Impedance IIIa

Study of the insertion reaction by impedance

Application to the characterization of batteries

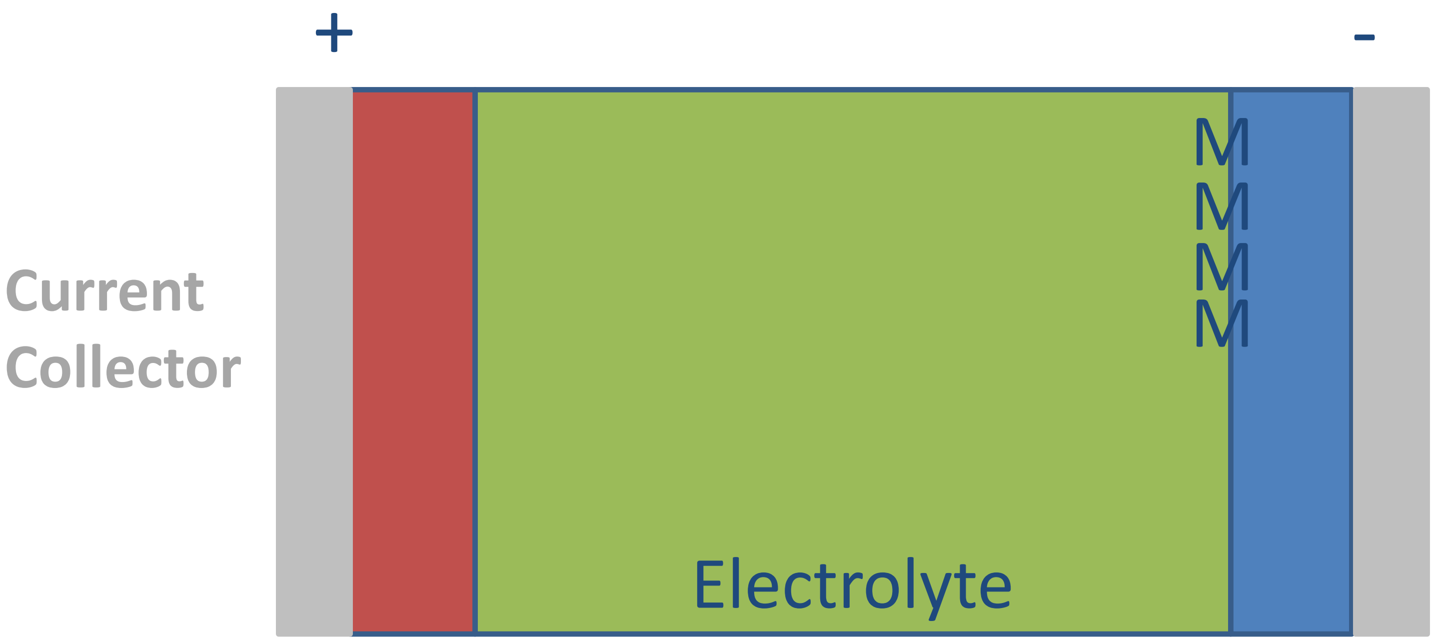
Objective

Understand to which mechanisms correspond the impedance graphs obtained on batteries.

Outline

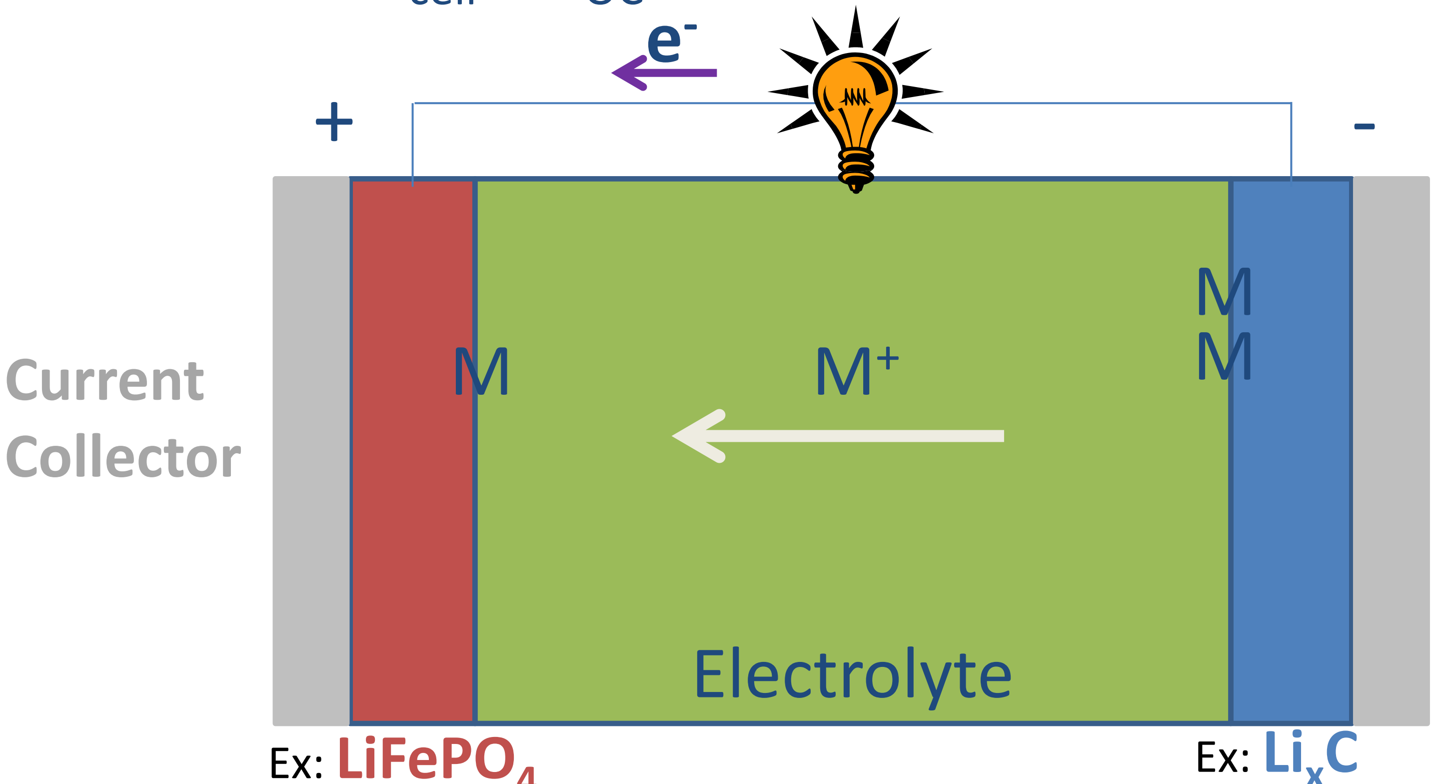
Outline

1. Initial state (charged) : $E_{cell} = E_{OC}$



E_{cell} = Cell voltage = potential difference between the positive electrode and the negative electrode.

2. Discharge: $E_{cell} < E_{OC}$ (charged) (Spontaneous reactions)

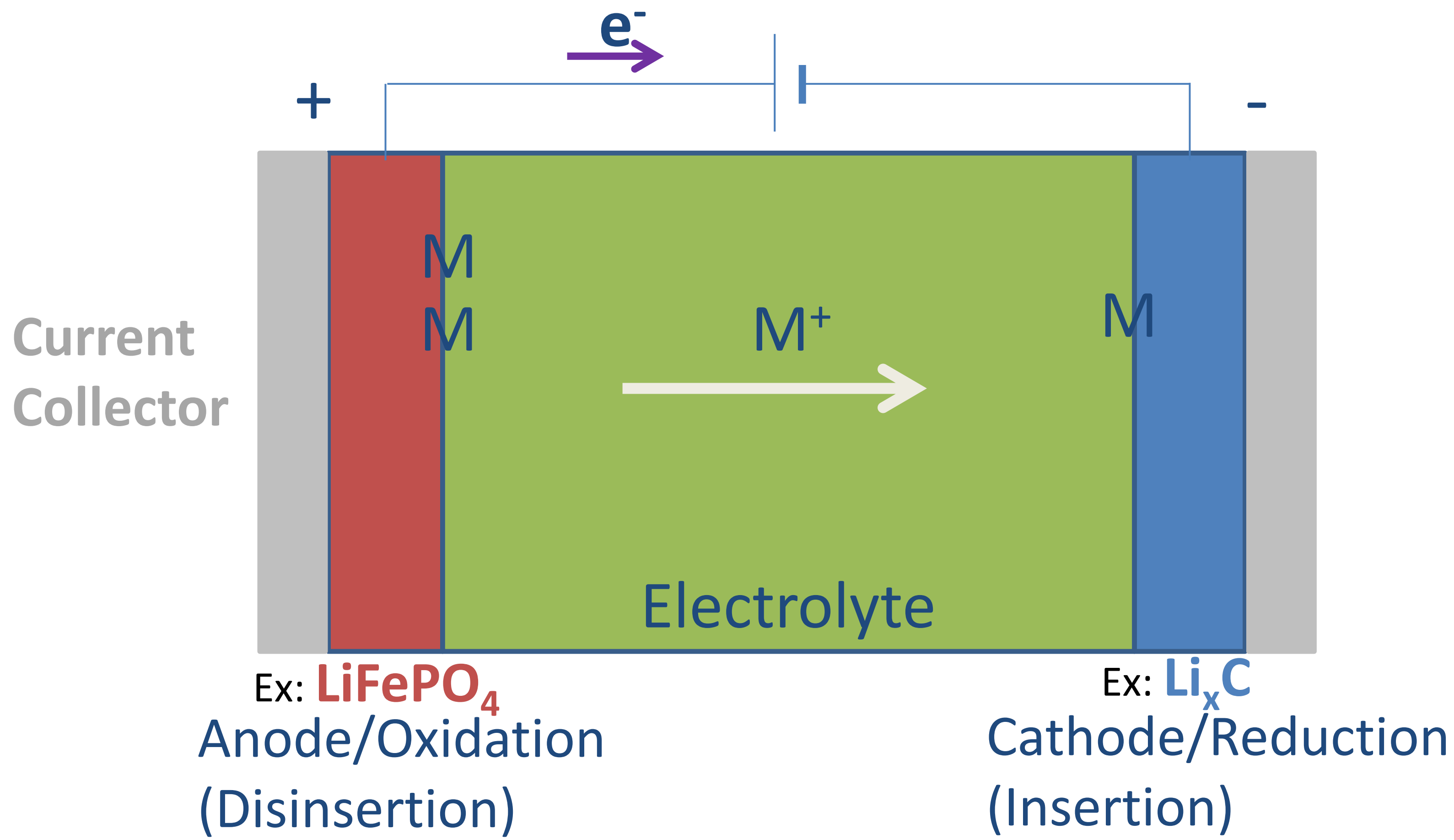


Cathode/Reduction (Insertion)

Anode/Oxidation (Disinsertion)

The Li battery

3. Charge : $E_{cell} > E_{OC}$ (discharged) (Forced reactions)



Outline

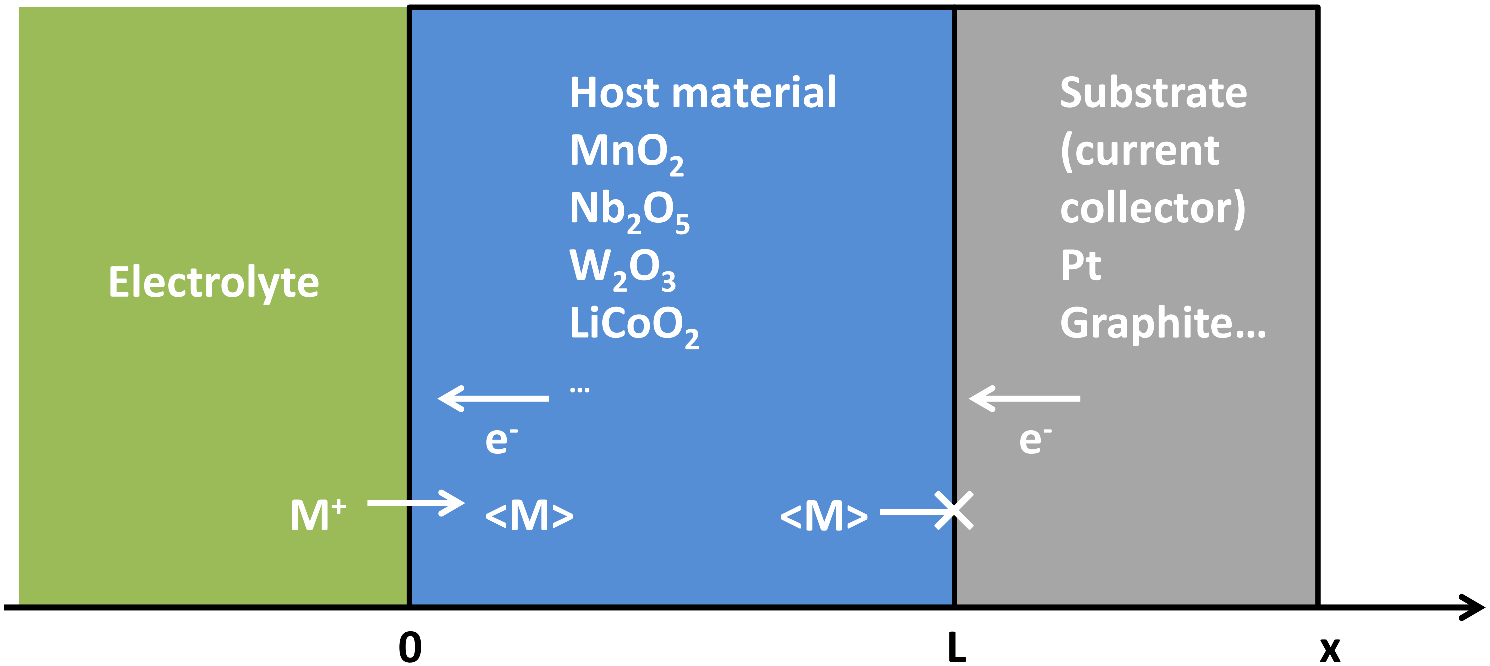
1. **Introduction : the Li battery**

2. **The insertion reaction with restricted diffusion**
    1. Mechanism
    2. Expression of the Faradaic impedance
    3. Equivalent circuit
    4. Experimental data
    5. Other mechanisms

3. **The insertion reaction with semi-infinite diffusion**

4. **The insertion reaction with bounded diffusion**

Let us consider one electrode of the battery.



$$\mathbf{M}^{+} + <> + \mathbf{e}^{-} \underset{K_d}{\overset{K_i}{\leftrightarrow}} < \mathbf{M} >$$

No inserted species can flow in the substrate.

At the host/substrate interface, $J_{<M>}(L,t) = 0$

Mechanism

$$\mathbf{M}^{+} + \langle\rangle + \mathbf{e}^{-} \underset{K_d}{\overset{K_i}{\leftrightarrow}} \langle \mathbf{M} \rangle$$

Insertion reaction rate $v_i(t)$

$$v_i(t) = K_i(t) M^{+}(0,t) <> (0,t)$$

with $K_i(t) = k_i \exp[-\alpha_i f E(t)]$

Desinsertion reaction rate $v_d(t)$

$$v_d(t) = K_d(t) < M > (0,t)$$

with $K_d(t) = k_d \exp[\alpha_d f E(t)]$

$f = F/(RT)$

Symmetry factors : $\alpha_i + \alpha_d = 1$

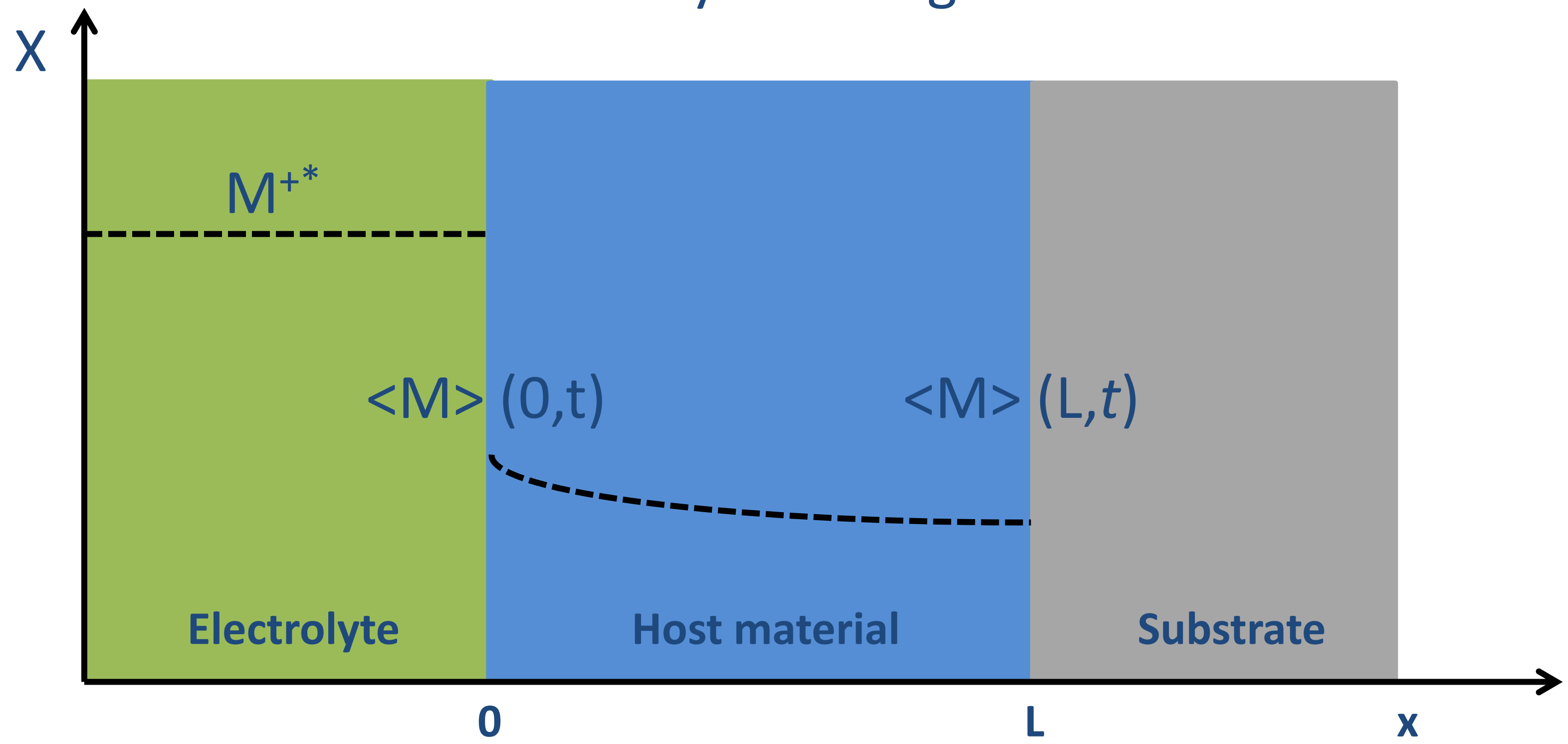
Global reaction rate $v(t)$

$$v(t) = v_i(t) - v_d(t)$$

$$v(t) = K_i(t) M^{+}(0,t) <> (0,t) - K_d(t) < M > (0,t)$$

$$i = i_f(t) + i_c(t) = -Fv(t) + C_{dc} dE/dt$$

Non-steady state regime



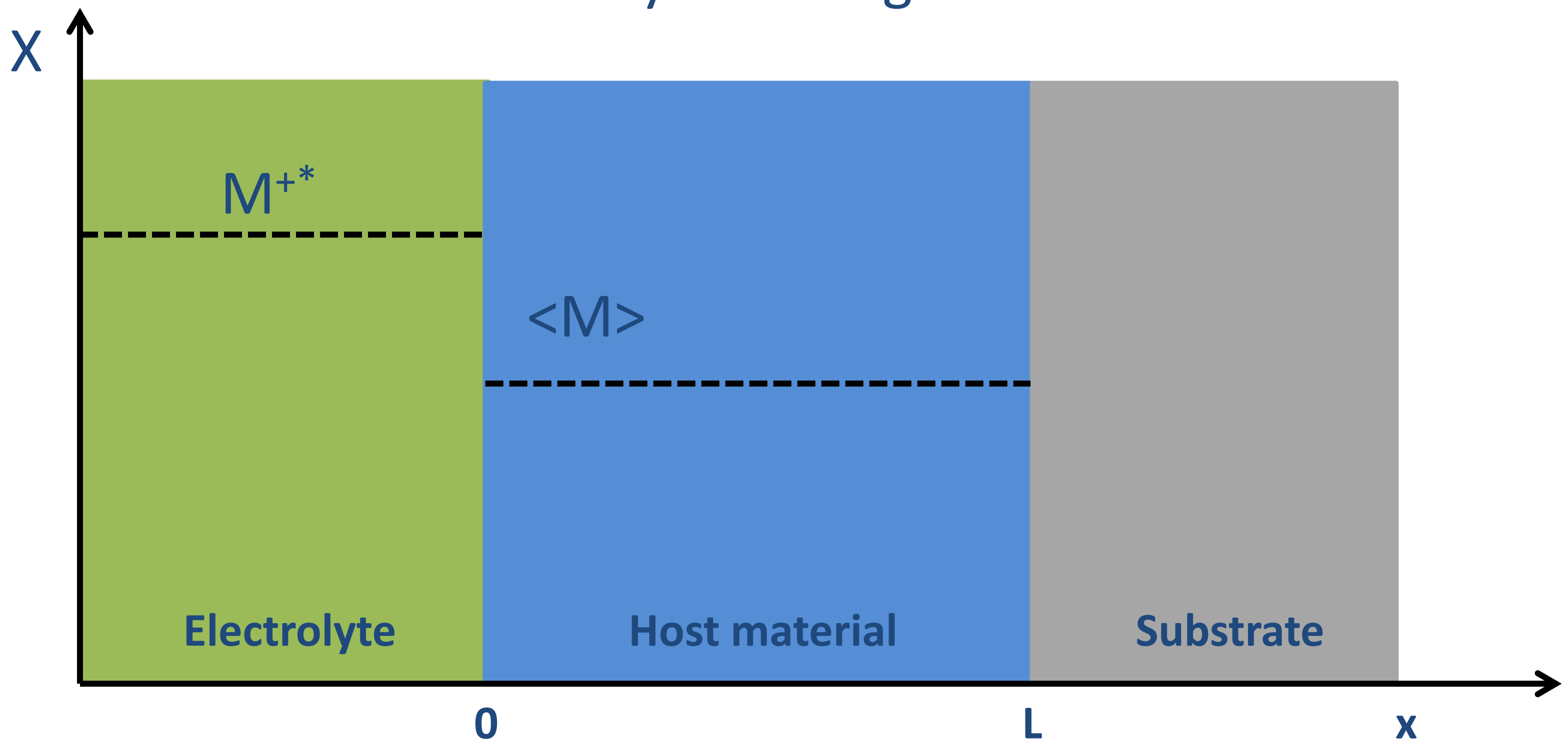
$$\partial \langle M\rangle(x,t)/\partial t = D_{\langle M\rangle}\partial^2\langle M\rangle(x,t)/\partial x^2$$

$$J_{\langle M\rangle}(0,t) = v(t) = -i_f(t)/F$$

$$J_{\langle M\rangle}(L,t) = 0$$

Mechanism

Steady-state regime



$$D_{<M>} d^2 <M>(x)/dx^2 = 0 \Rightarrow <M>(x) = <M>$$

In the steady-state regime, the applied potential E is an equilibrium potential $i_f = -Fv = 0$

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Faradaic Impedance

The Faradaic current is expressed as : $i_f(t) = -Fv(t)$

The Taylor development of the Faradaic current followed by its Laplace transformation leads to an expression of the Faradaic impedance :

$$Z_f(p) = \frac{\Delta E(p)}{\Delta i_f(p)} = R_{ct} + Z_{<M>}(p)$$

R_{ct} is the charge transfer resistance = $\lim_{\omega \to 0} Z_f(\omega)$

$Z_{<M>}$ is the impedance related to the concentration of the inserted species <M>.

Faradaic Impedance

$Z_{<\mathrm{M}>}(p)$ can be written :

$$Z_{<\mathrm{M}>}(p) = R_{<\mathrm{M}>} \frac{\coth\sqrt{\tau_{\mathrm{d}<\mathrm{M}>} p}}{\sqrt{\tau_{\mathrm{d}<\mathrm{M}>} p}}$$

$$Z_{\mathrm{f}}(p) = R_{\mathrm{ct}} + R_{<\mathrm{M}>} \frac{\coth\sqrt{\tau_{\mathrm{d}<\mathrm{M}>} p}}{\sqrt{\tau_{\mathrm{d}<\mathrm{M}>} p}}$$

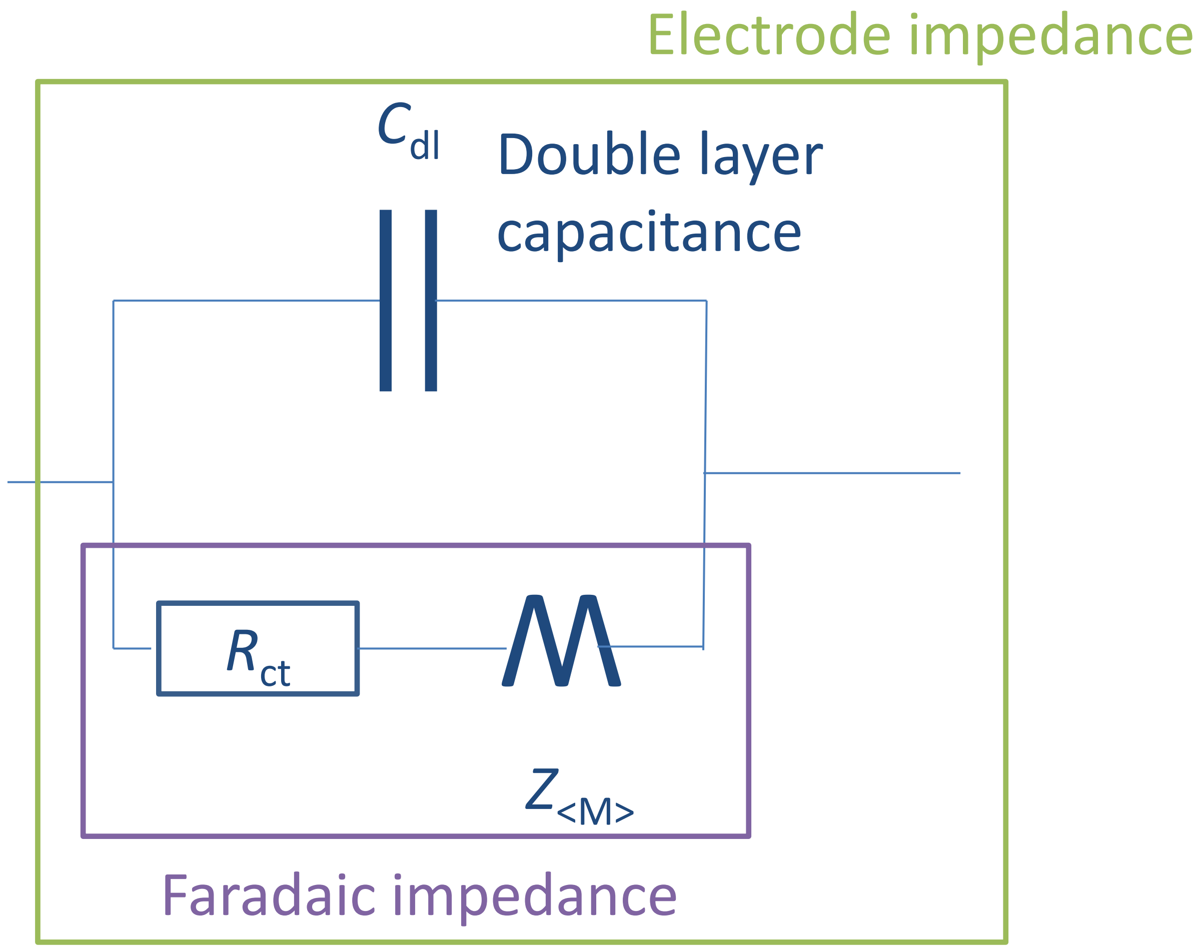
This impedance is equivalent to an electrical circuit.
The impedance of such a circuit can be displayed in a Nyquist diagram.

In this case, $p = j\omega = j2\pi f$ with f the frequency (Hz).
$\tau_d = L^2/D$

Outline

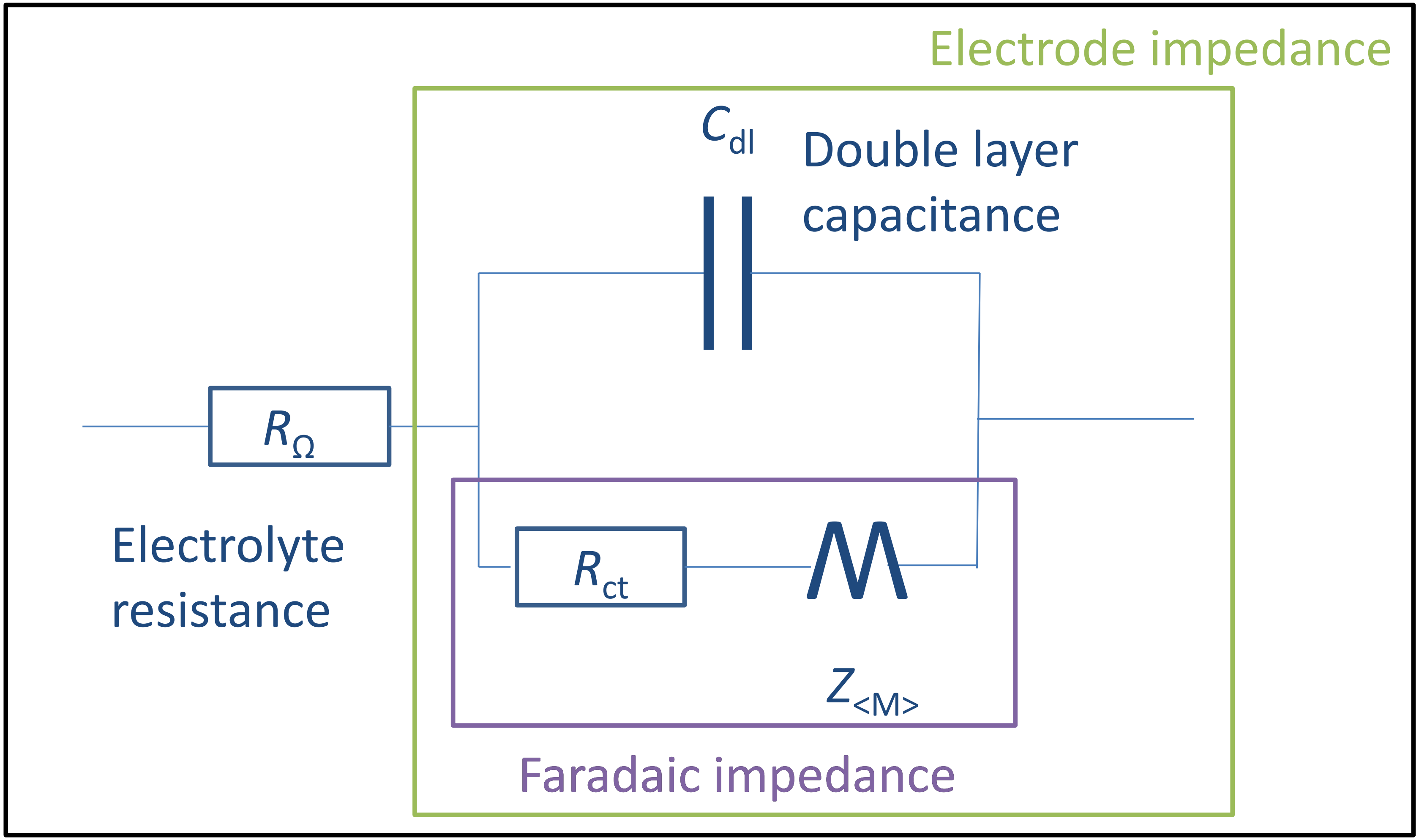
Faradaic impedance

Equivalent Circuit



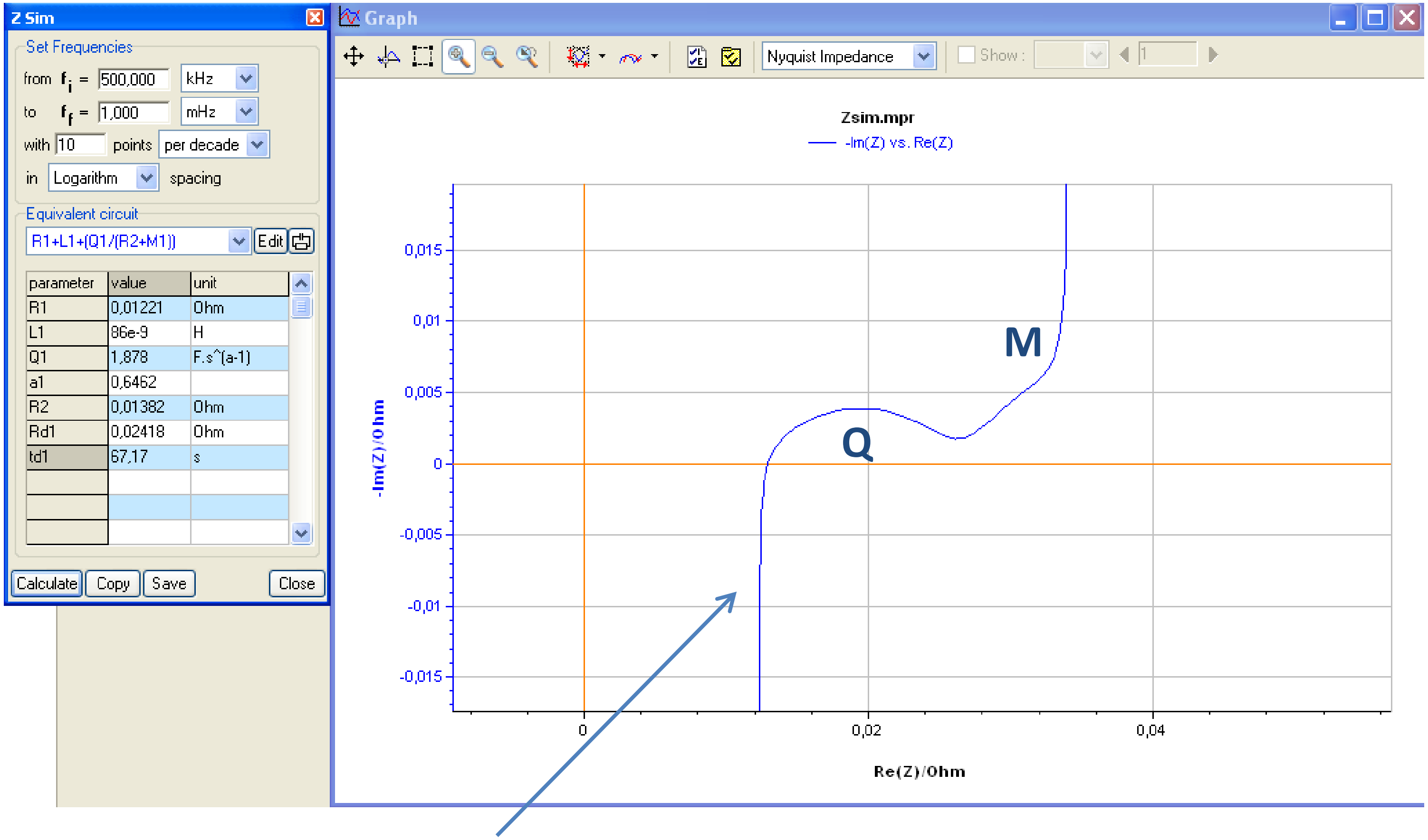
The insertion reaction with restricted diffusion

Equivalent Circuit



Total measured impedance

Simulated impedance graph using ZSim



Inductance component L (due to cell connections, wires…)

Outline

H_2 insertion

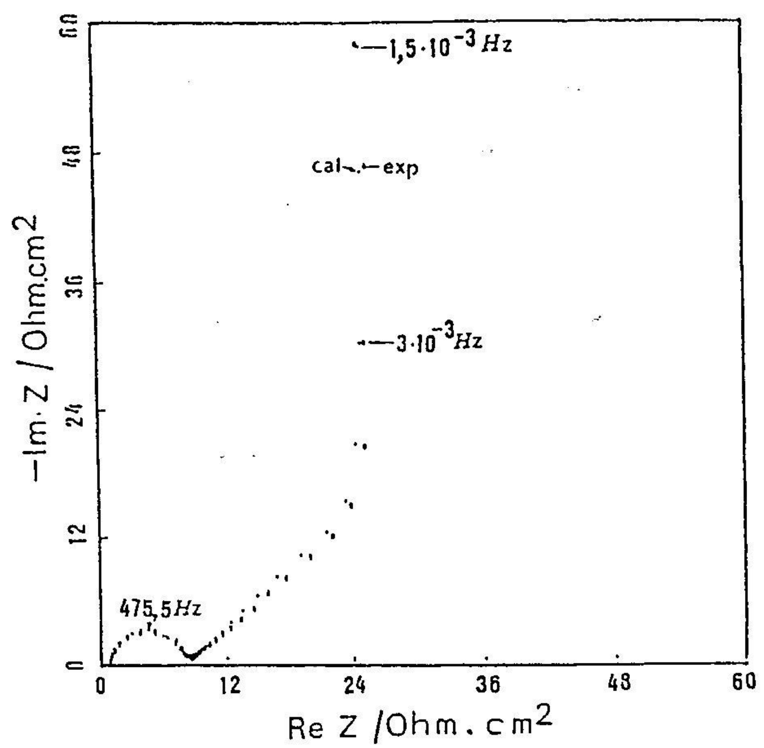


Fig. 3 : Experimental impedance diagram for a Pd electrode 100µm thick ; potential 115 mV (RHE) ; solution 1 M H_2SO_4 ; temperature 20 °C.

From J.S. Chen, J. –P. Diard, R. Durand, C. Montella, Electrochemistry and Materials Science of Hydrogen Absorption and Adsorption, Electrochemistry Society Meeting, B.E. Conway, G. Jerkiewicz (ed.), San Francisco, (1994) p. 207

H_2 insertion

Obtained on a Pd electrode with P_{H2} = 12 mbar

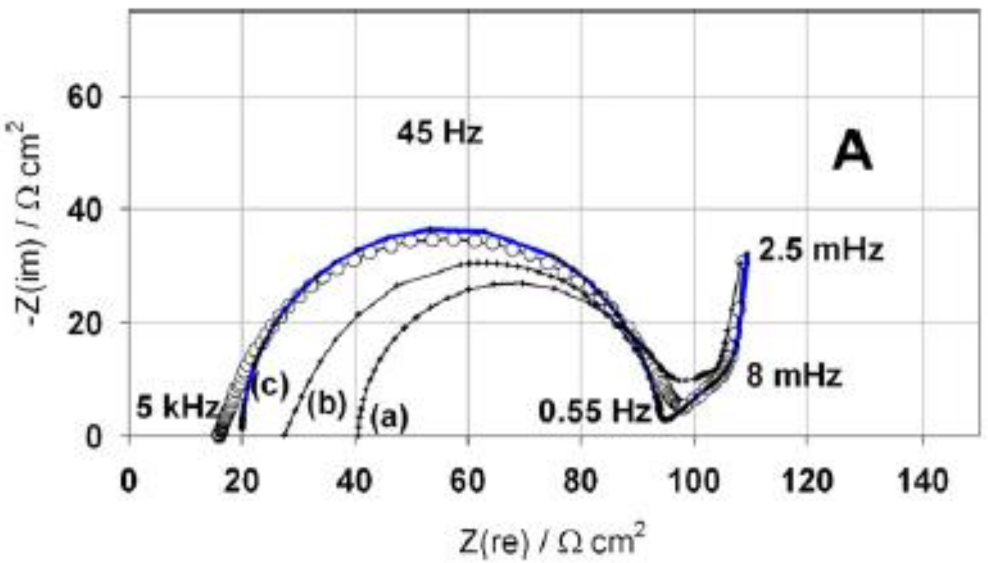
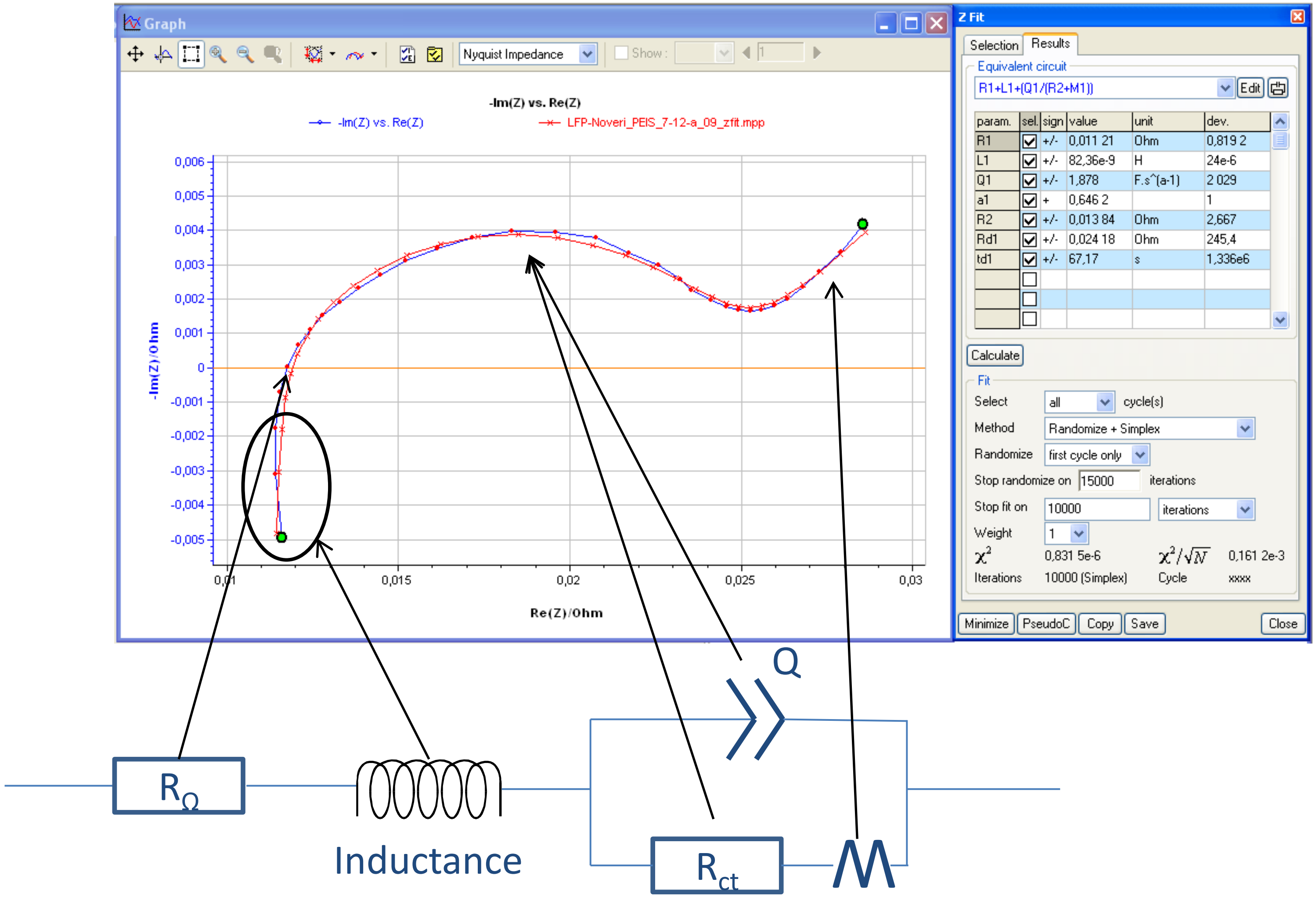


Fig. 6. Electrochemical impedance diagrams measured on Pd–H at 298 K, H/Pd = 0.01 and E = +60 mV NHE. (○) Experimental harmonic; (+) experimental non-harmonic with (a) Δt = 50 µs; (b) Δt = 25 µs; (c) Δt = 2.5 µs; (–) model from Eq. (5).

From P. Millet, R. Ngameni, Electrochim. Acta 56 (2011) p. 7907

Experimental Data

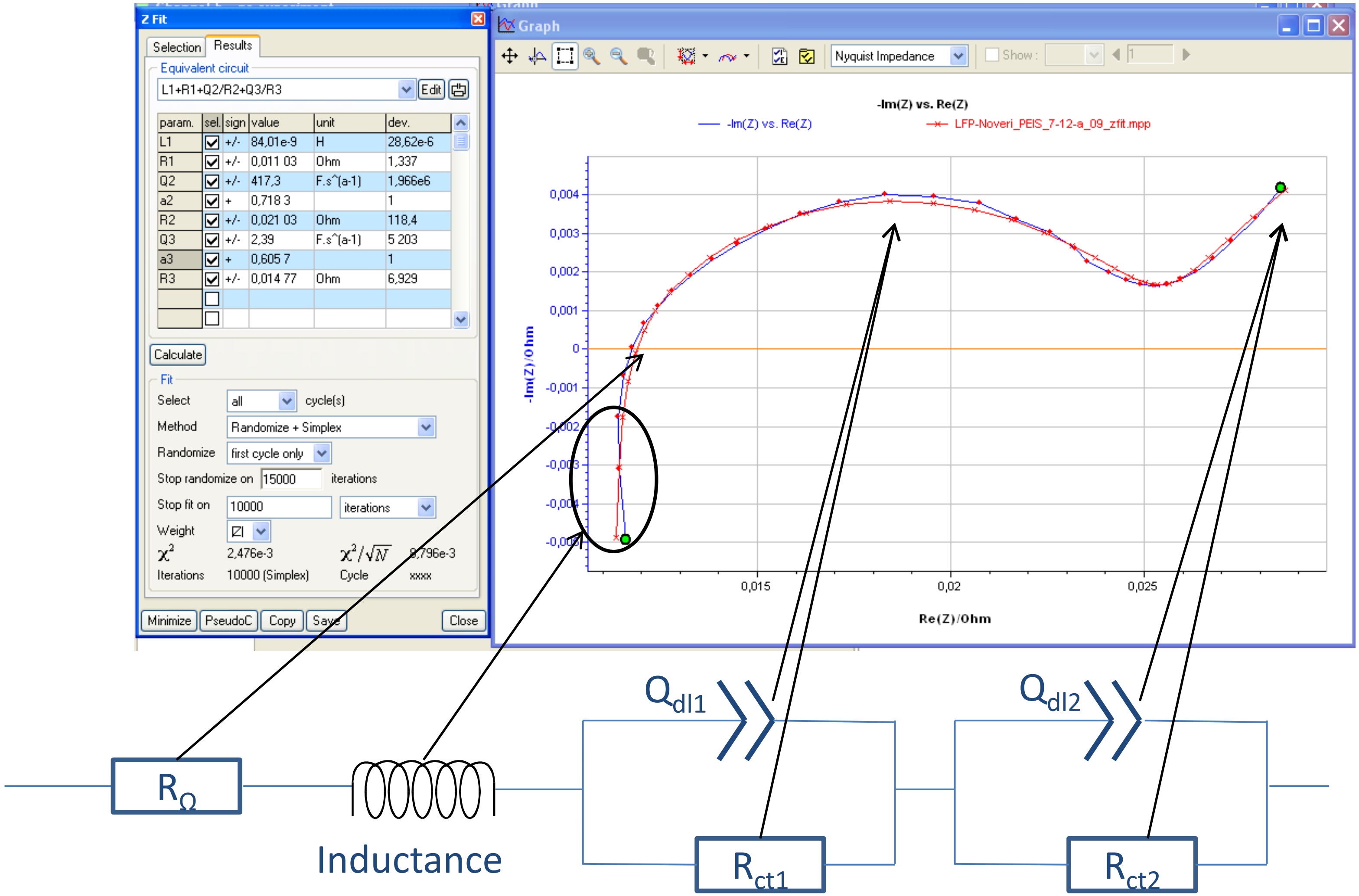
$LiFePO_4$ battery : the use of ZFit



The insertion reaction with restricted diffusion

Experimental Data

$LiFePO_4$ battery : the use of ZFit



Which EC should be chosen ?

The insertion reaction with restricted diffusion

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5. **The Solid Electrolyte Interphase**

Other more complicated insertion reactions are possible

1. Insertion with preliminary electrosorption

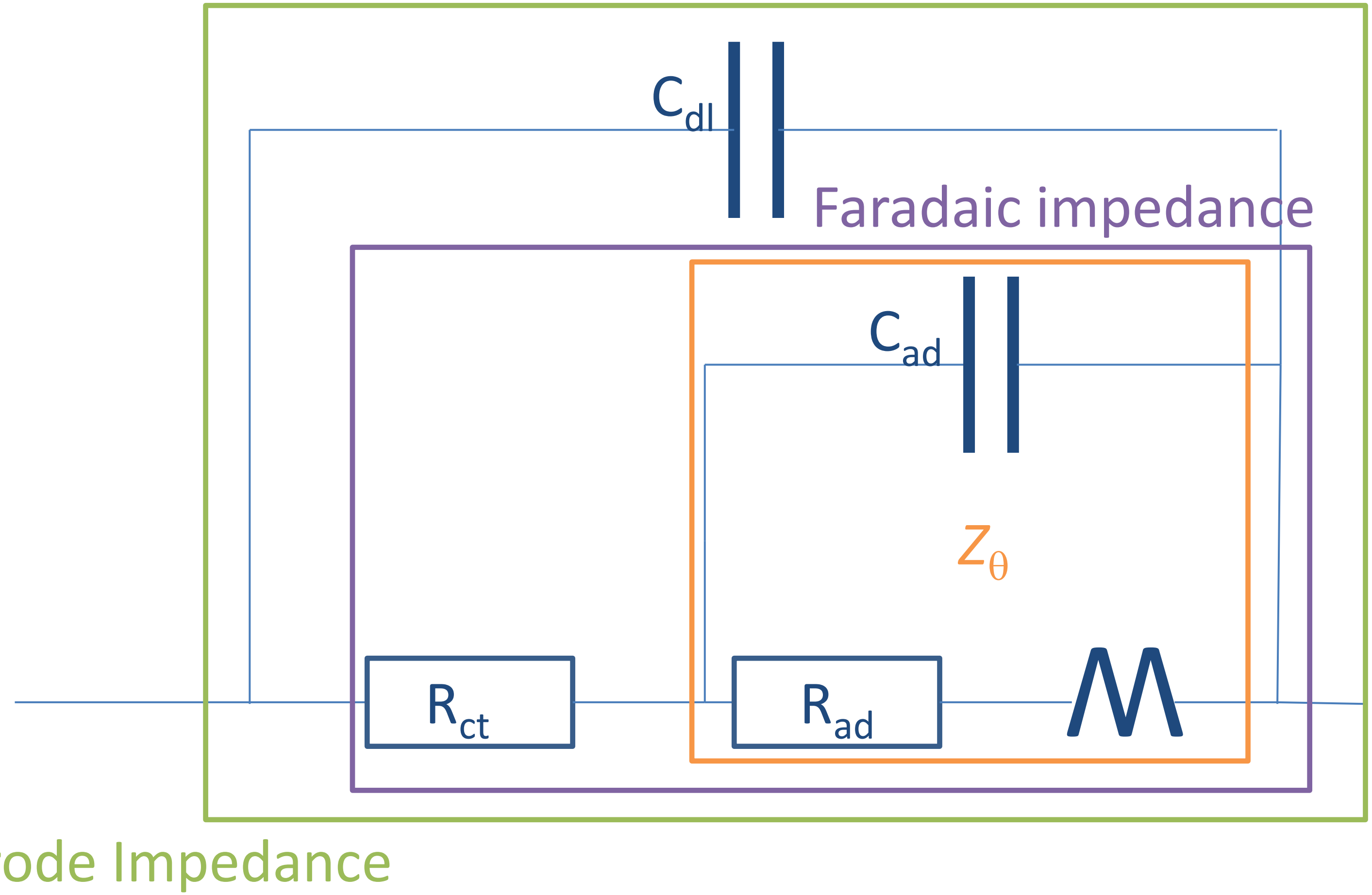
Electrosorption : $\mathbf{M}^{+} + \mathbf{s} + \mathbf{e}^{-} \underset{K_o}{\overset{K_r}{\leftrightarrow}} \mathbf{M}, \mathbf{s}$

Insertion : $\mathbf{M}, \mathbf{s} + <> \underset{k_d}{\overset{k_a}{\leftrightarrow}} < \mathbf{M} > + \mathbf{s}$

Electrosorption + Insertion

Faradaic impedance $Z_f(\omega) = R_{ct} + Z_\theta(\omega)$.

$Z_\theta(\omega)$ is the impedance related to the electroadsorbed species.



2. Insertion with preliminary adsorption

Adsorption :

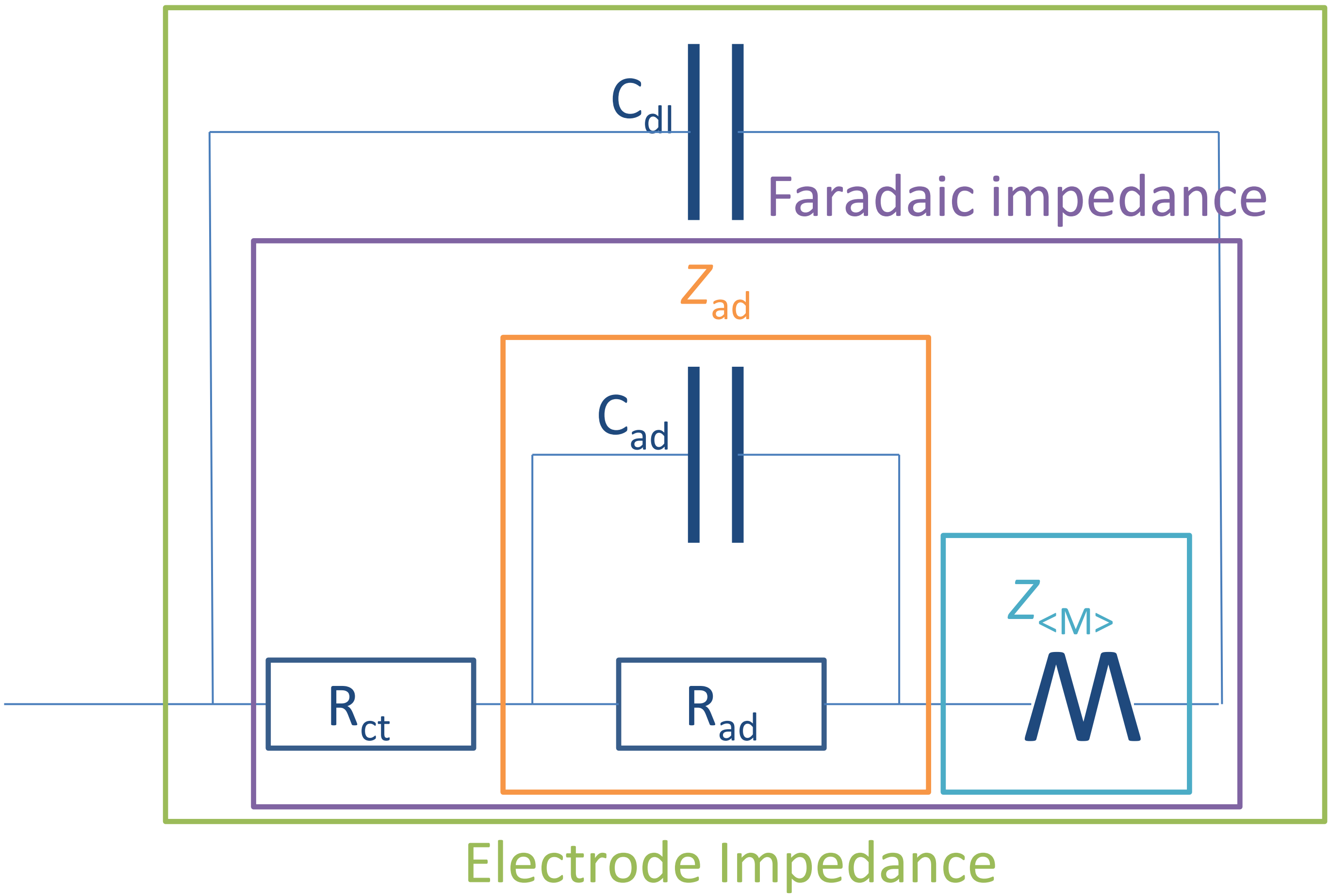
$$\mathbf{M}^{+} + \mathbf{s} \underset{k_\mathrm{d}}{\overset{k_\mathrm{a}}{\leftrightarrow}} \mathbf{M}^{+}, \mathbf{s}$$

Insertion :

$$\mathbf{M}^{+}, \mathbf{s} + \mathbf{e}^{-} + <> \underset{K_\mathrm{o}}{\overset{K_\mathrm{r}}{\leftrightarrow}} < \mathbf{M} > + \mathbf{s}$$

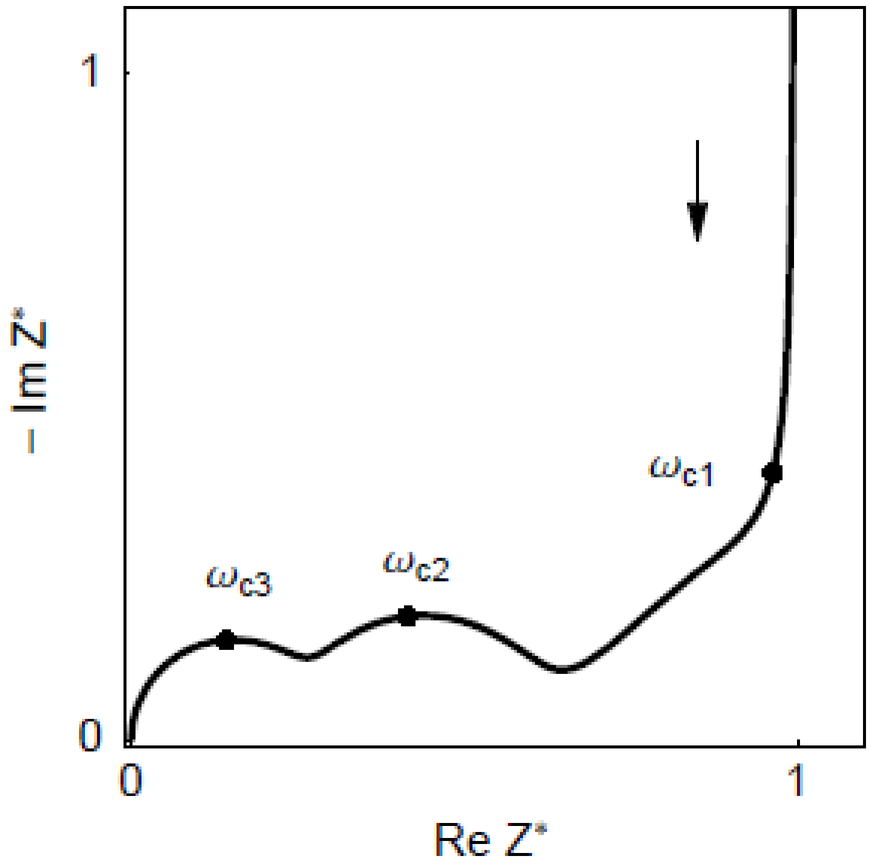
Adsorption + Insertion

Faradaic impedance = $Z_f(\omega) = R_{ct} + Z_{ad}(\omega) + Z_{<M>}(\omega)$



Adsorption + Insertion

Simulated Nyquist Plot

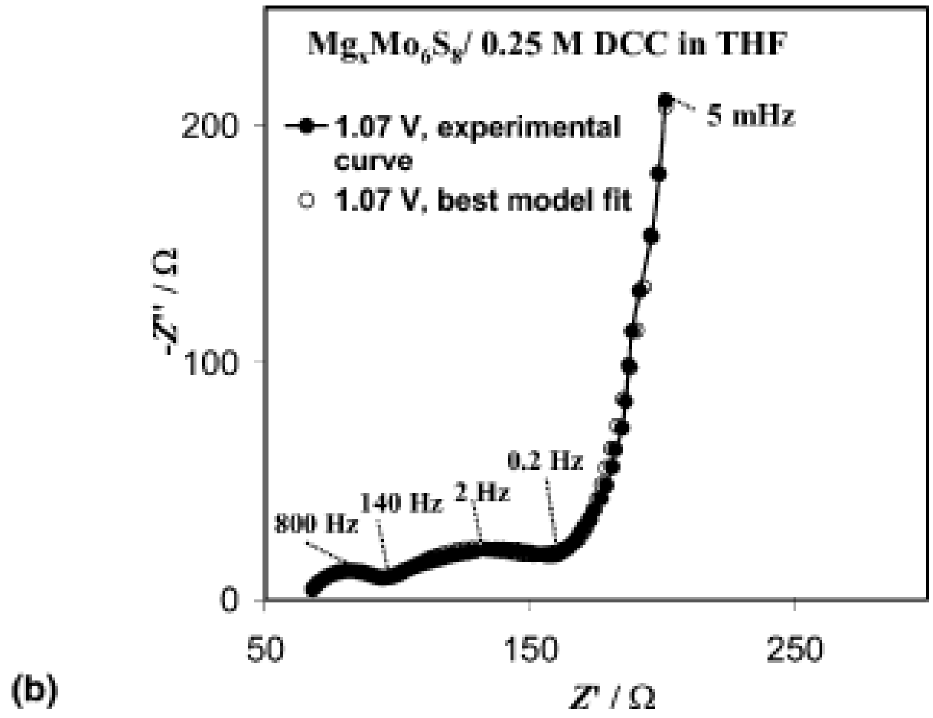


The insertion reaction with restricted diffusion

Adsorption + Insertion

Experimental Data

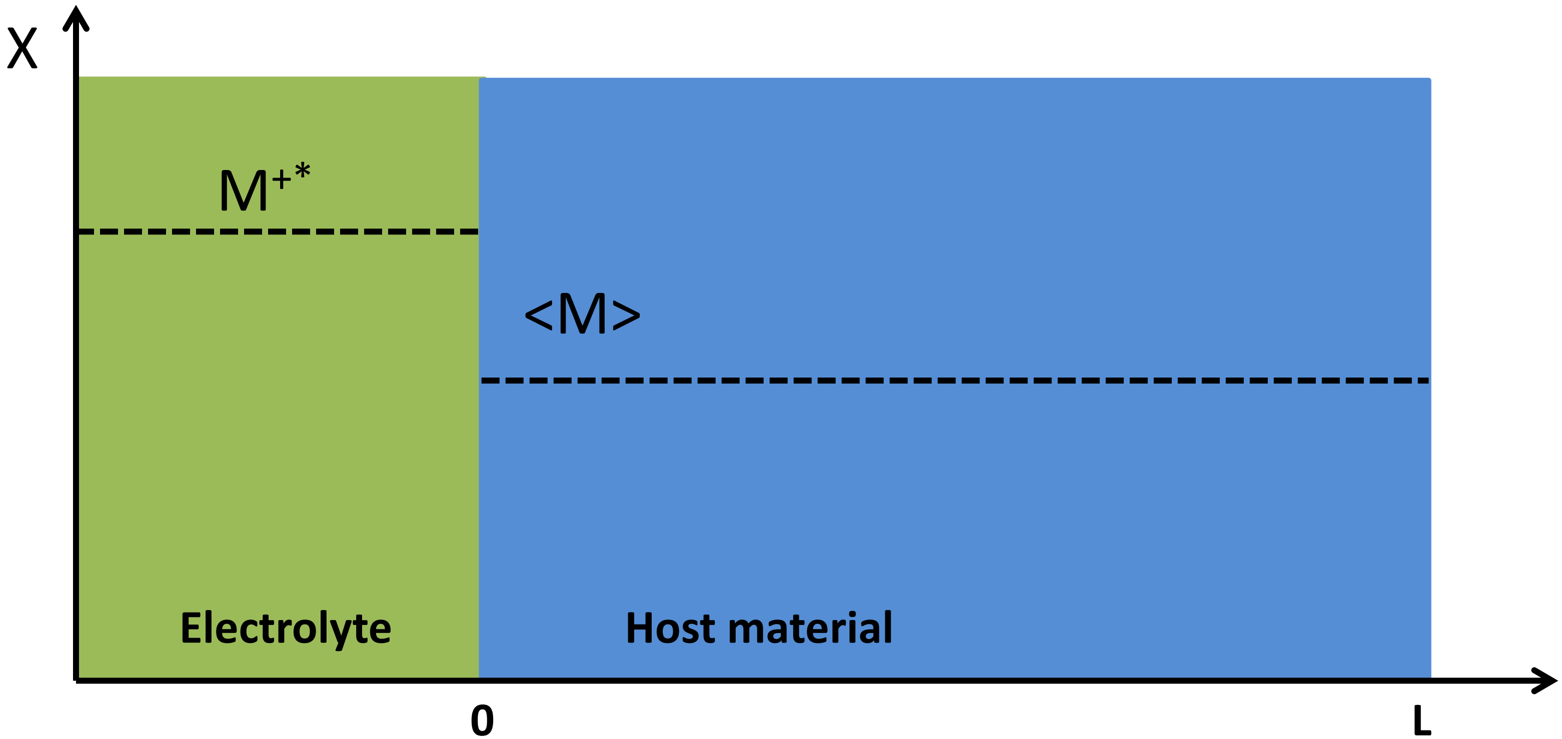
From M.D. Levi et al, J. Electroanal. Chem, 569, 2004



Mg-ion insertion into the Chevrel electrode ($M_xMo_6S_8$, $0 < x < 2$ for Mg and $0 < x < 4$ for Li)

Outline

Mechanism



The case for which the length of the host material is very large is a limit case of the direct insertion with restricted diffusion where either L is very large or $D_{<M>}$ is very small.

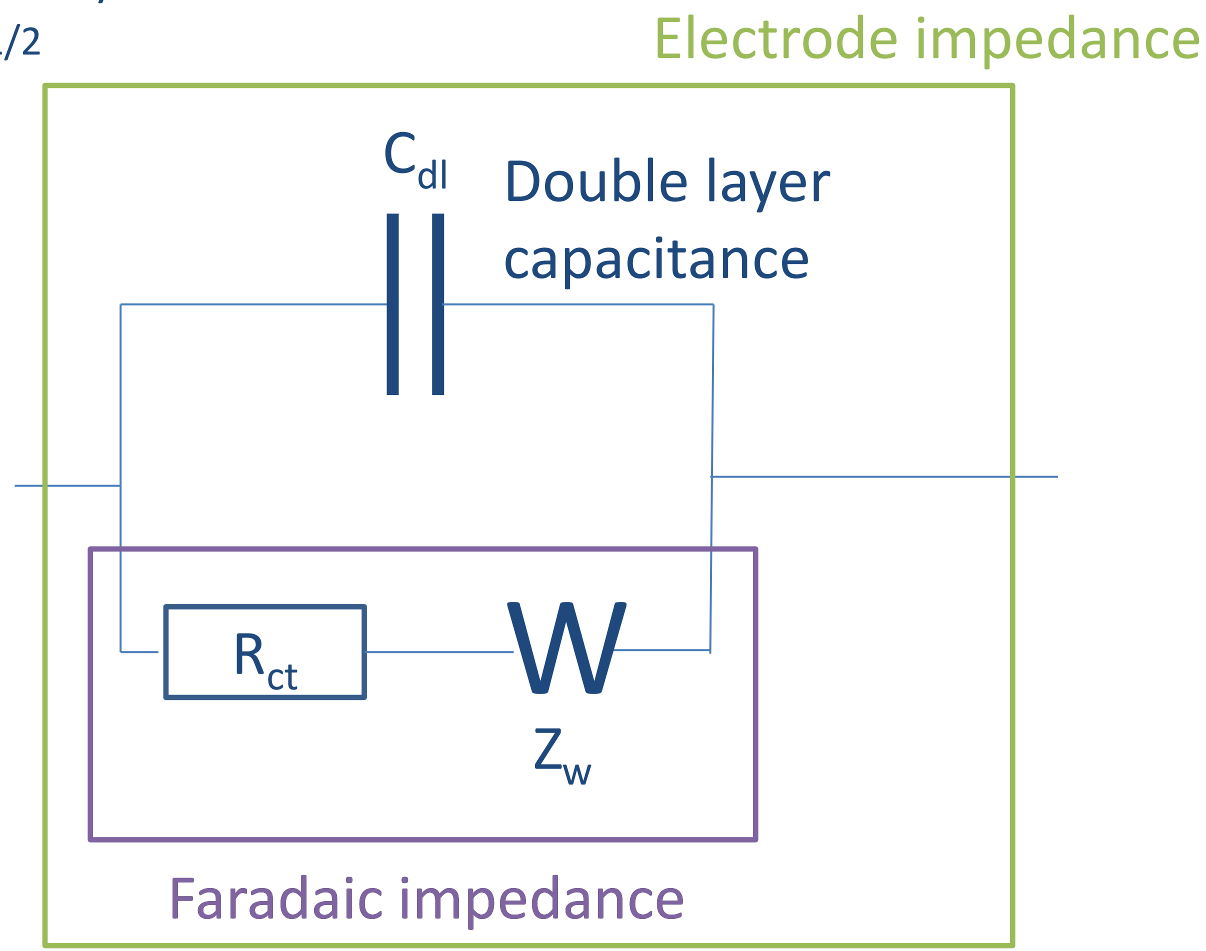
Equivalent Circuit

The impedance component of a diffusion in a semi-infinite media is called a Warburg component. It is symbolized by the letter W.

$$Z_w(\omega) = \sigma(1-j)/(j\omega)^{1/2}$$

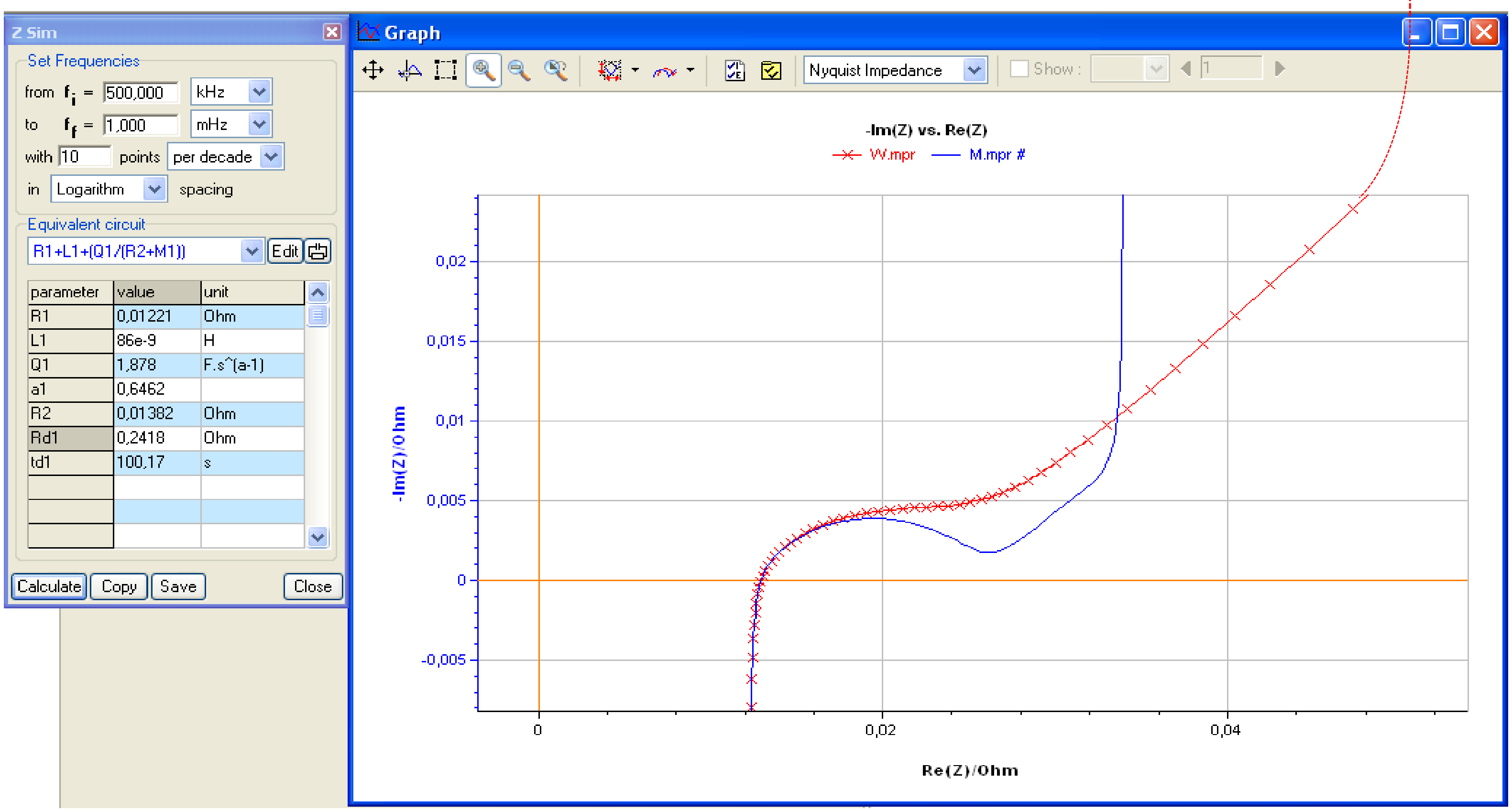
$$Z_f(\omega) = R_{ct} + Z_w(j\omega)$$

Such a circuit is called
a **Randles** circuit



Nyquist Plot

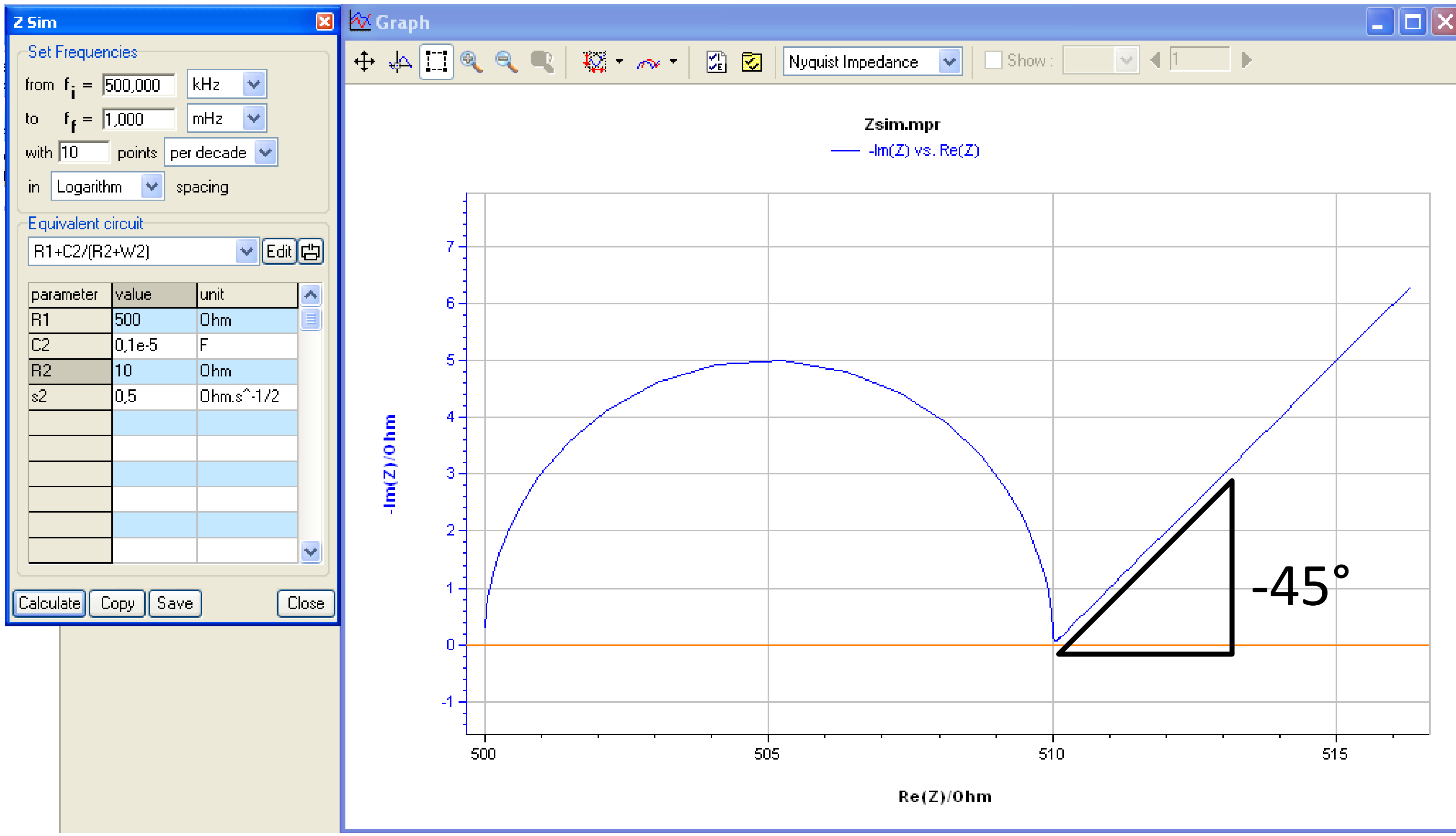
The vertical component on the Nyquist diagram is shifted to the much lower Frequencies, the time constant τ_{d1} (= $L^2/D_{<M>}$) is much larger.



R_{d1} = 0,2418 Ω instead of 0,02418 Ω, τ_{d1} = 100,17 s instead of 67,17 s

Nyquist Plot

Simulated impedance graph using ZSim



Randles circuit + electrolyte resistance

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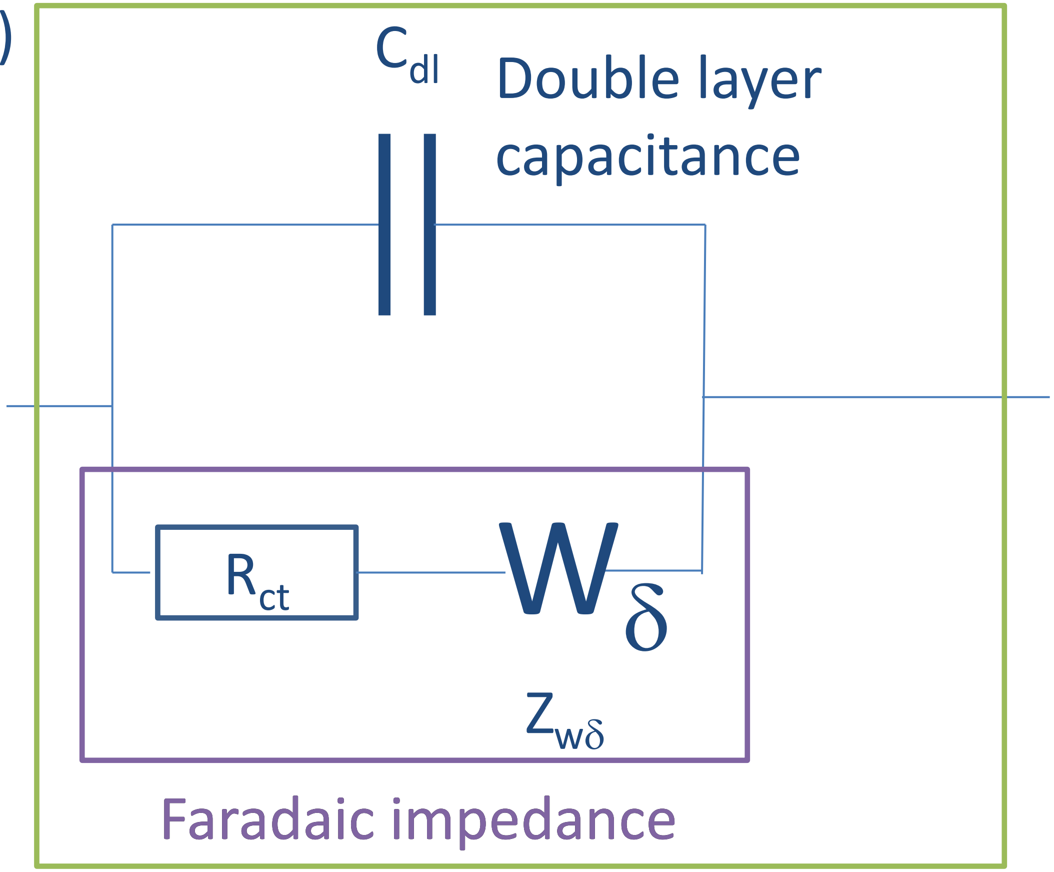
Equivalent Circuit

The impedance component of a bounded diffusion is a W_δ component.

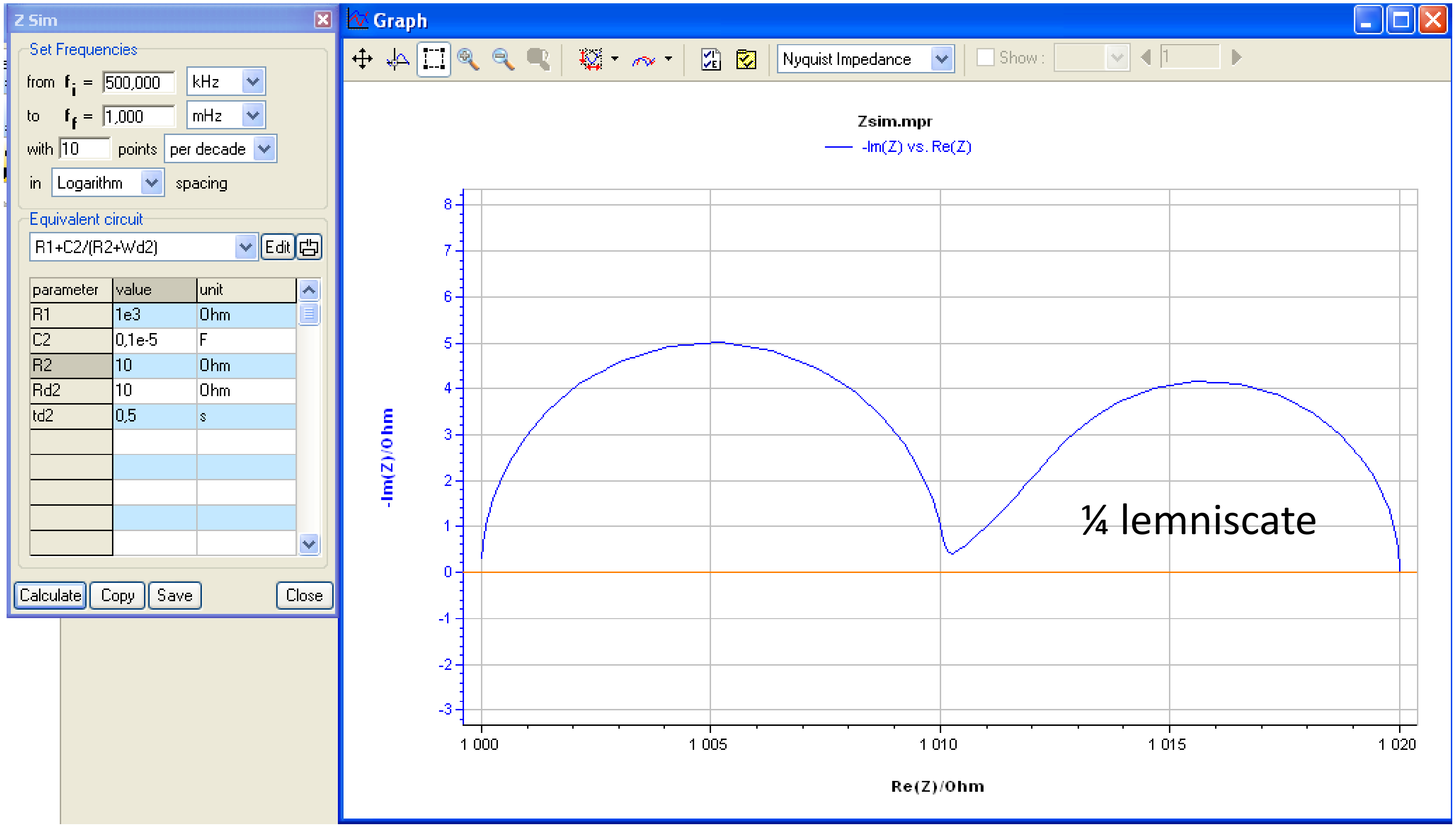
$$Z_{w\delta}(j\omega) = R_d \, th(\tau_d j\omega)^{1/2} / (\tau_d j\omega)^{1/2}$$

$$Z_f(j\omega) = R_{ct} + Z_{w\delta}(j\omega)$$

Electrode impedance



Simulated impedance graph using ZSim



What have we learned ?

- The reaction that takes place in a battery undergoing a charge or discharge is an insertion.
- The insertion involves a diffusion of the inserted species in three different conditions : restricted, semi-infinite, bounded.
- The insertion mechanism can be direct or involve a preliminary electrosorption or adsorption.
- For all these conditions, we now know :
    - The expression of the Faradaic impedance
    - The equivalent circuit
    - The Nyquist diagrams of the impedance

Now what ?

- Having this knowledge, we now how to interpret impedance data obtained on batteries.

- The next tutorial Impedance IIIb will show what useful characteristics of the batteries can be obtained from the impedance data.

References

Bio-Logic Website : www.bio-logic.info
http://www.bio-logic.info/potentiostat/notesifil.html

Faradaic Impedances

Mathematica Player files :

Direct Insertion

http://www.bio-logic.info/potentiostat/notes/20080131%20-%20Insertion1-ZmmaP.nbp

Electrosorption + Insertion

http://www.bio-logic.info/potentiostat/notes/20080307%20-%20IndirectInsertion1-mmaP.nbp

Adsorption + Insertion

http://www.bio-logic.info/potentiostat/notes/20080312%20-%20IndirectInsertion2-mmaP.nbp

Equivalent Circuits
http://www.bio-logic.info/potentiostat/iecl/20101004%20-%20RandlesCircuit-mmaP.nbp