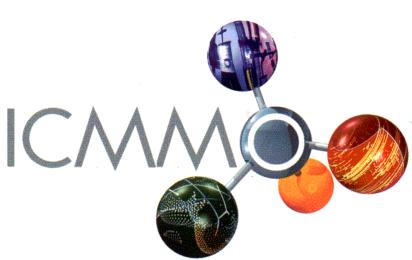


Correlation between electro-chemical and chemical impedance spectroscopies for analyzing the hydriding kinetics of palladium foils

NGAMENI JIEMBOU Joseph Rostand

Sous la direction de:

Pierre MILLET

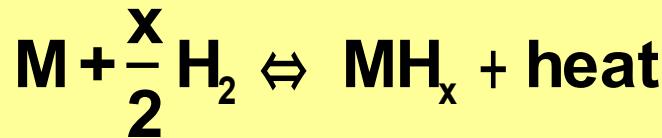


ICMMO, faculté d'Orsay

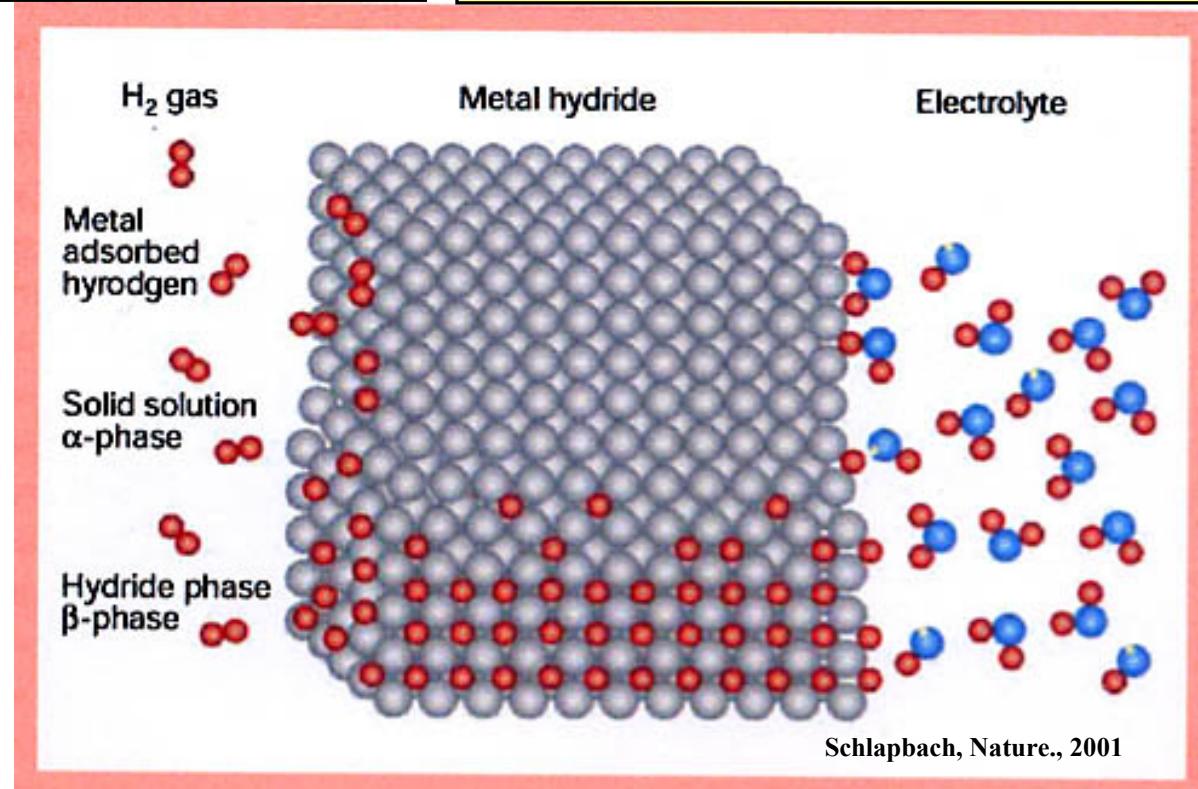


Hydrogen sorption by metals

Chemical (gas phase)



Electro-chemical (alkaline media)



Thermodynamics

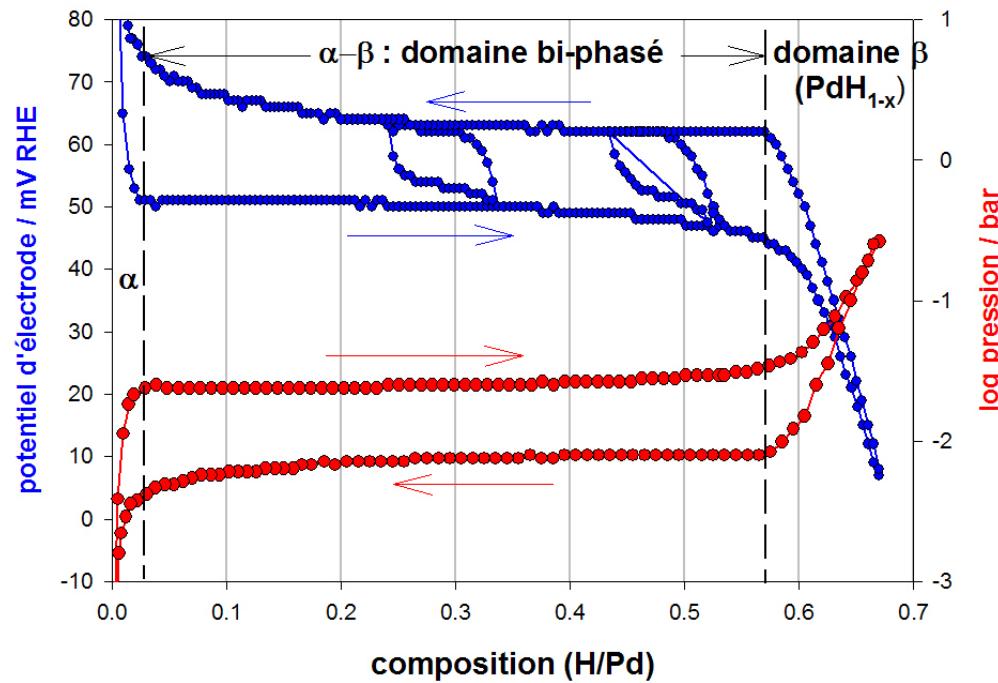


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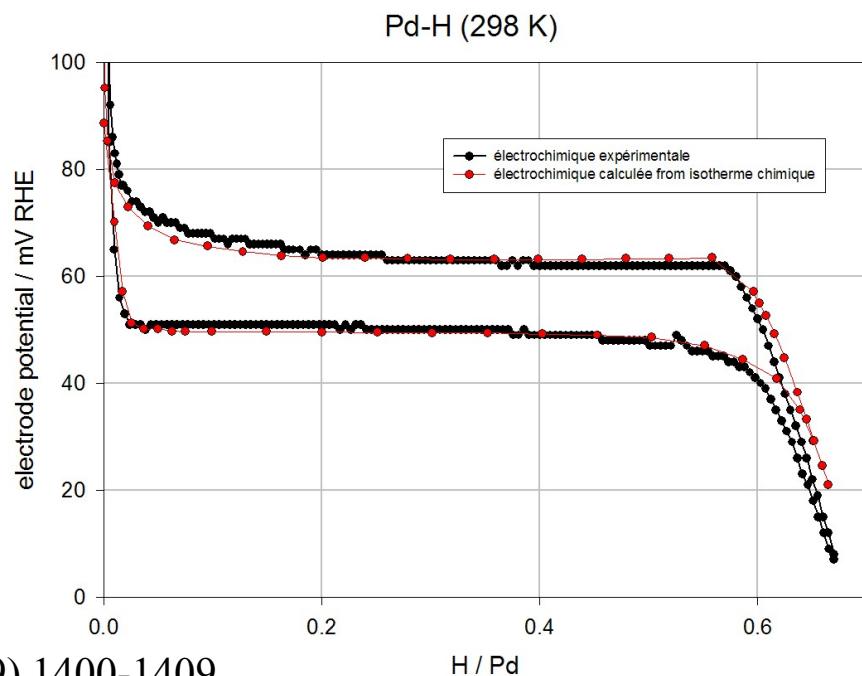
Thermodynamics of metal-H₂ systems

Palladium massif



$$\Delta E = - \frac{RT}{2F} \ln P_{H_2}$$

large hysteresis
in both cases



T.B. Flanagan and F.A. Lexis, trans. Faraday Soc., 55 (1959) 1400-1409



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Kinetic analysis

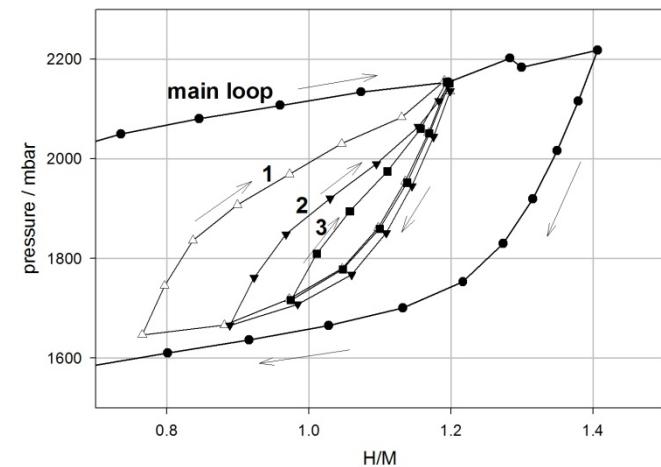
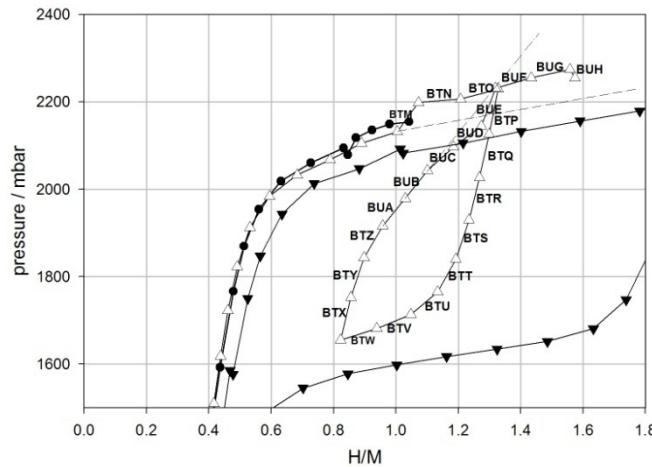
Methodologies

Harmonic analysis

linear systems and reversible transformations



Non-harmonic analysis



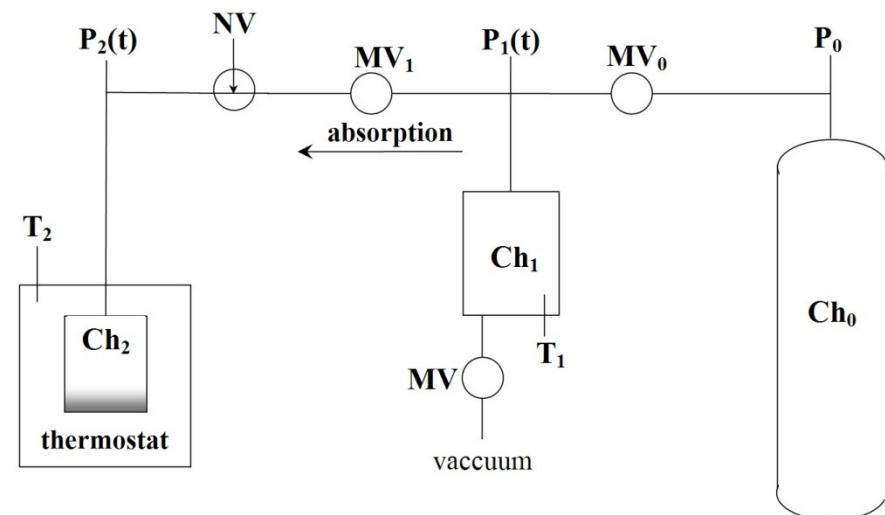
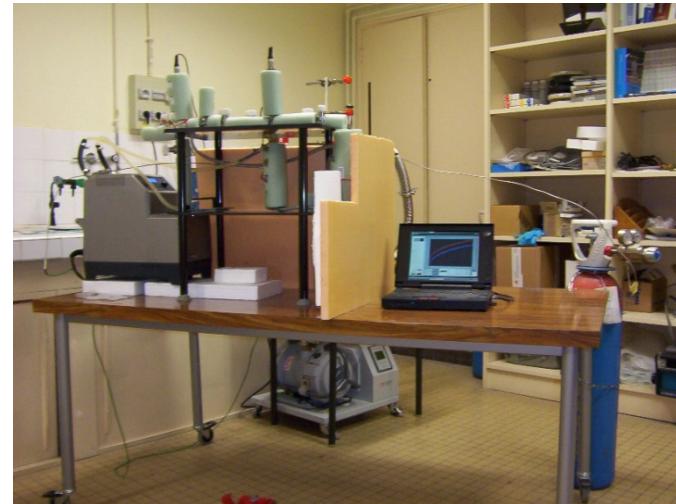
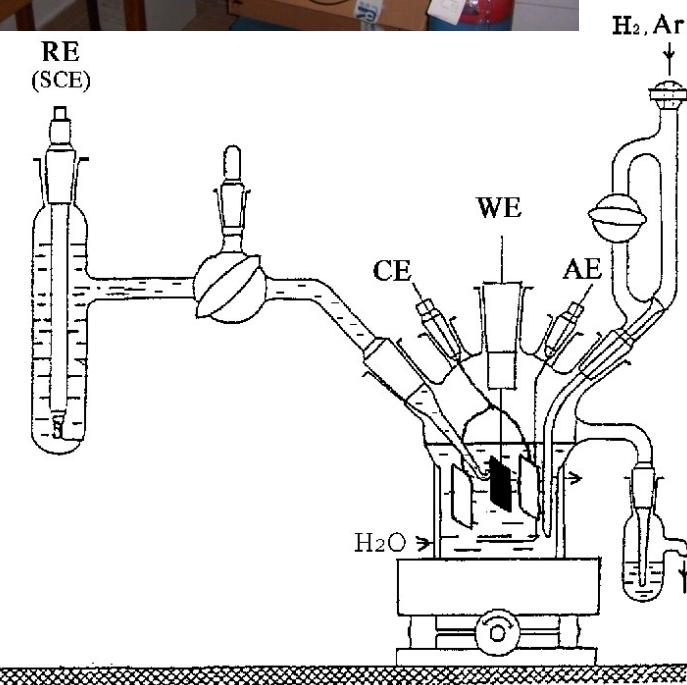
Transfer function :

$$H(\omega) = \frac{TF[s(t)]}{TF[e(t)]}$$

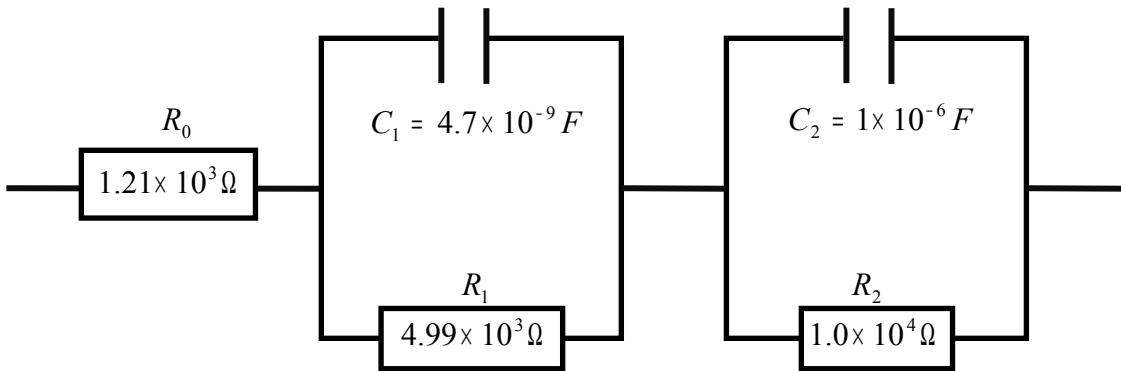
EIS

Experimental section

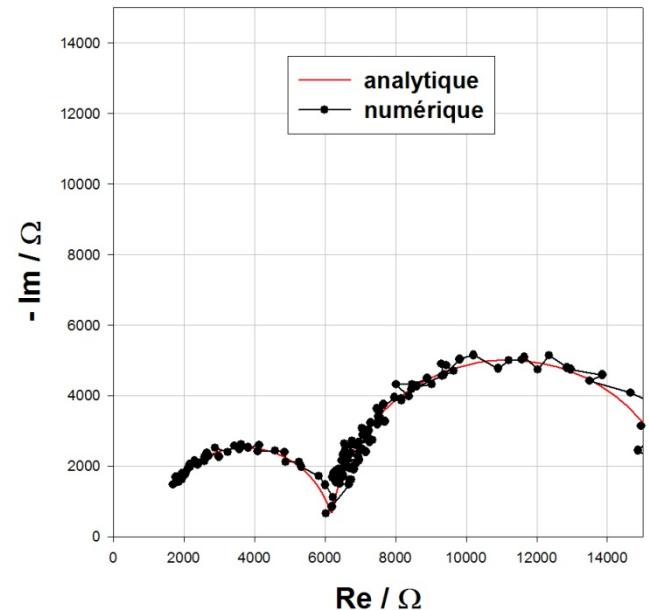
PIS



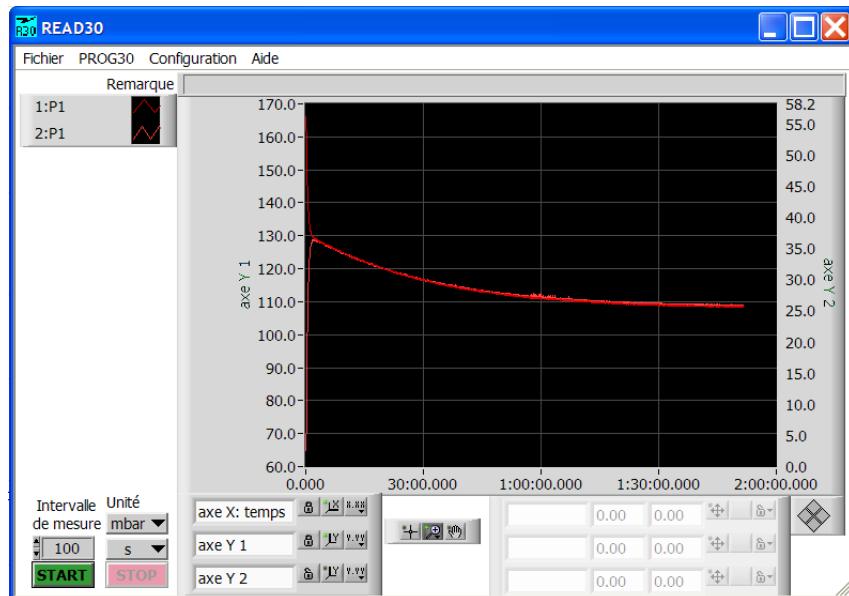
non-harmonic EIS



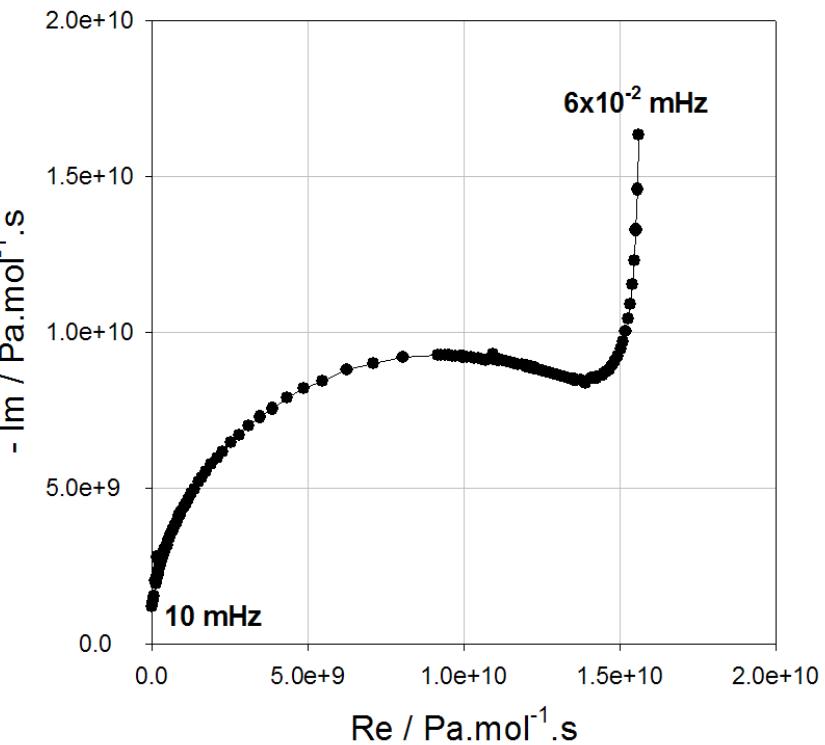
$$Z(\omega) = \frac{TF[E(t)]}{TF[I(t)]}$$



non-harmonic PIS



$$Z(\omega) = \frac{TF[P(t)]}{TF[dn/dt(t)]}$$



H insertion mechanisms



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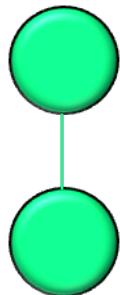
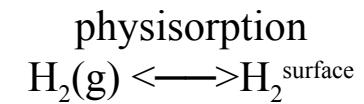


Chemical insertion of H₂

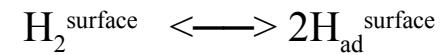
(mechanism)

Gas phase

metal

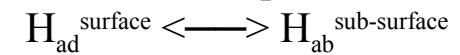


Dissociation



Surface diffusion

Absorption



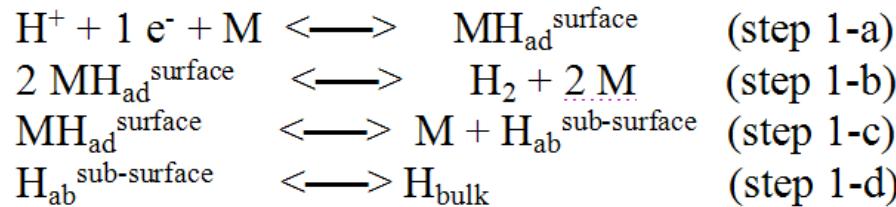
Volume Diffusion



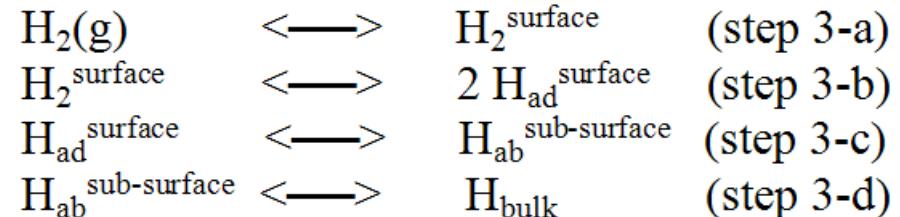
Phase Transformation

Comparison of insertion mechanism

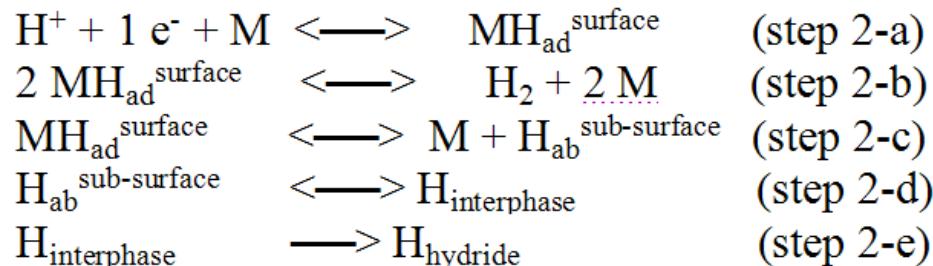
EIS single-phase domains



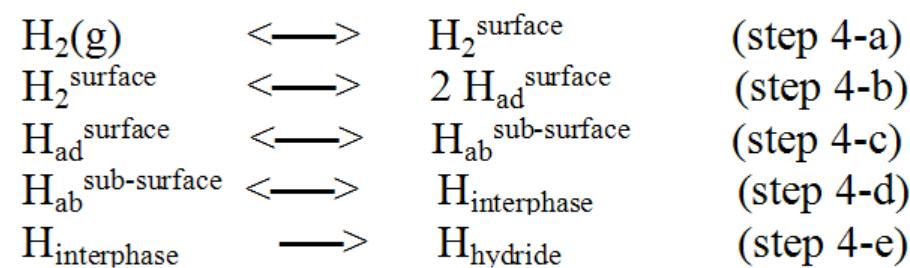
PIS single-phase domains



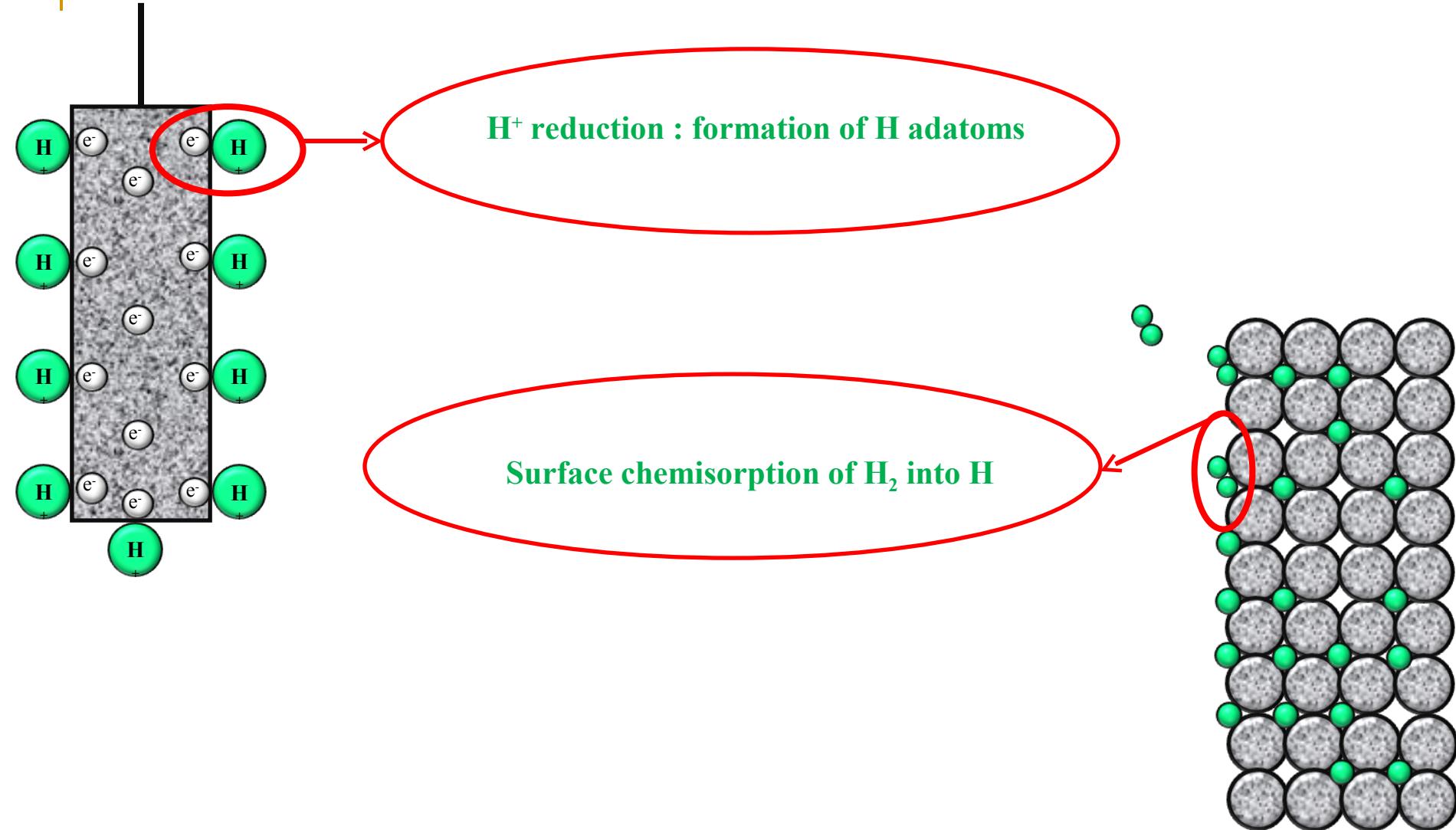
EIS two-phase domains



PIS two-phase domains



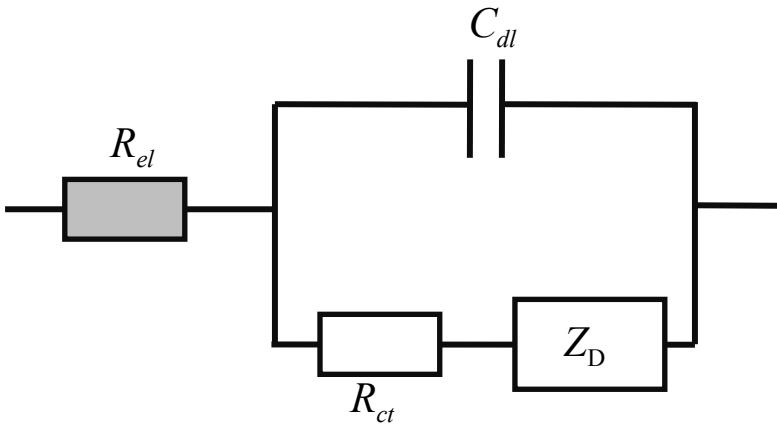
Insertion mechanisms : only surface step differs



Models for insertion in single-phase domains

Electrical model insertion of H₂

Electrochemical



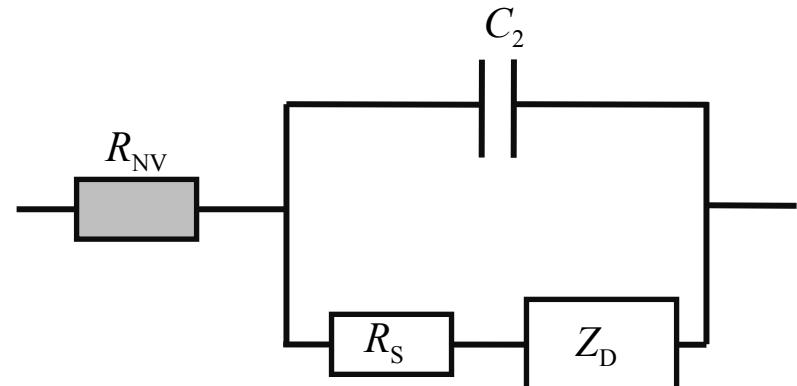
$$Z^{EC}(\omega) = R_{el} + \left[\frac{1}{jC_{dl}\omega + \left(\frac{1}{R_{ct} + Z_D^{EC}} \right)} \right]$$

$$Z_D^{EC,film}(p) = R_D^{EC,film} \frac{\coth(u^p)}{u^p}$$

$$R_D^{EC,film} = \frac{\delta}{FD_H} \left(-\frac{\partial E}{\partial C_H} \right)$$

$$u = j \frac{\omega \delta^2}{D_H}$$

Chemical



$$Z^C(\omega) = R_{NV} + \left[\frac{1}{jC_2\omega + \left(\frac{1}{R_S + Z_D^{C,film}} \right)} \right]$$

$$Z_D^{C,film}(p) = R_D^{C,film} \frac{\tanh(u^p)}{u^p}$$

$$R_D^{C,film} = \frac{\delta}{FD_H} \left(\frac{\partial P}{\partial C_H} \right) \quad u = j \frac{\omega \delta^2}{D_H}$$



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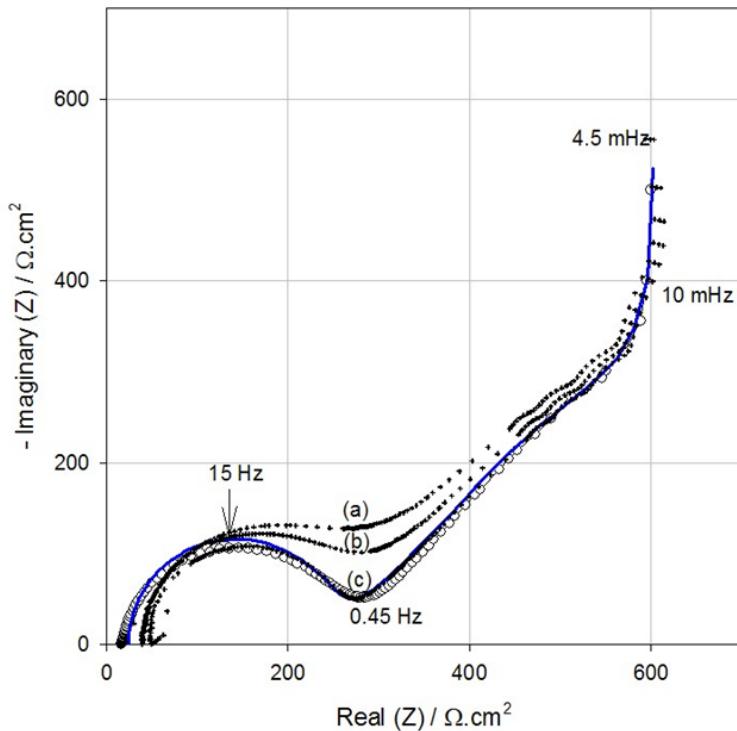
Results



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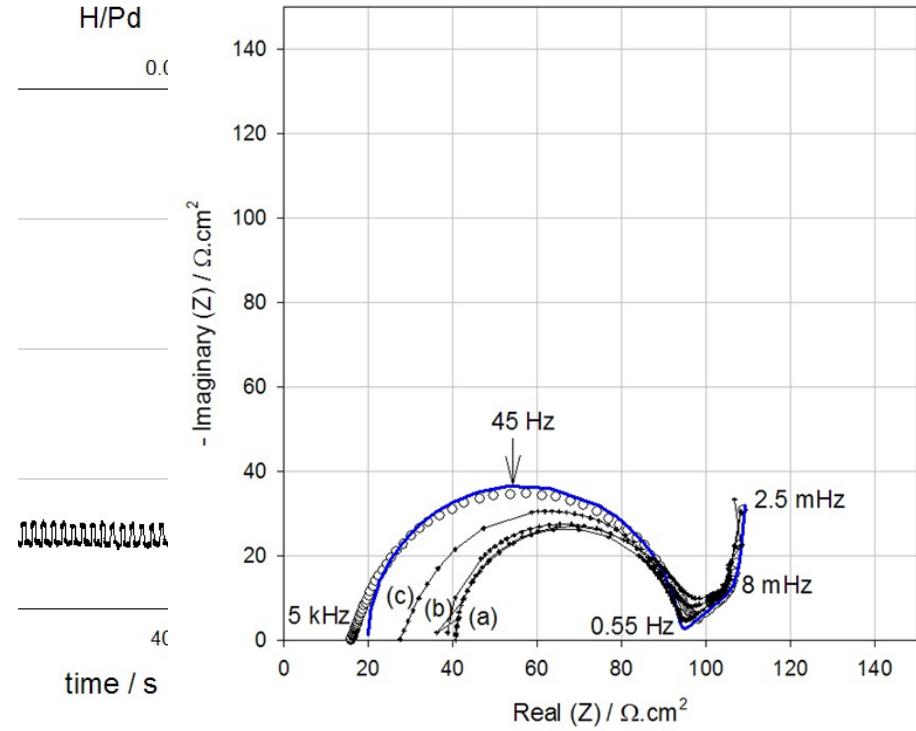


NHEIS in single-phase domains



electrochemical impedance diagrams measured on Pd-H at 298 K at $E = +160$ mV NHE.

- (o) experimental harmonic;
- (+) experimental non-harmonic with :
- (f) $Dt = 50$ ms; (b) $Dt = 25$ ms;
- (c) $Dt = 2.5$ ms; (—) model impedance



electrochemical impedance diagrams measured on Pd-H at 298 K at $E = +60$ mV NHE.

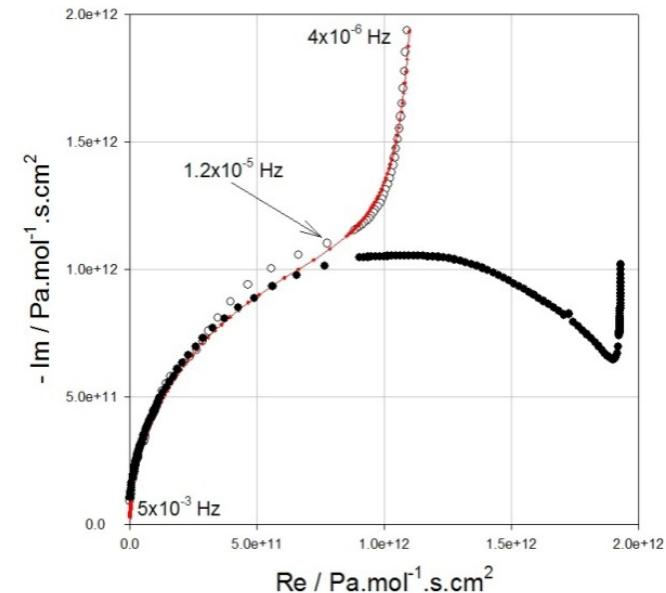
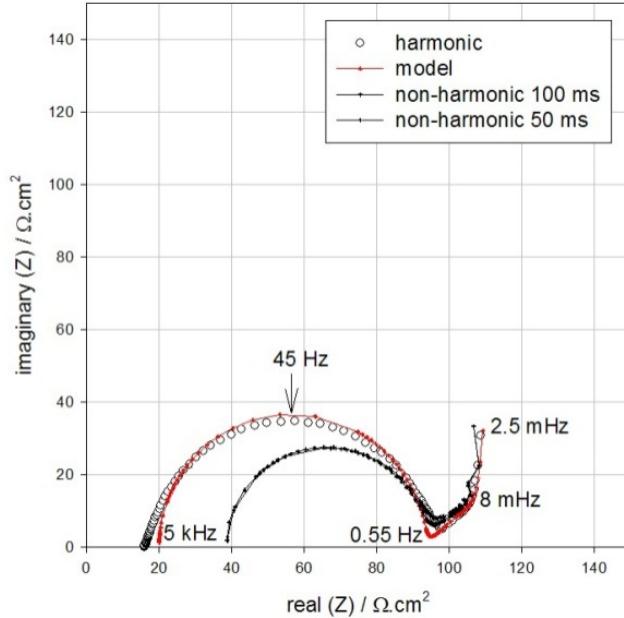
- (o) experimental harmonic;
- (+) experimental non-harmonic with :
- (f) $Dt = 50$ ms; (b) $Dt = 25$ ms;
- (c) $Dt = 2.5$ ms; (—) model impedance

Comparison of EIS and PIS

E=+60mV

$$\Delta E = - \frac{RT}{2F} \ln P_{H_2}$$

P_{H₂}=9.82 mbar

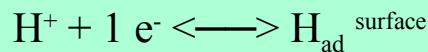


R_{el} $\Omega \cdot \text{cm}^2$	τ_c s	C_{dl} $\mu\text{F} \cdot \text{cm}^{-2}$	R_{ct} $\Omega \cdot \text{cm}^2$	R_D $\Omega \cdot \text{cm}^2$	
20	3.65×10^{-3}	50	73	43.7	
D_H $\text{cm}^2 \cdot \text{s}^{-1}$	$-(\partial E / \partial C_H)$ $\text{V} \cdot \text{mol}^{-1} \cdot \text{cm}^3$	R_{in} $\Omega \cdot \text{cm}^2$	C_{in} $\text{F} \cdot \text{cm}^{-2}$	τ_{in} s	p
2.7×10^{-7}	230	14.6	2.12	30.9	0.48

R_{NV} $\text{Pa} \cdot \text{mol}^{-1} \cdot \text{s} \cdot \text{cm}^2$	τ_c s	C_2 $\text{mol} \cdot \text{Pa}^{-1} \cdot \text{cm}^{-2}$	R_s $\text{Pa} \cdot \text{mol}^{-1} \cdot \text{s} \cdot \text{cm}^2$	R_D $\text{Pa} \cdot \text{mol}^{-1} \cdot \text{s} \cdot \text{cm}^2$
0	12400	6.2×10^{-9}	2×10^{12}	3.6×10^9
D_H $\text{cm}^2 \cdot \text{s}^{-1}$	$\partial P / \partial C_H$ $\text{Pa} \cdot \text{mol}^{-1} \cdot \text{cm}^3$	R_{in} $\text{Pa} \cdot \text{mol}^{-1} \cdot \text{s} \cdot \text{cm}^2$	C_{in} $\text{mol} \cdot \text{Pa}^{-1} \cdot \text{cm}^{-2}$	τ_{in} s
2.8×10^{-7}	2.6×10^3	1.2×10^9	2.5×10^{-8}	30

Comparaison of rate parameters (298 K)

electrochemistry



$$R_{\text{ct}}/R_{\text{in}} = 5$$

$$\tau_c = R_{\text{ct}} \cdot C_{\text{dl}} = 3.65 \times 10^{-3} \text{ s}$$
$$f_c = 10 \text{ kHz}$$

Comparison of surface rates

$$R_s/R_{\text{ct}} = 333$$

Electrochemical formation of surface H ad-atoms is much faster than the chemical process

High frequency time constant and sampling rate

Chemical insertion of H_2 in palladium foil is much slower than electrochemistry insertion.

chemistry



$$R_s/R_{\text{in}} = 1667$$

$$\tau_c = R_s \cdot C_2 = 12400 \text{ s}$$
$$f_c = 5 \times 10^{-3} \text{ Hz}$$

Conclusion and perspectives

- Because of hysteresis, harmonic spectroscopies cannot be used to analyze the hydriding kinetics of metals and intermetallic compounds
- Experimental electrochemical impedance diagrams have been obtained on Pd using potential steps
- Experimental chemical impedance diagrams have been obtained on Pd using PIS analysis
- Main kinetic differences between electrochemical and chemical processes have been determined quantitatively
- We are currently investigating the phase-transformation process in two-phase domains using EIS and PIS
- We are also thinking about hyper-permeation from low-temperature plasma experiments



Thank you for your
attention



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