fuel cell fractional modelling

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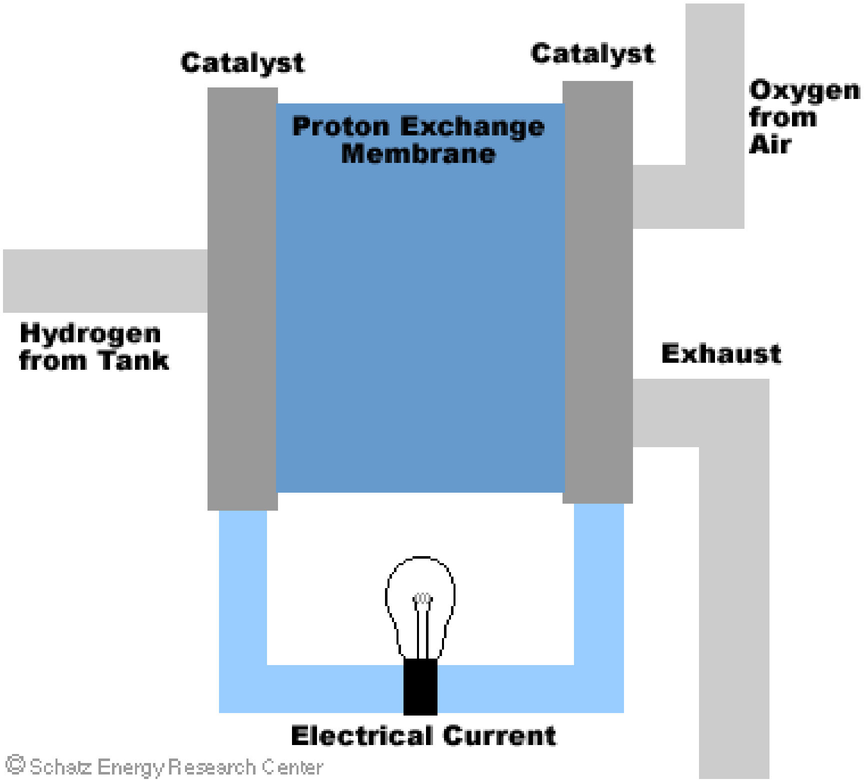
Fuel cell principle



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2 gaz diffusion electrodes:

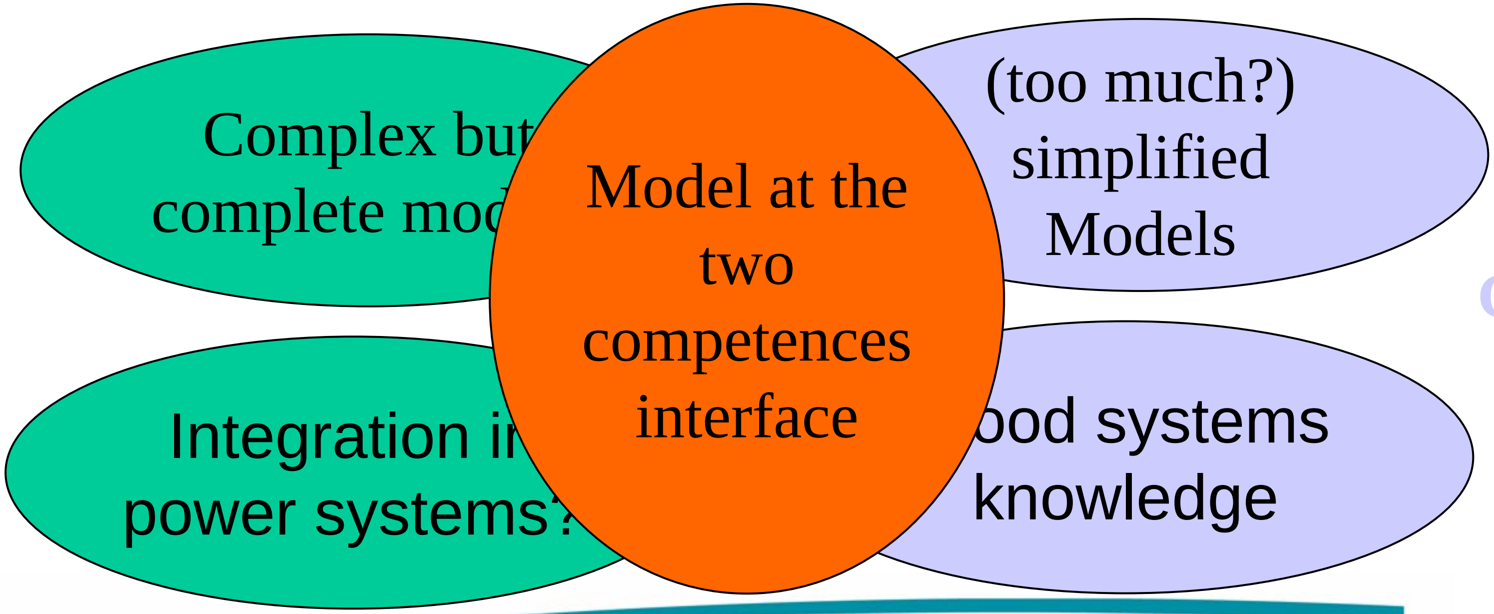
anode:
  hydrogen oxidation

cathode:
  oxygen reduction

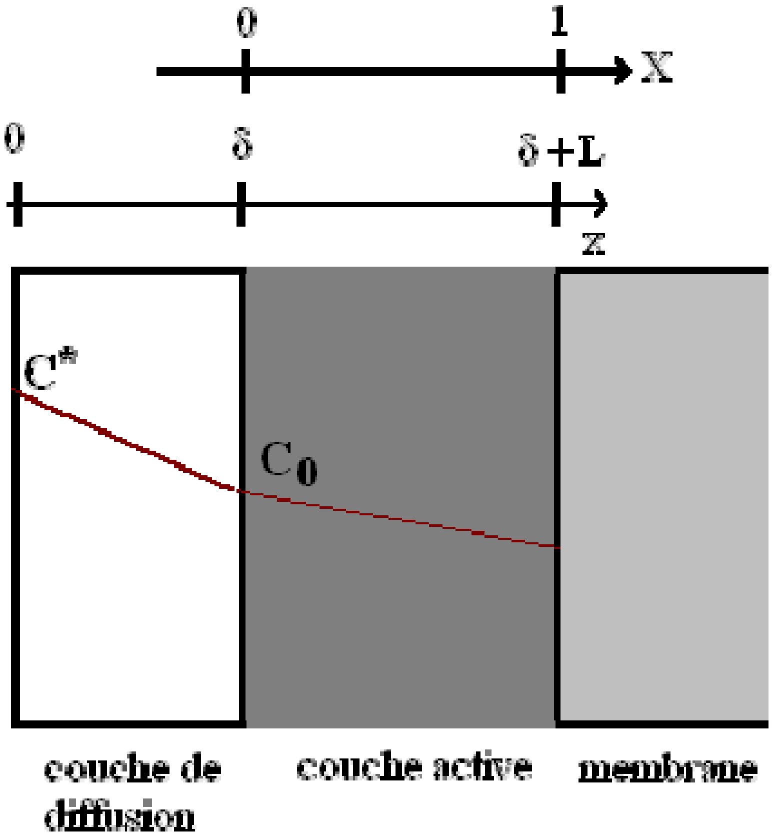
an electrolyte:
  a polymer

Study context

- New energy sources use
- Technology still badly controlled in a "Systems" application



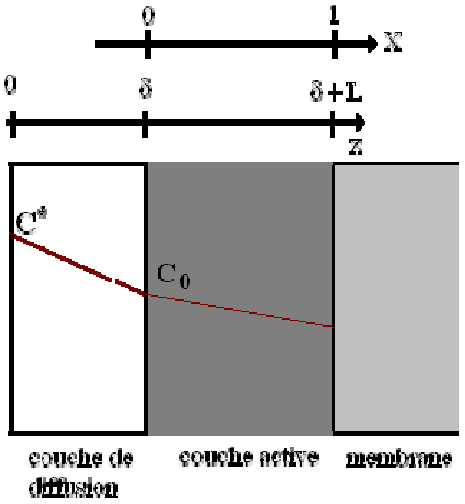
Fuel cell modeling



Three characteristic areas for each electrode:

- The diffusion layer
- the active layer
- the membrane

Active layer



- delocalization of the reaction in all the volume
- mass onservation:

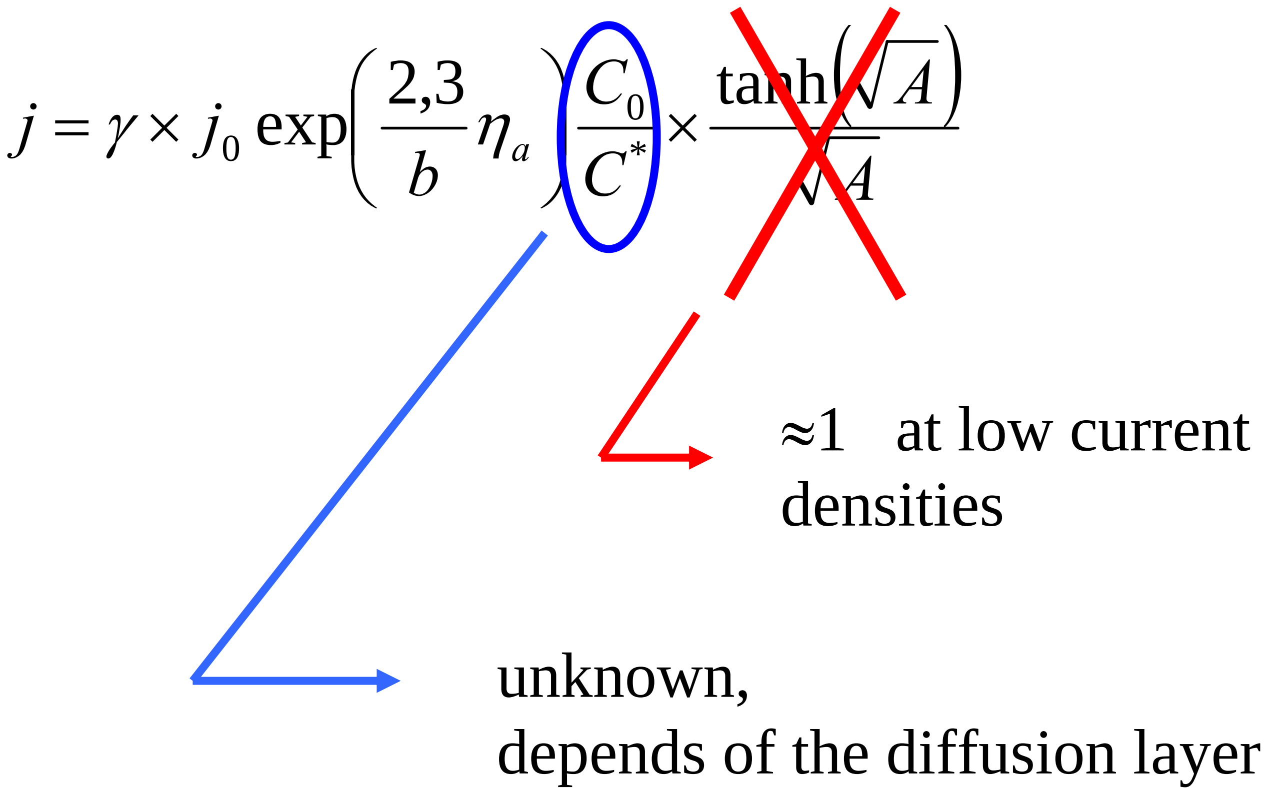
$$D\frac{\partial^2 C}{\partial x^2} = \pm\frac{\gamma}{L}\frac{j}{nF}$$

Reaction consumption

Tafel kinetic law

$$j = j_0\left[\exp\left(\frac{2,3}{b}\eta\right)\frac{C}{C^*}\right]$$

Active layer

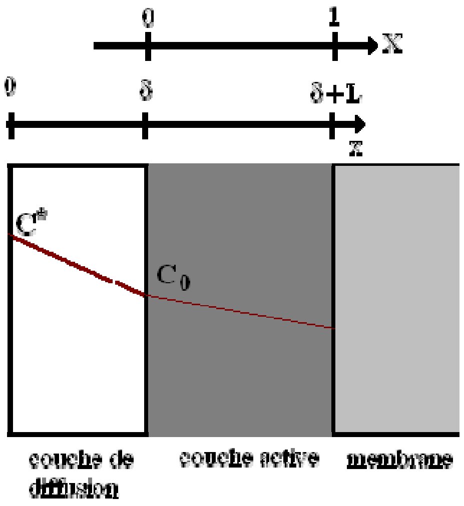


$$j = \gamma \times j_0 \exp\left(\frac{2{,}3}{b}\eta_a\right)\boxed{\left(\frac{C_0}{C^*}\right)} \times \cancel{\frac{\tanh\left(\sqrt{A}\right)}{\sqrt{A}}}$$

≈1 at low current densities

unknown,
depends of the diffusion layer

Diffusion layer



Fick diffusion law

$$D_{eff}\frac{\partial^2 C}{\partial x^2}=0$$

No reaction
We obtain:

$$\frac{C_0}{C^*}=1-\frac{j}{j_{\lim}}$$

$$\frac{j_{\lim}}{nF}=-D_{eff}\frac{0-C^*}{\delta}$$

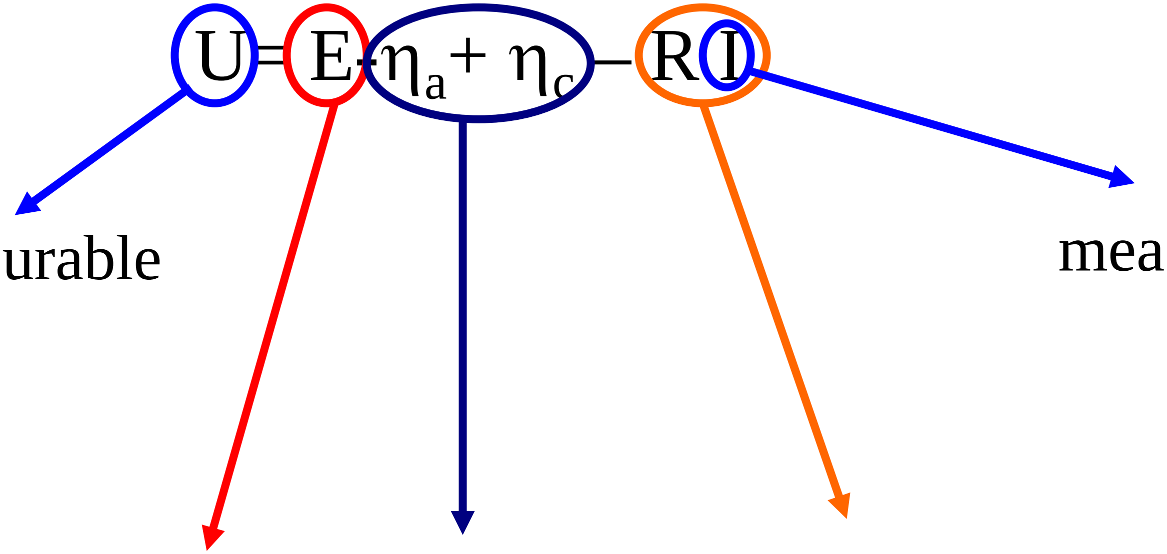
Current density expression

- We obtain:

$$j = \underbrace{\gamma}_{\text{Roughness factor}} \times \underbrace{j_0 \exp\left(\frac{2{,}3}{b}\eta\right)}_{\text{kinetic}} \underbrace{\left(1 - \frac{j}{j_{\lim}}\right)}_{\text{Diffusion limitation}}$$

Fuel cell voltage

Fuel cell voltage equation



$$U = E - \eta_a + \eta_c - RI$$

measurable

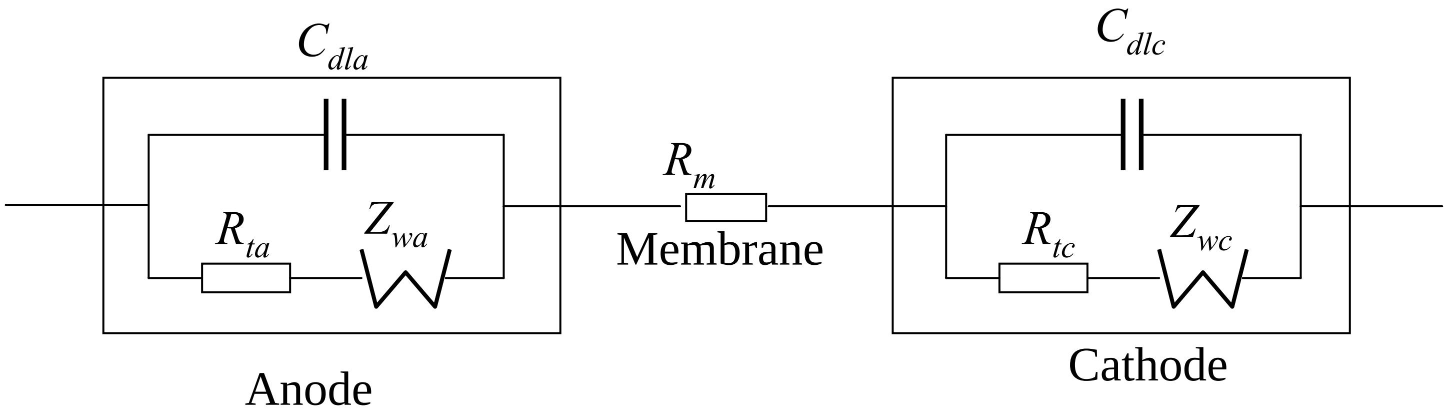
measurable

Thermodynamic potential

Over-potential

Ohmic loss

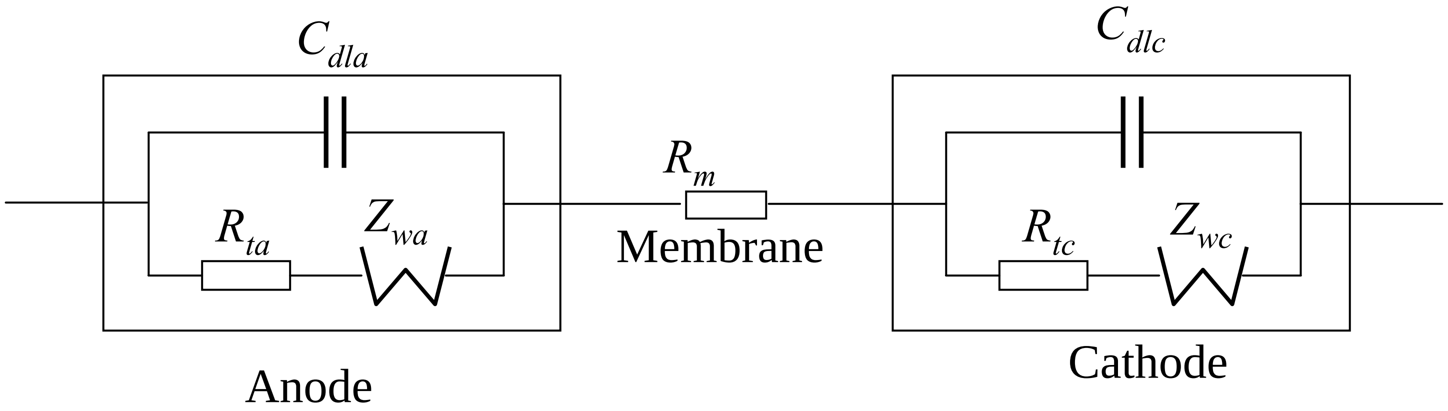
Fuel cell Impedance



3 elements per electrodes:

- Rti: mass transfer resistance
- Z_{wi}: Warburg impedance : diffusion limitation
- C_{dli}: double layer capacitance: charge accumulation at the membrane/active layer interface

Fuel cell impedance



$$Z_{Total}(\omega) = Z_a(\omega) + R_m + Z_c(\omega)$$

$$Z_{electrode}(w) = \frac{1}{{}^{1}\!/\!_{Z_{fk}(s)} + iwC_{dl}^{eff}}$$

avec $Z_{fk}(w) = R_{tk} + Z_{Wk}(w)$

Fuel cell impedance

$$R_{tk} = \frac{1}{\partial j_k \big/ \partial \eta_k} = \frac{1}{\gamma_k \, j_{ok} \, \dfrac{2.3}{b_k} \; exp\left(\frac{2.3 \left| \eta_k \right|}{b_k} \right) \left(1 - \dfrac{j}{j_{lk}} \right)}$$

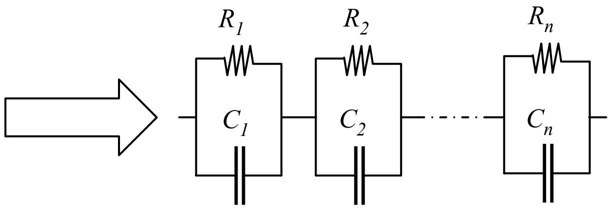
$$Z_{Wk}(w) = \frac{\partial j_k \big/ \partial C_k}{\partial j_k \big/ \partial \eta_k} \; \frac{\delta}{n_e \; F \; D_k^{eff}} \; \frac{\tanh(\sqrt{i w \tau_k})}{\sqrt{i w \tau_k}}$$

$$Z_{Wk}(w) = A_k(j) \, \frac{\tanh(\sqrt{i w \tau_k})}{\sqrt{i w \tau_k}}$$

Fuel cell impedance

- 2 models were studied :
  - Foster series development

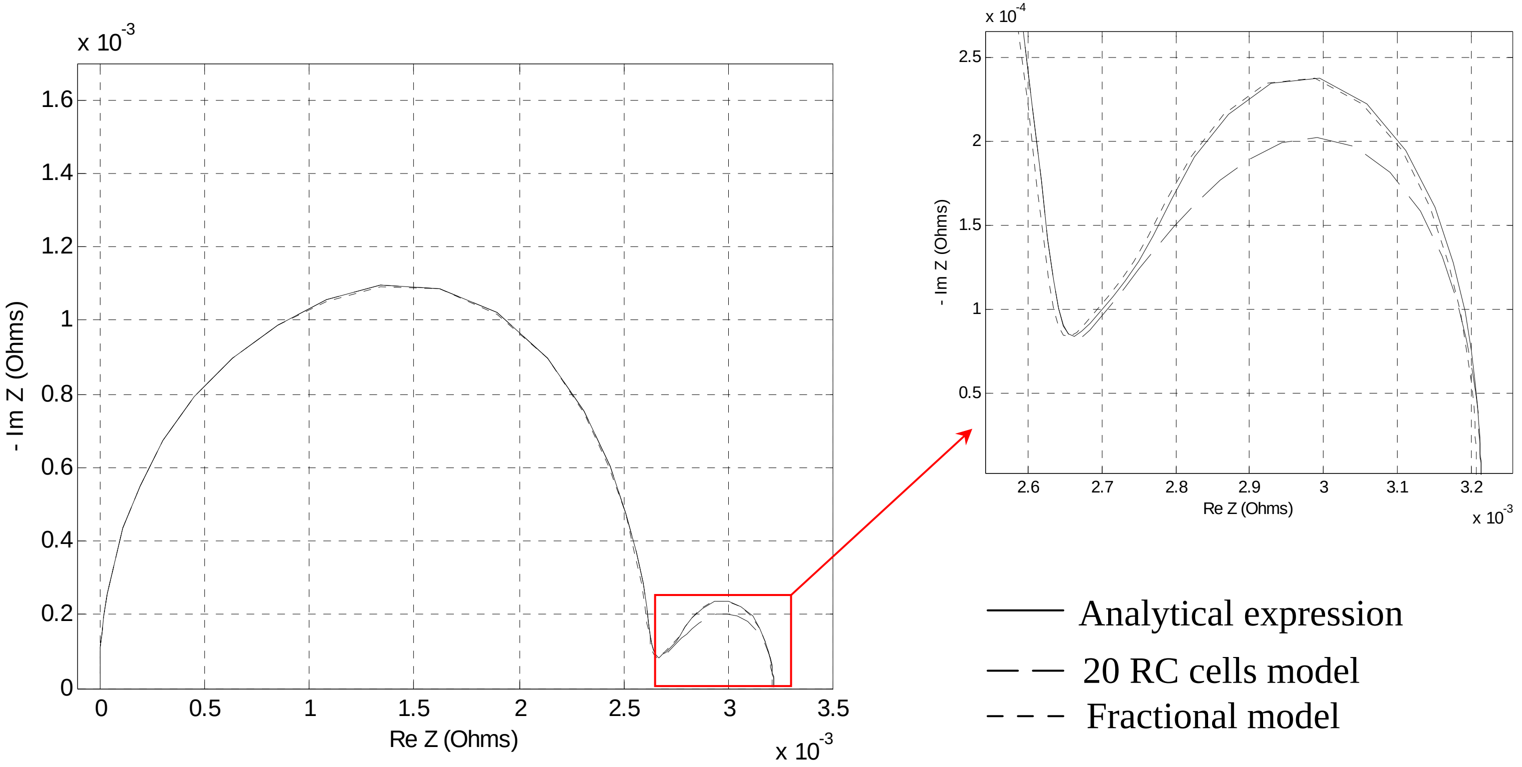
$$Z_{Wk}(s) = 2A_k(j)\sum_{n=1}^{\infty}\frac{1}{s\tau_k + \left[\frac{\pi(2n-1)}{2}\right]^2}$$



  - First order Taylor development
    - ↳ Fractional model (half order)

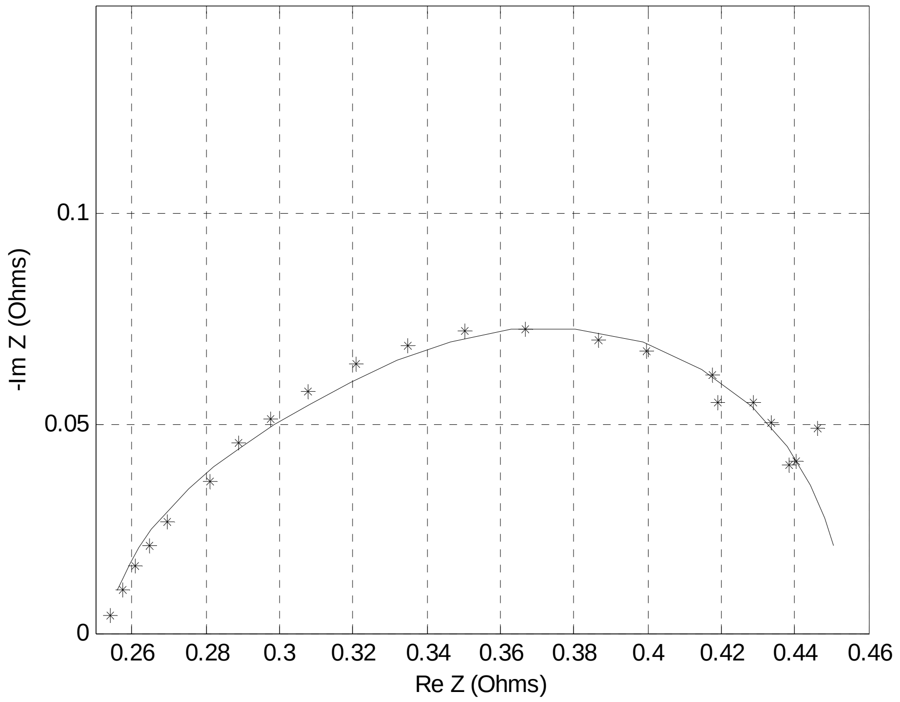
$$\boxed{Z_{Wk}(s) = \frac{A_k(j)}{\sqrt{1+s\tau_k}}}$$

Models comparison



Bad agreement between analytical expression and 20 RC cells model at low frequencies (diffusion arc)

Results: comparison between experimental and half order model spectra



- Good adequacy between model and the experiment

Conclusion

- Reduction of the number of parameters to be identified
- No losses of information on the chemical phenomena

Application

500 W demonstrator development (FC + storage) allowing :

- Energy optimization of the unit (command laws),
- Validation of fuel cell and storage fractional models,
- Study of the external parameters influence (T, P, H_20, …)