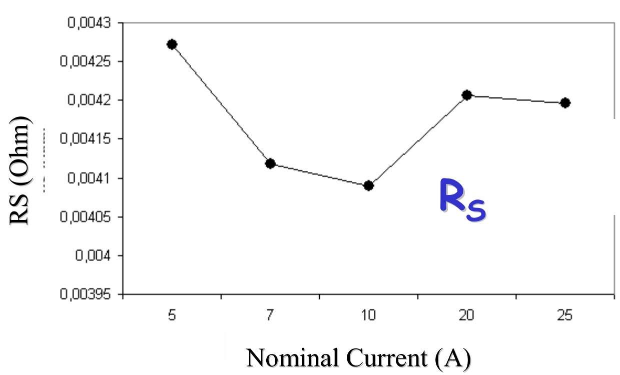


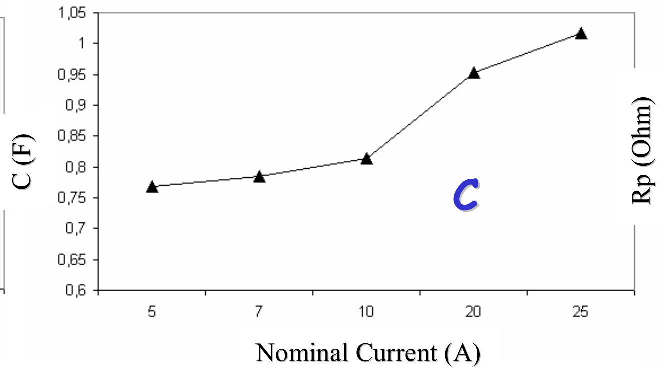
Analogy models (electrical circuits) (1/2)

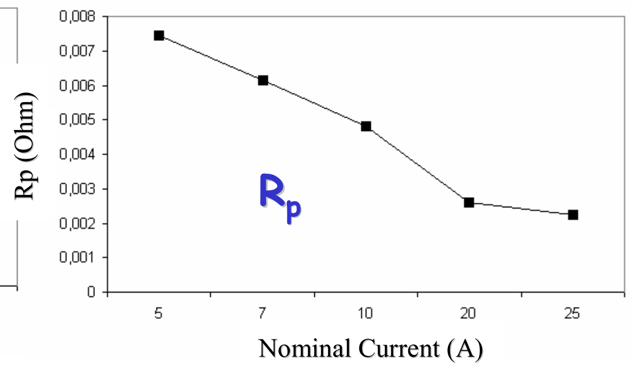




[Franco et al. (2004)]







- No intrinsic dependence on current, reactant pressures and temperature [Conway (1989)], [Hitz (2002)], Kornyshev (1999)], no direct link with the physical parameters.
- No take into account of the volumetric electrode structure.
- Different possible circuits for similar impedance responses.

Analogy models (electrical circuits) (2/2)

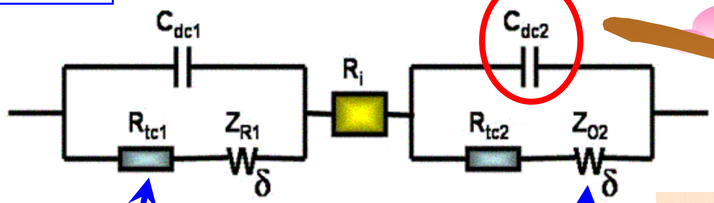
Impedances: analytical expressions from elementary phenomena

$$R_1 \xrightarrow{k_1} O_1 + n_1 e^-$$

$$O_2 + n_2 e^- \xrightarrow{k_2} R_2$$

[Walkiewicz et al. (2001)]

$$C_{dc1} = \frac{1}{i\omega C_1}$$



$$R_{tc1} = \frac{1}{j_{01}\gamma n_1 f \alpha_{01} \exp(\alpha_{01} n_1 f \eta_1^*)\left(1 - \frac{j}{n_1 F m_{R1} R_1^*}\right)}$$

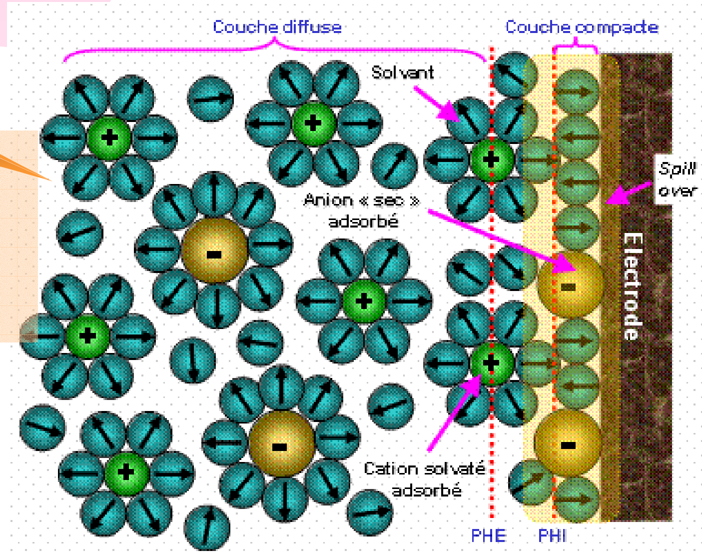
$$\eta = E - E_{th}$$

$$Z_{O2} = \frac{\left(\frac{\tanh(\sqrt{i\omega\tau_2})}{\sqrt{i\omega\tau_2}}\right)}{\alpha_{r2} n_2^2 F f m_{O2} O_2^* \left(1 - \frac{j}{n_2 F m_{O2} O_2^*}\right)}$$

Changing electrochemical reaction

New analytical computing of impedance (sometimes impossible)

One speaks about an *electrochemical double layer capacity* <u>uncoupled</u> from electrochemical reactions impedances…



- **Kinetic impedances no taking into account absence of supporting electrolyte in Nafion®.**
- **Static theory: local validity.**
- **Needs to recalculate impedances if changes or new couplings in reactions or transport (analytical expressions not always possible): not reusable.**
- **Difficult link with irreversible thermodynamics.**

- **Double layer capacity derived from an equilibrium theory [Chapman (1932)], [Schmickler (1985)], [Amokrane (1996)].**
- **Statistical mechanics, MC, MD models.**
- **Interface behaviour in presence of electrochemical reactions and in absence of supporting electrolyte ?**
- **What is the meaning of « double layer » in the PEFC electrode case?**

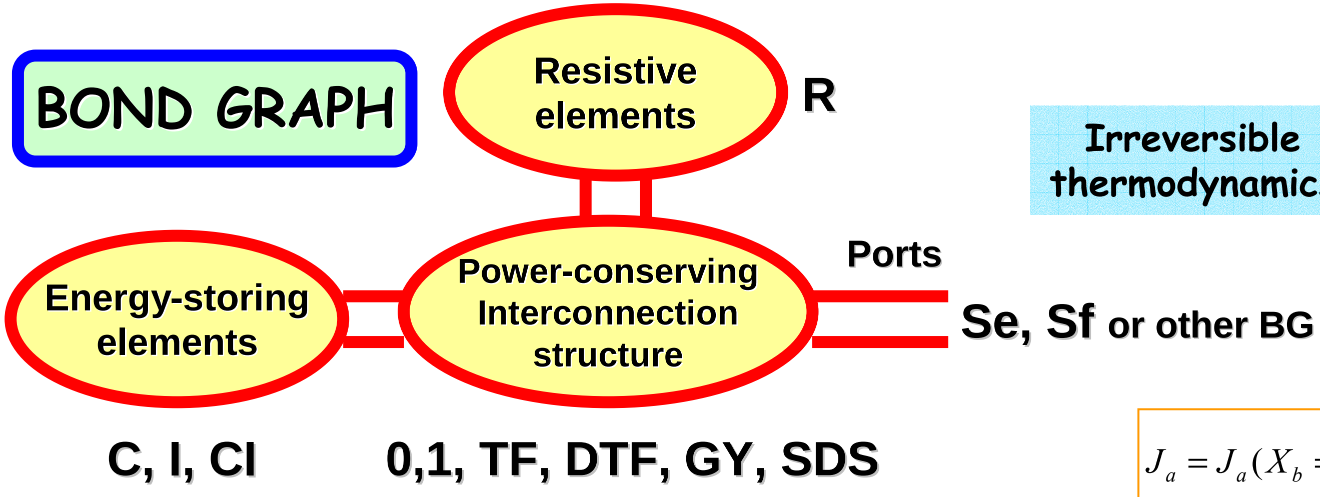
Our research objectives

- Model centred on <u>electrochemical phenomena.</u>
- Model linking irreversible thermodynamics with electrical circuits theory, allowing interdomain couplings: port-based, <u>hierarchical</u> approach, <u>energetically consistent</u> in all participating domains and at all relevant space and time scales.
- <u>Dynamical model</u>: transient regimes, physicochemical aging mechanisms, transient experiments interpretation (diagnostics)…
- <u>Predictive model</u>: sensitivity to working conditions (I,T,P) and constructor parameters (design).
- <u>Modular and modulable model</u>: reusability into/with another electrochemical contexts.

Bond Graph modelling seems to be the optimal approach

Irreversible thermodynamics and infinite-dimensional Bond Graphs

Franco et al., in Proceedings of the 5th Mathmod conference, Vienna (2006).



Irreversible thermodynamics

Balance equation

$$\frac{\partial C_a}{\partial t} = -\nabla . J_a$$

Flux / Effort

$$J_a = \sum_{b=1}^{n} L_{ab} X_b$$

Markoffian system

$$J_a = J_a(X_b = 0) + \sum_{b=1}^{n} \frac{\partial J_a}{\partial X_b} X_b + \frac{1}{2!} \sum_{b,c=1}^{n} \frac{\partial^2 J_a}{\partial X_b \partial X_c} X_b X_c + ..$$

- Representation of the power flux network type: constitutive and conservation equations.
- This formalism allows to represent the complexity of interconnection of physical phenomena in agreement with the axioms of non equilibrium thermodynamics.
- Feedback in model decisions.
- « Infinite dimensional »: extension of classical 0D Bond Graphs to continuum systems [Maschke and van der Schaft (1995)].

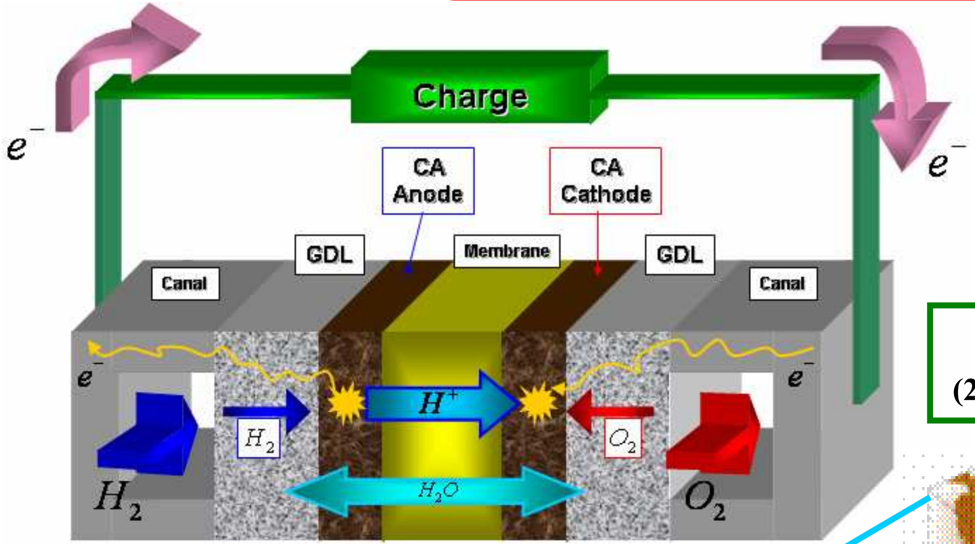
Unified formulation of electrochemistry and its coupling with transport phenomena in the PEFC active layers.

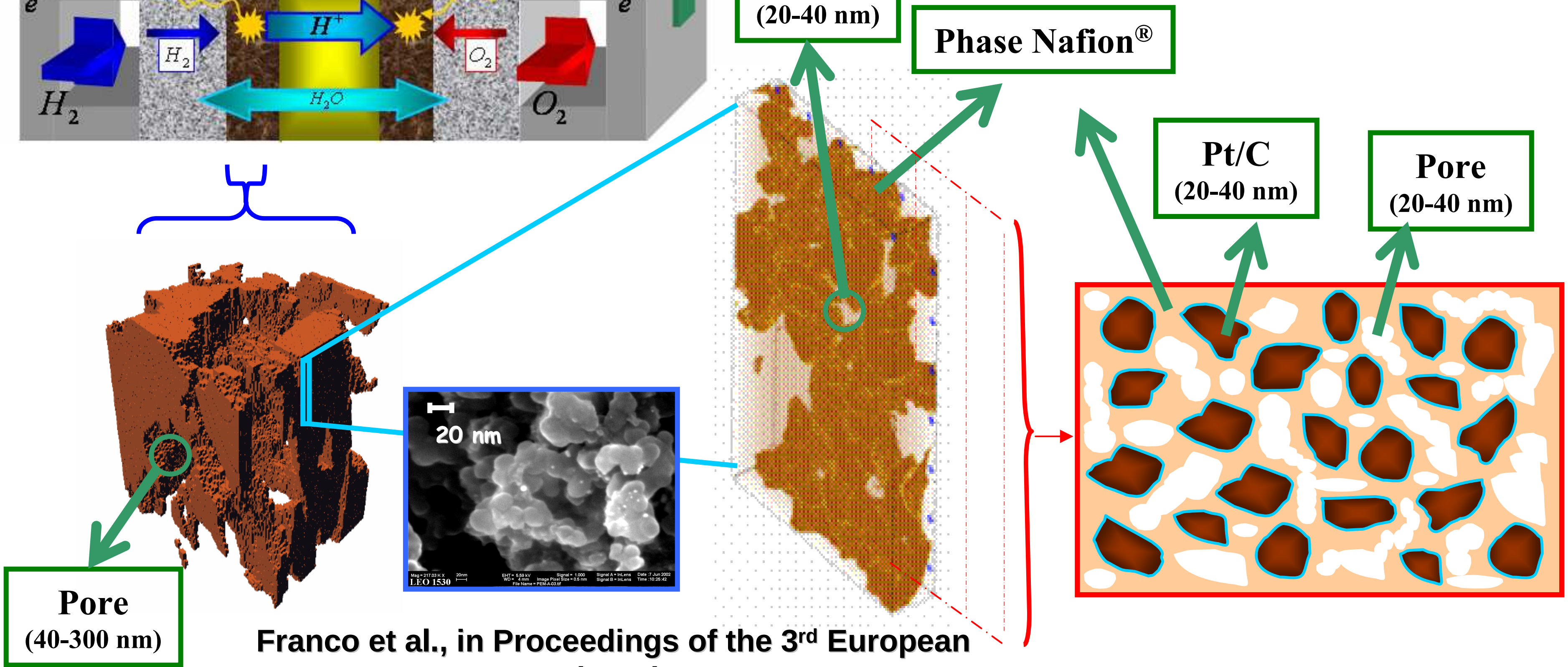
Only <u>two</u> scalar potentials in our model : chemical potentials, electrostatic potentials.

Volumetric electrode "real" structure

At the NANOscopic scale the three phase boundary doesn't exist.

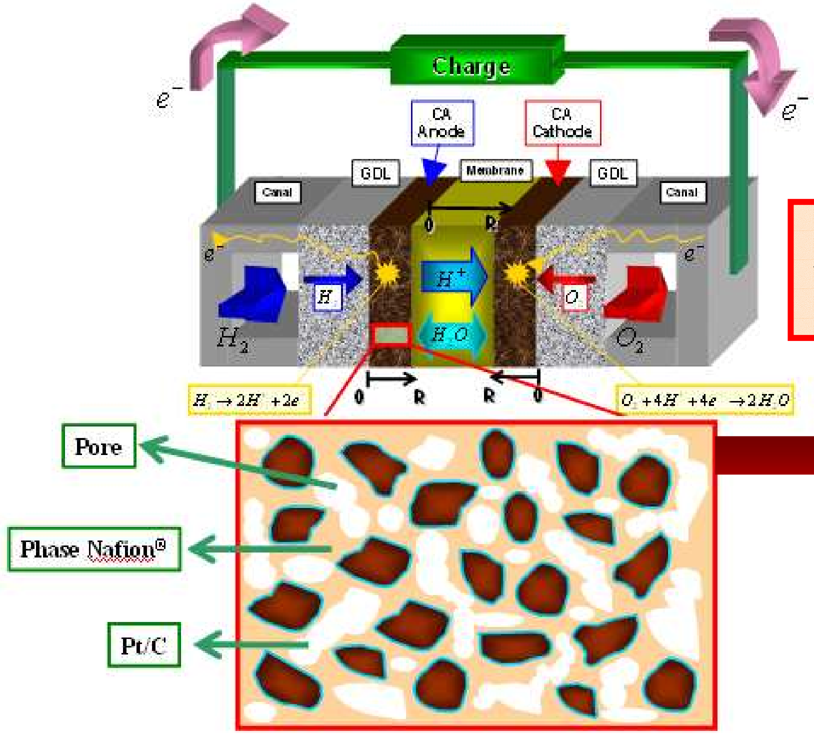
[Inaba (1996)] [Gerbaux (1996)] [Kornyshev (1999)] [Franco et al. (2003-2005)]





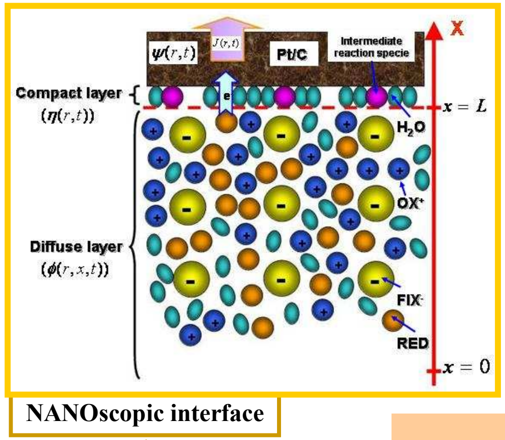
Franco et al., in Proceedings of the 3rd European PEFC Forum, Luzern (2005).

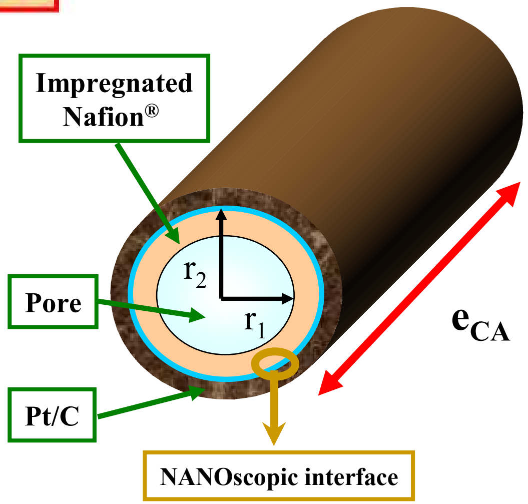
Volumetric electrode <u>modelled</u> structure

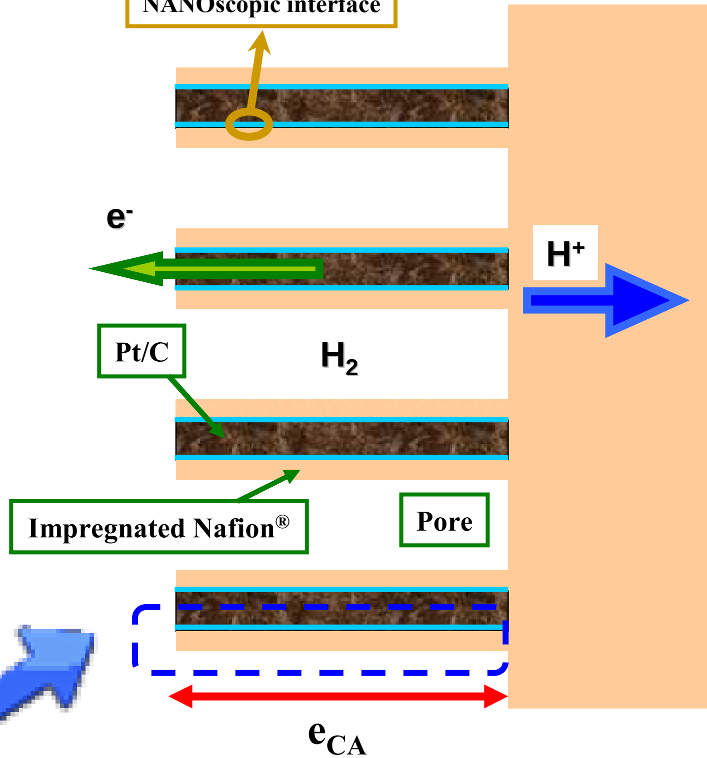


Active surface per volume unit of electrode (*specific active area*)

$$\gamma(m^2/m^3)$$





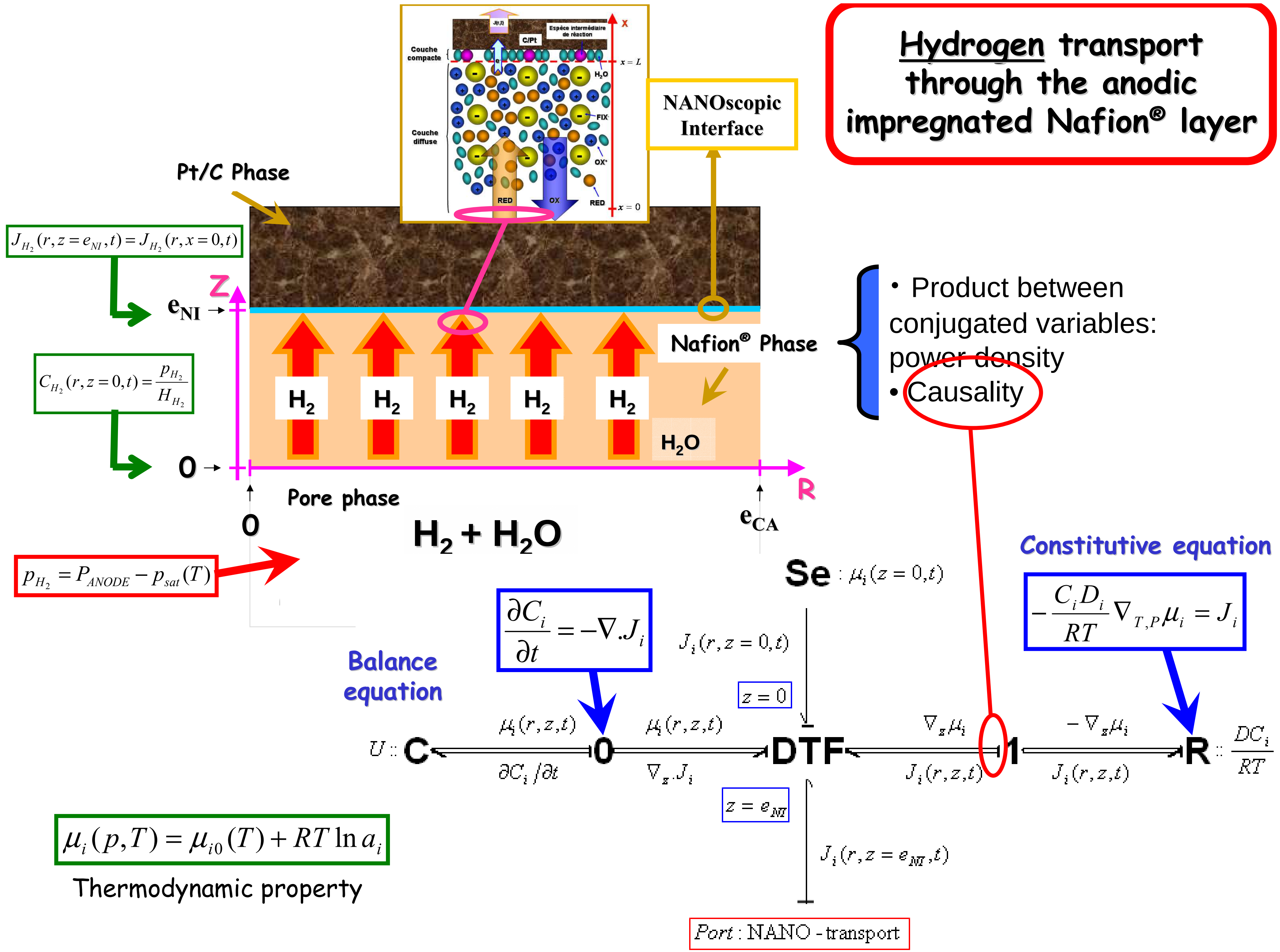


- Isothermal model
- Pure gases (H_2, O_2)
- Fully vapour saturated gases
- Water transport not considered
- Volumetric homogeneous electrode

$$r_1 \approx 15-40nm$$

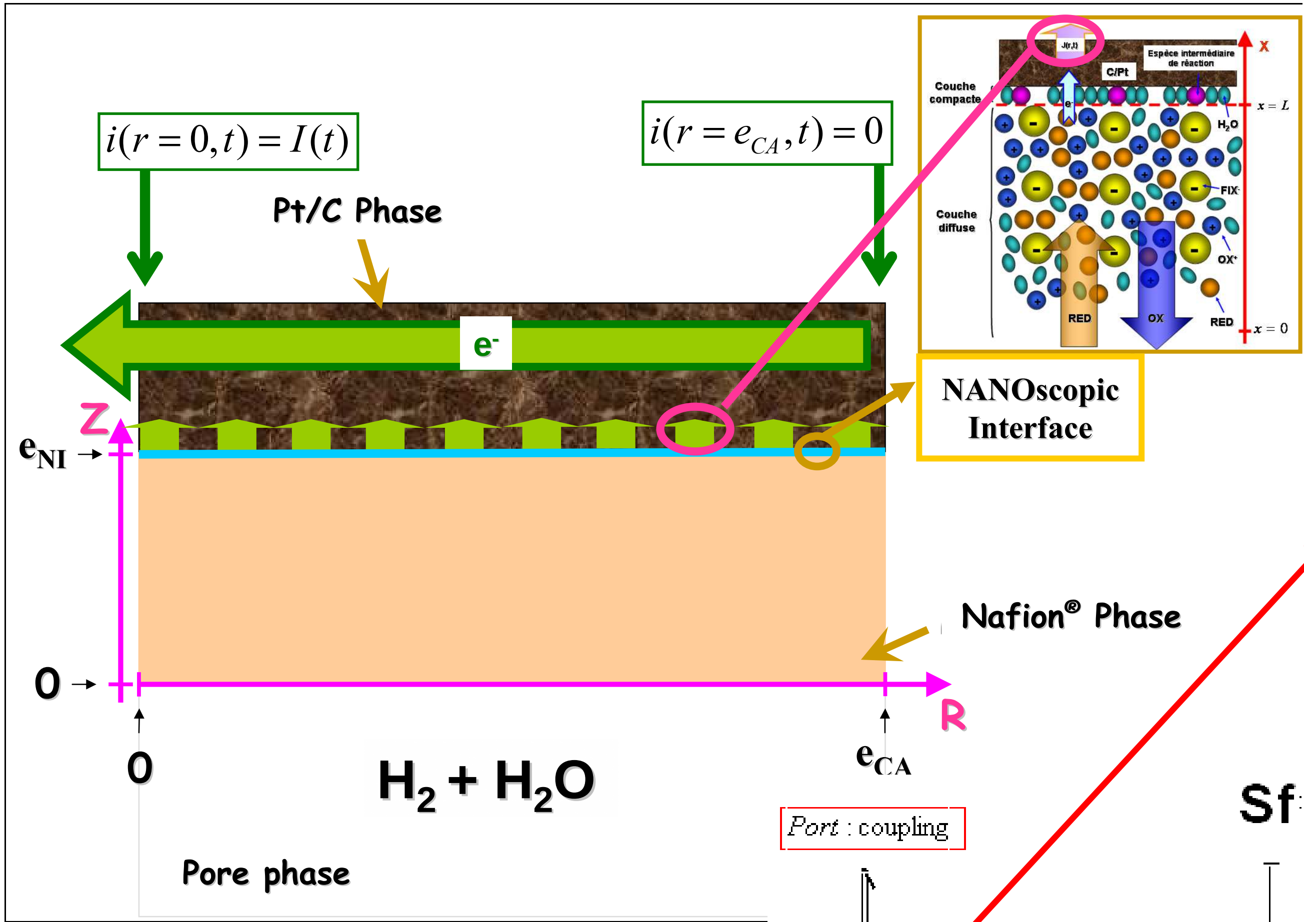
$$r_2 - r_1 \leq 0.1\mu m$$

$$\approx 5-10\mu m$$



Hydrogen transport through the anodic impregnated Nafion® layer
NANOscopic Interface
Couche compacte
Couche diffuse
C/Pt
Espèce intermédiaire de réaction
$x = L$
$x = 0$
RED
OX
Pt/C Phase
$J_{H_2}(r, z = e_{NI}, t) = J_{H_2}(r, x = 0, t)$
e_{NI}
Z
$C_{H_2}(r, z = 0, t) = \frac{p_{H_2}}{H_{H_2}}$
0
H_2
H_2O
Nafion® Phase
R
Pore phase
0
e_{CA}
$H_2 + H_2O$
$p_{H_2} = P_{ANODE} - p_{sat}(T)$
• Product between conjugated variables: power density
• Causality
Constitutive equation
$-\frac{C_i D_i}{RT} \nabla_{T,P} \mu_i = J_i$
Se : $\mu_i(z = 0, t)$
$\frac{\partial C_i}{\partial t} = -\nabla . J_i$
Balance equation
$J_i(r, z = 0, t)$
$z = 0$
U :: C
$\mu_i(r,z,t)$
$\partial C_i / \partial t$
0
$\mu_i(r,z,t)$
$\nabla_z . J_i$
DTF
$\nabla_z \mu_i$
$J_i(r,z,t)$
1
$-\nabla_z \mu_i$
$J_i(r,z,t)$
R :: $\frac{DC_i}{RT}$
$z = e_{NI}$
$J_i(r, z = e_{NI}, t)$
$Port$: NANO - transport
$\mu_i(p,T) = \mu_{i0}(T) + RT \ln a_i$
Thermodynamic property

Electron transport through the anodic electrode thickness

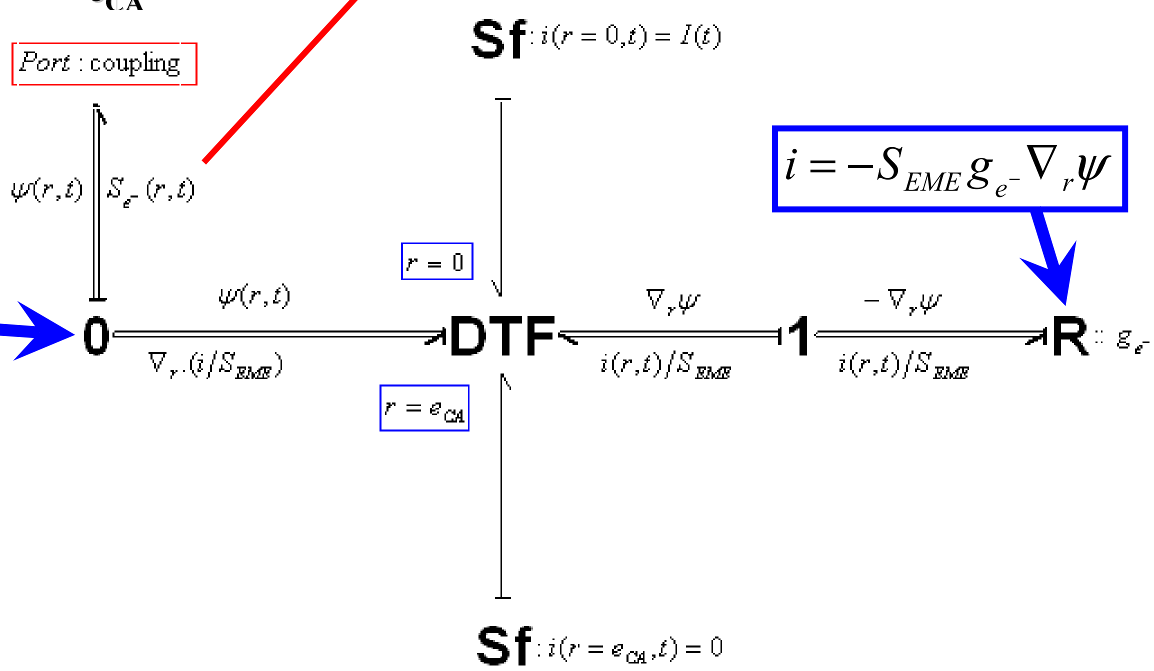


Coupling between scales

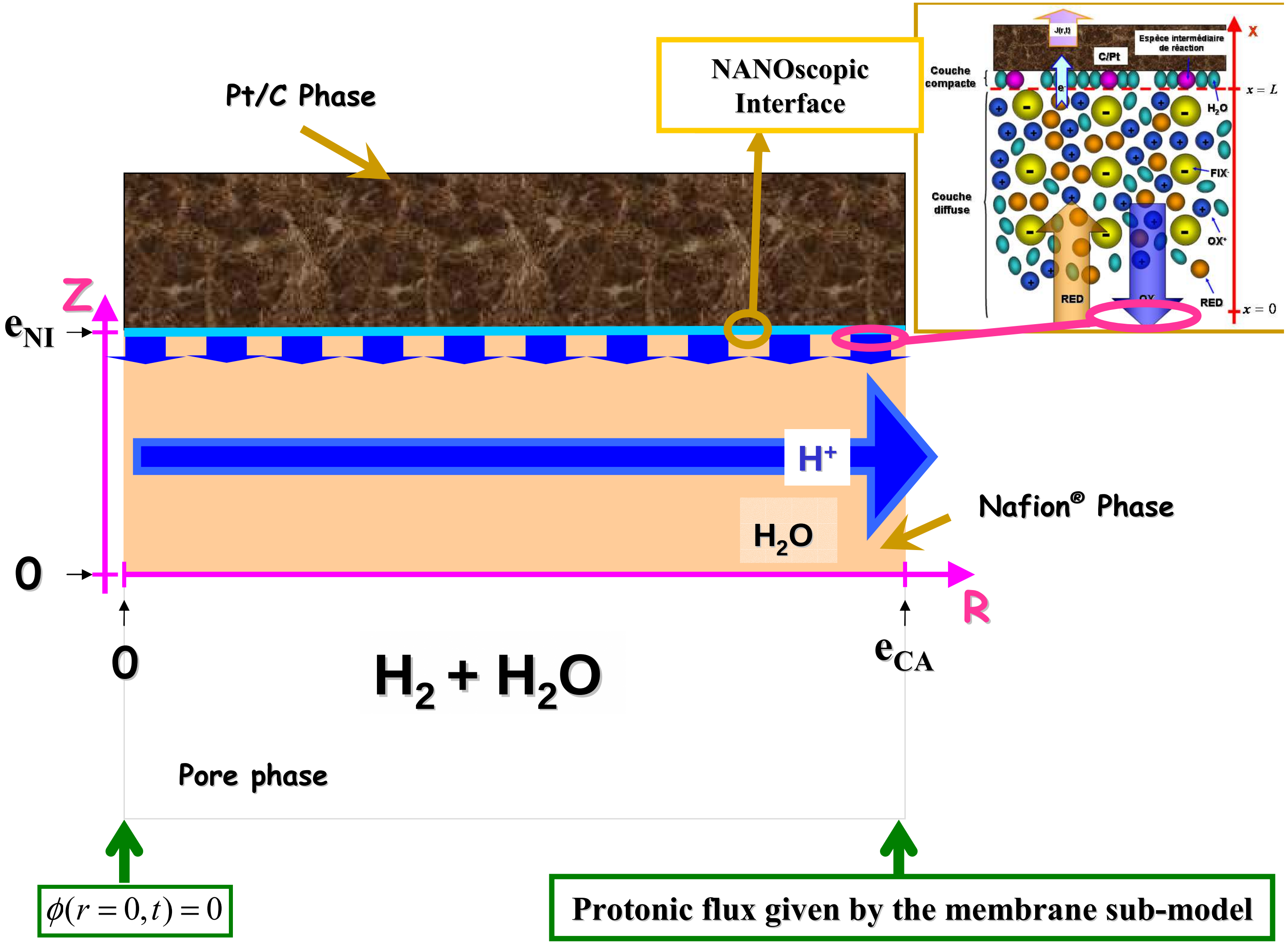
$$S_{e^-}(r,t)=J(r,t)\gamma$$

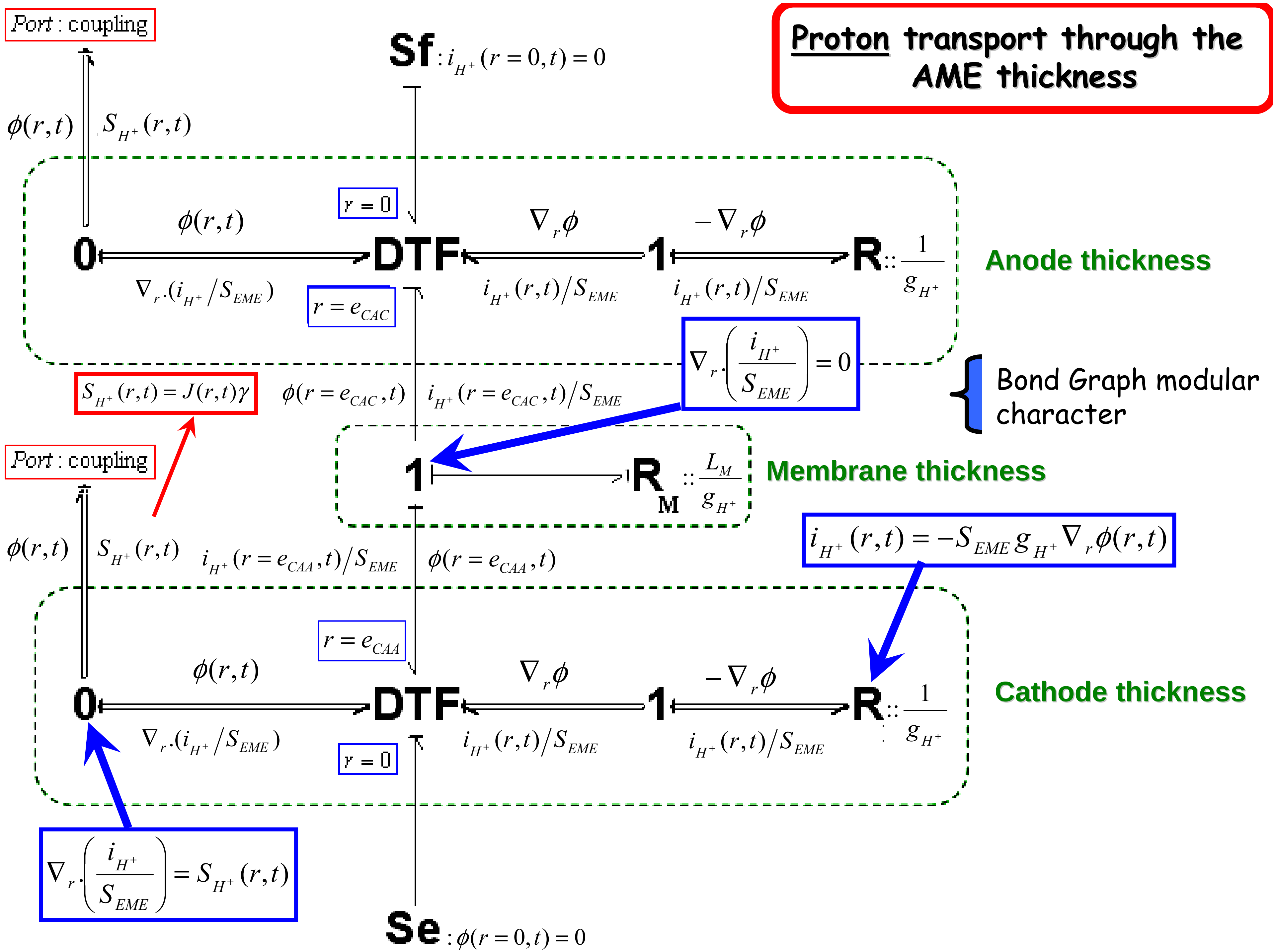
$$\nabla_r\cdot\left(\frac{i}{S_{EME}}\right)=S_{e^-}(r,t)$$

$$i=-S_{EME}\,g_{e^-}\nabla_r\psi$$



Proton transport through the anodic electrode thickness

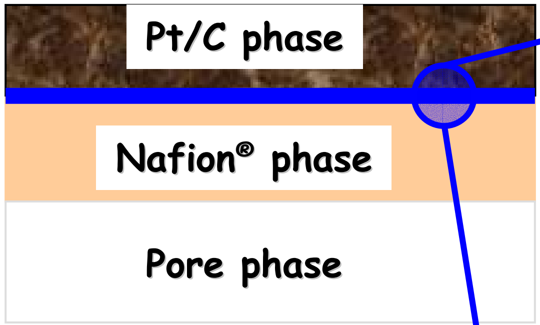


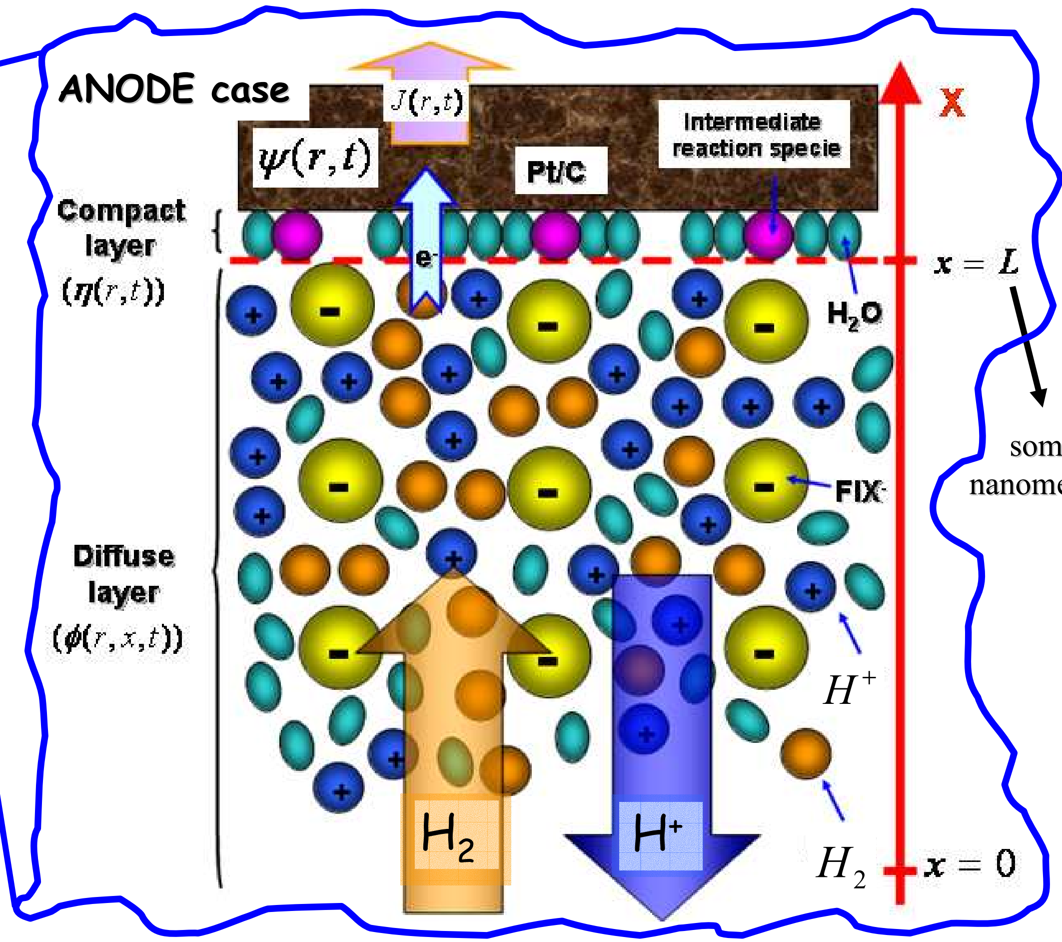


Proton transport through the AME thickness
Port : coupling
Sf : $i_{H^+}(r=0,t)=0$
$\phi(r,t)$
$S_{H^+}(r,t)$
$r=0$
$\nabla_r\phi$
$-\nabla_r\phi$
0
DTF
1
R
$\frac{1}{g_{H^+}}$
Anode thickness
$\nabla_r.(i_{H^+}/S_{EME})$
$r=e_{CAC}$
$i_{H^+}(r,t)/S_{EME}$
$\nabla_r.\left(\frac{i_{H^+}}{S_{EME}}\right)=0$
Bond Graph modular character
$S_{H^+}(r,t)=J(r,t)\gamma$
$\phi(r=e_{CAC},t)$
$i_{H^+}(r=e_{CAC},t)/S_{EME}$
$R_M :: \frac{L_M}{g_{H^+}}$
Membrane thickness
$i_{H^+}(r,t)=-S_{EME}\,g_{H^+}\nabla_r\phi(r,t)$
$i_{H^+}(r=e_{CAA},t)/S_{EME}$
$\phi(r=e_{CAA},t)$
$r=e_{CAA}$
Cathode thickness
$\nabla_r.\left(\frac{i_{H^+}}{S_{EME}}\right)=S_{H^+}(r,t)$
Se : $\phi(r=0,t)=0$

NANOscale sub-model

Franco et al., Journal of the Electrochemical Society 156, 6 (2006).

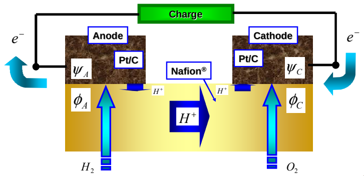




Assumptions: Isotropic and homogeneous electrolyte structure (solid matrix), no interprotonic interaction, no solvatation, no convection, punctual species.

NANOscopic interface

Franco A.A., PhD Thesis UCBL-1, 2005LYO10239 (2005).



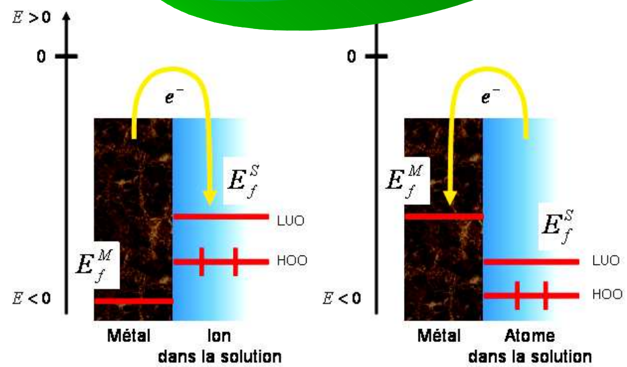
Electric potentials paradox

NANOscopic interface

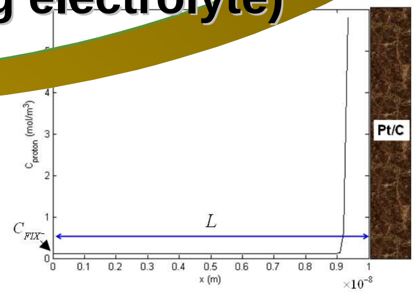
Dynamical electrochemical double layer at the Pt/C-Nafion interface in presence of electrochemical reactions.

Intermediates adsorption at the compact layer.

Compatibility between irreversible thermodynamics and Quantum Marcus' theory



Diffusion/Migration coupling for proton transport in Nafion® (no electroneutrality/ no supporting electrolyte)



<u>Strong coupling</u> between EDL and Electrochemical Reactions

Diffuse layer sub-model

Gas transport

Diffusion

$$-\frac{C_i D_i}{RT}\nabla_{T,P}\mu_i = J_i$$

Proton transport

Diffusion, migration

$$-\frac{C_{H^+} D_{H^+}}{RT}\nabla_{T,P}\tilde{\mu}_{H^+} = J_{H^+}$$

Balance equation

$$\frac{\partial C_i}{\partial t} = -\nabla . J_i$$

$$\tilde{\mu}_{H^+} = \mu_{H^+} + F\phi$$

Absence of supporting electrolyte

No Electroneutrality

Coupling between migration and diffusion

$$\frac{F}{\varepsilon_{CD}}(C_{H^+} - C_{FIX}) = \varepsilon_{CD}\upsilon_{CD}\frac{\partial^2\phi}{\partial t^2} - \nabla_x{}^2\phi$$

$$\nabla_x{}^2\vec{A} - \upsilon_{CD}\varepsilon_{CD}\frac{\partial^2\vec{A}}{\partial t^2} = -\upsilon_{CD}\vec{J}_{H^+}$$

Conservation equations

$$\nabla\times\vec{H} - F\vec{J}_{H^+} = \frac{\partial\vec{D}}{\partial t}$$

$$-\nabla\times\vec{E} = \frac{\partial\vec{B}}{\partial t}$$

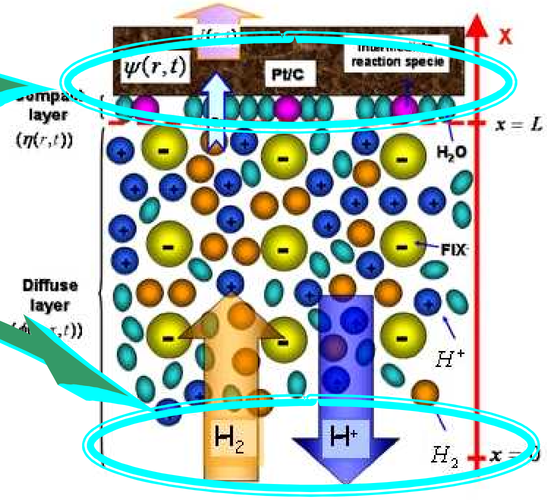
Constitutive equations

$$\vec{H} = \upsilon_{CD}{}^{-1}\vec{B}$$

$$\vec{E} = \varepsilon_{CD}{}^{-1}\vec{D}$$

Maxwell's theory as a port-Hamiltonian system [Maschke et van der Shaft (2004)] [Franco et al. (2005)]

$$J(r,t) = \frac{S_{e^-}(r,t)}{\gamma}$$



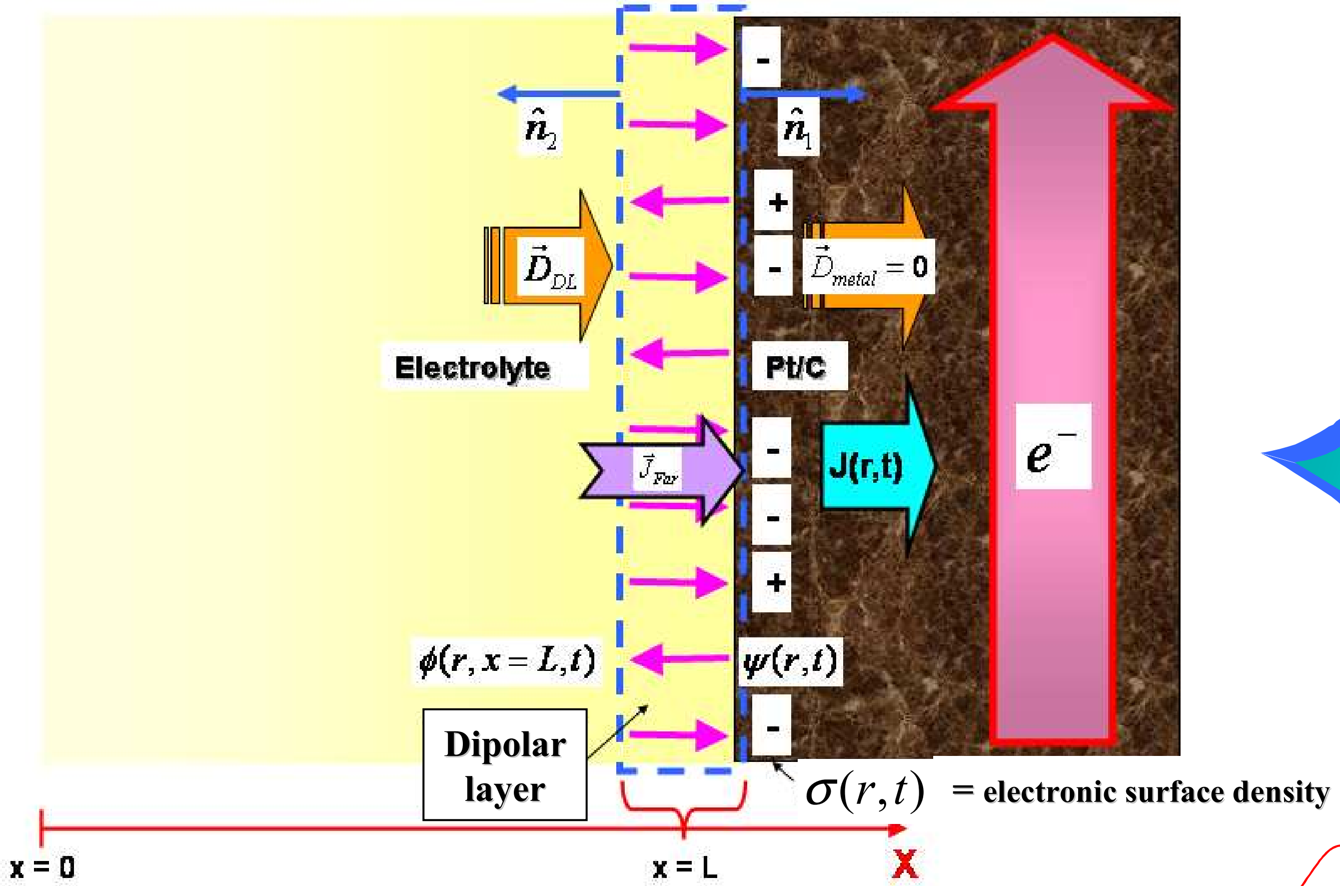
$$C_{H_2}(r,x=0,t) = C_{H_2}(r,z=e_{NI},t)$$

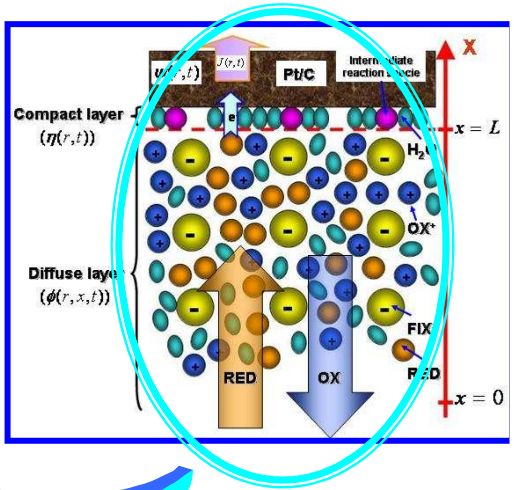
$$\left\{J_{H_2}(r,z=e_{NI},t) = J_{H_2}(r,x=0,t)\right\}$$

$$C_{H^+}(r,x=0,t) = C_{H^+}(r,t)$$

$$\left\{S_{H^+}(r,t) = \gamma\vec{J}_{H^+}(r,x=0,t)\right\}$$

D'Alembert's equation: boundary condition at x = L





$$\left\| -\nabla \phi(r, x = L, t) \right\| = \frac{\sigma(r,t)}{\varepsilon_{CC}}$$

Gauss' theorem

$\sigma(r,t)$

$$J(r,t) - FJ_{H^+}(r, x = L, t) = -\frac{\partial \sigma(r,t)}{\partial t}$$

Charge conservation at x = L

$$J(r,t) + FJ_{H^+}(r, x = L, t) = \frac{\partial \sigma(r,t)}{\partial t}$$

Coupling between electrochemical reactions and dipolar adsorption

[Harrington et Conway (1987)} [Franco et al. (2003-2005)]

Tafel	$H_2 + 2s \leftrightarrow 2Hs$
Heyrovsky	$s + H_2 \leftrightarrow Hs + H^+ + e^-$
Volmer	$Hs \leftrightarrow s + H^+ + e^-$

Damjanovic 1	$O_2 + H^+ + e^- + s \leftrightarrow O_2Hs$
Damjanovic 2	$O_2Hs + H_2O + 2s \leftrightarrow 3OHs$
Damjanovic 3	$OHs + H^+ + e^- \leftrightarrow H_2O + s$

[Damjanovic et al. (1967)] [Jacob et al. (2004)] [Franco et al. (2003-2005)]

$$1 = \theta_s + \theta_{Hs} + \vec{\theta} + \overleftarrow{\theta}$$

No interaction between intermediates

$$1 = \theta_s + \theta_{O_2Hs} + \theta_{OHs} + \vec{\theta} + \overleftarrow{\theta}$$

$$v_{TAF} = k_{TAF}\theta_s^2 C_{H_2}(r,L,t) - k_{-TAF}\theta_{Hs}^2$$

$$v_{HEY} = k_{HEY}\theta_s C_{H_2}(r,L,t)e^{(1-\alpha_{HEY})f\eta(r,t)} - k_{-HEY}\theta_{Hs}C_{H^+}(r,L,t)e^{-\alpha_{HEY}f\eta(r,t)}$$

$$v_{VOL} = k_{VOL}\theta_{Hs}e^{(1-\alpha_{VOL})f\eta(r,t)} - k_{-VOL}\theta_s C_{H^+}(r,L,t)e^{-\alpha_{VOL}f\eta(r,t)}$$

$$v_1 = k_1\theta_s C_{H^+}(r,L,t)C_{O_2}(r,L,t)e^{-\alpha_1 f\eta(r,t)} - k_{-1}\theta_{O_2Hs}e^{(1-\alpha_1)f\eta(r,t)}$$

$$v_2 = k_2\theta_{O_2Hs}\Theta_{H_2O}\theta_s^2 - k_{-2}\theta_{OHs}^3$$

$$v_3 = k_3\theta_{OHs}C_{H^+}(r,L,t)e^{-\alpha_3 f\eta(r,t)} - k_{-3}\theta_s\Theta_{H_2O}e^{(1-\alpha_3)f\eta(r,t)}$$

$$\frac{n_s^{\max}}{N_A}\frac{d\theta_{Hs}}{dt} = -v_{VOL} + v_{HEY} + 2v_{TAF}$$

$$J_{H_2}(r, x = L, t) = -(v_{TAF} + v_{HEY})$$

$$J_{H^+}(r, x = L, t) = v_{HEY} + v_{VOL} = J_{Far}/F$$

Frumkin's Overpotential

$$\eta(r,t) = \psi(r,t) - \phi(r, x = L, t)$$

(Frumkin, Marcus, Bockris, Franco)

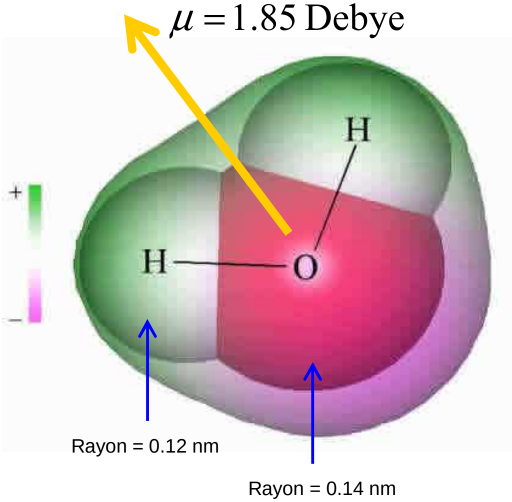
$$\frac{n_s^{\max}}{N_A}\frac{d\theta_{O_2Hs}}{dt} = v_1 - v_2 \qquad \frac{n_s^{\max}}{N_A}\frac{d\theta_{OHs}}{dt} = 3v_2 - v_3$$

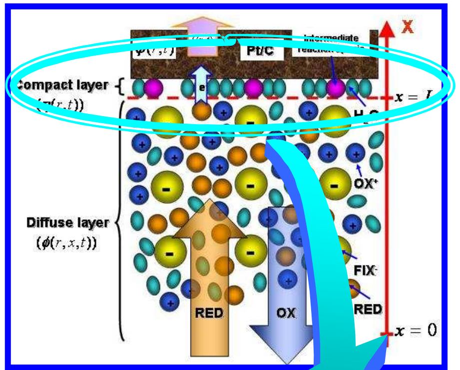
$$J_{O_2}(r, x = L, t) = -v_{Dmj1}$$

$$J_{H^+}(r, x = L, t) = -(v_{Dmj1} + v_{Dmj3}) = -J_{Far}/F$$

How η is linked to σ ?

Reaction rates ➡ **Functions of** $\eta(r,t)$





Experimental:
Benderskii (1982),
Climent (2002)

Stern layer

Dipolar water layer: generates interface discontinuity of electric potential

$$\eta(r,t) = \Delta\varphi_1 + \Delta\varphi_2 = f(\sigma)$$

Depends on the thickness of the water layer.

Depends on the dipolar nature of the water layer.

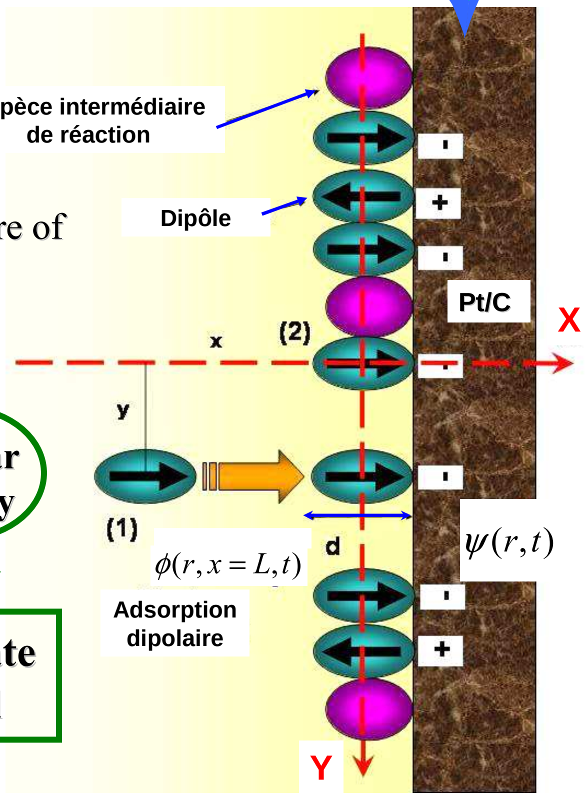
$$\Delta\varphi_1 = -\frac{\sigma}{\varepsilon_{CC}} d$$

Application of Gauss theorem and Poisson integral

$$\Delta\varphi_2 = \frac{\Gamma(\sigma)}{\varepsilon_{CD}} = \frac{\mu(\vec{n} - \overleftarrow{n})}{\varepsilon_{CD}}$$

Dipolar density

Two-state model



Franco et al., 207th Meeting of the Electrochemical Society, Quebec paper #1256 (2005).

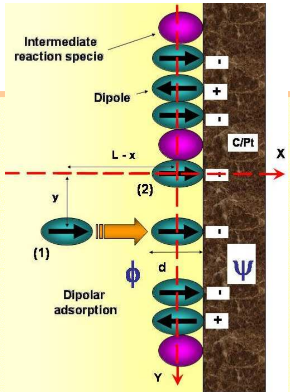
[Watts-Tobin (1961)]
[Bockris (1977)]
[Schmickler (1983)]
[Conway (1992)]
[Franco et al. (2003)]

Water adsorption and resulting dipolar density

$$H_2O + s \overset{\rightleftarrows}{\leftrightarrow} H_2O - s$$

Chemical energy — **Electrostatic energy** — **Interdipolar interaction energy**

$$\frac{\overset{\rightleftarrows}{n}}{n_S \Theta_{H_2O}} = \overset{\rightleftarrows}{K} = \exp\left[-\frac{\Delta G_C^0}{RT} \mp \frac{\mu\sigma}{RT\varepsilon_{CC}} \mp \frac{A\mu^2}{RTd^3}\left(\frac{\vec{n} - \overleftarrow{n}}{n^* + \vec{n} + \overleftarrow{n}}\right)\right]$$



$$\vec{F} = (\vec{p}_1.\nabla)\vec{E} = \frac{1}{4\pi\varepsilon}(\vec{p}_1.\nabla)[\nabla[\vec{p}_2.\nabla\left(\frac{1}{r}\right)]]$$

$$\vec{\theta} = \frac{\vec{n}}{n^{\max}} = \frac{\vec{n}}{n^* + \vec{n} + \overleftarrow{n}}$$

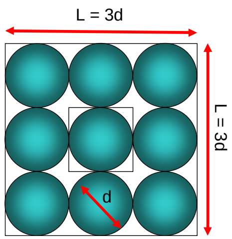
$$\overleftarrow{\theta} = \frac{\overleftarrow{n}}{n^{\max}} = \frac{\overleftarrow{n}}{n^* + \vec{n} + \overleftarrow{n}}$$

$$\vec{\theta} - \overleftarrow{\theta} = \frac{\vec{n} - \overleftarrow{n}}{n_S + \vec{n} + \overleftarrow{n}}$$

$$\begin{cases} X = \dfrac{\mu\sigma}{kT\varepsilon_{CC}} + \dfrac{A\mu^2}{kTd^3}(\vec{\theta} - \overleftarrow{\theta}) \\ a = 2e^{-\frac{\Delta G_C^0}{RT}} \end{cases}$$

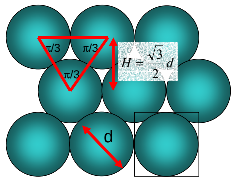
Change of variables

Packaging type 1



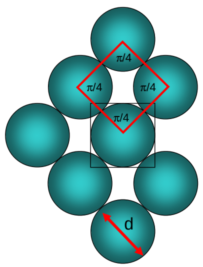
$$n^{\max} = \frac{9}{(3d)^2} = \frac{1}{d^2}$$

Packaging type 2



$$n^{\max} = \frac{\left(3\times\frac{1}{6}\right)}{\left(\frac{\sqrt{3}}{4}d^2\right)} = \frac{2}{\sqrt{3}d^2} \cong \frac{1.1547}{d^2}$$

Packaging type 3



$$n^{\max} = \frac{\left(4\times\frac{1}{4}\right)}{d^2} = \frac{1}{d^2}$$

$$n^{\max}$$

$$\frac{a\,Sinh[X]}{\dfrac{n^*}{n_s\Theta_{H_2O}} + a\,Cosh[X]} = \sigma\frac{d^3}{\varepsilon_{CC}A\mu} - X\frac{kTd^3}{A\mu^2}$$

Transcendental equation

$$X(\sigma)$$

$$\Delta\varphi_2 = \frac{\Gamma(\sigma)}{\varepsilon_{CD}} = \frac{\mu(\vec{n} - \overleftarrow{n})}{\varepsilon_{CD}} = -\frac{a n_s \Theta_{H_2O}\mu Sinh[X(\sigma)]}{\varepsilon_{CD}}$$

Compact layer as a modulated-variable capacitance with σ

$$\eta(r,t) = \Delta\varphi_1 + \Delta\varphi_2 = f(\sigma)$$

$$\frac{1}{C_{CC}(\sigma)} = \frac{d\eta}{d\sigma}$$

State variable: electronic charge surface density

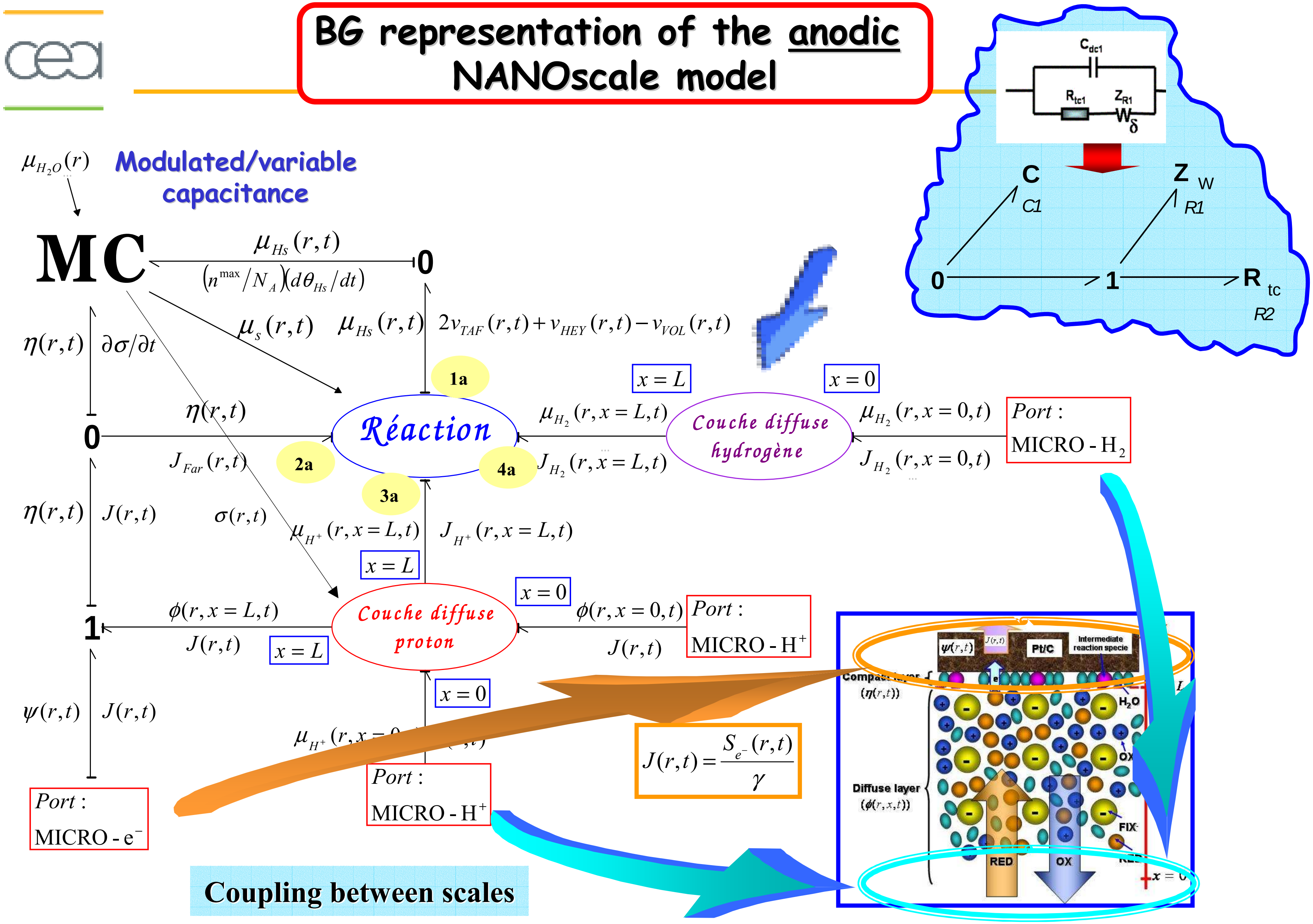
$$C_{CC}(\sigma) = \frac{1}{\dfrac{d\eta}{d\sigma}} = \frac{1}{+\dfrac{d}{\varepsilon_{CC}} + \dfrac{a\Theta_{H_2O} n_S \mu Cosh[X(\sigma)]}{\varepsilon_{CD}} \dfrac{\kappa}{\dfrac{\left(\dfrac{n^*}{n_s\Theta_{H_2O}} Cosh[X(\sigma)] + a\right)a}{\left(\dfrac{n^*}{n_s\Theta_{H_2O}} + aCosh[X(\sigma)]\right)^2} + \beta}}$$

When n_S towards 0
(full coverage with water molecules)

$$C_{CC} \cong C_{Stern} = \frac{\varepsilon_{CC}}{d}$$

Stern's capacitance

BG representation of the anodic NANOscale model



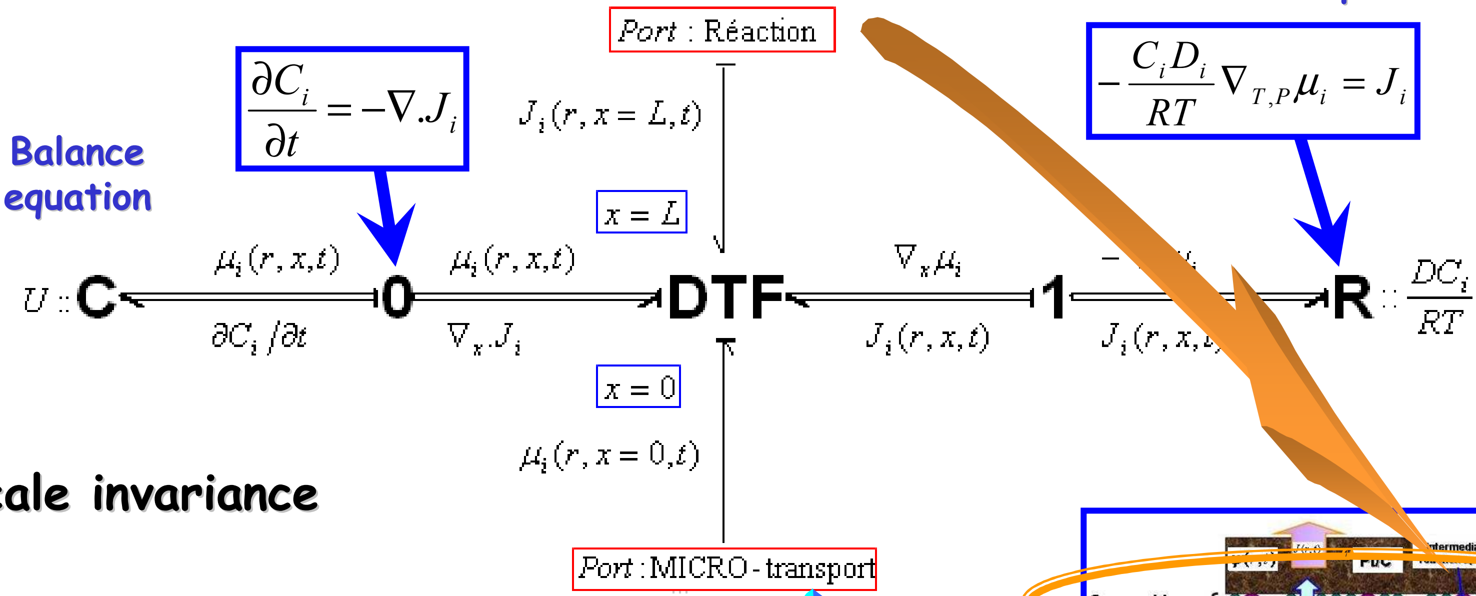
Anodic « hydrogen diffuse layer » BG

Constitutive equation

$$-\frac{C_i D_i}{RT}\nabla_{T,P}\mu_i = J_i$$

Balance equation

$$\frac{\partial C_i}{\partial t} = -\nabla . J_i$$

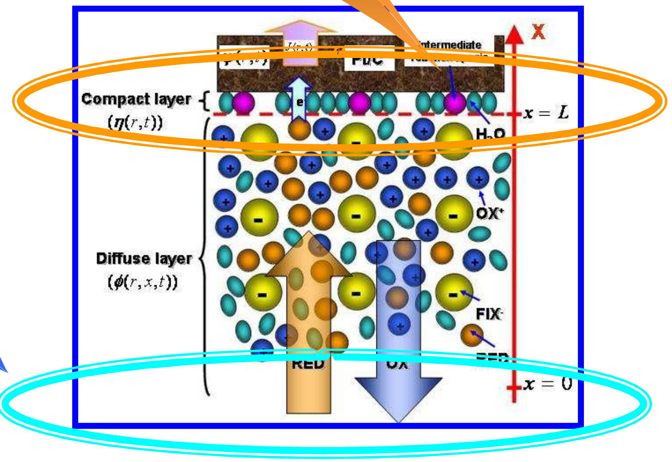


Scale invariance

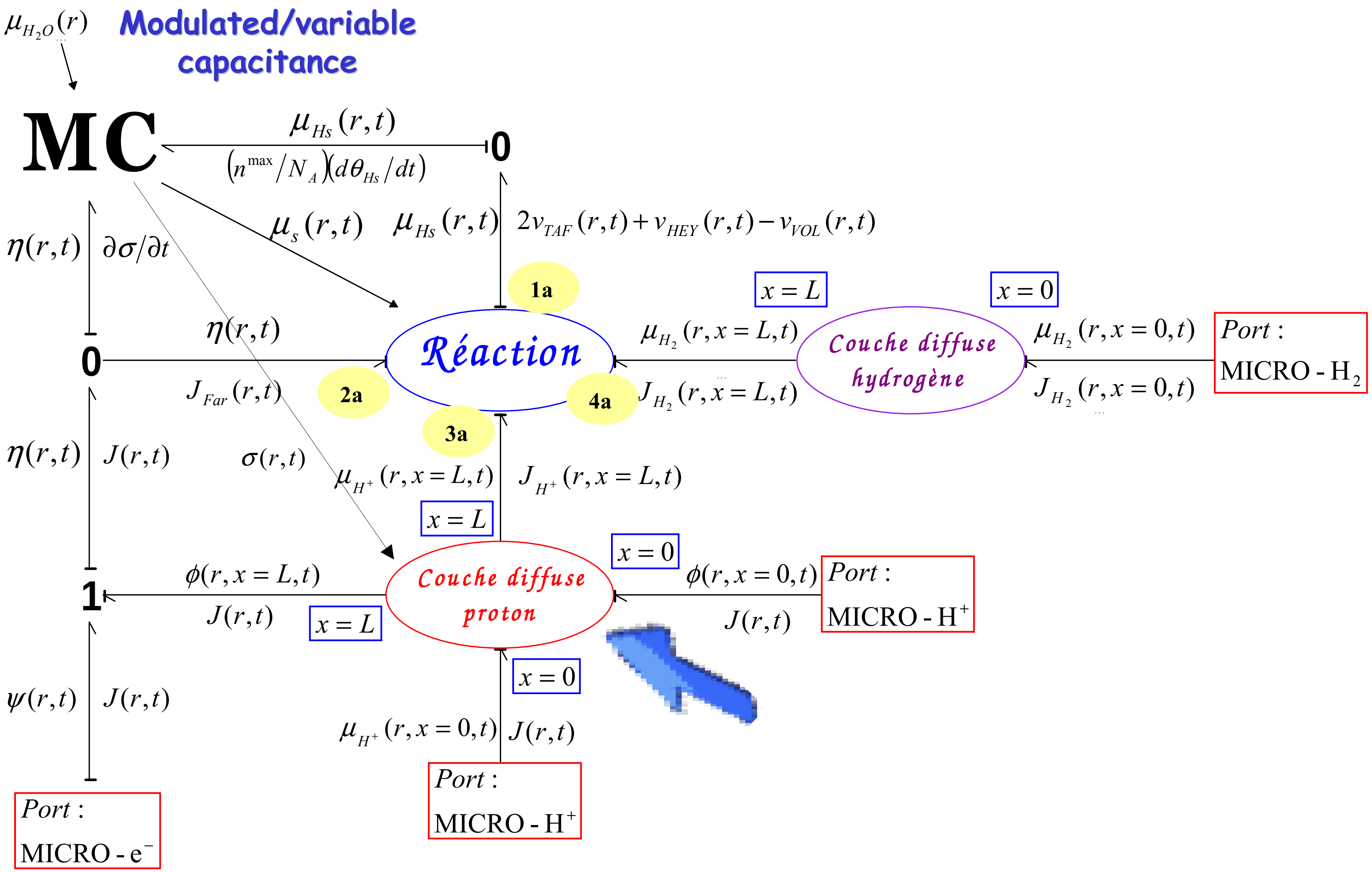
Coupling between scales

$$C_{H_2}(r, x = 0, t) = C_{H_2}(r, z = e_{NI}, t)$$

$$\left\{ J_{H_2}(r, z = e_{NI}, t) = J_{H_2}(r, x = 0, t) \right\}$$

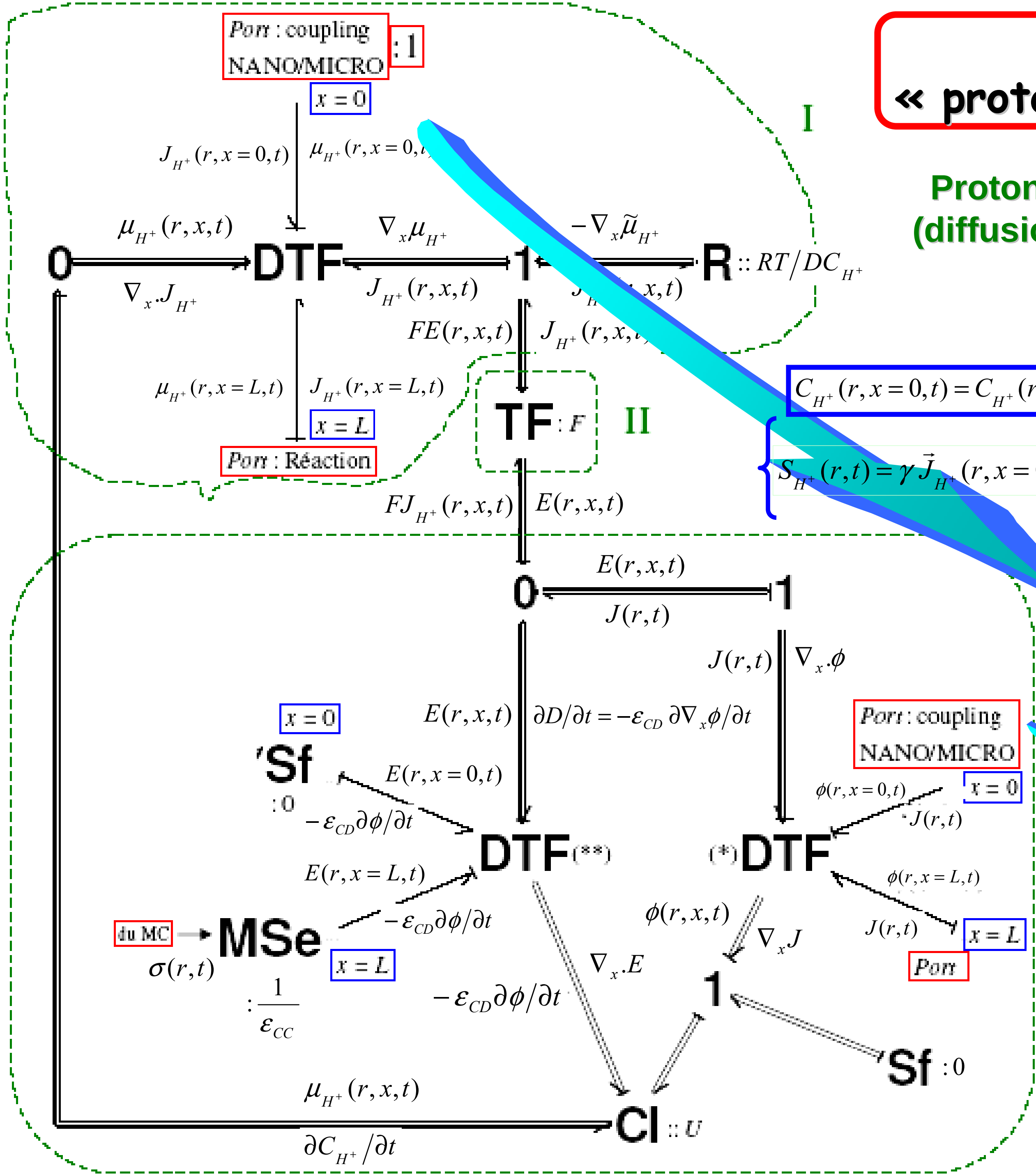


BG representation of the anodic NANOscale model



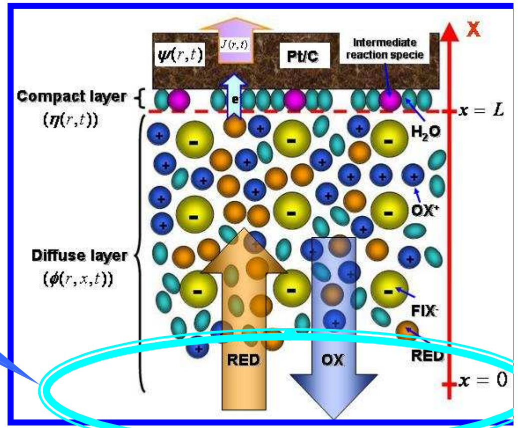
Anodic « proton diffuse layer » BG

Protonic transport (diffusion/migration)



$$C_{H^+}(r,x=0,t)=C_{H^+}(r,t)$$

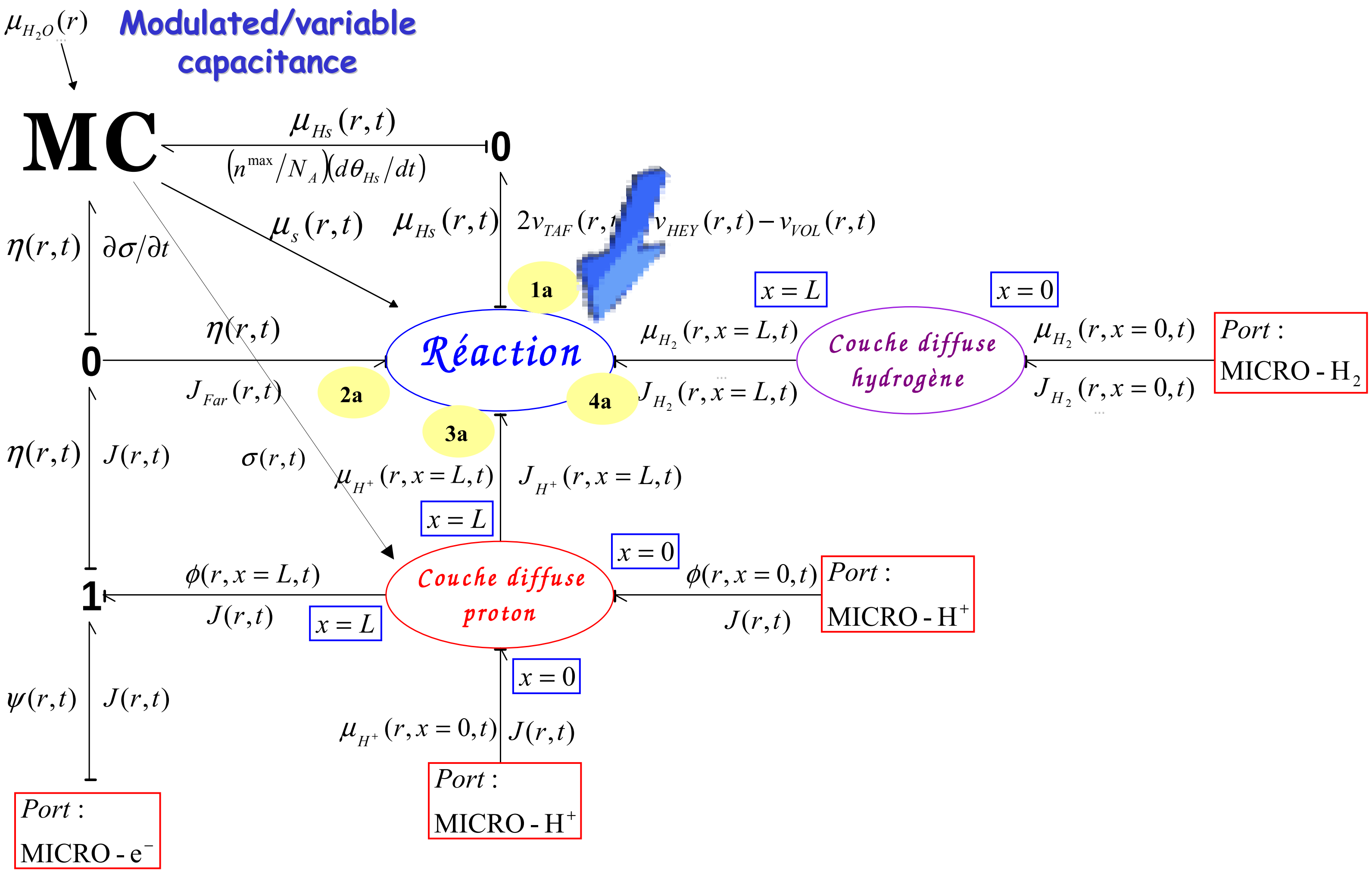
$$S_{H^+}(r,t)=\gamma\,\vec{J}_{H^+}(r,x=0,t)$$



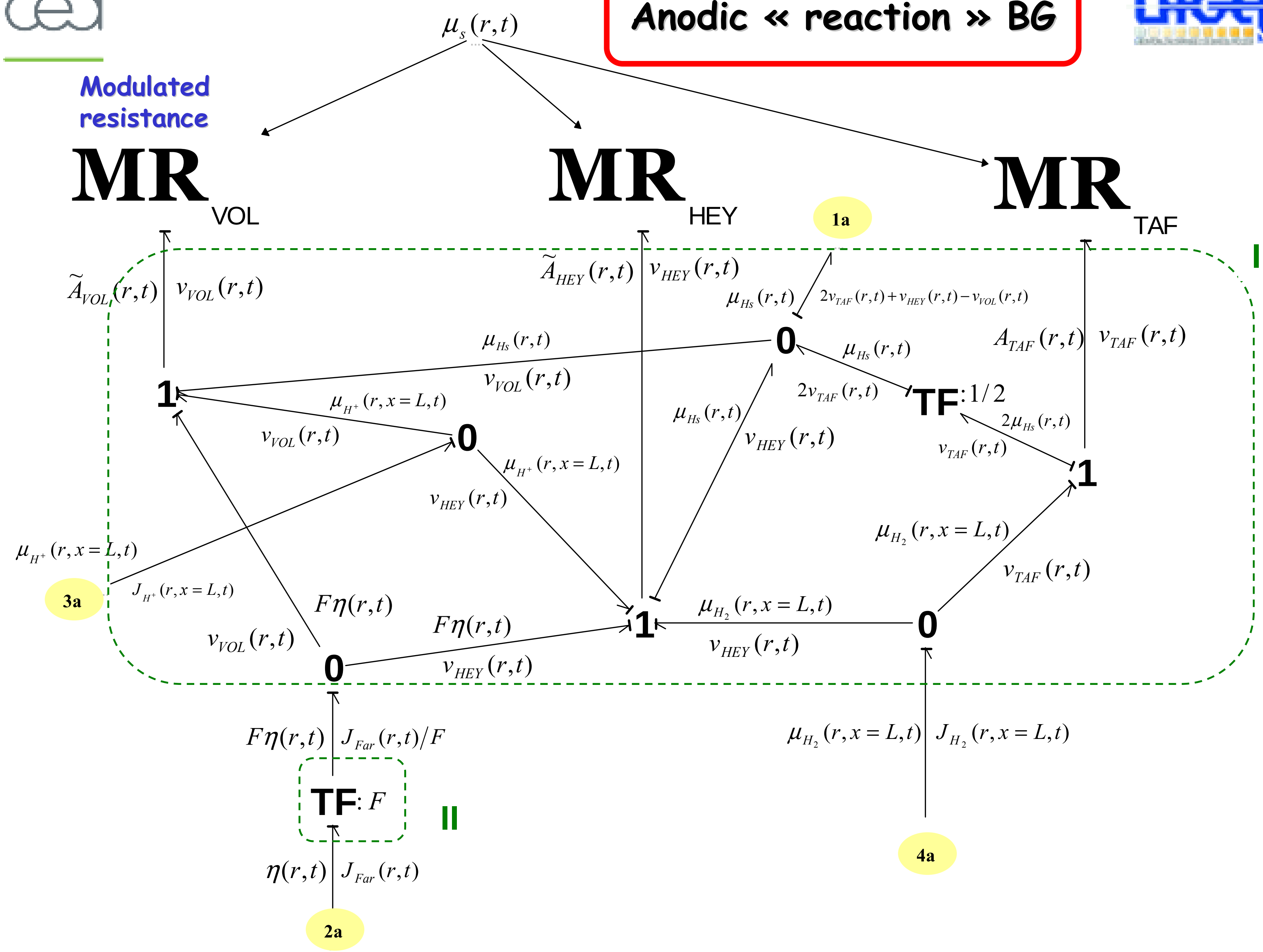
$$\phi^{NANO}(r,x=0,t)=\phi^{MICRO}(r,t)$$

Ionic potential dynamics coupled with proton accumulation

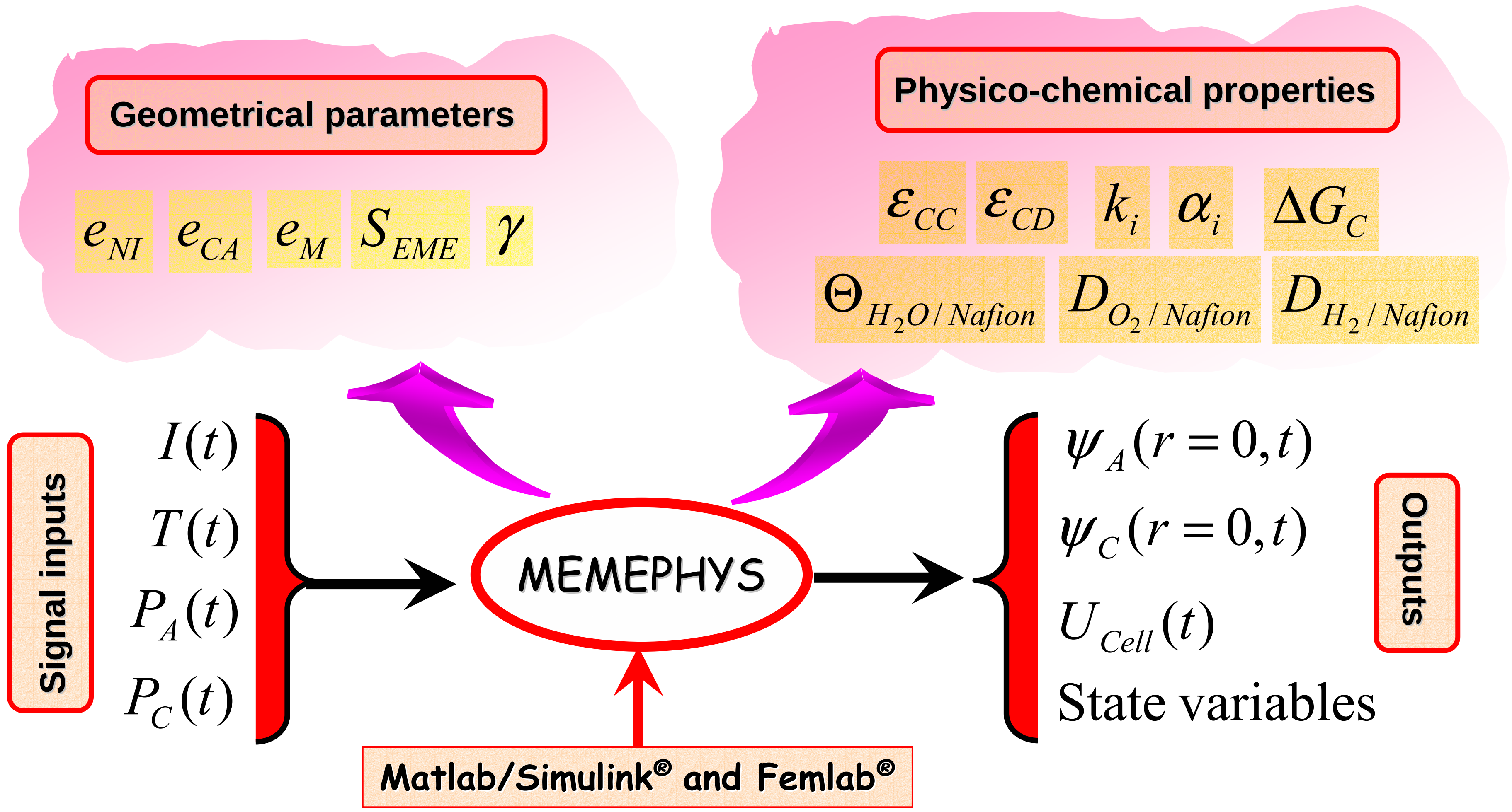
BG representation of the anodic NANOscopic model



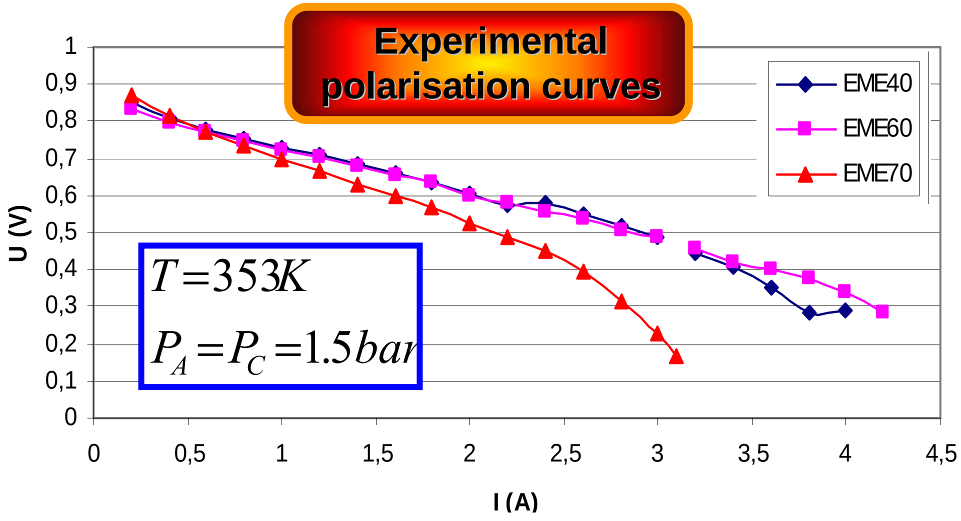
Anodic « reaction » BG



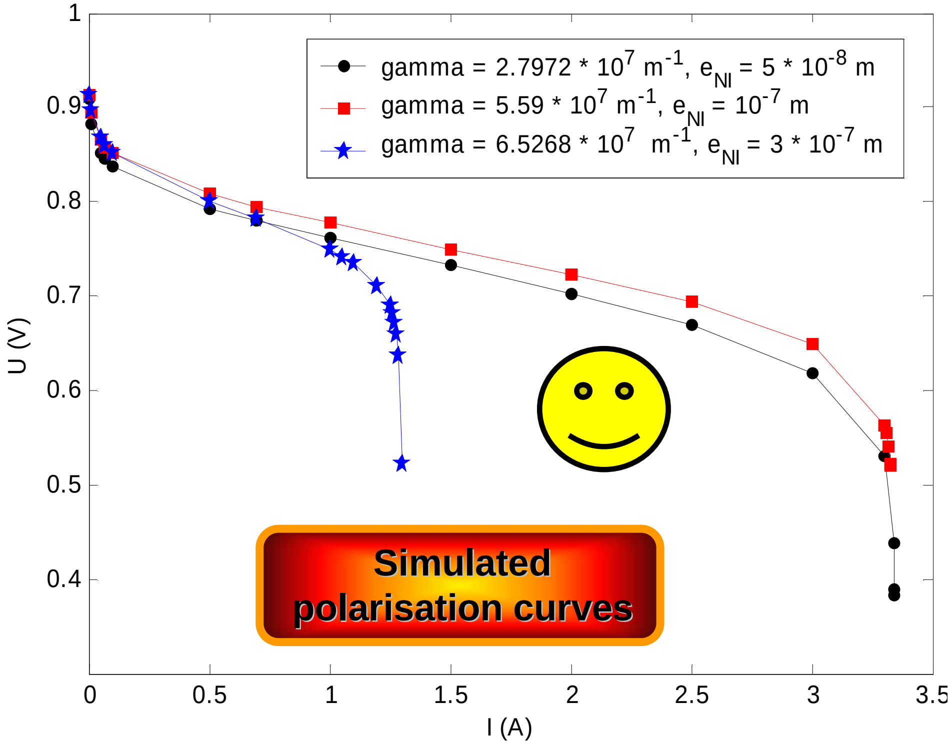
M.E.M.E.PHYS. simulation algorithm

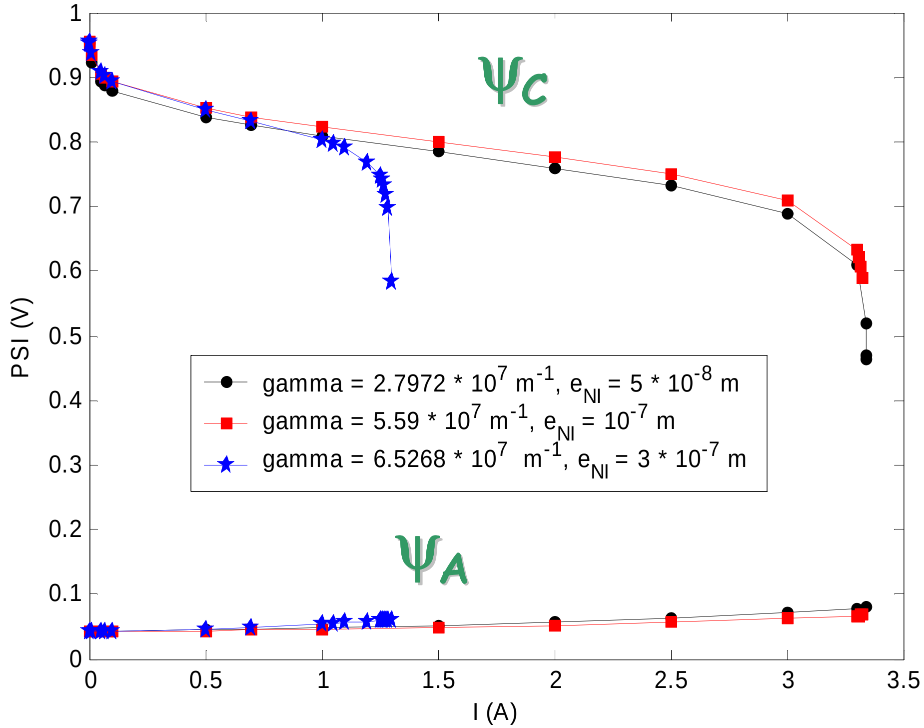


Electrodes design: finding optimums between Nafion® and Platinum loadings



AME	Chargement surfacique moyen en Pt (mg/cm²)	γ moyen (m²/m³)	Epaisseur électrodes (µm)	Epaisseur Membrane (µm)
EME 40%	0.5	2.7972×10^{7}	15	50 (Nafion® 112)
EME 60%	0.7	5.59×10^{7}	15	50 (Nafion® 112)
EME 70%	0.9	6.52681×10^{7}	15	50 (Nafion® 112)

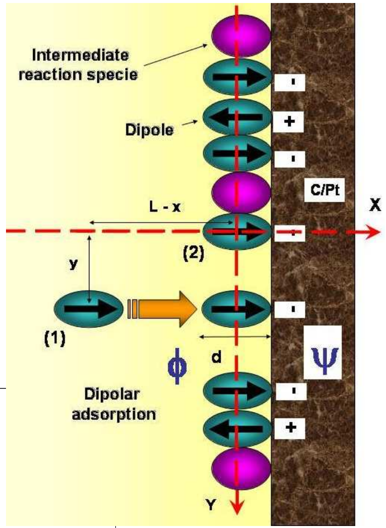


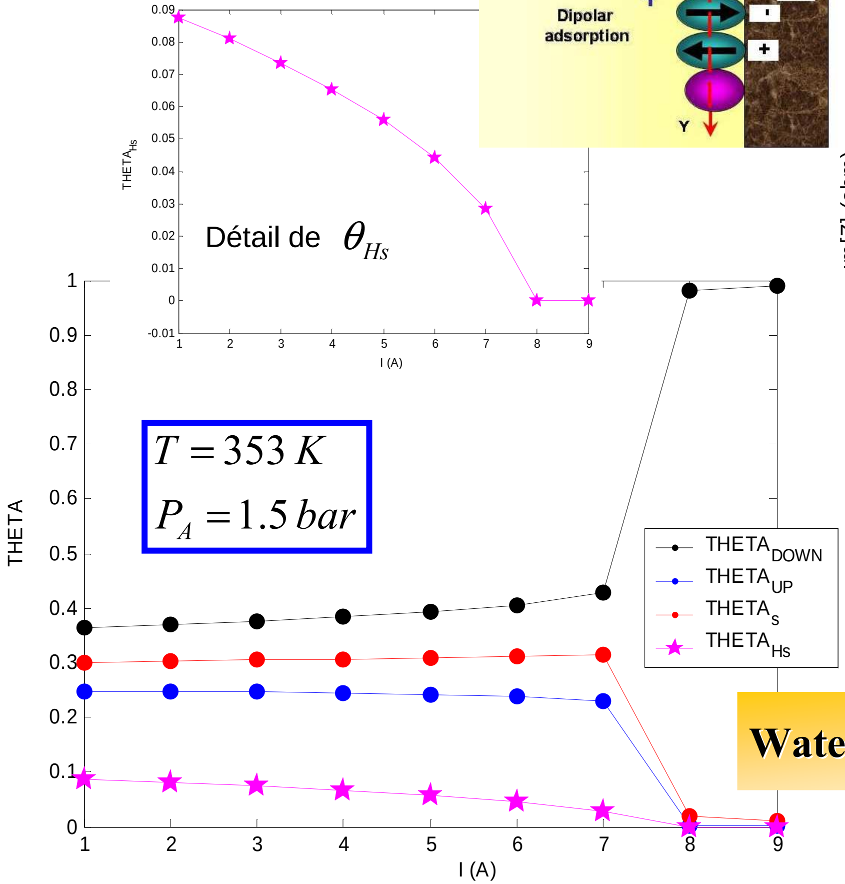


Diagnostics (1/4)

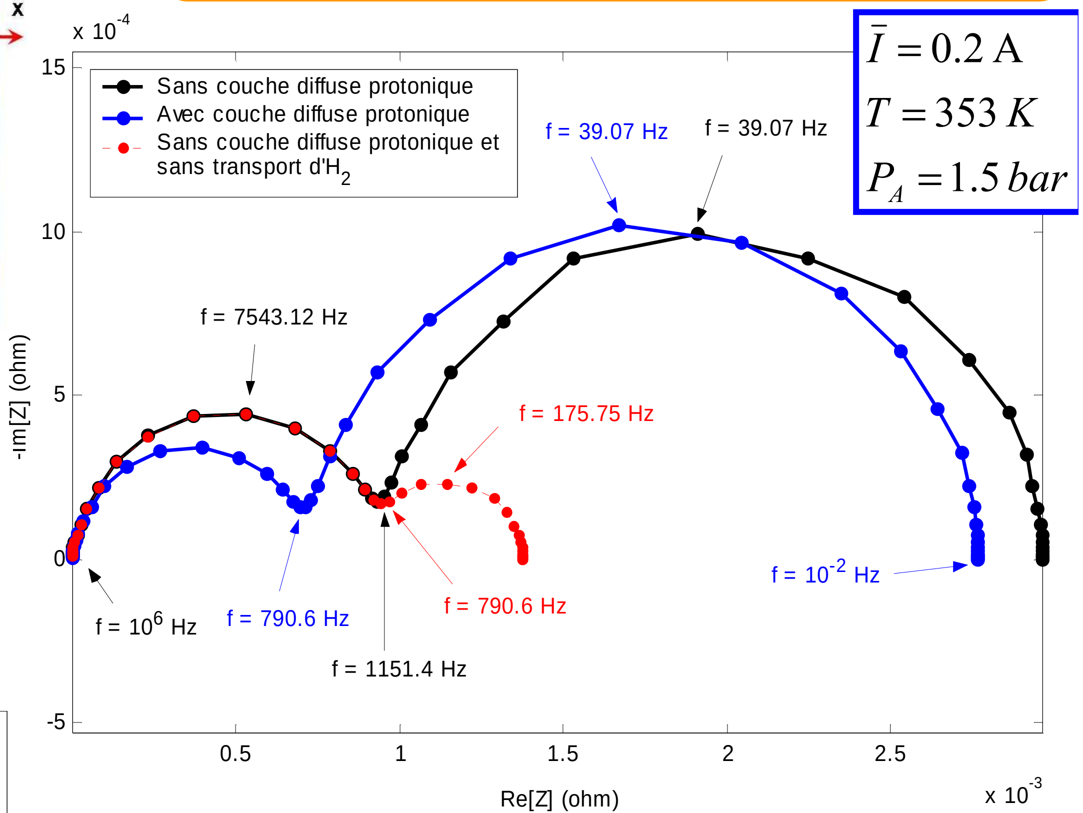
Stationary surface coverages

$$\vec{\theta} > \overleftarrow{\theta} \Rightarrow \eta^{Frumkin}$$





Contribution of different phenomena to the anodic NANOmodel



Water molecules parasite intermediate adsorption

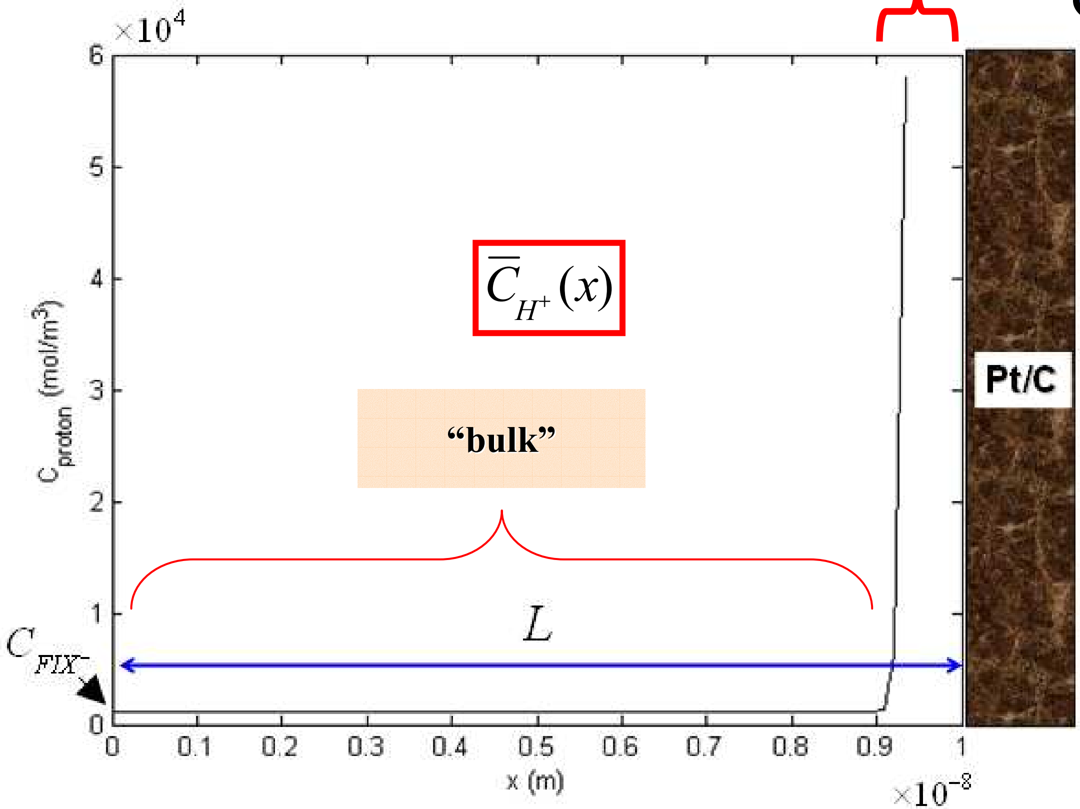
Diagnostics (2/4)

Anodic stationary proton diffuse layer profile

Diffuse layer thickness

$$\begin{cases} -\dfrac{\varepsilon_{CD}}{F}\dfrac{\partial^4\phi}{\partial x^4}-\dfrac{\varepsilon_{CD}}{RT}\dfrac{\partial^3\phi}{\partial x^3}\dfrac{\partial\phi}{\partial x}-\dfrac{\varepsilon_{CD}}{RT}\left(\dfrac{\partial^2\phi}{\partial x^2}\right)^2+\dfrac{FC_{FIX}}{RT}\dfrac{\partial^2\phi}{\partial x^2}=0 \\ \delta=\dfrac{1}{F}\sqrt{\dfrac{\varepsilon_{CD}RT}{C_{FIX}}} \end{cases}$$

Debye's length



Characteristic length: electric screen length

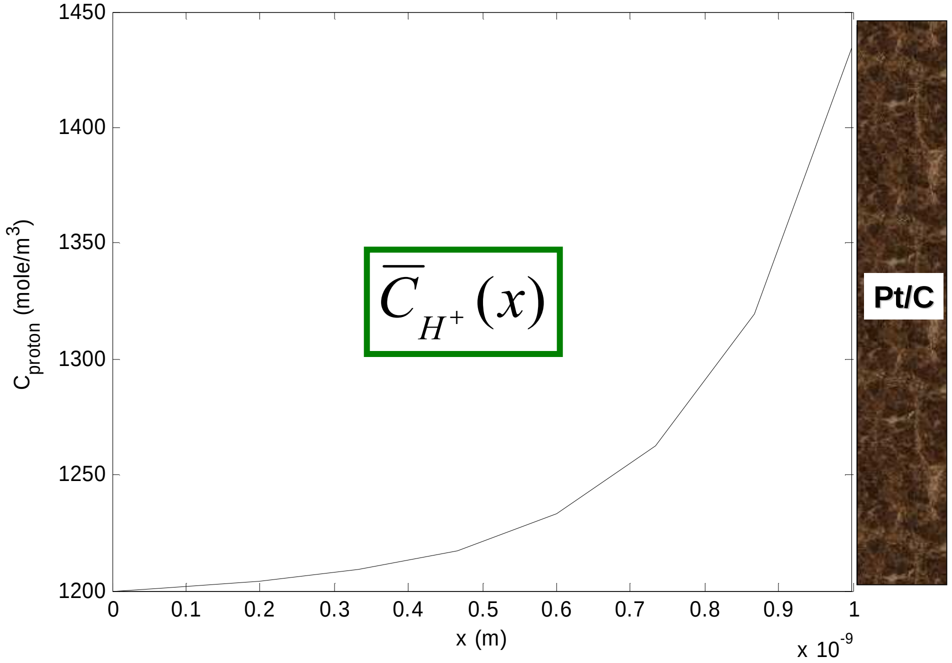
$I = 7$ A

$T = 353\ K$

$P_A = 1.5\ bar$

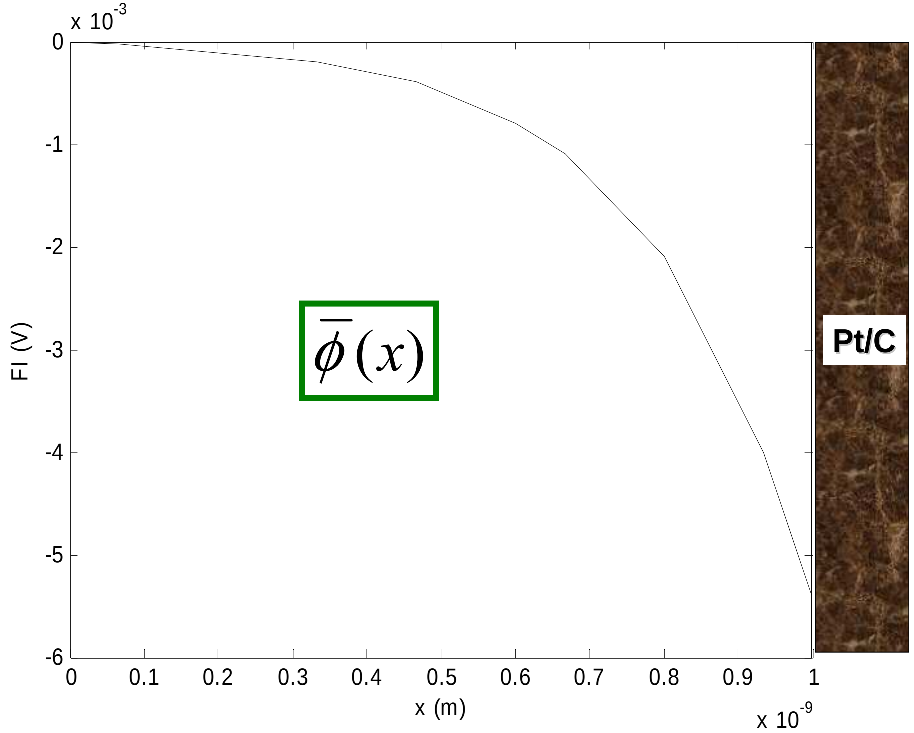
$\Theta_{H_2O} = 1$

Constant proton concentration in the bulk because constant C_{FIX}



Anodic equilibrium proton concentration diffuse layer profile

$$I = 0\text{ A}$$
$$T = 353\,K$$
$$P_A = 1.5\,bar$$
$$\Theta_{H_2O} = 1$$



Anodic equilibrium potential diffuse layer profile

Non uniform proton concentration at equilibrium conditions

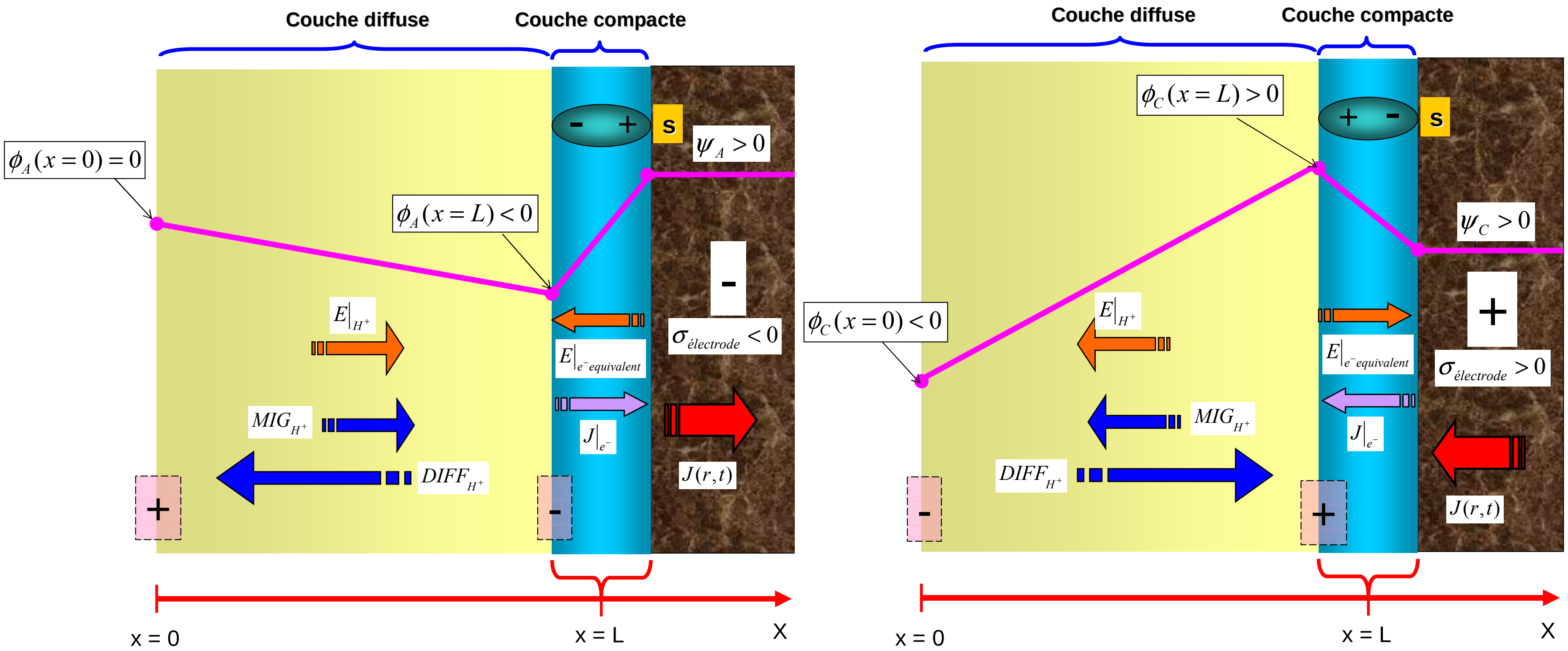
F

Diagnostics (4/4)

Electric potential and flux profiles through the NANOscopic models

Anodic NANOmodel

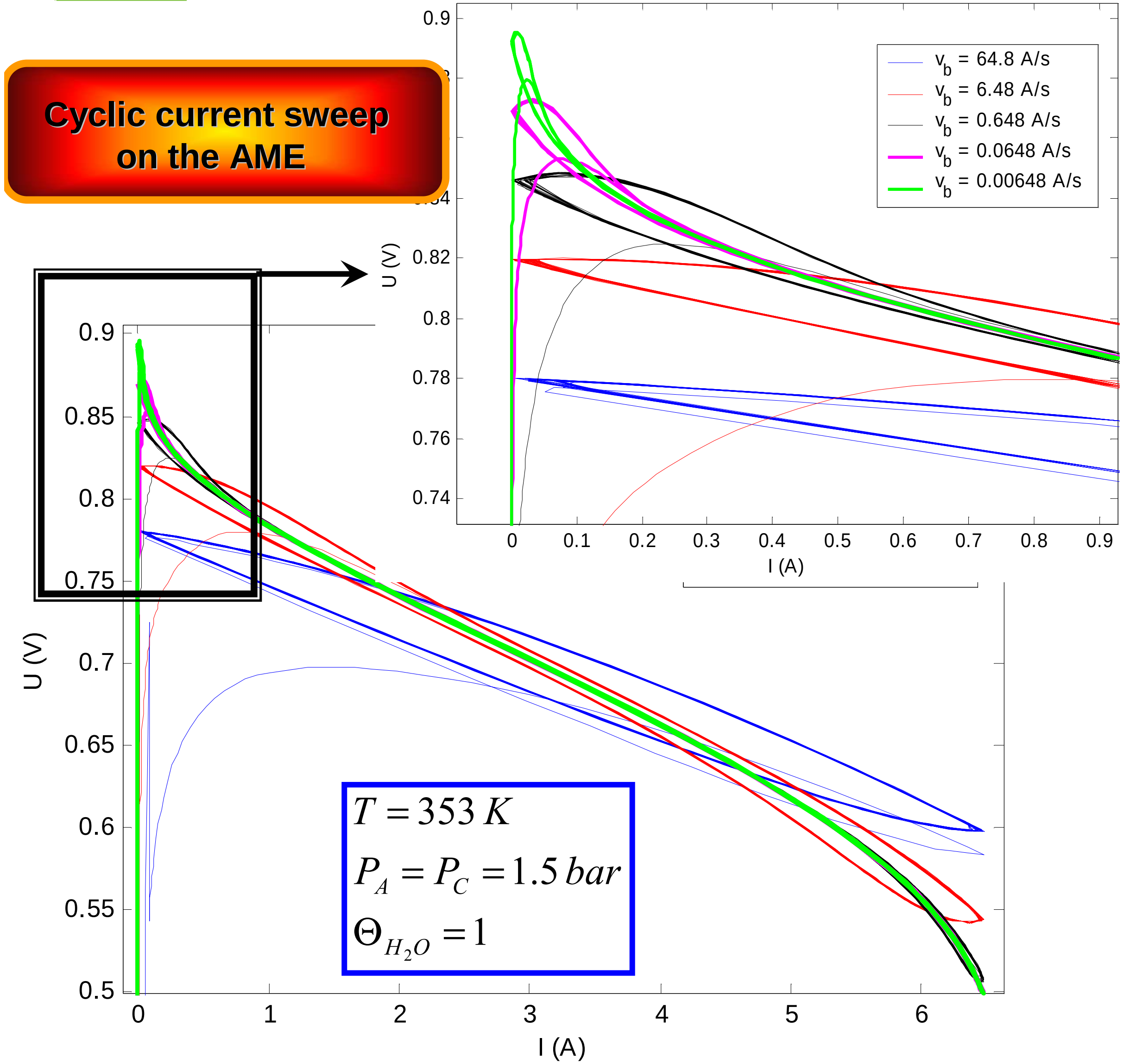
Cathodic NANOmodel



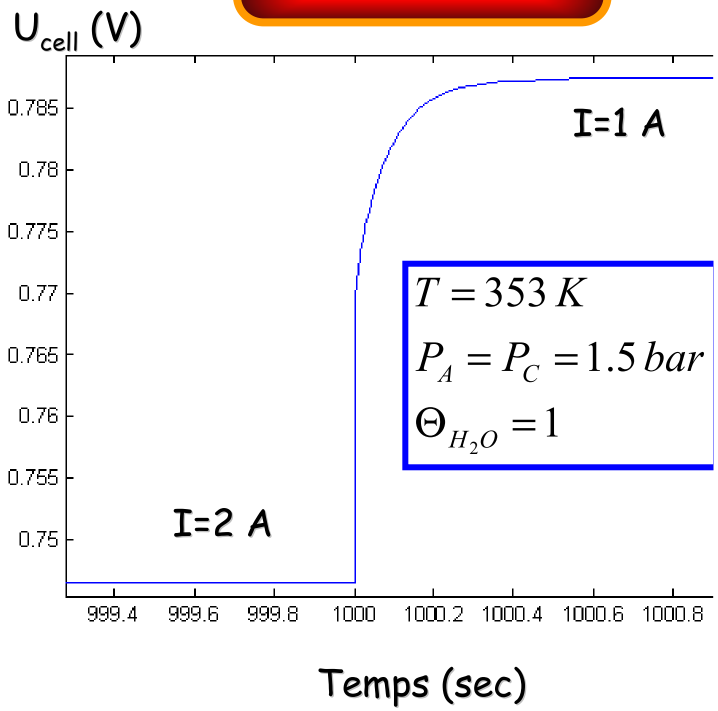
Protons in the diffuse layer go up the electric potential ! (migration and diffusion forces: opposed)

Transient response simulation

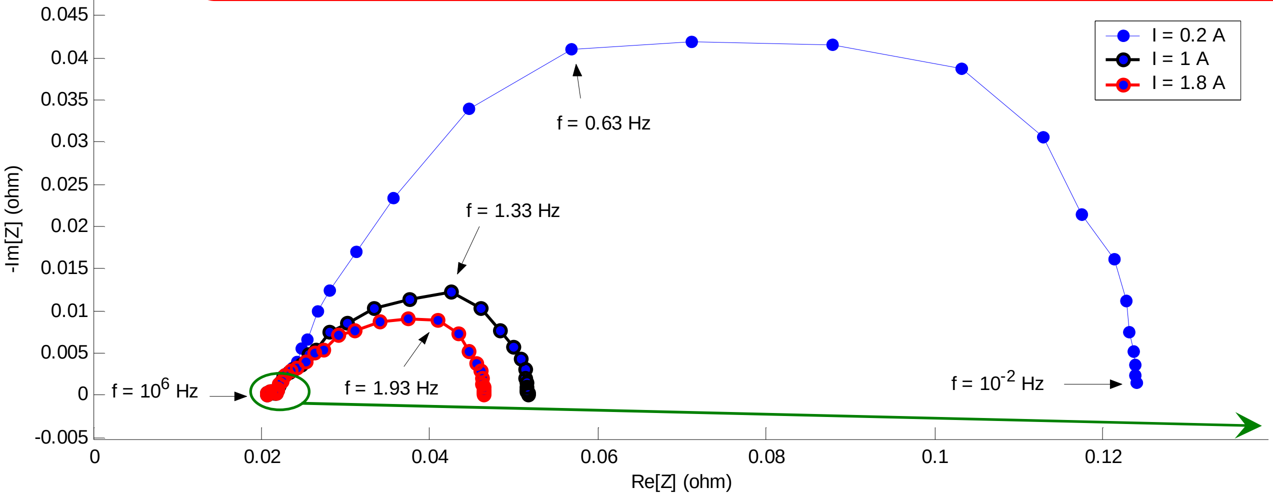
Cyclic current sweep on the AME

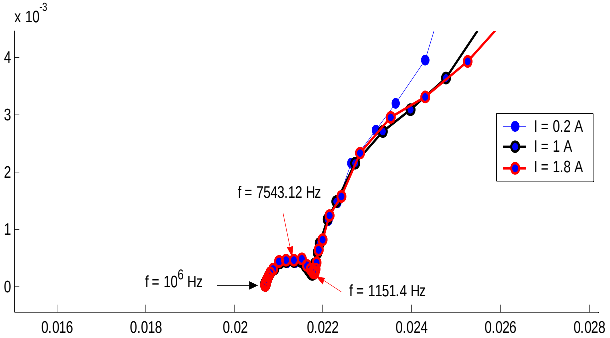


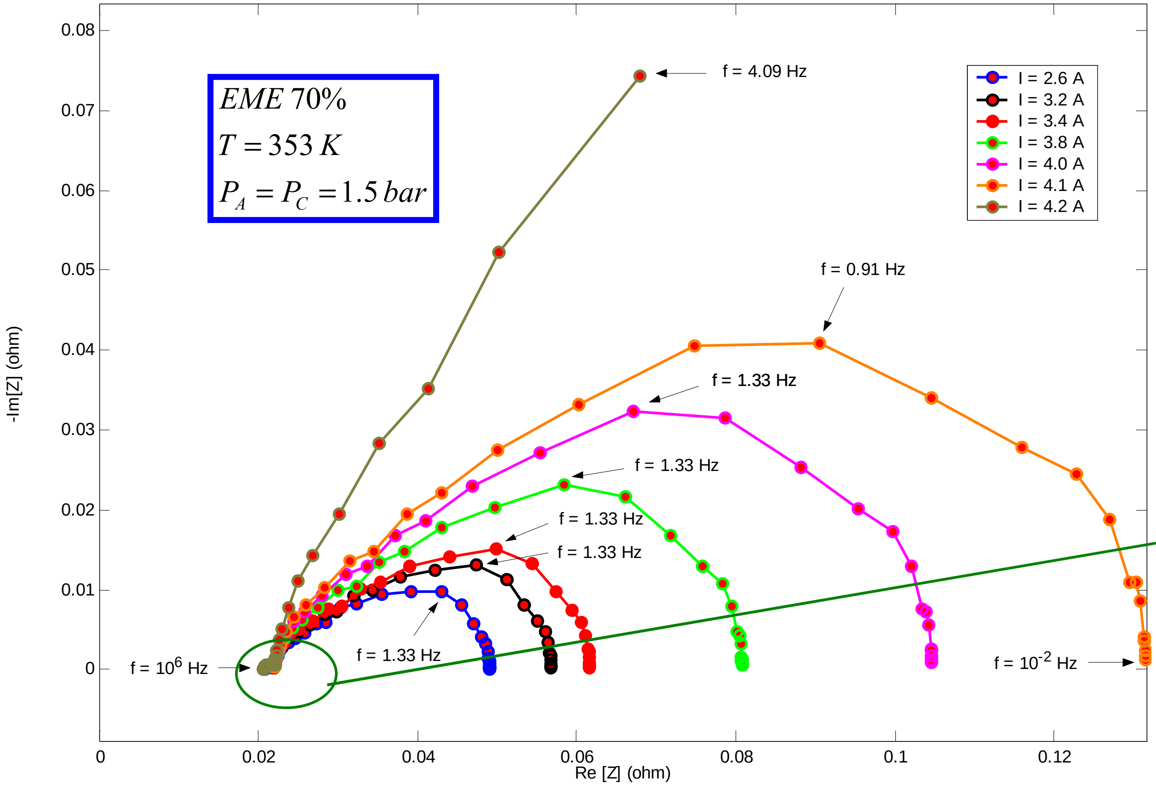
Current steps on the AME



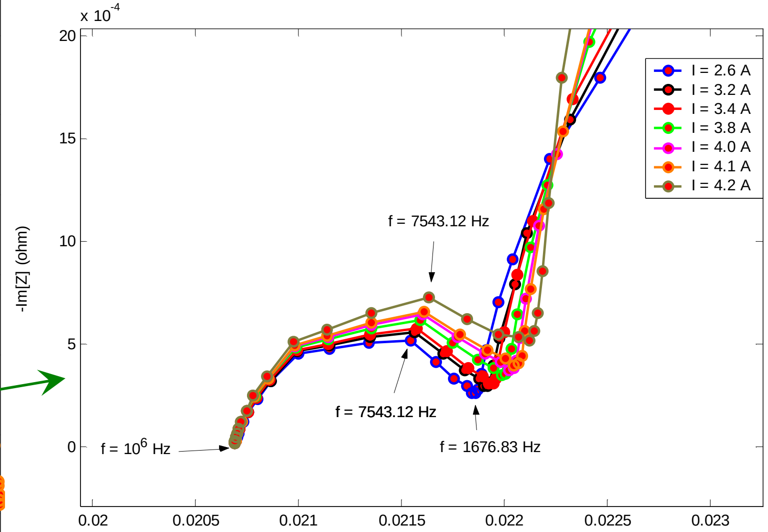
MEMEPHYS EIS sensitivity to the nominal current







Simulated AME impedance spectra



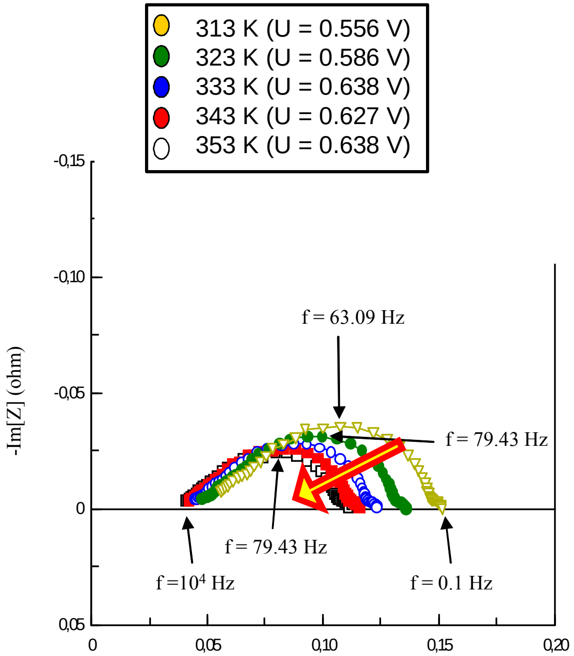
MEMEPHYS EIS sensitivity to the temperature

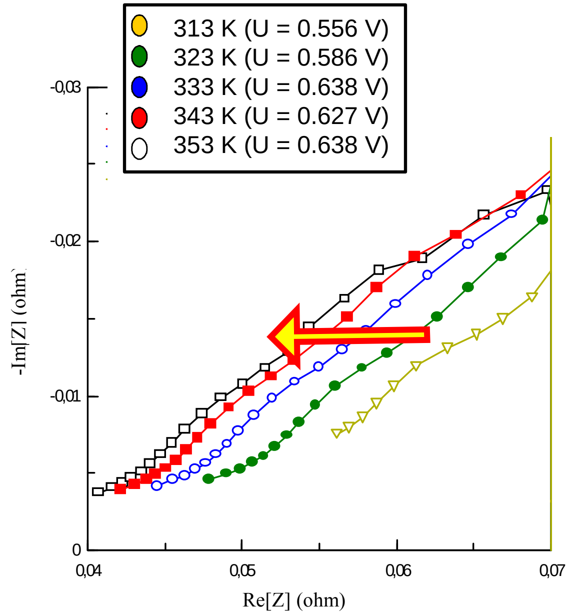
Experimental AME impedance spectra

EME 60%

$\bar{I} = 2\ A$

$P_A = P_C = 1.5\ bar$

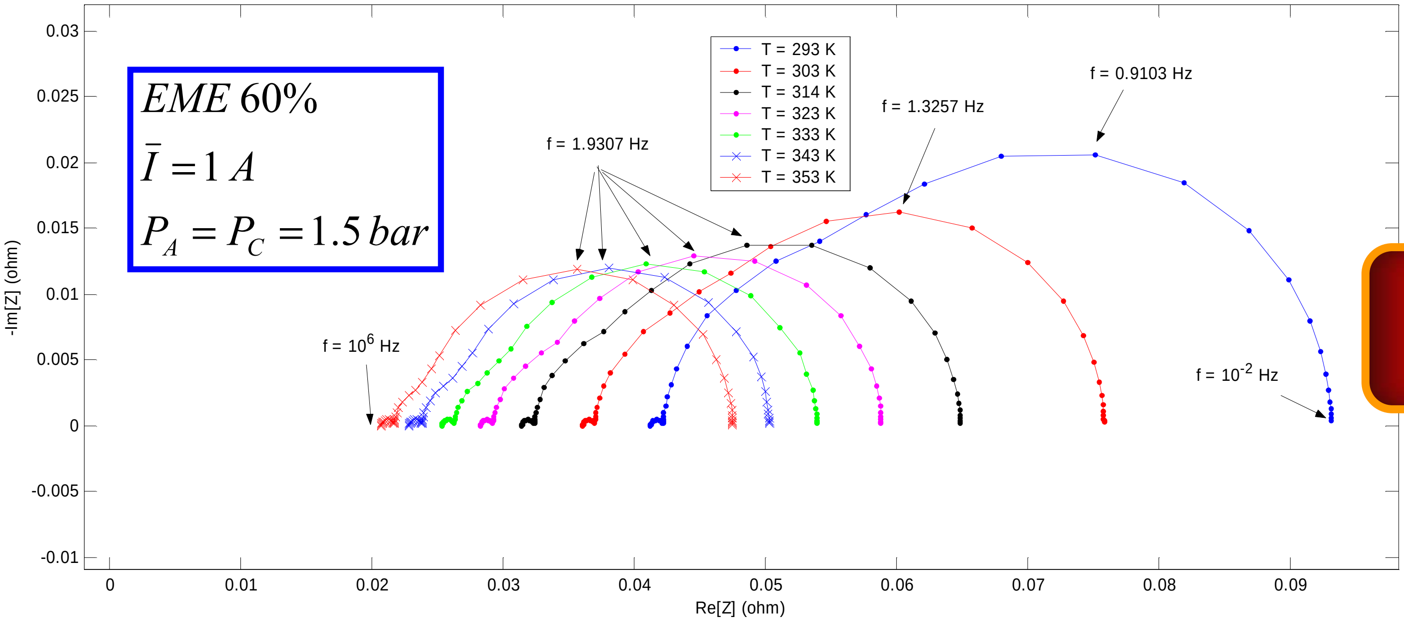




EME 60%

$\bar{I} = 1\ A$

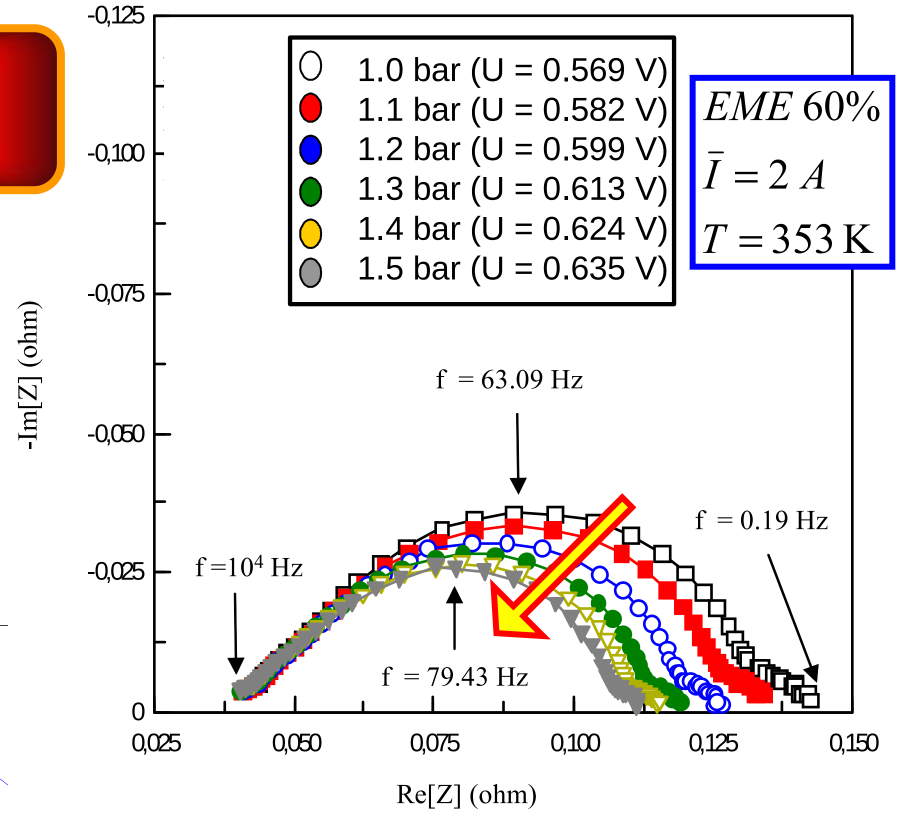
$P_A = P_C = 1.5\ bar$



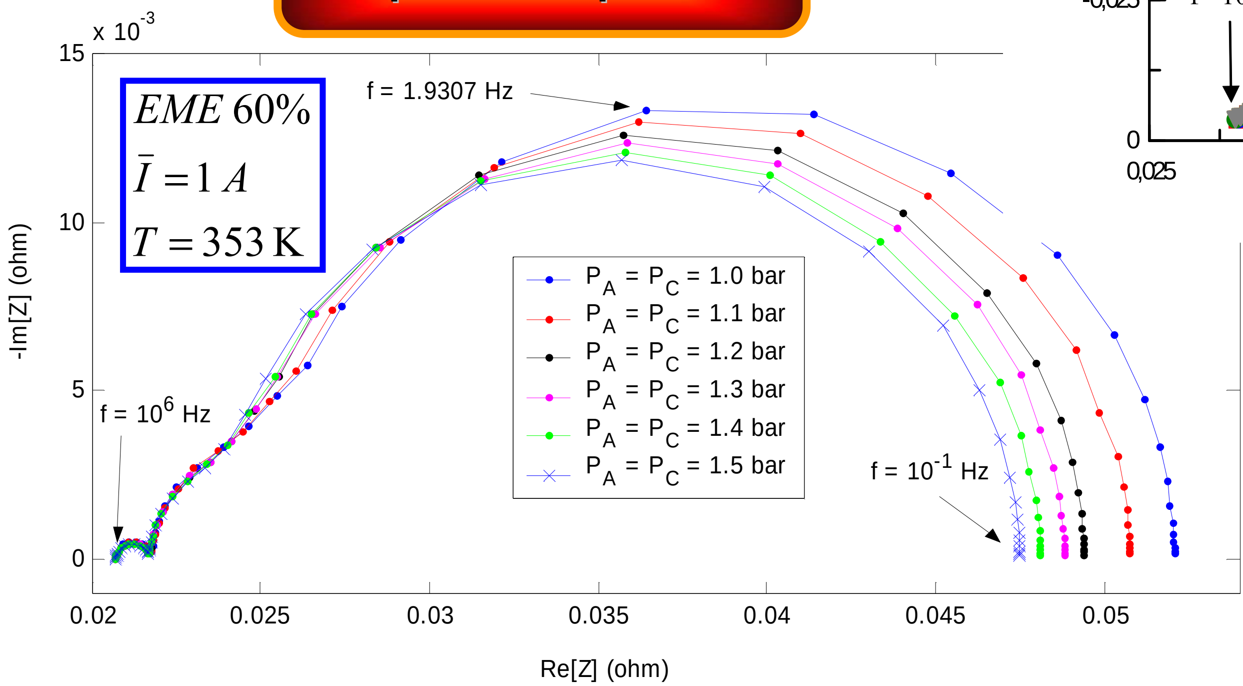
Simulated AME impedance spectra

MEMEPHYS EIS sensitivity to the reactant pressures

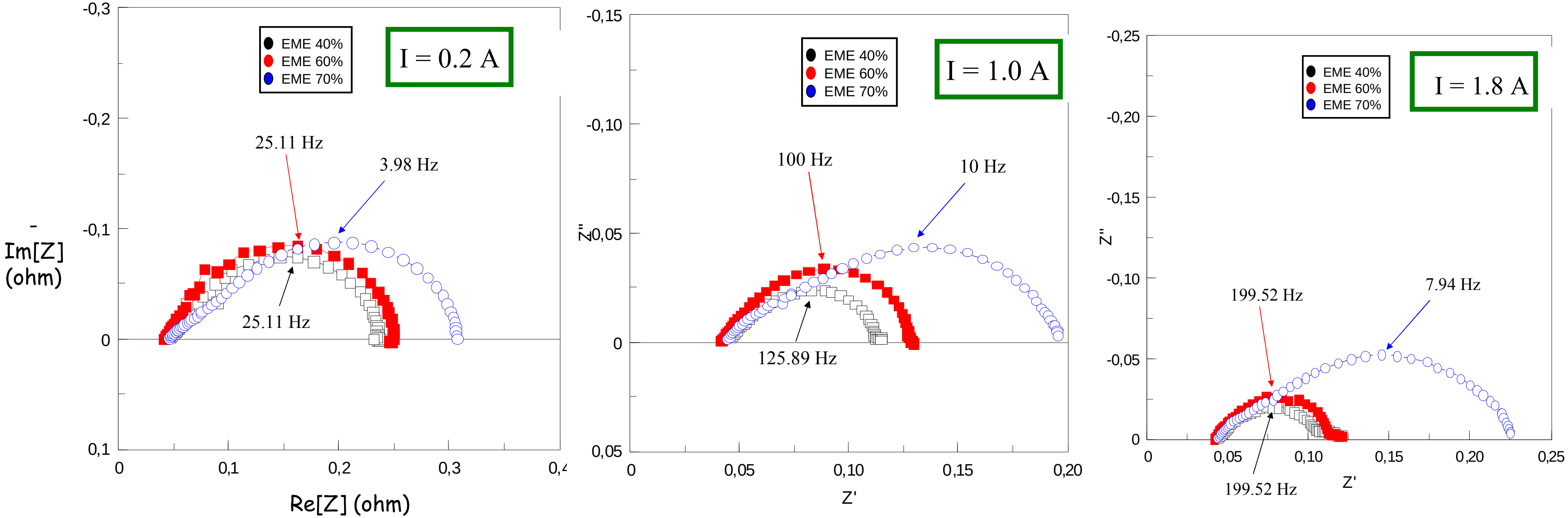
Experimental AME impedance spectra

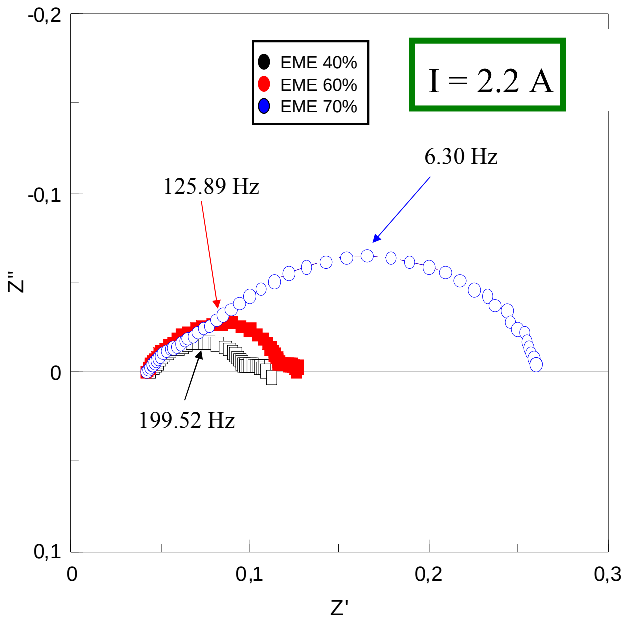


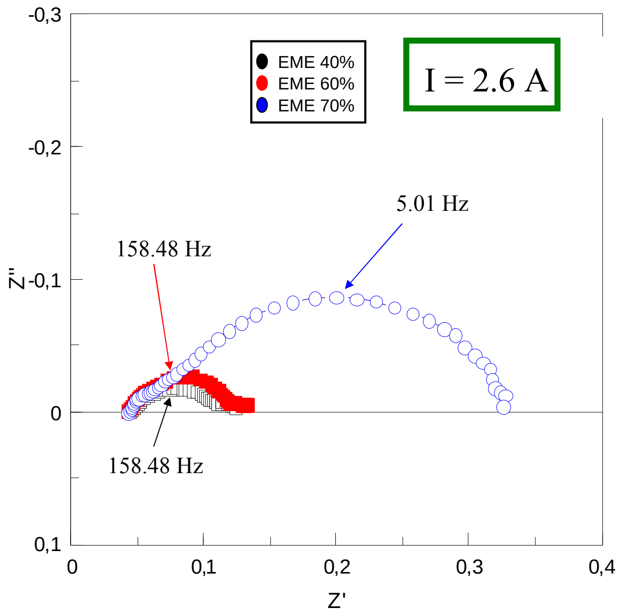
Simulated AME impedance spectra



Experimental EIS sensitivity to electrodes composition







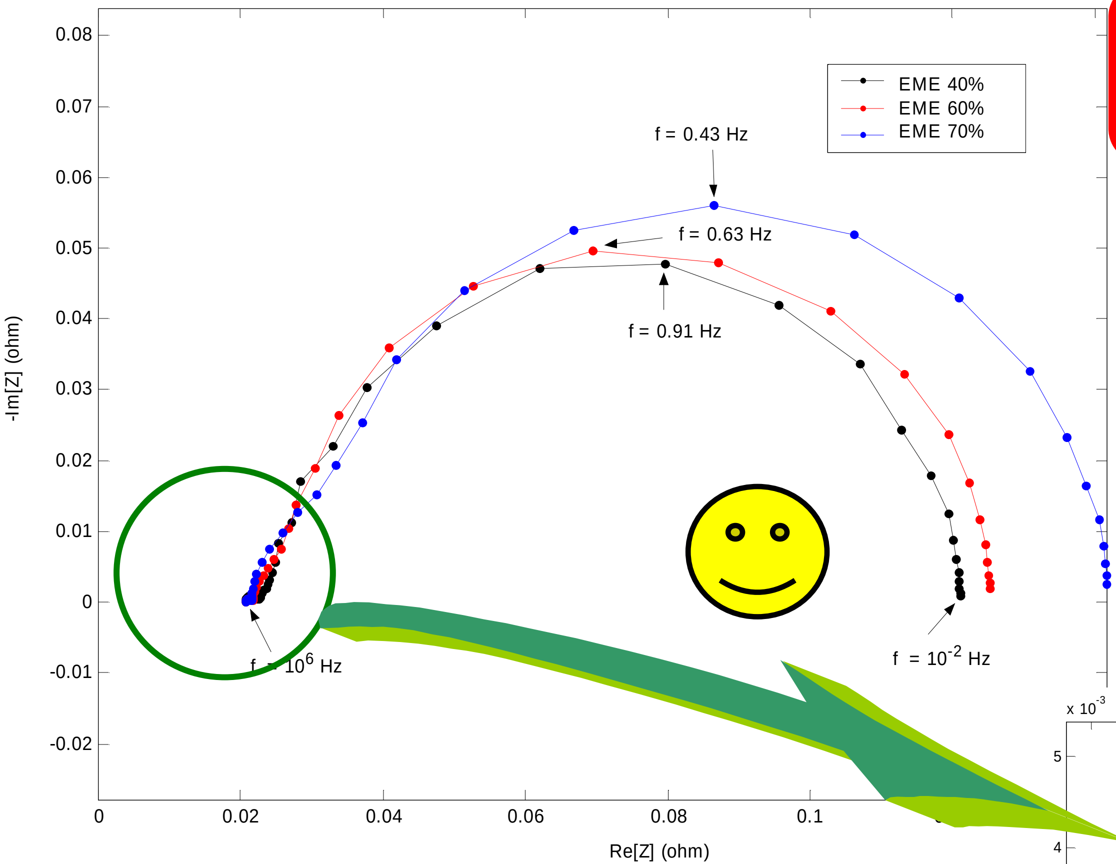
$T = 353\,K$

$P_A = P_C = 1.5\,bar$

$Amp : 5\,\%$ de $\bar{I}$

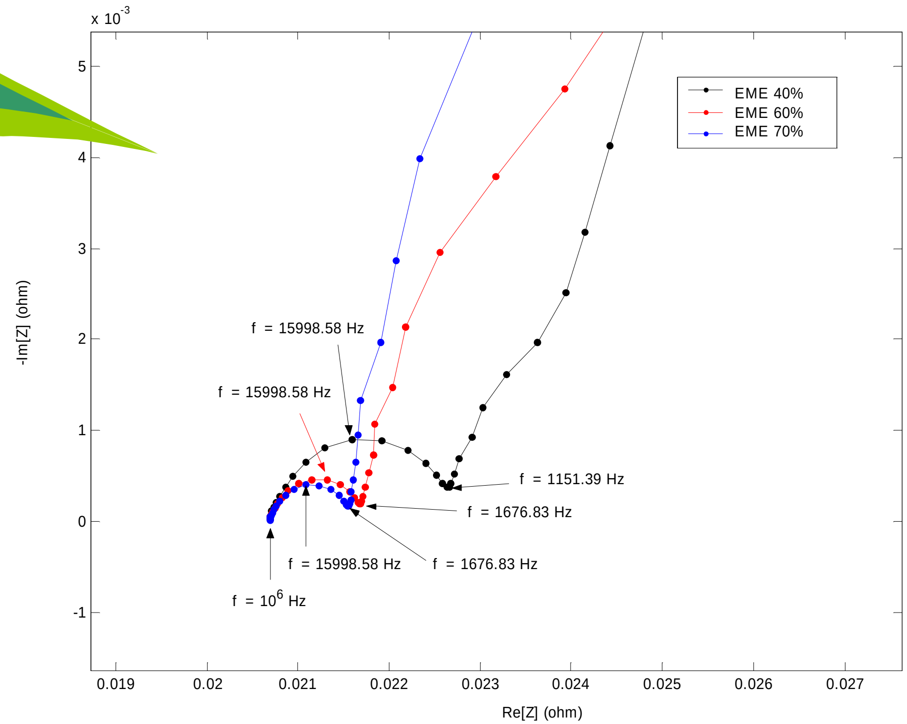
$10kHz - 0.07\,Hz$

MEMEPHYS EIS sensitivity to electrodes composition



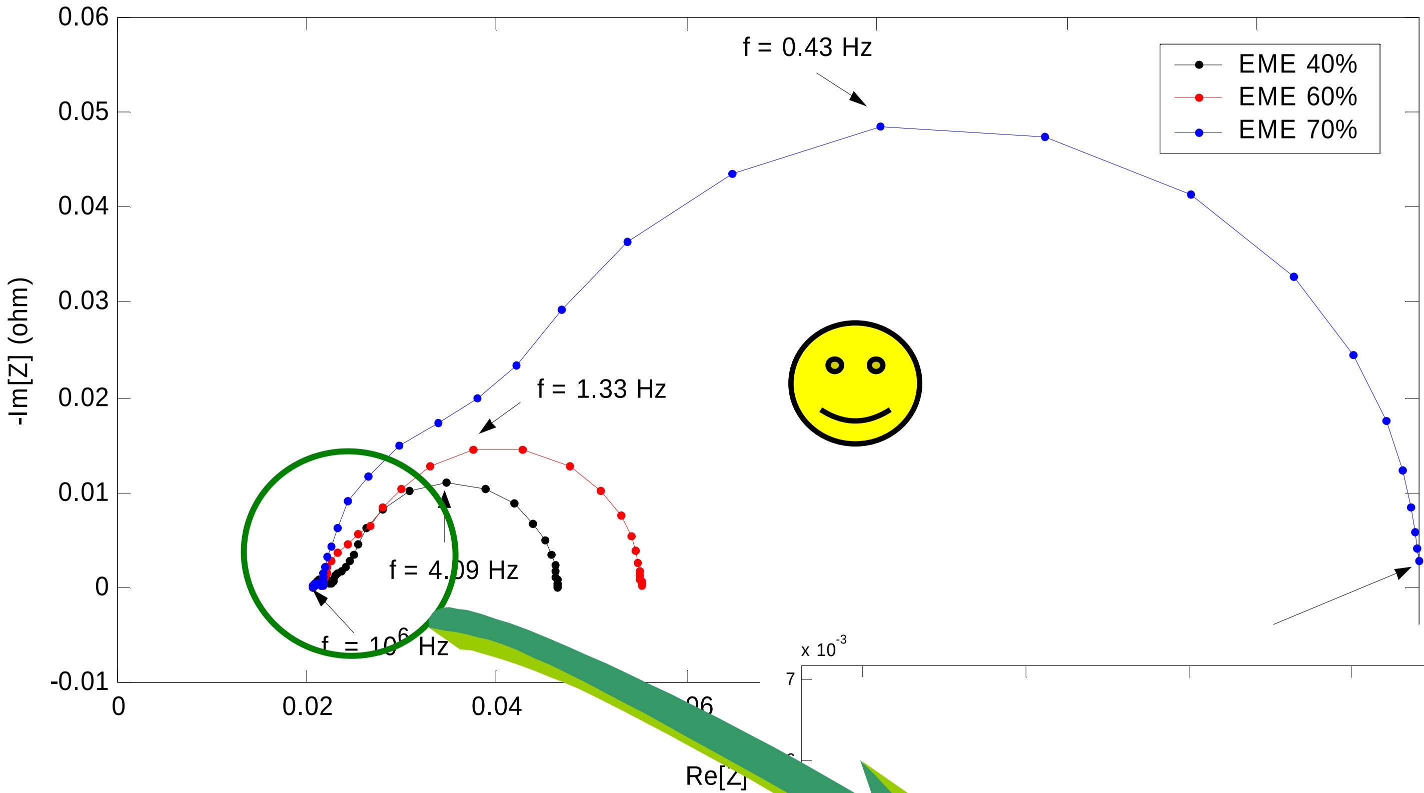
Simulated AME impedance spectra

$$T = 353\,K$$
$$P_A = P_C = 1.5\,bar$$
$$\bar{I} = 0.2\,A$$



e_{NI} (m)

EME 40%	10^{-8}
EME 60%	10^{-7}
EME 70%	3×10^{-7}

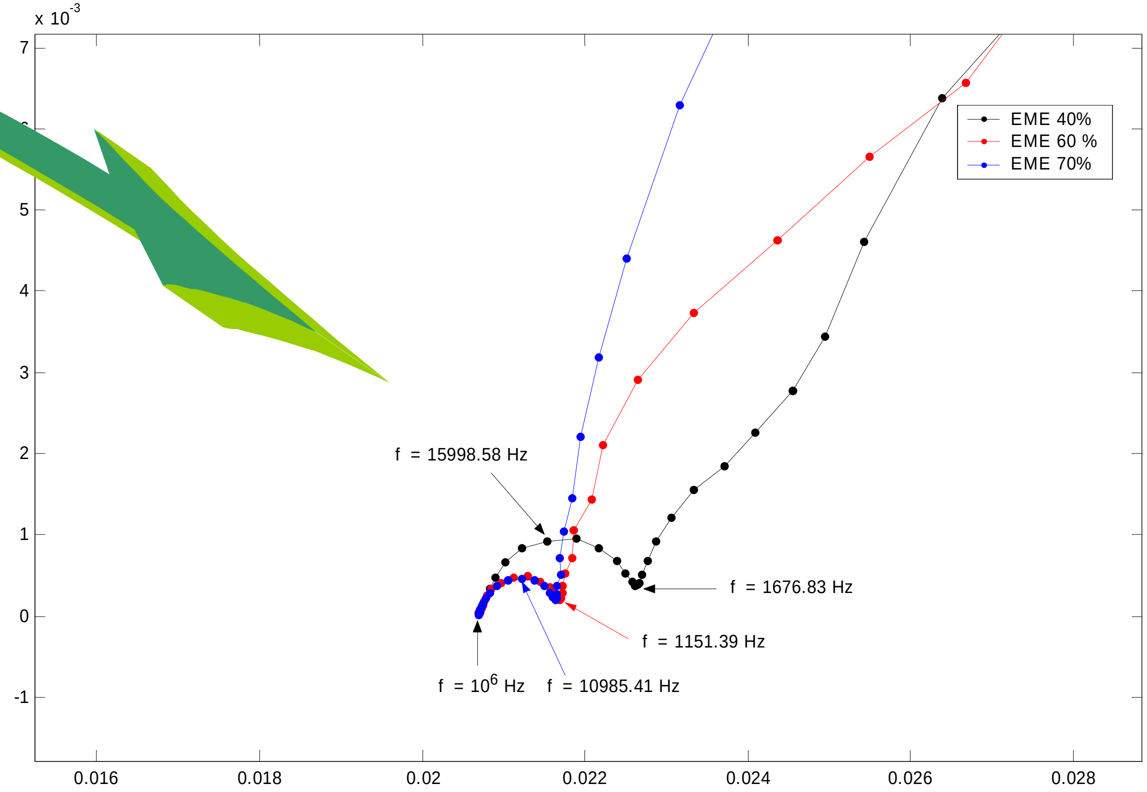


Simulated AME impedance spectra

$T = 353\ K$

$P_A = P_C = 1.5\ bar$

$\bar{I} = 1A$



e_{NI} (m)

EME 40%	10^{-8}
EME 60%	10^{-7}
EME 70%	3×10^{-7}

Concluding remarks (1/3)

- Mechanistic model of the electrochemical dynamics in a MEA of PEFC.
- Consistent approach with irreversible thermodynamics and electrodynamics.
- Multiscale model (very different geometrical scales are involved).
- Dynamical model: transient regimes, physicochemical aging mechanisms, transient experiments interpretation…working PEFC !
- Predictive model: sensitivity to working conditions (I,T,P), morphology and composition of the electrodes (design).
- Possible to evaluate contributions of different layers (microscopic and nanoscopic) and physical phenomena (diagnostics).
- Port-based, hierarchical approach (infinite dimensional Bond Graphs): modular and modulable model (coupling with other/additional physico-chemical phenomena is possible).
- Reusable model: possible to extend in other electrochemical contexts (Acid Pb and Li-Ion batteries, SOFC…).
- MEMEPHYS simulations in good qualitative agreement with experimental results under different working conditions and electrode compositions.

Concluding remarks (2/3)

Ab-initio (DFT, QMD…)
Molecular Dynamics
Monte Carlo

H. Pitsch (Stanford)
E. Spohr (Juelich)
W. Bessler (Heildelberg)

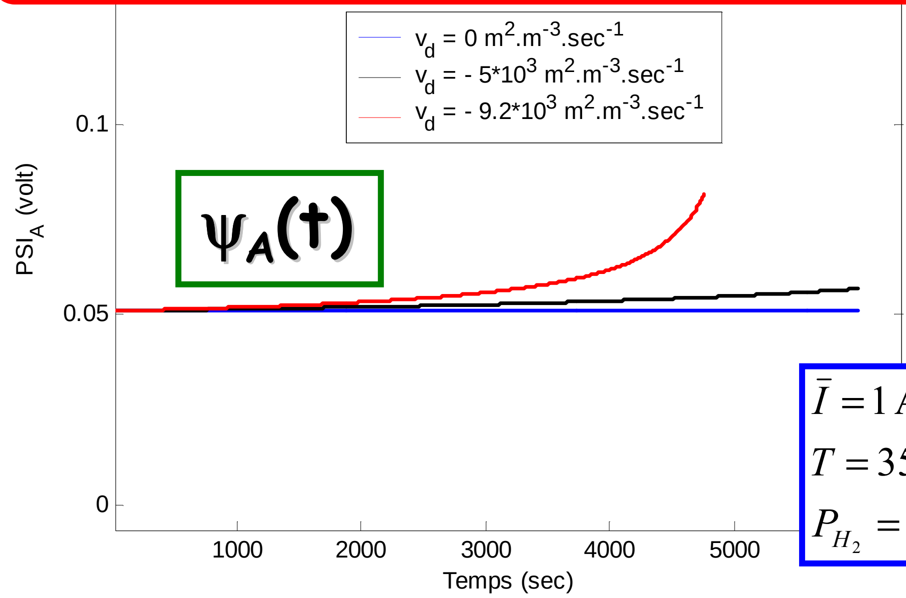
MEMEPHYS
(irreversible thermodynamics/electrodynamics on the basis of infinite-dimensional Bond Graphs)

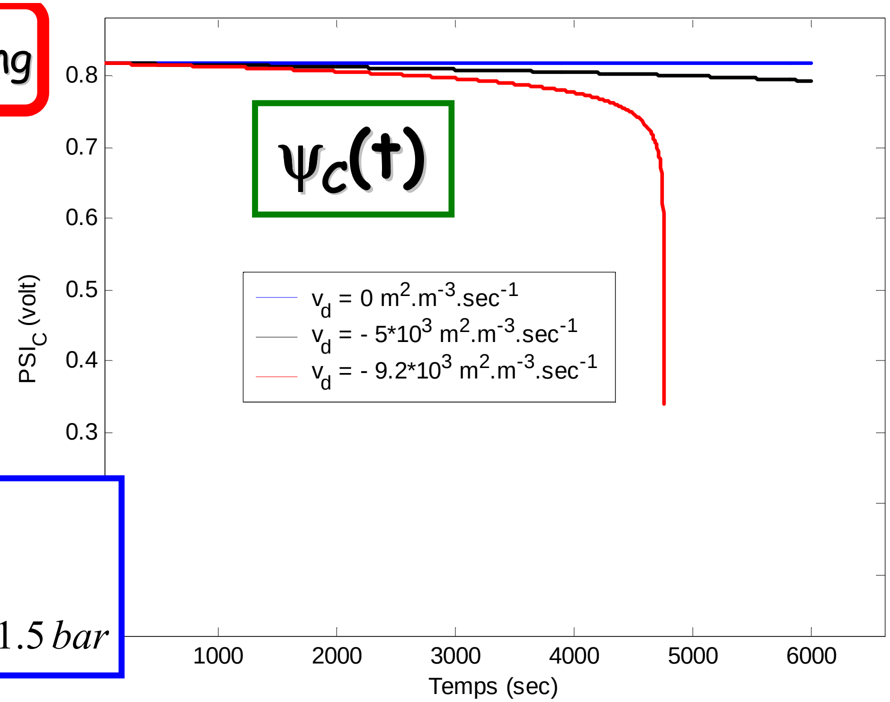
Reactions parameters, intermediates interaction parameters, diffusion coefficients, species electrical interaction…

Experimental electrochemistry/ electrified interfaces physics

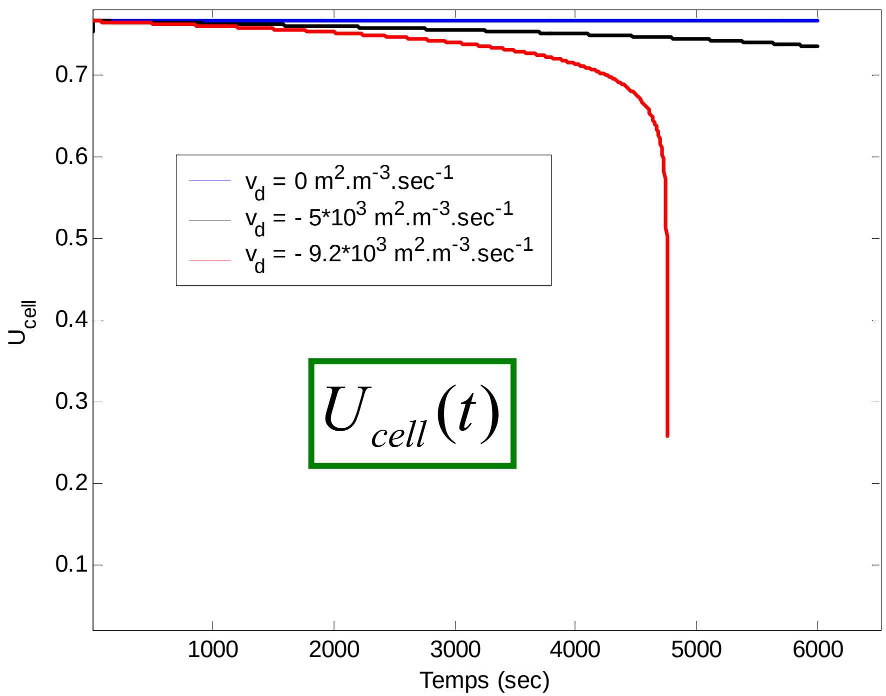
V. Climent (Alicante)

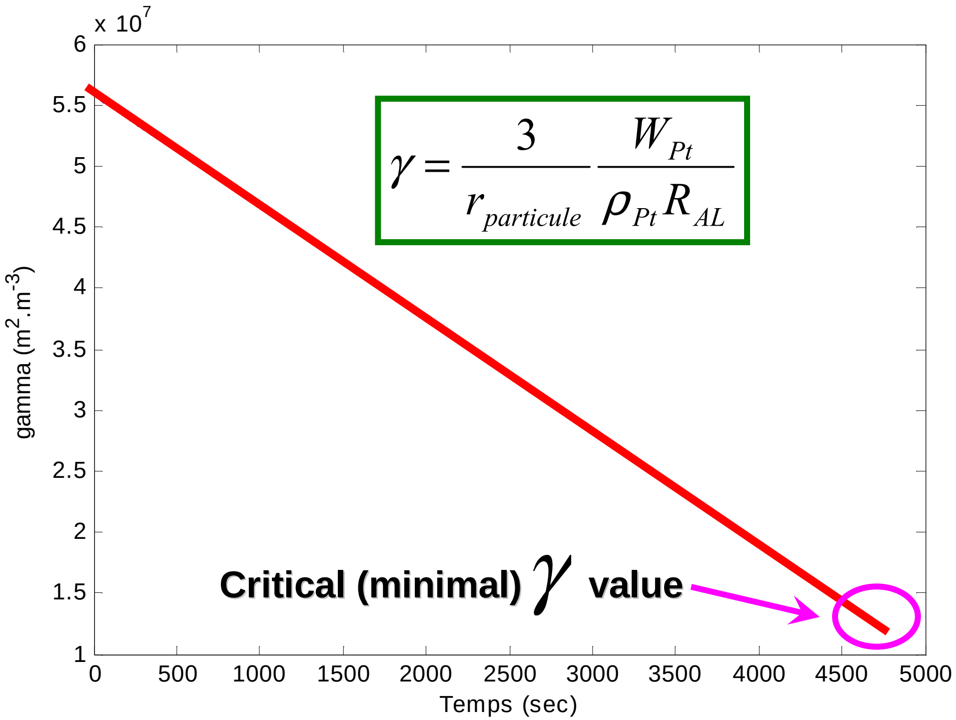
Concluding remarks (3/3): electrode aging modelling





$$\bar{I} = 1\,\mathrm{A}$$
$$T = 353\,K$$
$$P_{H_2} = P_{O_2} = 1.5\,bar$$





Thank you very much!

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