Impedance modeling of electrochemical systems

Application to PEMFCs and supercapacitors

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Outline

1. Hydrogen & Electrochemical Systems (HES) research group
2. Introduction to Electrochemical Impedance Spectroscopy (EIS)
3. Modeling of electrochemical storage devices → Supercapacitors (SCs)
4. Modeling of electrochemical generators → Polymer Electrolyte Membrane Fuel Cells (PEMFCs)
5. Concluding remarks

Outline

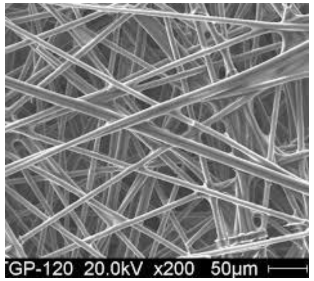
1. Hydrogen & Electrochemical Systems (HES) research group
   - Scientific context
   - Topics – Issues - Approach
   - Instrumented cells
   - *In-situ* characterization

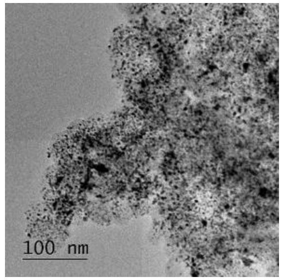
Research activities at LEMTA (director: P. Boulet)

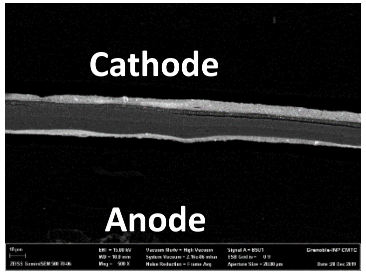
- ❑ Energy and Transfer
- ❑ Fluid Media, Rheophysics
- ❑ MRI for Engineering
- ❑ **Energy Carriers**
  - Heat Management (B. Rémy)
  - Management of Electrical Energy (S. Pierfederici)
  - **Hydrogen and Electrochemical Systems**
    - ✓ 9 researchers and engineers (J. Mainka, julia.mainka@univ-lorraine.fr)
    - ✓ 12 (+4) PhDs, post-docs and internships

1. HES research group → Scientific context

Material sciences

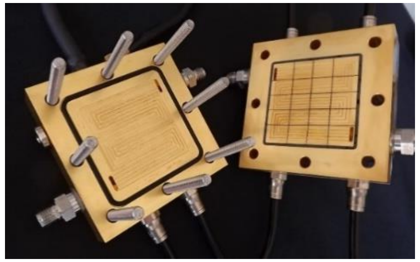


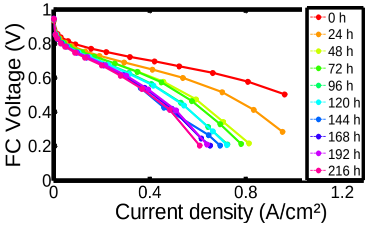


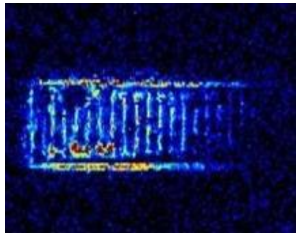


Membranes, catalysts, bipolar plates…

HES group @ lemta







Membrane-Electrode Assemblies (MEA) and components of Fuel Cells (FC) and other electrochemical systems

Electrical engineering

Systems for industrial and commercial applications…

1. HES research group → Principal applications

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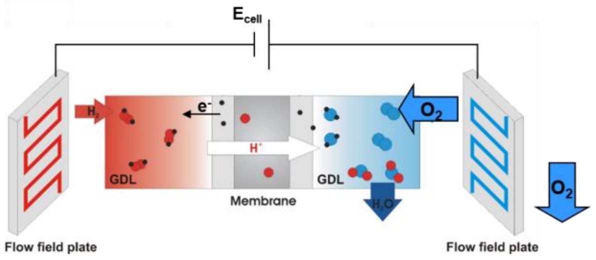
- Supercapacitors (SCs)
- Hybridization PEMFC-SC

2002 - 2006

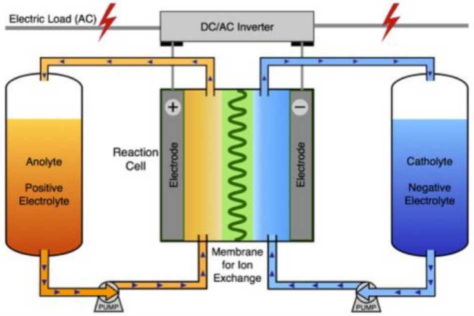
PEMFC



2009

NMR/MRI membranes


2015



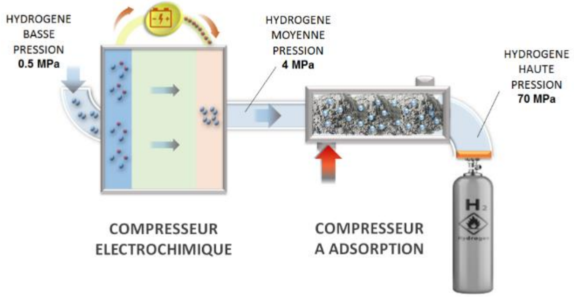
Redox flow-batteries

2016

KEMIWATT Your energy bank

2017

- DBFC
- PEMWE
- FC Management Systems
- H_2 Compression (electrochemical & adsorption/desorption 700 bar)



2019

- Electrode fabrication (spray)
- Catalysts
- AEMFC

esa

Joule-Thomson cooler

2022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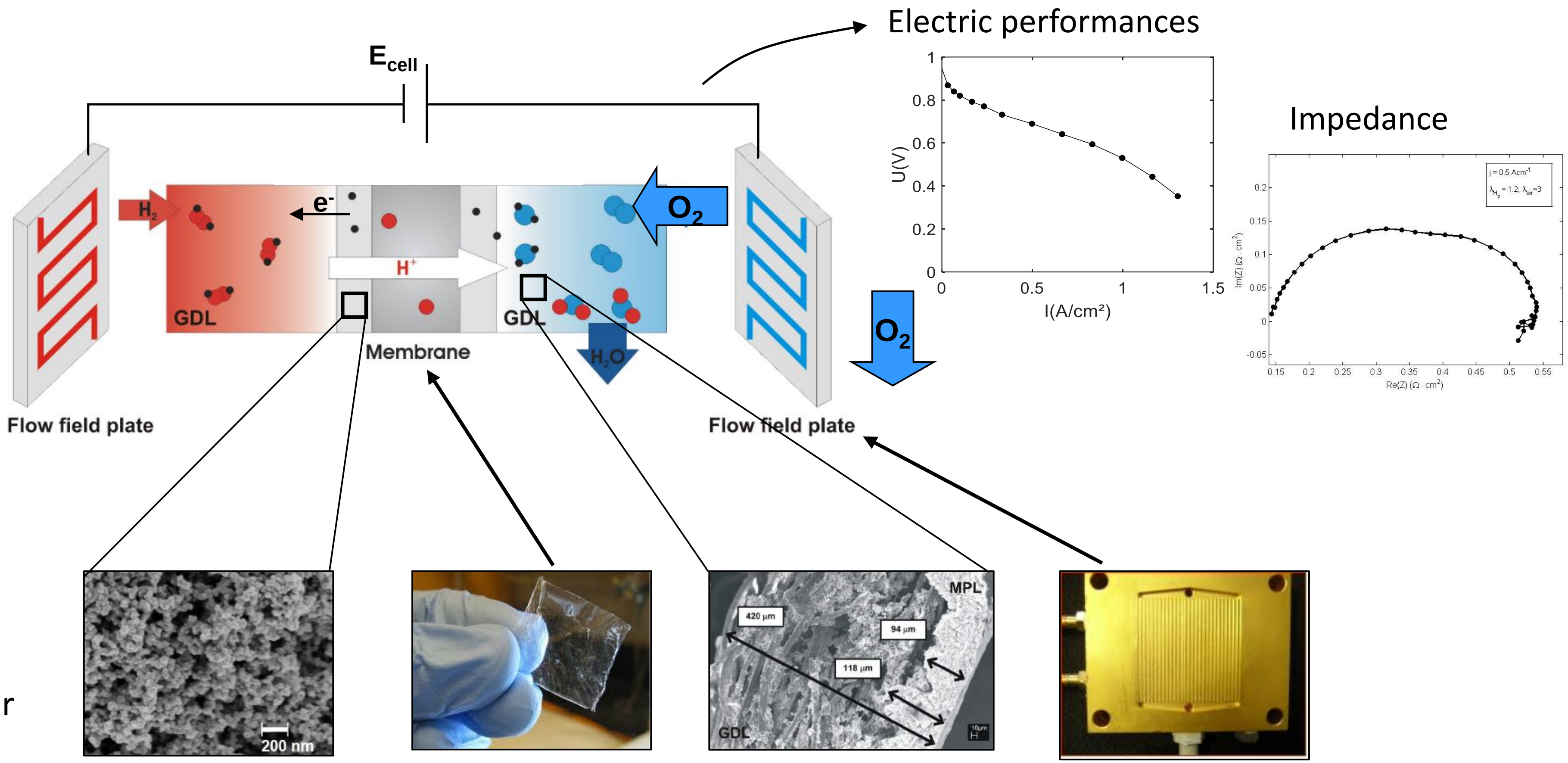
1. HES research group → Scientific approach

- **Macroscopic** phenomena

→ **Well-adapted measuring techniques**



Carter et al., Handbook of Fuel Cells, Wiley-VCH, 2009

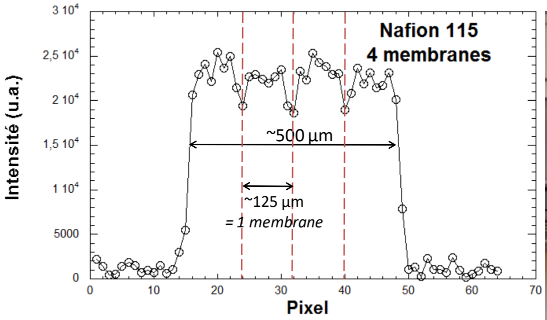
Gostick et al., J. Power Sources 156, 2006

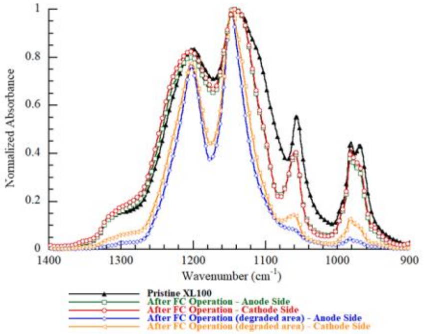
- **Microscopic** phenomena
  - Heat, charge and mass transfer
  - Water management
  - Degradation phenomena

→ **Appropriate description of physico-chemical processes and geometry**

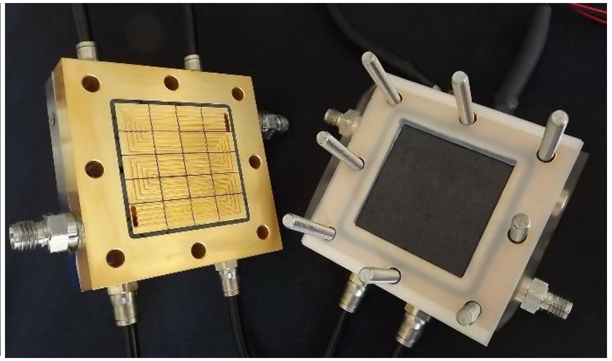
1. HES research group → Main topics & issues

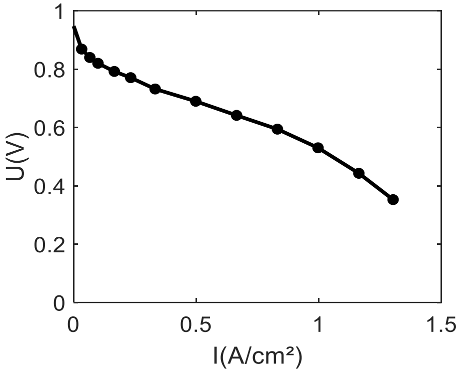
Ex-situ analyses → Structure and properties (membranes)





In-situ analyses → Electric performances and durability





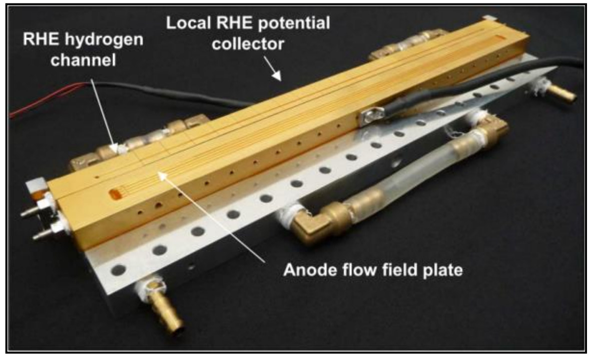
Innovating architectures → Systems

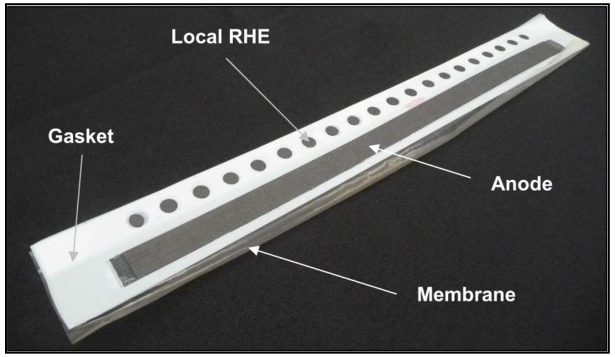
Main Issues → Performances & Durability

1. HES research group → Instrumented cells

- **Segmented cells** → Measurement of local performances and working conditions for durability studies

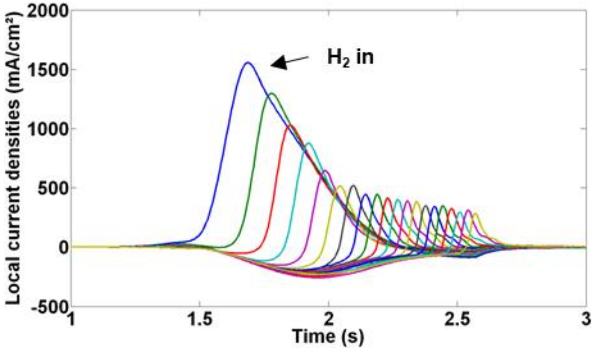
  - **Linear cells** (30 x 1cm² - 5 parallel flow fields)



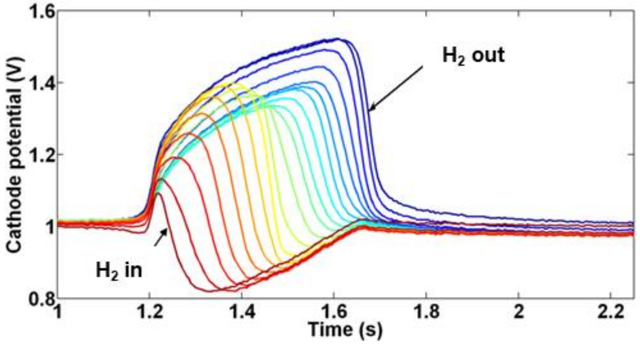


PEMFC dégradation Start & Stop

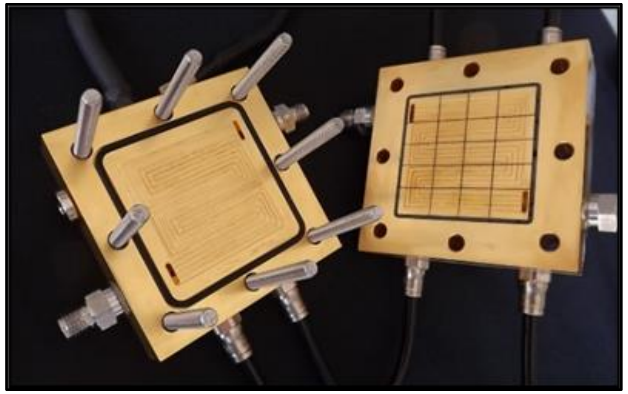
Local currents

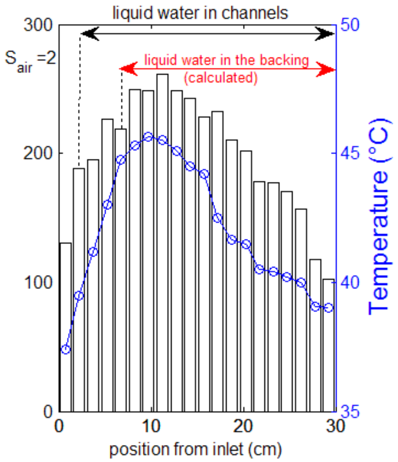


Cathode potentials

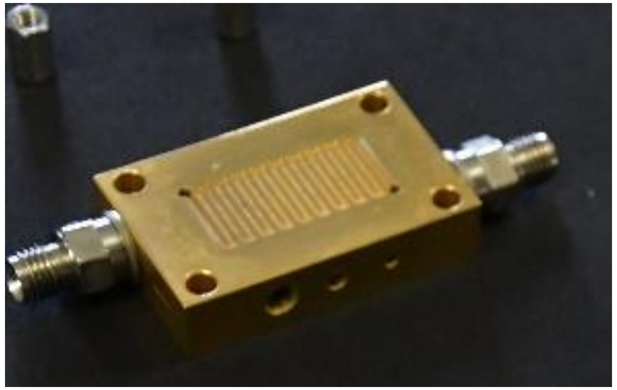


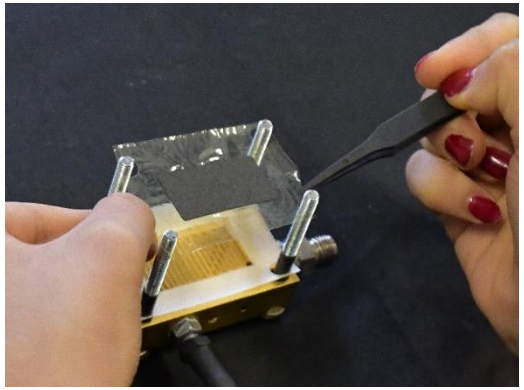
  - **Standard geometries** (5cm x 5cm)





- **Single cells (7.6cm²)** → Test of new materials

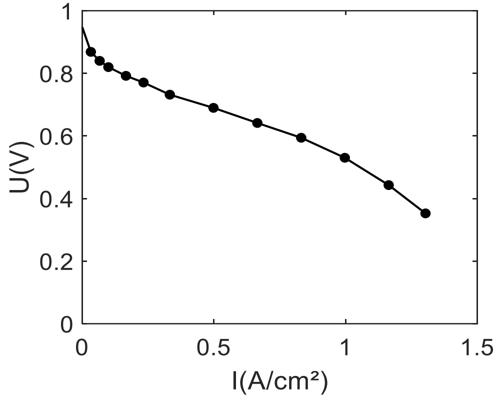




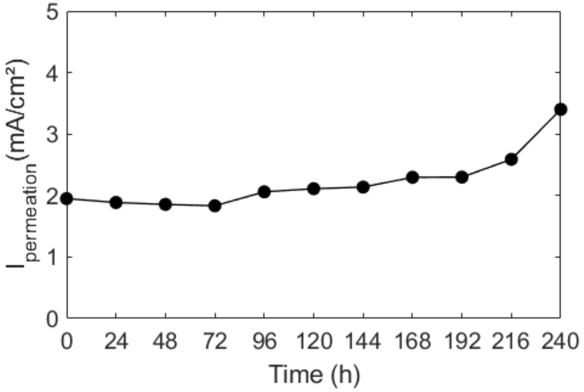
1. HES research activities → In-situ characterization

❑ Steady-state methods

Polarization curves

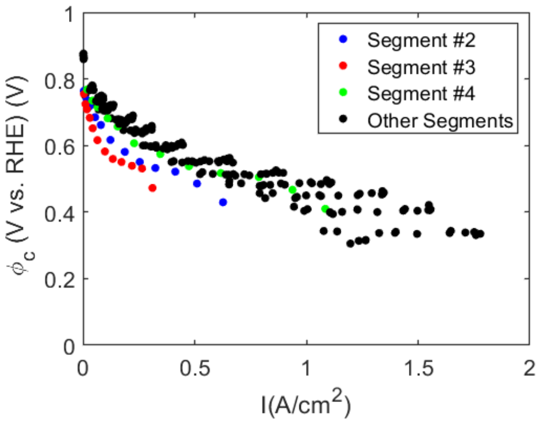


H_2 permeation current

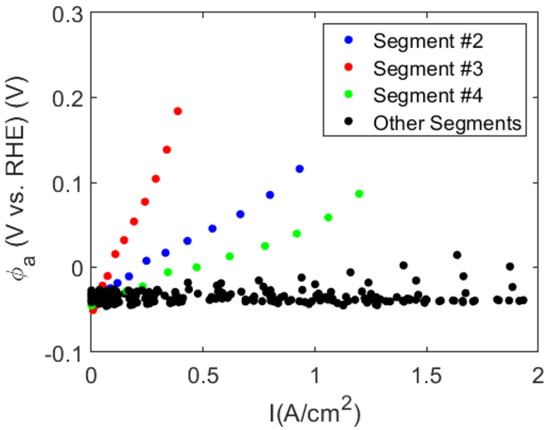


Electrode potentials

Cathode

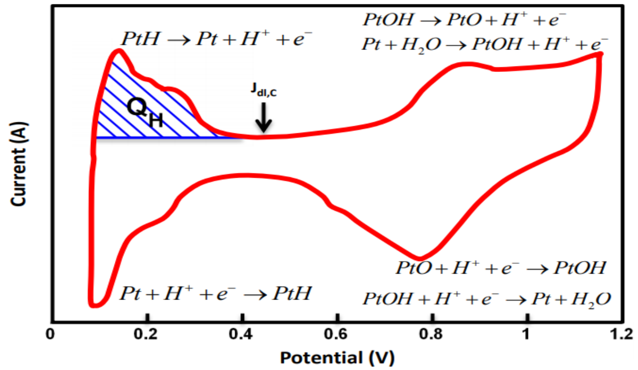


Anode



❑ Transient methods

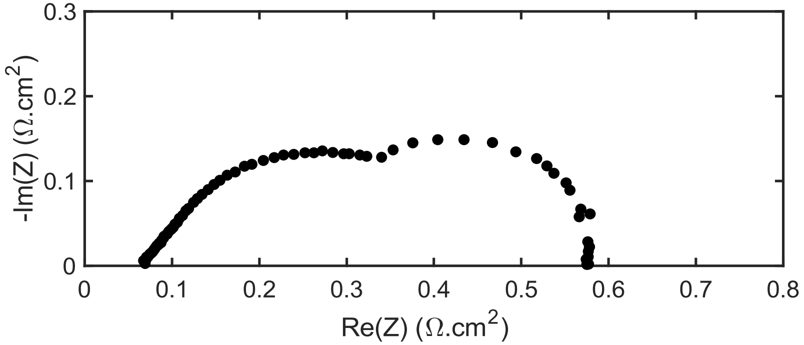
Cyclic Voltammetry



→ ElectroChemical Surface Area (ECSA)

$$ECSA = \frac{Q_H}{210\ \mu C/cm^{-2}_{Pt} . L_{Pt}}$$

Electrochemical Impedance Spectroscopy



→ Electrochemical parameters
→ Voltage drop sources

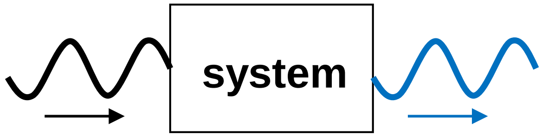
Outline

2. Introduction to EIS - Principle

- **Electrochemical Impedance Spectroscopy (EIS)** is a common technique used to **analyze the performance** of electrochemical systems such as fuel cells and supercapacitors

- **Method**: application of a small sinusoidal perturbation to a system and measurement of the associated dynamic response

$\Delta I(t) = \Delta\bar{I}\mathrm{e}^{i\omega t}$ $\Delta U(t) = \Delta\bar{U}e^{i(\omega t+\Phi)}$



Transfer function

$\omega = 2\pi f$: angular frequency

Impedance

$$Z = \frac{\Delta U(t)}{\Delta I(t)} = \frac{\Delta\bar{U}e^{i(\omega t+\Phi)}}{\Delta\bar{I}e^{i\omega t}} = \bar{Z}e^{i\Phi} = Z' + i\,Z''$$

→ Separate *in-situ* analysis of microscopic phenomena occuring at different time scales in the frequency domain

- Two possible modes according to the control variable
  - **Potentiostatic mode** : voltage variation imposed → current perturbation measured
  - **Galvanostatic mode** : current variation imposed → voltage perturbation measured

- **Requirements**
  - Stable operating conditions
  - Linearity between input (stimulus) and output (response) signal
  - Causality

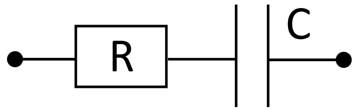
2. Introduction to EIS – Graphical representation

❑ Nyquist plot

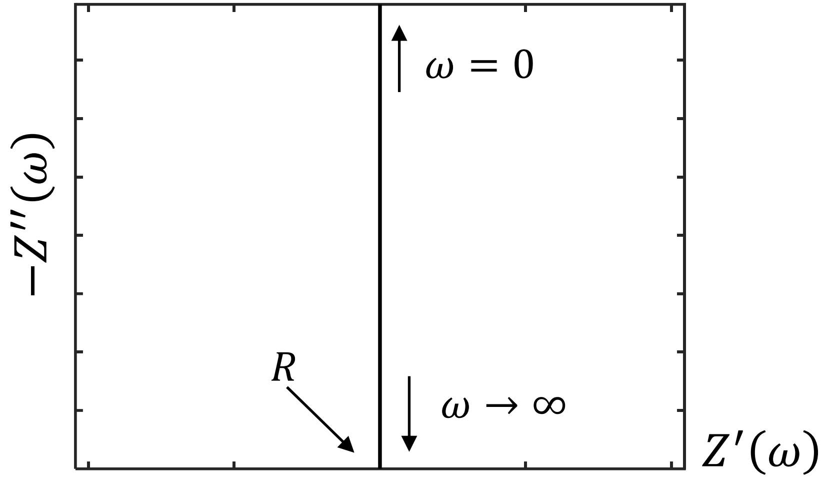
Cartesian form of the impedance $\mathbf{Z} = \boldsymbol{Z'} + \boldsymbol{i}\,\boldsymbol{Z''}$ → representation of the negative imaginary part $-Z''$ vs. the real part Z' for a given angular frequency $\omega = 2\pi f$

Examples

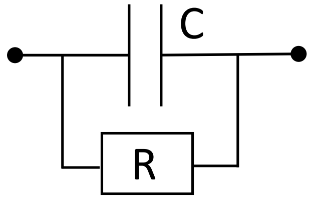
- R - C series connection



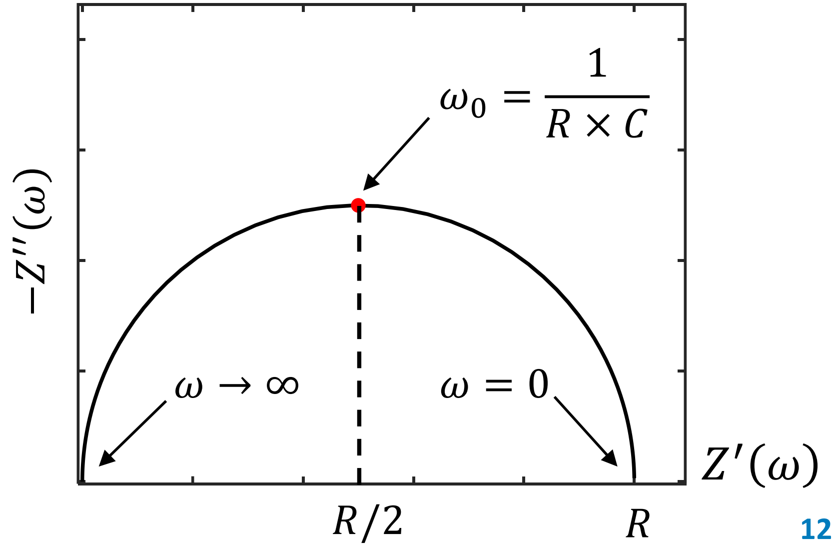
$$Z(\omega) = Z_R + Z_C = R + \frac{1}{i\omega C}$$



- R - C parallel connection



$$Z(\omega) = \left(\frac{1}{Z_R} + \frac{1}{Z_C}\right)^{-1} = \frac{1}{\frac{1}{R} + i\omega C}$$



2. Introduction to EIS – Interpretation

❑ Main modeling approaches [1]

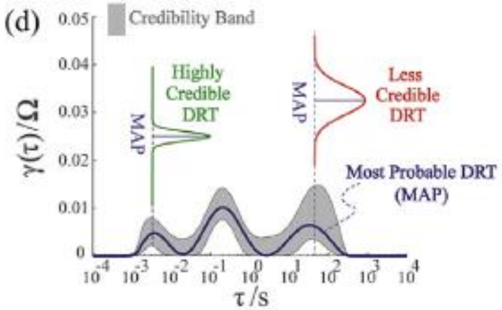
Physical models

- Derived from problem specific physical phenomena
- Yield information about the phenomena governing the operation of the system
- More challenging to solve → generally limited to single components and/or simple systems

$$i2\pi f\tau_{ion}(\mu^*_{ion} - \mu^*_{eon}) = \Delta\mu^*_{ion}$$
$$i2\pi f\tau_{eon}(\mu^*_{eon} - \mu^*_{ion}) = \Delta\mu^*_{eon}$$

Distribution of Relaxation Times (DRT) [2]

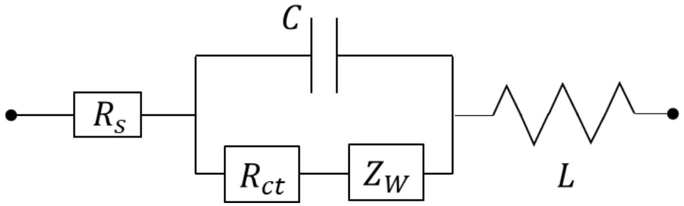
- Analysis of the system relaxation after the application of small signal perturbation
- Interpretation in terms of timescale distribution of the individual physical processes



$$Z(f) = R_0 + \int_{-\infty}^{\infty} \frac{\gamma(\tau)}{1 + i2\pi f\tau} d\tau$$

Equivalent Electrical Circuits (EECs)

- Assembly of electric components (resistors R, capacitors C, inductances L…)
- Objective: reproduce the impedance $Z(\omega)$ of a system
- Parameters ideally related to physical phenomena



[1] Ciucci, Current Opinion in Electrochem. 13, 2019
[2] Effat MB, Ciucci F, Electrochi. Acta 247, 2017

Outline

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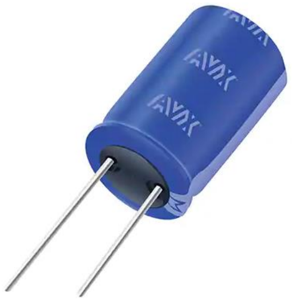
3. Modeling of electrochemical storage devices → Supercapacitors (SCs)

- Generalities
  - ✓ Operation principle
  - ✓ Characterization methods
- Usual EEC models
  - ✓ Electrical Double-Layer Capacitors (EDLCs)
  - ✓ Pseudo-Capacitors
- Application: characterization of hybrid Fiber-shaped SuperCapacitors (FSCs)



KYOCERA AVX

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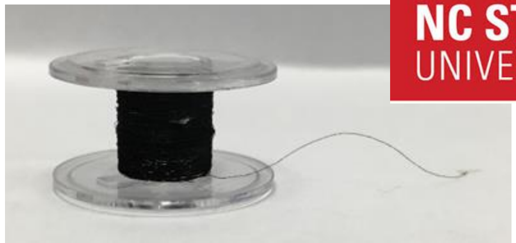


NC STATE UNIVERSITY

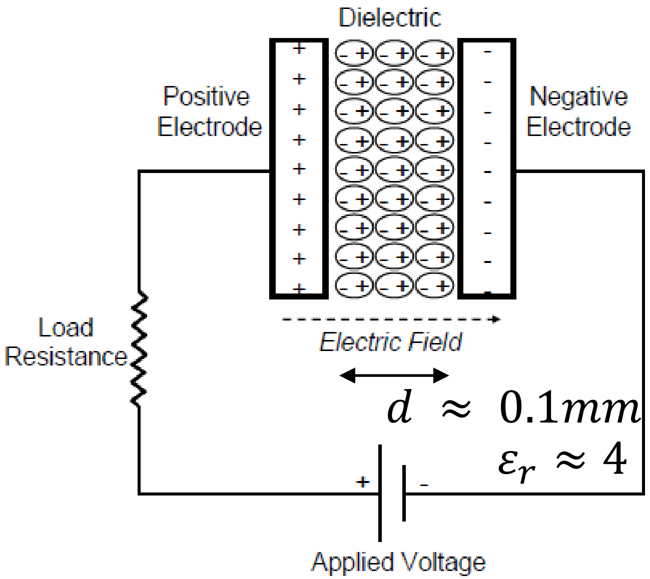
Energy recovery - SC equiped tram, Rio Janeiro Light Rail

Back–up power supply emergency exit (A380)

Voltage stabilization FC-SC hybridization

3. SC modeling – Operation principle

- **Classical** (dielectric) **capacitor**
  - Metal electrode → interface charge storage



$d \approx 0.1mm$

$\varepsilon_r \approx 4$

$$\frac{C}{S} = 3.5\ 10^{-5} \mu F.cm^{-2}$$

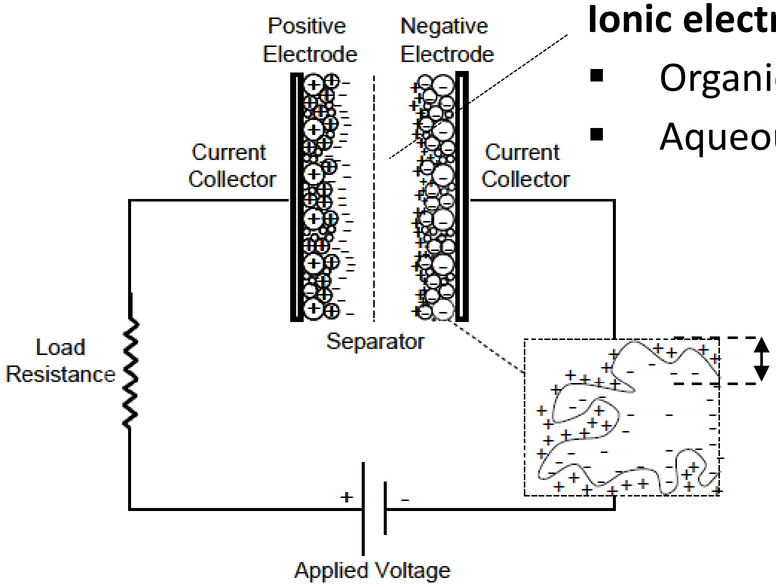
Audyn, 0.01µF, 400 V

Capacitance: $C = \varepsilon_0 \varepsilon_r \frac{S}{d}$

- **Supercapacitor** (electrical double-layer capacitor)
  - Porous electrode → double-layer charge storage

Ionic electrolyte (liquid solvent)

- Organic → up to 2.7 V
- Aqueous → up to 1 V

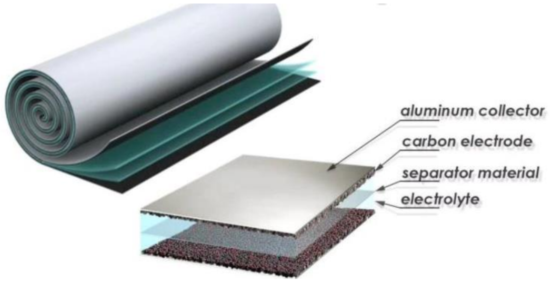


$d \approx 1nm$

$\varepsilon_r \approx 12$

$$\frac{C}{S} = 10\ \mu F.cm^{-2}$$

Maxwell, 5 F to 150 F, 2.7 V



[1] Halper and Ellenbogen, MITRE Nanosystem Group (2006)
[2] P. Guillemet, Polytech Nantes lecture (2015)

3. SC modeling – Operation principle

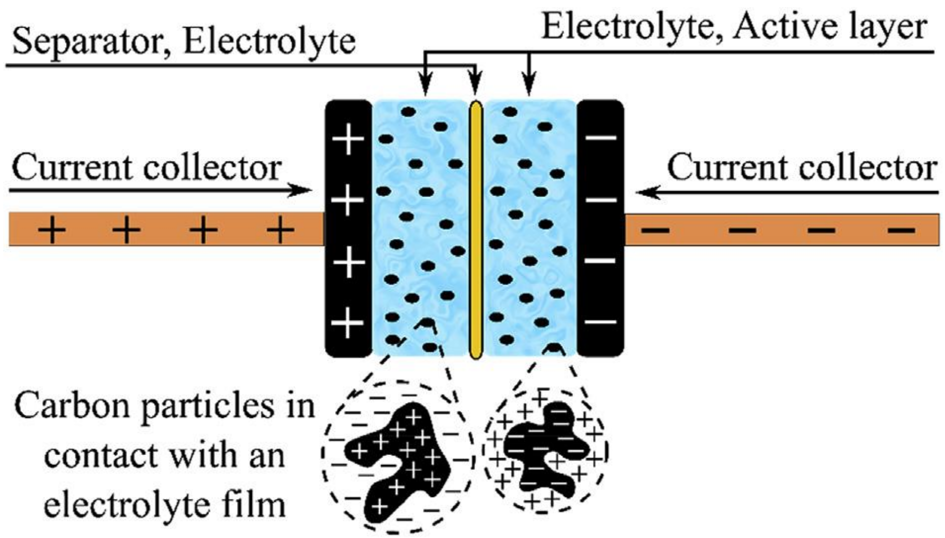
- **Distinction according charge storage mechanism [1]**

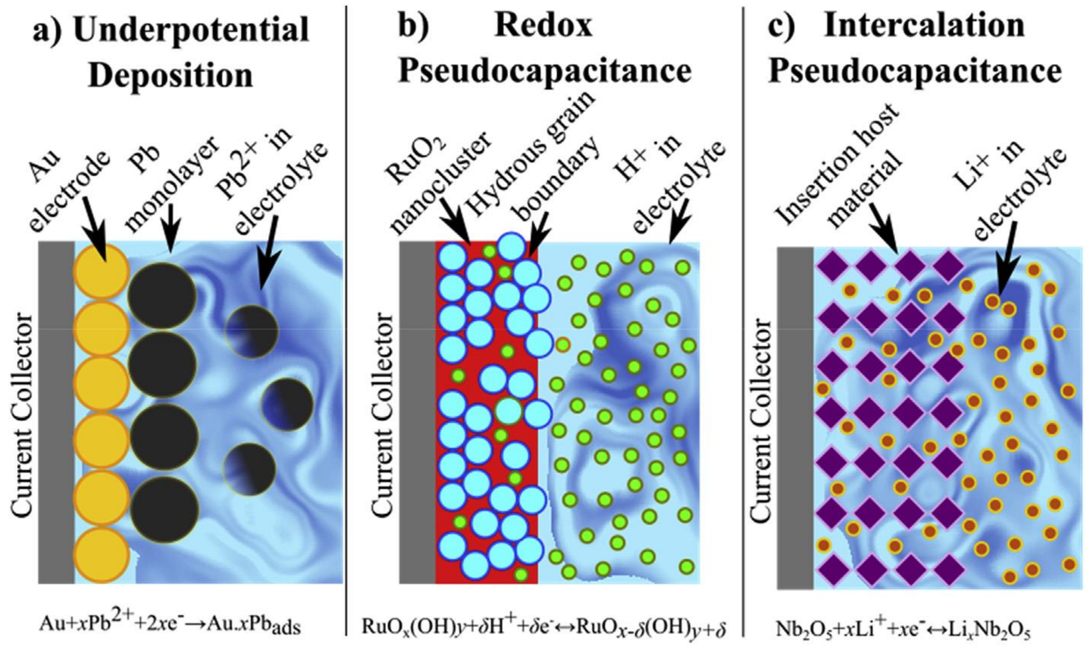
- **Electrical Double-Layer Capacitors (EDLCs)**

  Charge storage in the porous electrodes in a purely capacitive manner within an Electrical Double-Layer (EDL)

- **Pseudo-capacitors**

  Pseudo-capacitive charge storage through underpotential deposition, redox reactions and/or ion intercalation





[1] Da Silva et al., *Energy Storage Mater.*, **27**, 555-590 (2020)

3. SC modeling – Characterization methods

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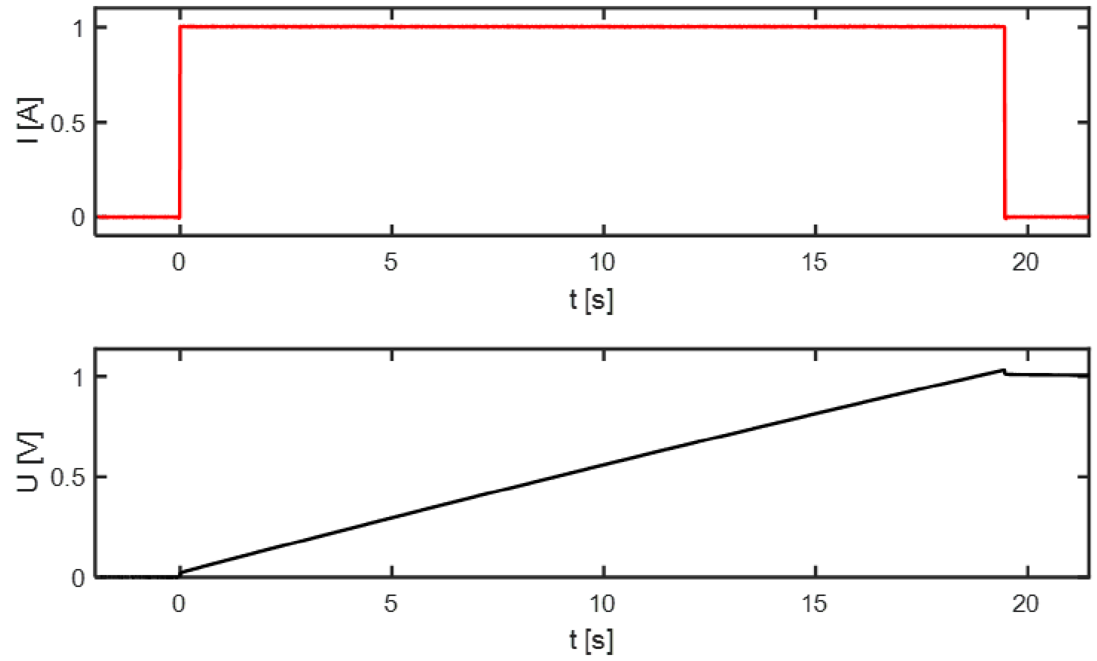
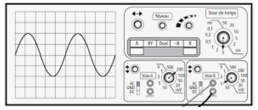
❑ **Time domain**

Charging/discharging curves

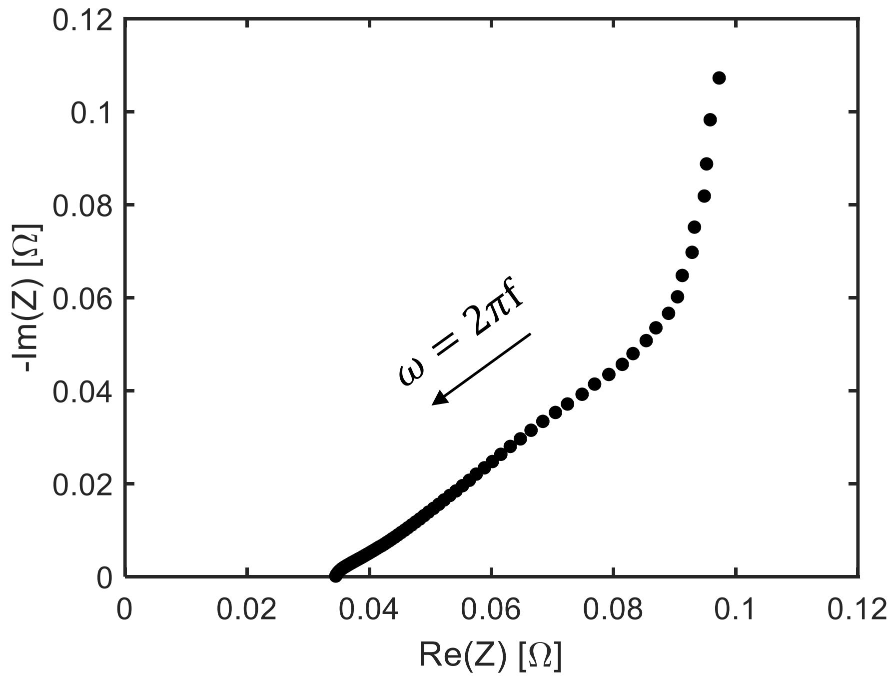


→ Analysis of **voltage** as a function of **time**.

❑ **Frequency domain**



Electrochemical Impedance Spectroscopy (EIS)



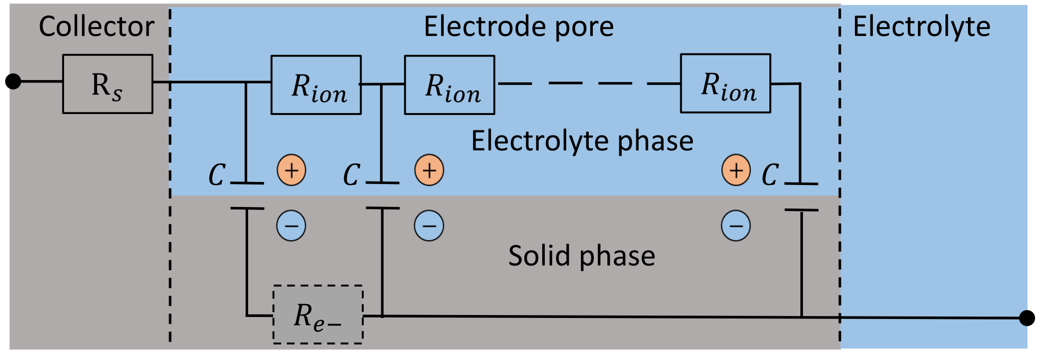
→ Analysis of **impedance** as a function of **frequency**.

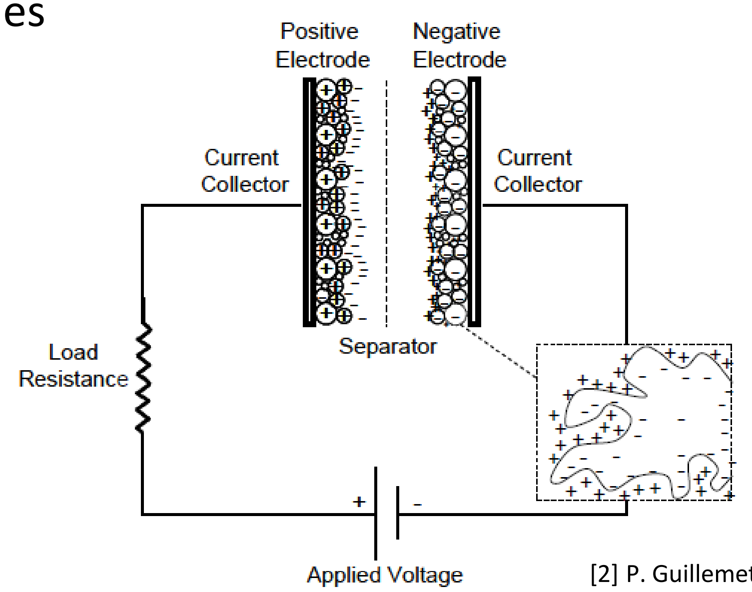
Interpretation usually done by using **equivalent electrical circuits** (**EECs**)

3. SC modeling – Usual EEC models

- **EDLCs:** electrostatic charge storage without self-discharge

Transmission Line Model (TLM) [1] → Volumetric (thick) electrodes





[2] P. Guillemet, Polytech Nantes lecture (2015)

Hypotheses

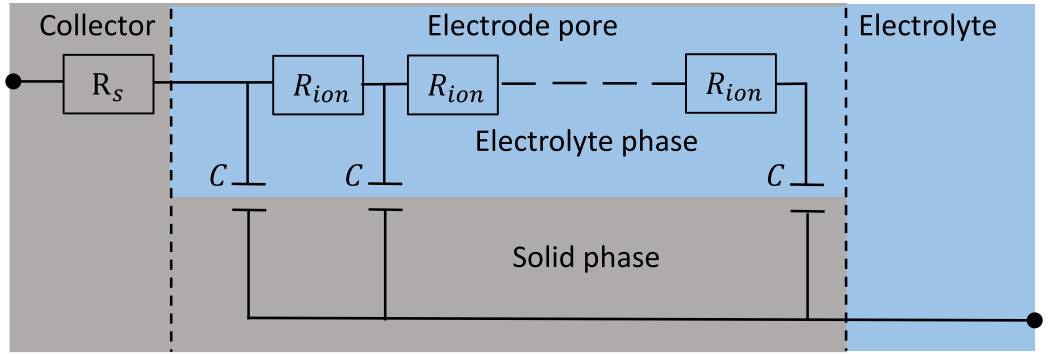
- Electrode composed of cylindrical identical pores with length equal to its thickness
- **Classic TLM***: **EDL charge storage** (no el-chem. reaction)
- Electric behavior described by an assembly of resistances end capacitors in series
- For conventional SCs : electronic resistance (active material) $\boldsymbol{R_{e-}}$ **negligible compared to** the ionic resistance $\boldsymbol{R_{ion}}$ (electrolyte).

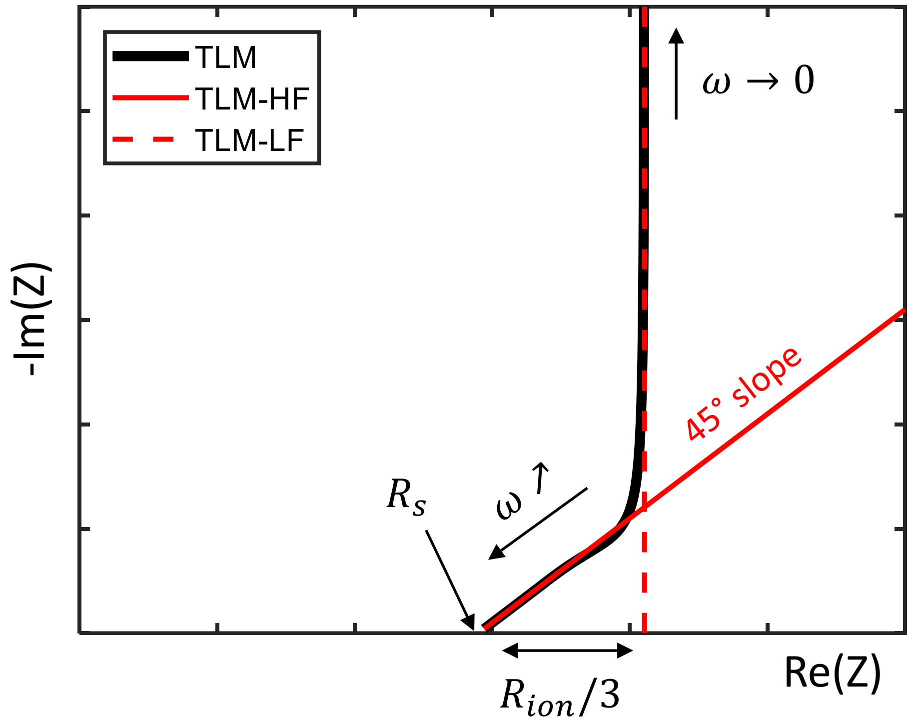
[1] De Levie, *Electrochim. Acta*, **8**, 751 (1963)

3. SC modeling – Usual EEC models

- **EDLCs:** electrostatic charge storage without self-discharge

Transmission Line Model (TLM) [1] → Volumetric (thick) electrodes





- **SC impedance**

$$\boxed{Z_{EDLC}(\omega) = R_s + Z_{TLM}(\omega) = R_s + \frac{R_{ion}}{\sqrt{i\omega C R_{ion}}}\coth\left(\sqrt{i\omega C R_{ion}}\right)}$$

- High frequency limit: $\lim_{\omega\to\infty} Z_{TLM} = \sqrt{\frac{R_{ion}}{i\omega C}}$

- Low frequency limit: $\lim_{\omega\to 0} Z_{TLM} = \frac{R_{ion}}{3} + \frac{1}{i\omega C}$

R_{ion} - ionic resistance (electrolyte)
C - EDL capacitance
R_s - series resistance (current collector + contacts)

[1] De Levie, *Electrochim. Acta*, **8**, 751 (1963)

3. SC modeling – Usual EEC models

- **EDLCs:** electrostatic charge storage with self-discharge

  Faradaic Tansmission Line Model (F-TLM) [1] → Volumetric (thick) electrodes

  → Connecting a leakage resistance R_f in parallel to C

  - **SC impedance**

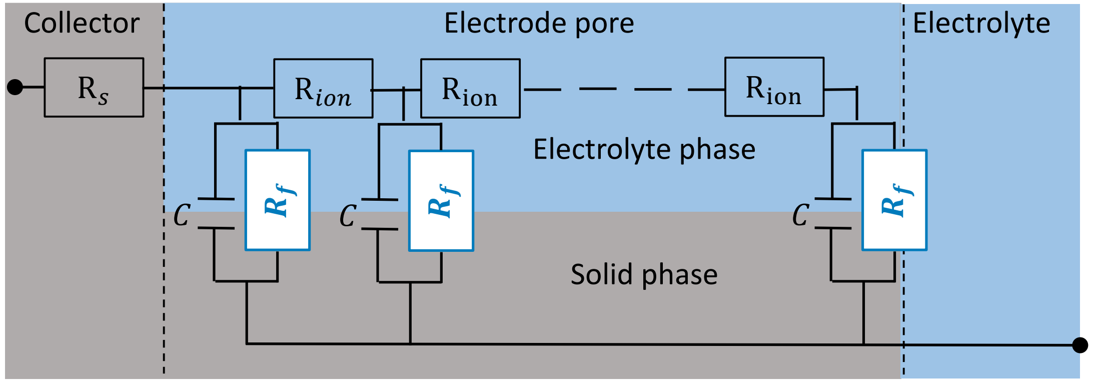
$$Z_{EDLC}(\omega) = R_s + Z_{F-TLM}(\omega)$$

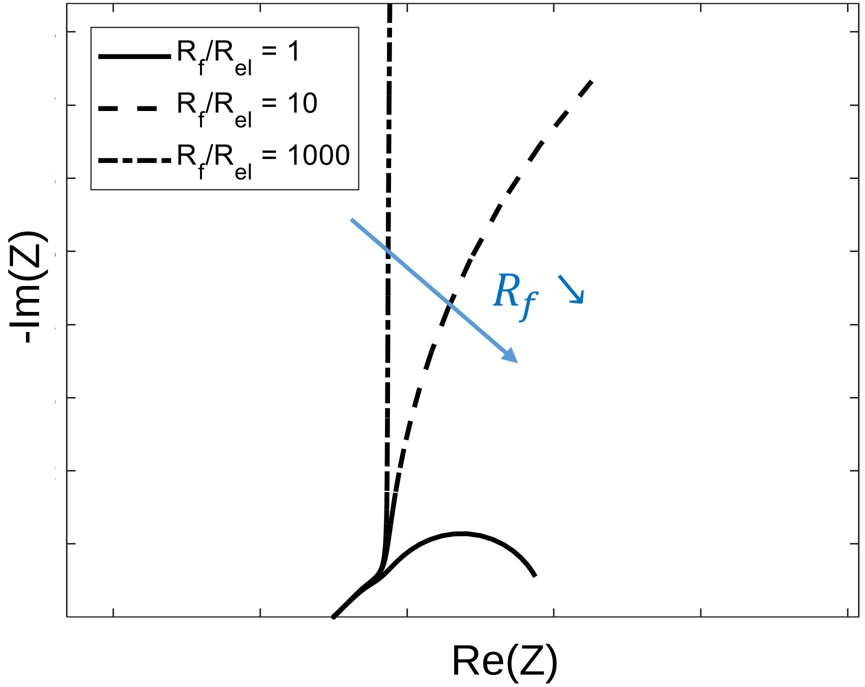
$$= R_s + \frac{R_{ion}}{\sqrt{\frac{R_{ion}}{R_f} + i\omega C R_{ion}}} \coth\left(\sqrt{\frac{R_{ion}}{R_f} + i\omega C R_{ion}}\right)$$

  - Limit for high leakage resistance R_f:

$$\lim_{R_f \to \infty} Z_{F-TLM} = \frac{R_{ion}}{\sqrt{i\omega C R_{ion}}} \coth\left(\sqrt{i\omega C R_{ion}}\right) = Z_{TLM}$$

→ **F-TLM** as a **general EEC for EDLCs** (with and without self-discharge)



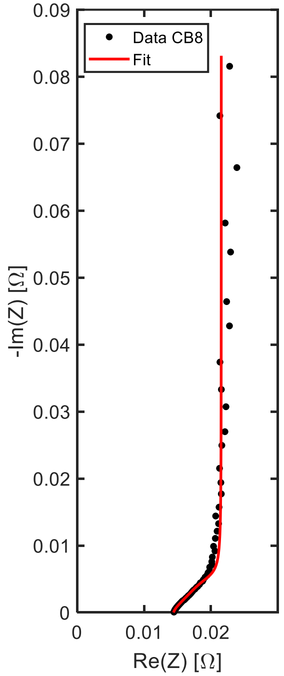


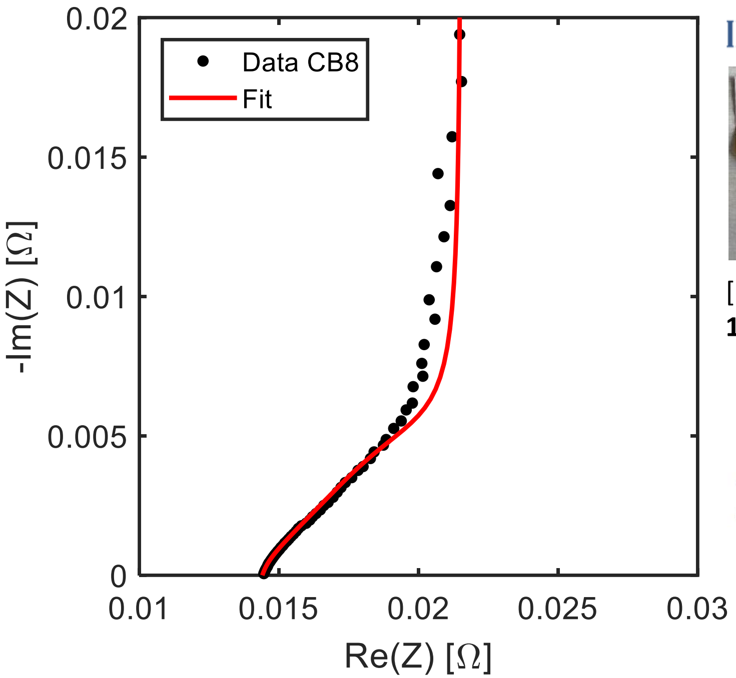
[1] Eikerling and Kornyshev, *J. Electroanal. Chem*, **475** (2), 107-123 (1999)

3. SC modeling – Usual EEC models

- **EDLCs:** characterization example [1] ($f = 0.1\ Hz - 40\ kHz$)

CB8 @ 0.1V (aqueous electrolyte)





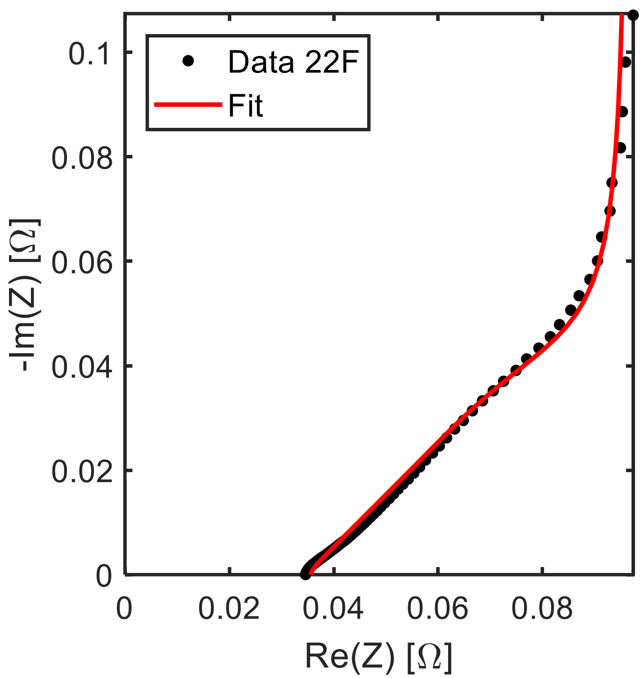
IMN INSTITUT DES MATÉRIAUX JEAN ROUXEL

[2] Taleb et *al., Fuel Cells,* **18** (3), 299-305 (2018)

ASTRID

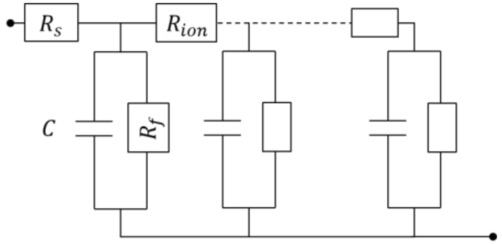
ANR DGA

22F @ 0.1V (organic electrolyte)



nichicon

Least-Square Fitting	R_s [mΩ]	R_{ion} [mΩ]	R_f [Ω]	C [F]
CB8	14	23	$5\ 10^{12}$	19
22F	35	186	$5\ 10^{12}$	16



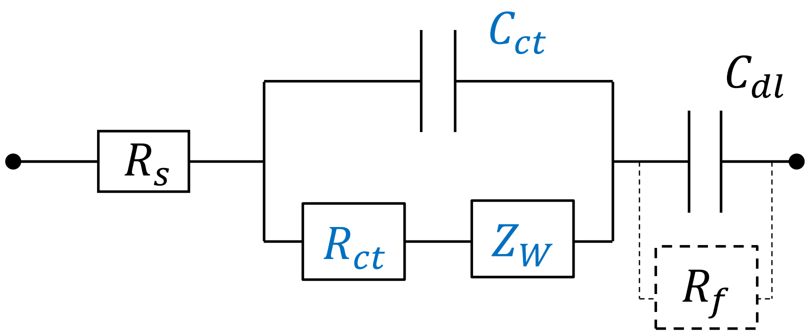
→ **F-TLM well-adapted for EDLC impedance modeling**

[1] Mainka et al., 235th ECS Meeting, Dallas – USA, May 26-30, 2019

3. SC modeling – Usual EEC models

- **Pseudo-capacitors:** EDL + electrochemical charge storage (redox reactions)

Usual EEC: **Randles circuit** [1] → Interfacial (thin) electrodes

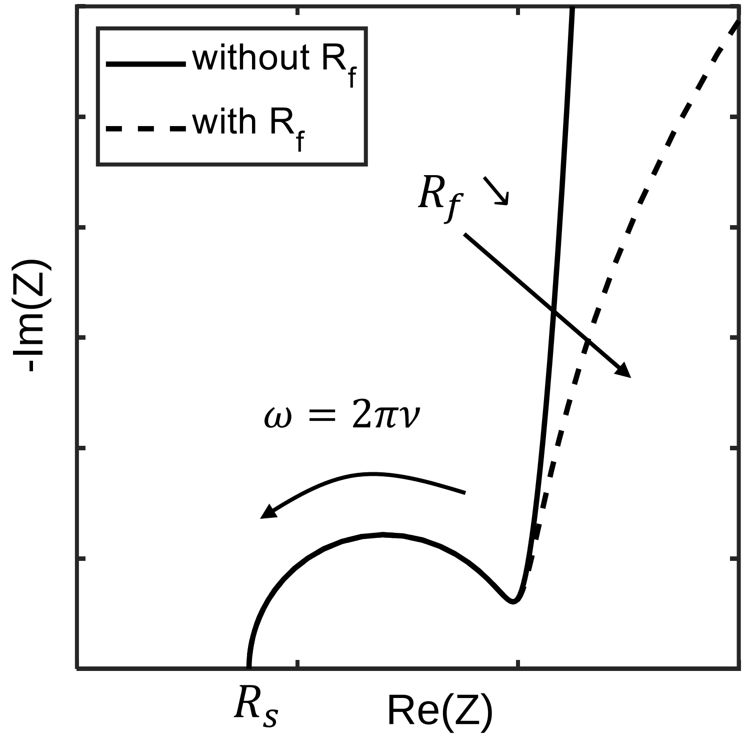


- **SC impedance**

$$Z_{SC}(\omega) = R_s + Z_{Randles} + \frac{1}{i\omega C_{dl}}$$

$$= R_s + \underbrace{\left(\frac{1}{R_{ct} + Z_w(\omega)} + i\omega\, C_{ct}\right)^{-1}}_{\text{el.-chem. contribution}} + \underbrace{\frac{1}{i\omega C_{dl}}}_{\text{EDL contribution}}$$

with $Z_w(R_d, \tau_d) = R_d \frac{\tanh\sqrt{i\omega\tau_d}}{\sqrt{i\omega\tau_d}}$ - Warburg diffusion impedance



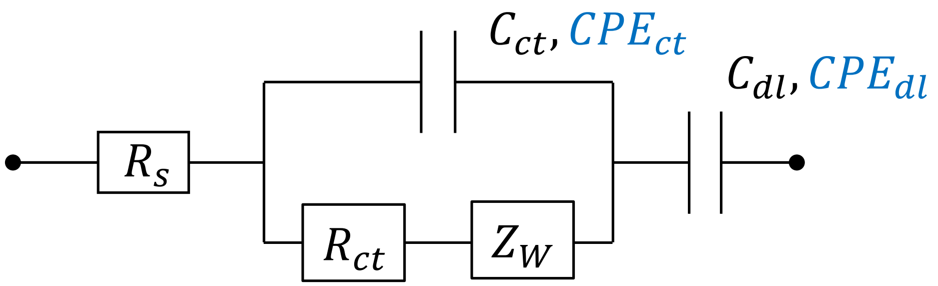
R_{ct} - charge transfer resistance
C_{dl} - double-layer capacitance

[1] Masarapu et al., *ACS Nano, 3* (8), 2199-2206 (2005)

3. SC modeling – Usual EEC models

- **Pseudo-capacitors:** EDL + electrochemical charge storage (redox reactions) → **ion diffusion in porous media**

  Usual EEC: **Randles circuit** [1] → Interfacial (thin) electrodes



- **SC impedance**

$$Z_{SC}(\omega) = R_s + \left(\frac{1}{\mathrm{R_{ct}} + \mathrm{Z_W}(\omega)} + \frac{1}{Z_{CPE\,ct}}\right)^{-1} + Z_{CPE_{dl}}$$

with $Z_{CPE\,ct/dl}(Q, \alpha) = \frac{1}{Q(i\omega)^{\alpha}}$ - **Constant phase element (CPE)**

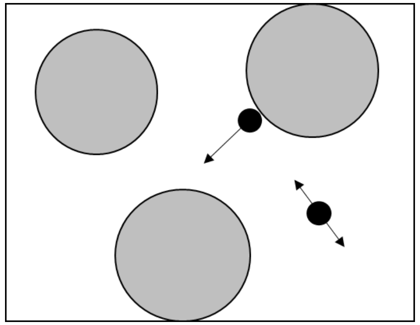
CPE parameter Q in $[\mathrm{F}.s^{\alpha-1}]$

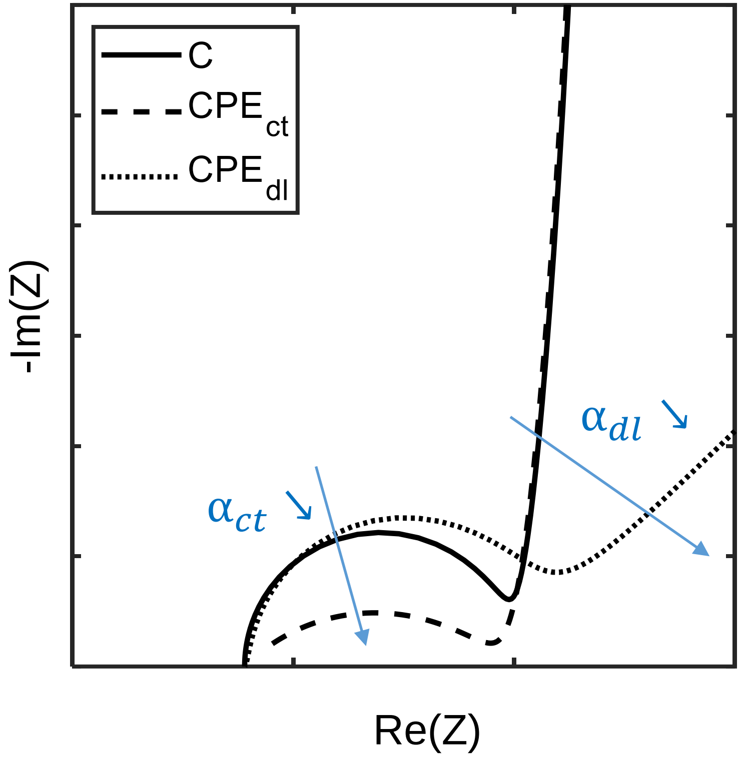
Exponent α in [-] → indicator for type of diffusion [1]

$0 < \alpha < 1$: subdiffusion (porous media)

$\alpha = 1$: normal diffusion

$\alpha > 1$: faster than normal diffusion



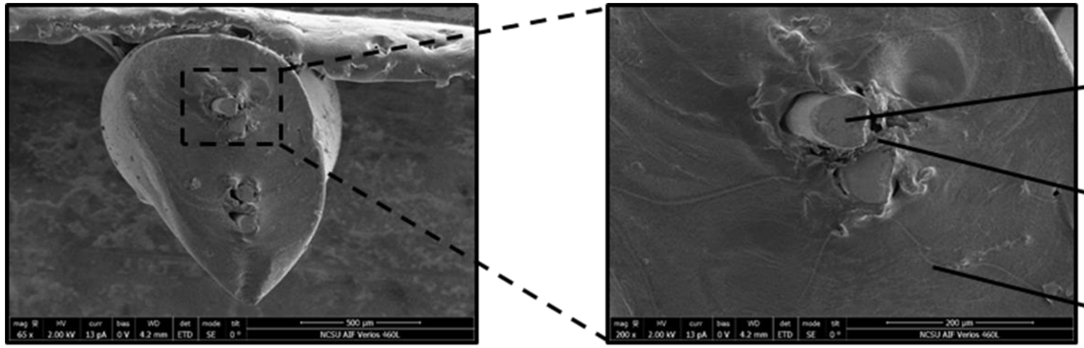


[1] Niya, Hoorfar, Electrochim. Acta **188**, 2016

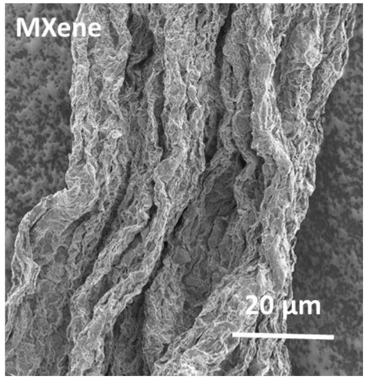
3. SC modeling – Characterization of hybrid FSCs [1]

- **Hybrid Fiber-shaped SuperCapacitors (FSCs)** → pseudo-capacitive FSCs

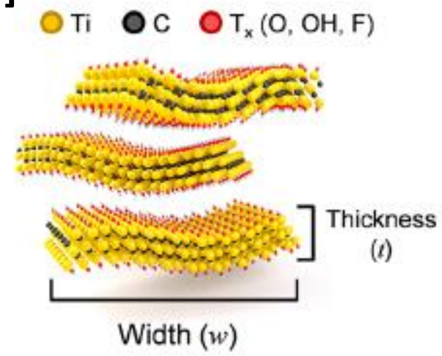
SEM image of SC fibers [2]



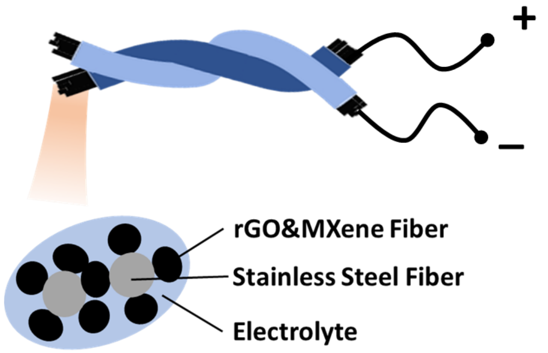
[2] He et al., *J. Mater. Chem. A*, 7, 6869~6876 (2019)



Chemical structure of MXene (Ti_3C_2X) [3]



[3]Zhang et al., *J. Mater. ACS Cent. Sci.*, 6, 254-265 (2020)



	FSC1
Electrode ▪ Diameter ≈ 500 µm ▪ Length 15 cm	40% rGO 60% MXene: Ti_3C_2X (X: -OH, -O, -F)
Current collector	Stainless steel
Electrolyte (aqueous polymer)	1M sulfuric acid (H_2SO_4) /Polyvinyl alcohol (PVA) solution

→ **Expected charge storage** : el-chem + EDL (capacitive + ion intercalation)

[1] Mainka et al., Electrochim. Acta 404, 139740 (2022)

3. SC modeling – Characterization of hybrid FSCs [1]

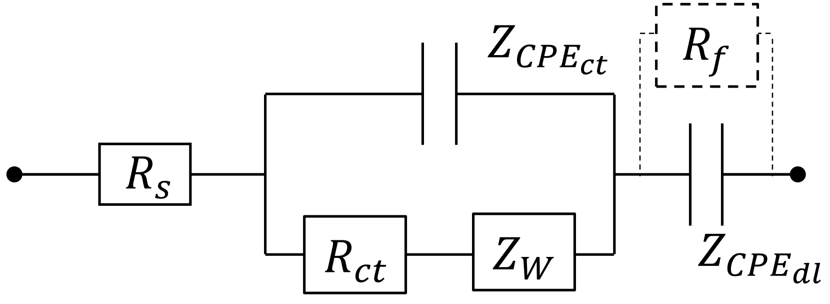
❑ Modeled charge storage mechanisms

- Electrochemical → Randles (thin electrode) vs. M-TLM (thick electrode)
- EDL (capacitive + ion intercalation) → constant phase element $Z_{CPE_{dl}}$

❑ EECs analyzed

Randles

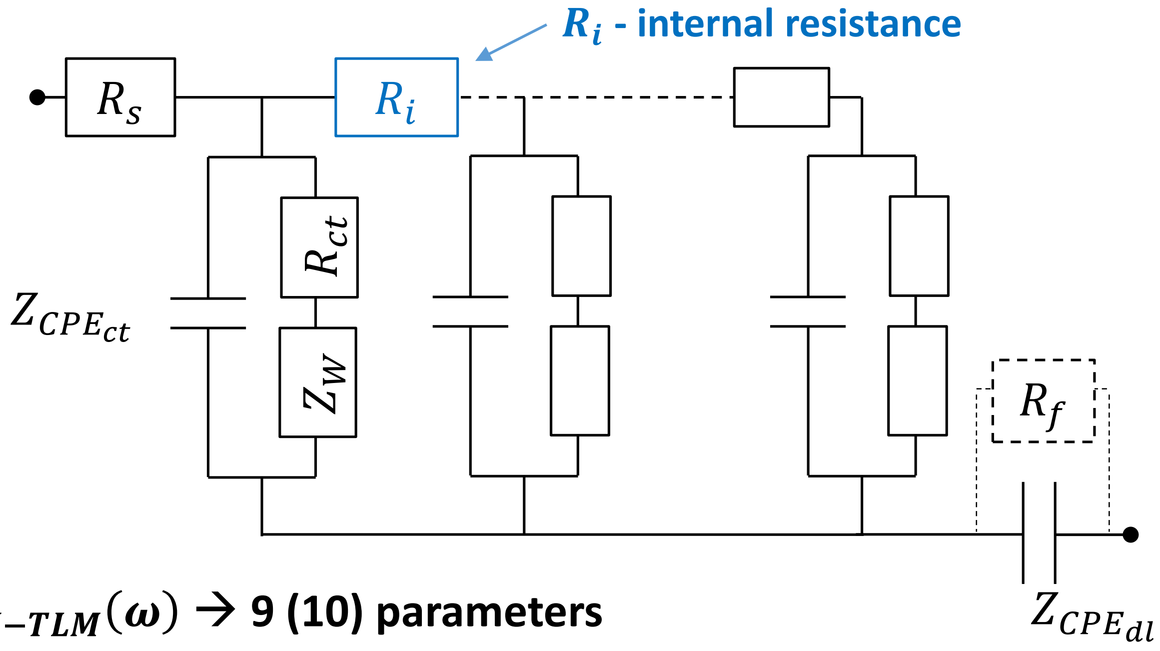
→ Interfacial (thin) electrodes



$Z_{Randles}(\omega)$ → **8 (9) parameters**

Modified - Transmission Line Model (M-TLM)

→ Generalization of Randles EEC for thick (long fiber) electrodes [1,2]

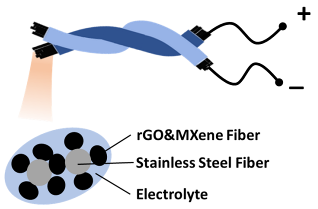


$Z_{M-TLM}(\omega)$ → **9 (10) parameters**

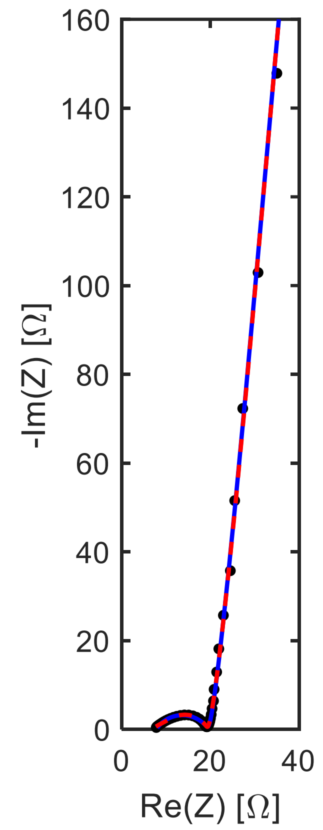
[1] Mainka et al., Electrochim. Acta (2022)
[2] Touhami et al., *J. Electrochem. Society* (2019)

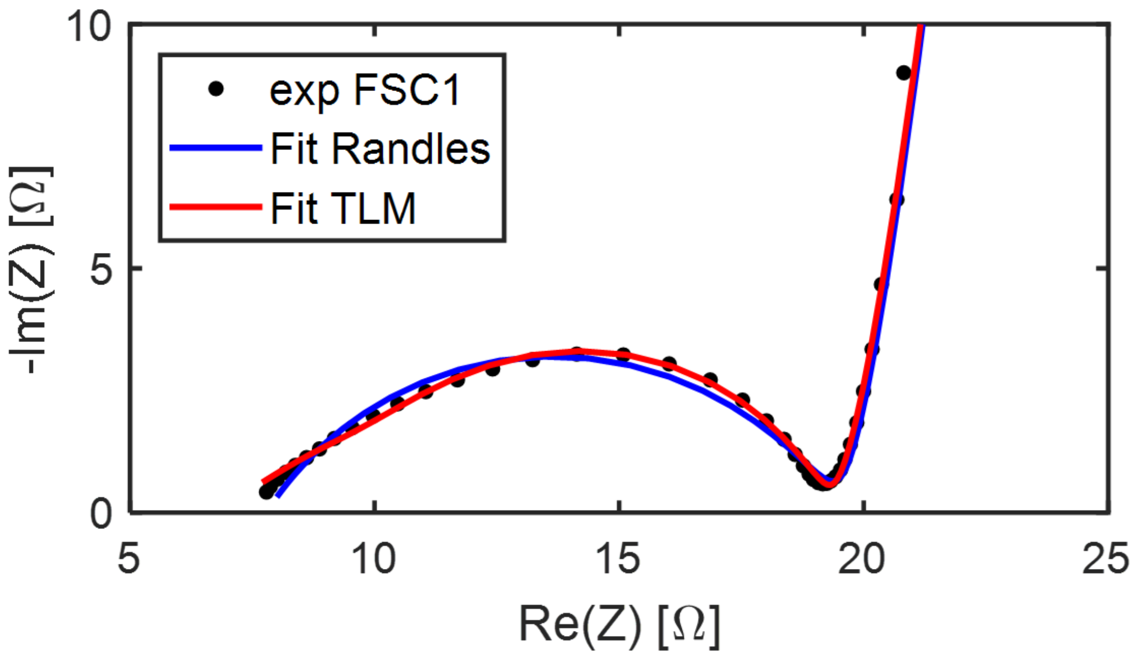
3. SC modeling – Characterization of hybrid FSCs [1]

- **FSC1 data: pseudo-capacitors** (15 cm devices)

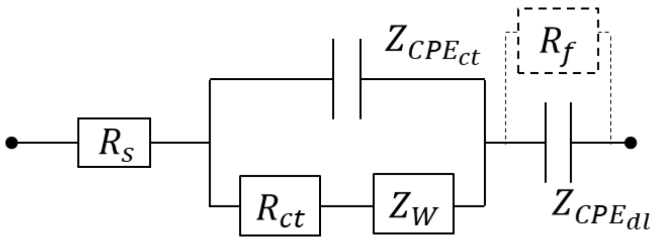


Frequencies : 1 mHz to 1MHz

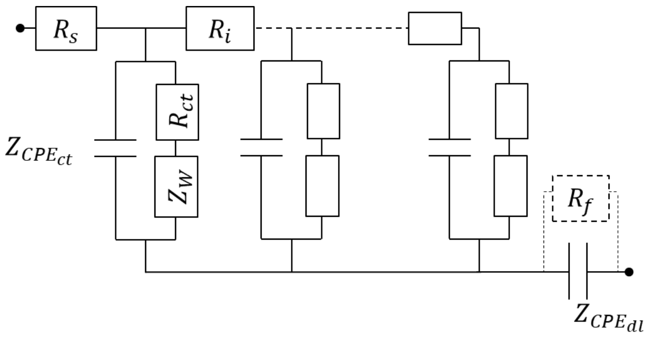




Randles EEC



M-TLM EEC

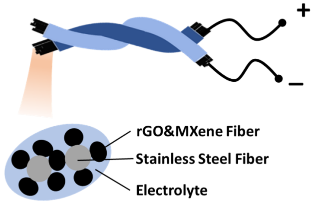


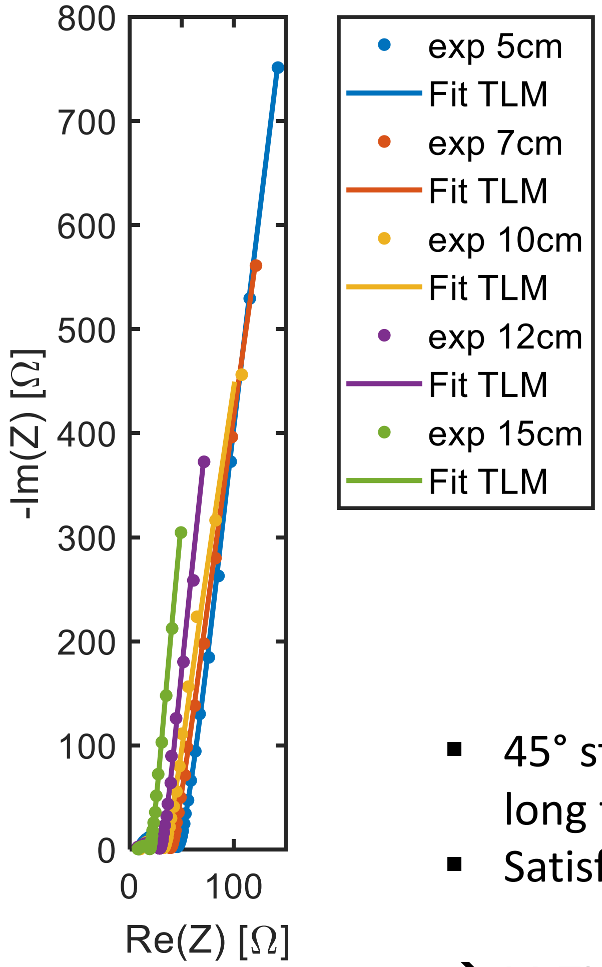
- **High frequencies** : only M-TLM able to fit the 45° straight line
- **Intermediate frequencies**: better fit of faradaic loop using M-TLM
- **Low frequencies**: satisfying fit quality for both models → self-discharge negligible

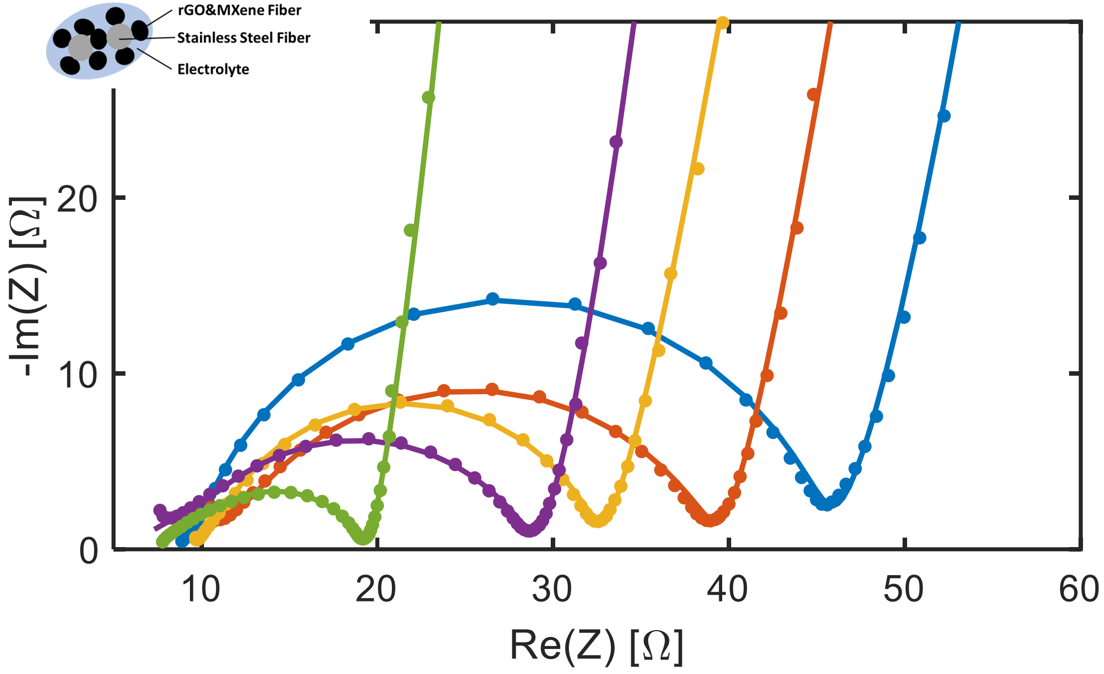
[1] Mainka et al., Electrochim. Acta (2022)

3. SC modeling – Characterization of hybrid FSCs [1]

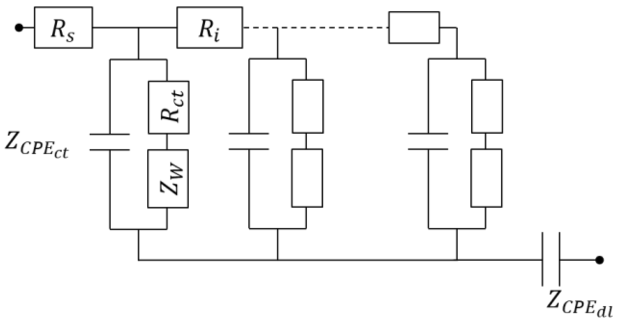
- FSC1 data: pseudo-capacitors



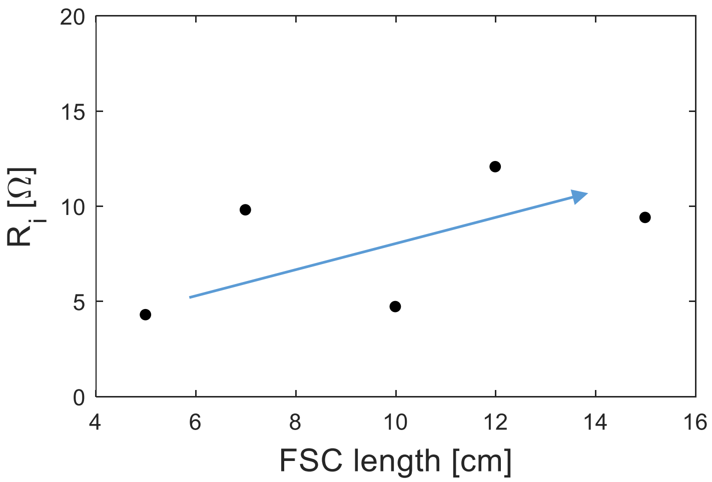




M-TLM EEC



Electrode internal resistance R_i

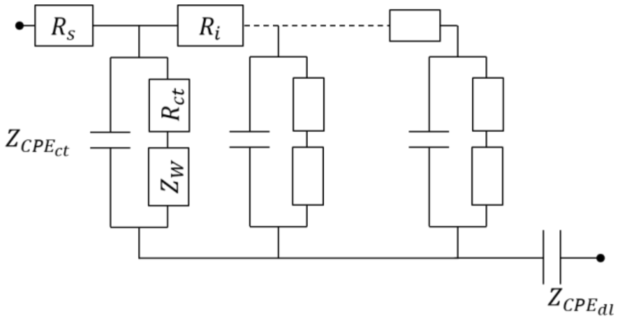


- 45° straight line at highest frequencies more developped for long fibers → R_i increases
- Satisfying fit quality also for short fibers

→ **M-TLM as generalized EEC able to fit all FSCs**

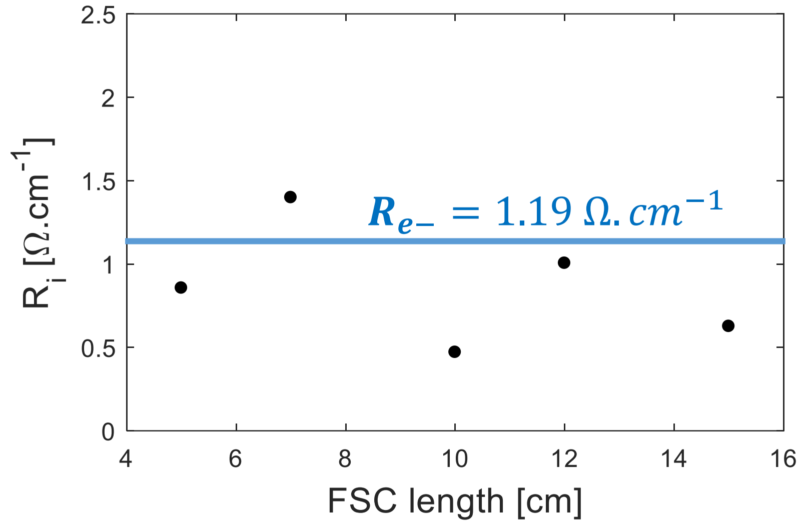
[1] Mainka et al., Electrochim. Acta 404, 139740 (2022)

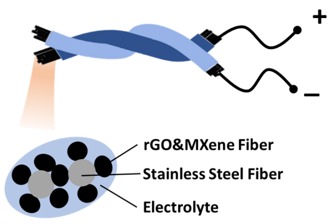
3. SC modeling – Characterization of hybrid FSCs [1]



Conventional SCs: electric resistance of the active material R_{e-} negligible compared to ionic resistance of the electrolyte $\boldsymbol{R_{ion}}$ → $\boldsymbol{R_i = R_{ion}}$

FSC1: pseudo-capacitors





FSC2 and FSC3: EDLCs

	FSC2	FSC3
$\boldsymbol{R_i}$ [$\boldsymbol{\Omega.cm^{-1}}$]	3.7	4.5
$\boldsymbol{R_{e-}}$[$\boldsymbol{\Omega.cm^{-1}}$]	2.5	4.7

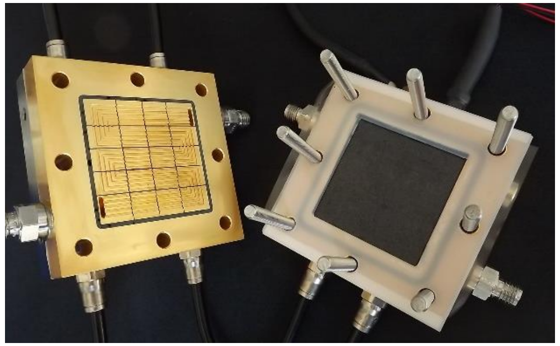
→ **Hybrid FSC**: R_i governed by the electron conducting phase of the electrode rather than by the ion conductive electrolyte (opposite to classical SCs) → $\boldsymbol{R_i = R_{e-}}$

[1] Mainka et al., Electrochim. Acta 404, 139740 (2022)

Outline

4. Modeling of electrochemical generators → Polymer Electrolyte Membrane Fuel Cells (PEMFCs)

- Generalities
  - ✓ Operation principle
  - ✓ Cell Impedance
- Membrane-Electrode Assembly (MEA) - Electrode EECs
  - ✓ Blocked-electrode model
  - ✓ *In operando* models (thick and thin electrodes)
- Focus on O_2 diffusion impedance
  - ✓ Identification of diffusion limiting layer
  - ✓ Difficulties at low frequencies
  - ✓ Example of alternative to Warburg impedance
- Application to PEMFC ageing analyses



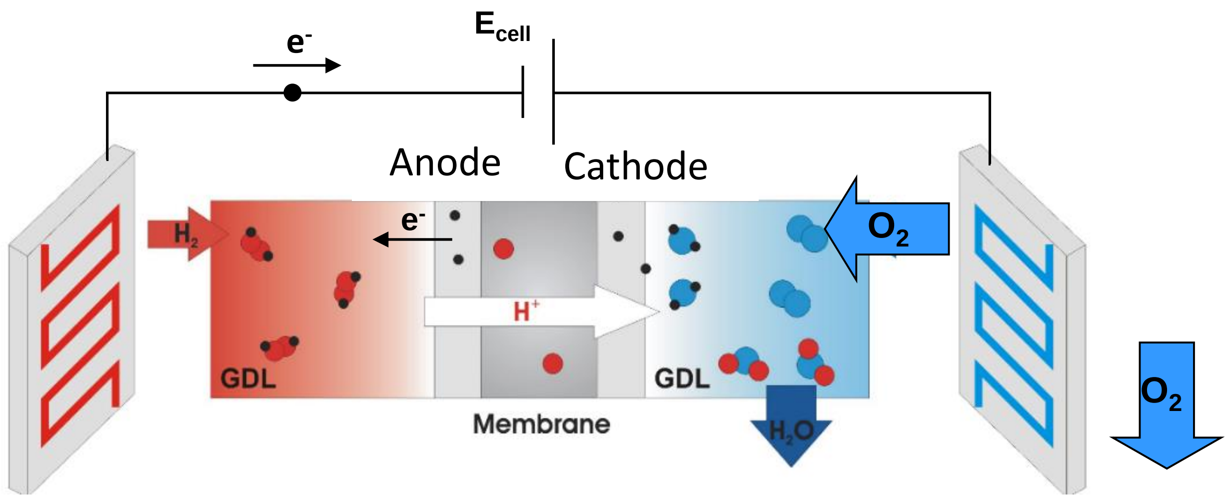
Hype taxi in Paris (2015)

Alstom Coradia iLint in Germany (2018)

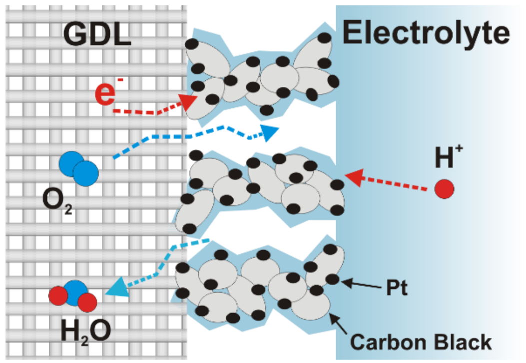
4. PEMFC modeling – Operation principle

❑ Membrane – Electrode Assembly (MEA)

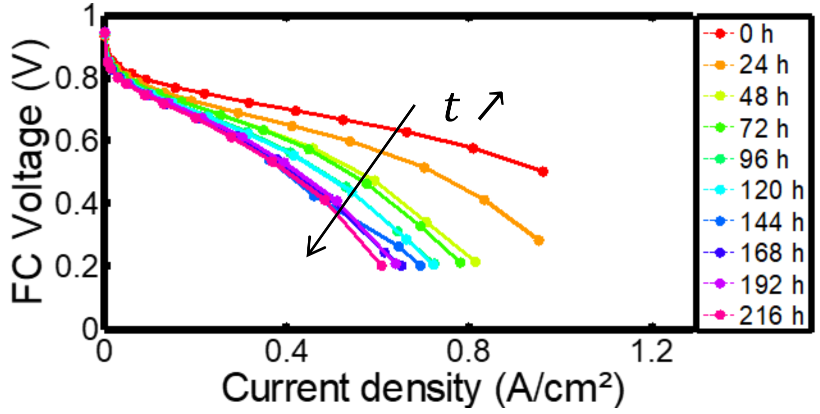
- Assembly of various media with different geometrical and physical properties
- Different coupled transport phenomena (charge, mass, heat)



Porous electrodes (cathode)



Polarization curve



Hydrogen oxidation reaction (HOR)

$$H_2 \rightarrow 2H^+ + 2e^-$$

Oxygen reduction reaction (ORR)

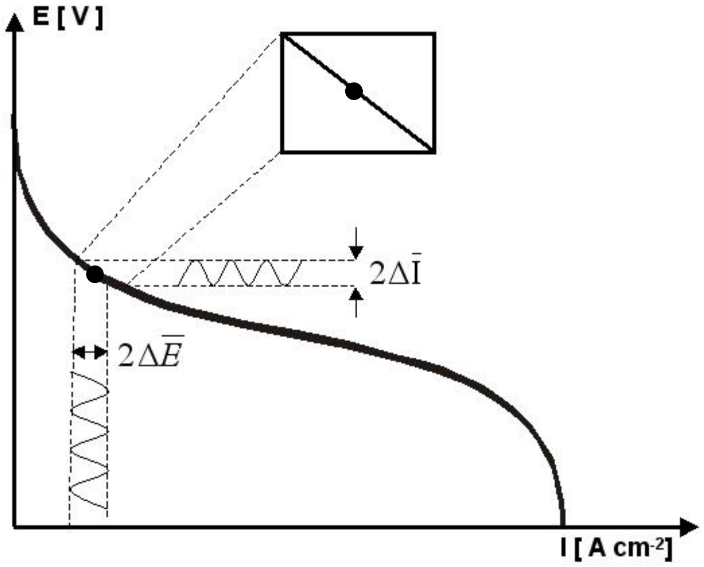
$$1/2\,O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

Global reaction: $H_2 + 1/2\,O_2 \rightarrow H_2O + \mathrm{Heat}$

[1] S. Abbou, Ph.D Thesis, UL (2015)

4. PEMFC modeling – Cell impedance

❑ EIS measurement and spectrum (Nyquist plot)

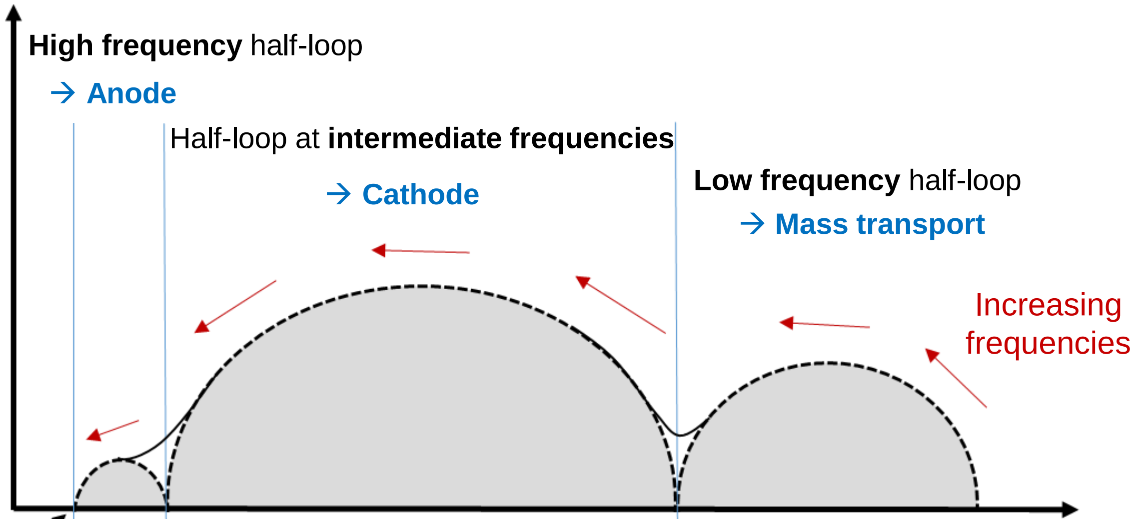


Conditions : linear and stationary system

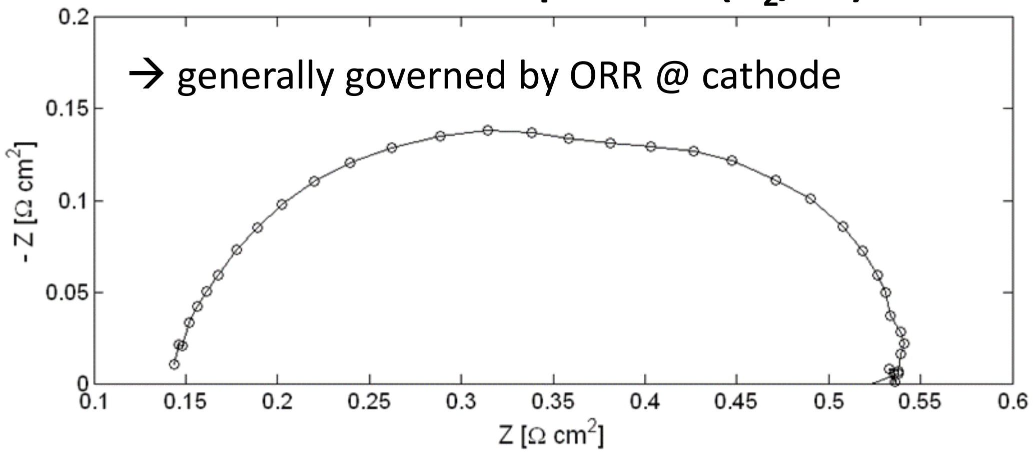
- Applying AC signals with small amplitudes ΔE/ΔI
- Approximatively linear behavior if [1]:

$$\Delta\bar{E} < E_T = \frac{RT}{F} \approx 29\ mV \qquad \text{(at 60°C)}$$

Ideal FC spectrum



Real PEMFC spectrum (H_2/air)



$RH_{air} = 76\%$
$RH_{H2} = 0\%$
$\langle j_{cell} \rangle_t = 0.5 Acm^{-2}$

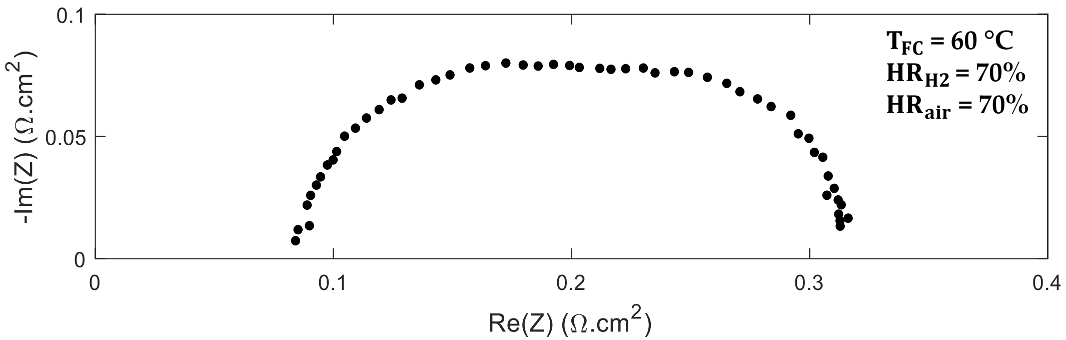
[1] Rubio et al., J. Power Sources 183(1), 2008

4. PEMFC modeling – Cell impedance

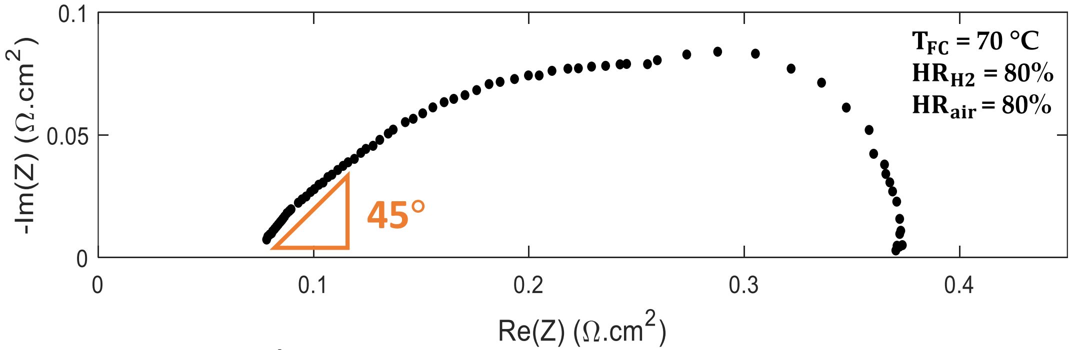
Real PEMFC spectra

- Impedance spectra of two **different MEAs and cells** (PEMFC under H_2/air @ 0.5 A/cm^2, f = 20 mHz-10 kHz)

Cell A (CCM Solvicore – thin electrode)

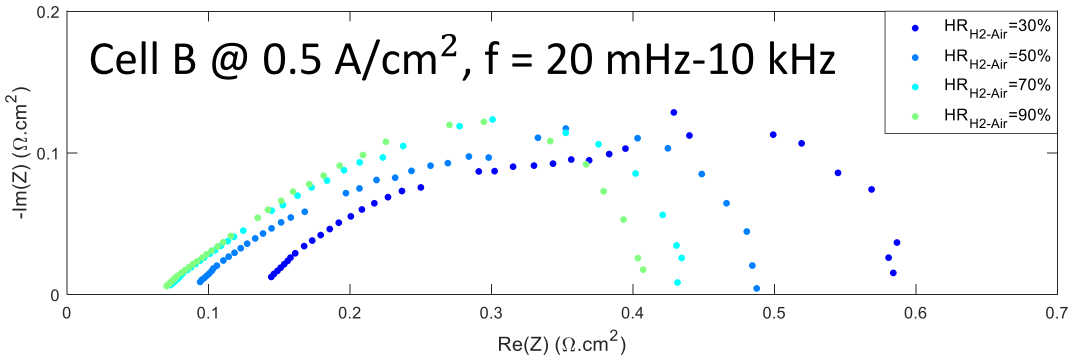


Cell B (hot-pressed GDE – thick electrode)

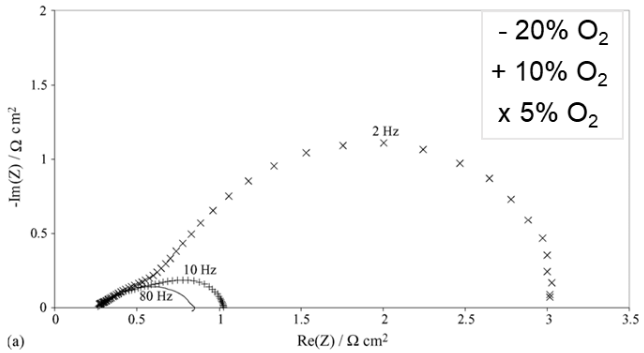


- Impedance spectra for **different operating conditions** (PEMFC under H_2/air)

Impact of relative humidity



Impact of oxygen supply [1]



→ **Appropriate impedance model (EEC)** strongly depends of the **MEA composition** and **FC operating conditions.**

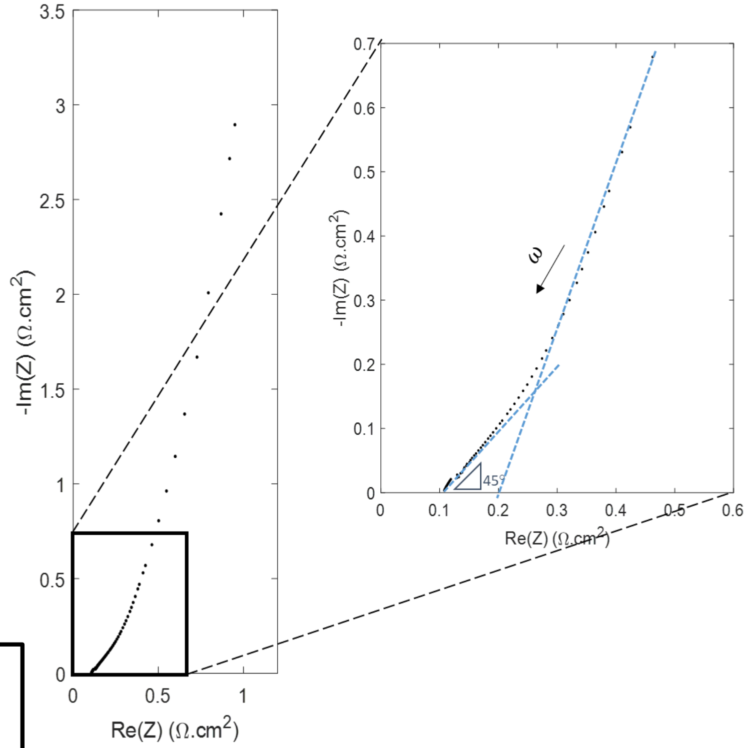
[1] Bultel et al., Electrochimica Acta (2005)

4. PEMFC modeling – Electrode EECs

❑ Blocked electrode (H_2/N_2 operation)

Nyquist plot [1]

- At low frequencies: steep increase of the imaginary part approaching a **vertical line** associated with a **purely capacitive behavior**
- At high frequencies: **straight line at 45°** associated with **proton conduction within the CCL**



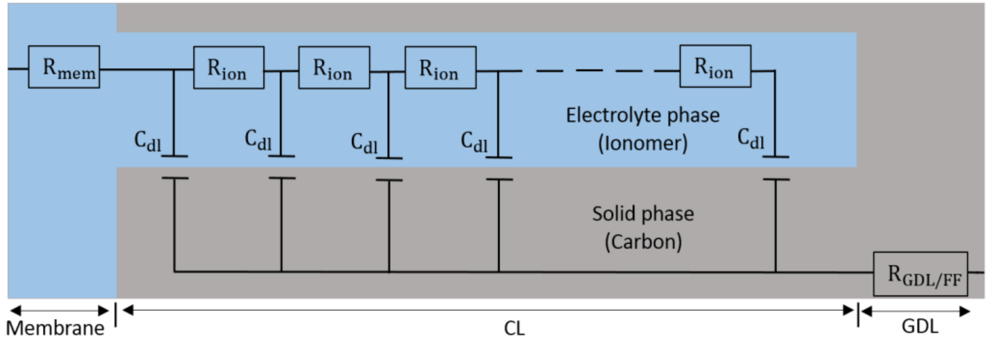
Cell B
T_{FC} = 70 °C
RH_{H2} = 80%
RH_{N2} = 80%
U = 0.5V
f = 1 Hz -10 kHz

EEC : Transmission Line Model (TLM) [1-2]

- **PEMFC impedance**

$$\boxed{Z_{PEMFC}(\omega) = R_{hf} + Z_{TLM}(\omega) = R_{hf} + \sqrt{\frac{R_{ion}}{i\omega C_{dl}}}\coth\left(\sqrt{i\omega R_{ion} C_{dl}}\right)}$$

R_{ion}: ionomer resistance in the CCL
C_{dl}: double-layer capacitance
R_{mem}: ionomer resistance in the membrane
$R_{GDL/FF}$: electronic resistance in the GDL/FF
$R_{hf} = R_{GDL/FF} + R_{mem}$: high-frequency resistance

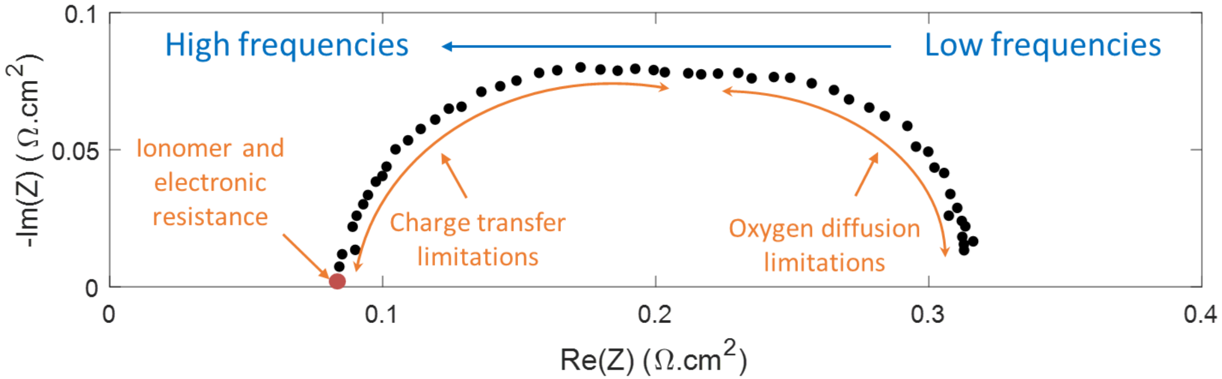


[1] S. Touhami et al, *J. Electrochem. Soc.* (2019)
[2] De Levie, *Electrochim. Acta* (1963)

4. PEMFC modeling – Electrode EECs

❑ H_2/air operation (in operando) – thin electrodes [1]

Cell A (CCM - SolviCore) – thin electrode

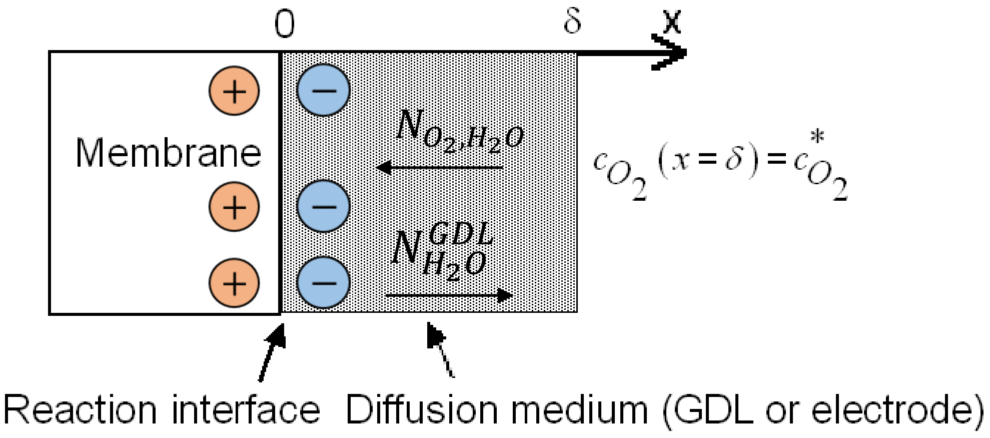


$T = 60°C$
$HR_{H2} = 70\%$
$HR_{air} = 70\%$

EEC : Randles circuit [2,3]

Hypotheses

- **Surface reaction**
- Isothermal and isobaric active layer (AL)
- Cathode place of water production: ohmic drops due to electron and ion conduction in the GDL and AL neglected
- 1D O_2 transport by binary diffusion only (Fick diffusion laws)
- Constant O_2 concentration at the GDL/channel interface
- Cathode limiting electrode – anode neglected



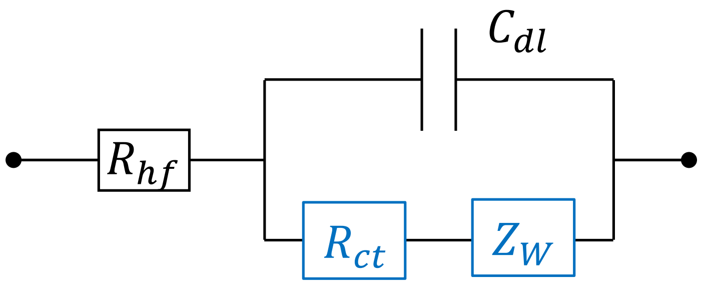
[1] S. Touhami et al, *J. Electrochem. Soc.* (2019)
[2] Randles, Discuss. Faraday, Soc. (1947)
[3] Warburg, Ann. Phys. Chem. (1899)

4. PEMFC modeling – Electrode EECs

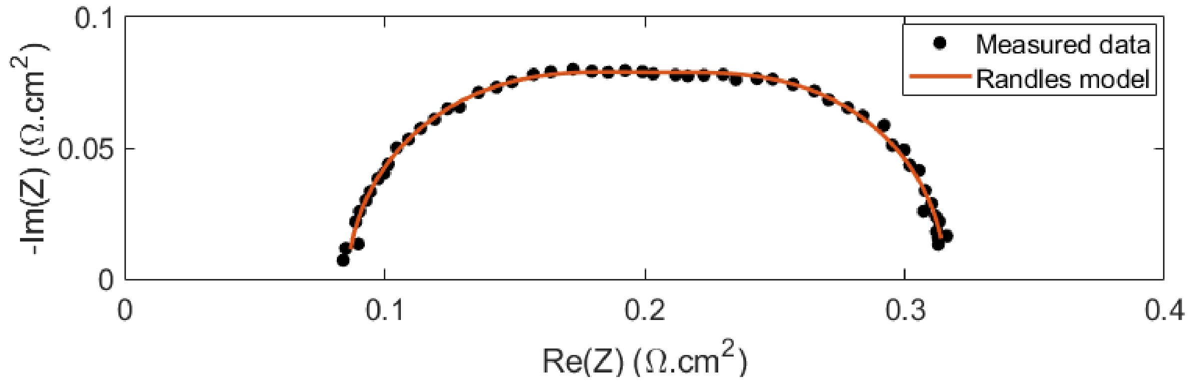
- H_2/air operation (in operando) – thin electrodes [1]

Randles circuit [2] (anode neglected)

- **PEMFC EEC** → Interfacial (thin) electrodes



Cell A (CCM - SolviCore) – thin electrode



- **PEMFC impedance**

$$Z_{PEMF}(\omega) = R_{hf} + Z_{Randles} = R_{hf} + \left(\frac{1}{R_{ct} + Z_w(\omega)} + i\omega\, C_{dl}\right)^{-1}$$

With $\boldsymbol{R_{ct} = \frac{b}{j}}$ **- charge transfer resistance**
C_{dl} - double layer capacitance
} Electrode reaction kinetics (here : ORR at the cathode)

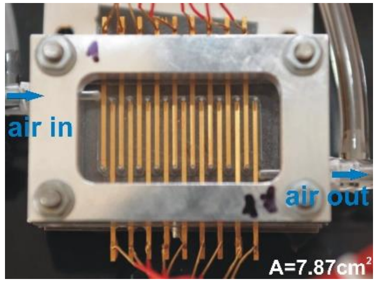
$Z_w(R_d, \tau_d) = R_d \dfrac{\tanh\sqrt{i\omega\tau_d}}{\sqrt{i\omega\tau_d}}$ - O_2 diffusion impedance (Warburg element [3])

[1] S. Touhami et al, *J. Electrochem. Soc.* (2019)
[2] Randles, Discuss. Faraday, Soc. (1947)
[3] Warburg, Ann. Phys. Chem. (1899)

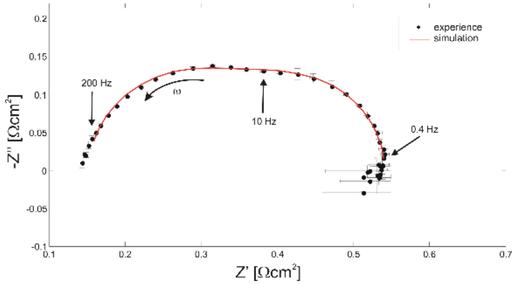
4. PEMFC modeling – Electrode EECs

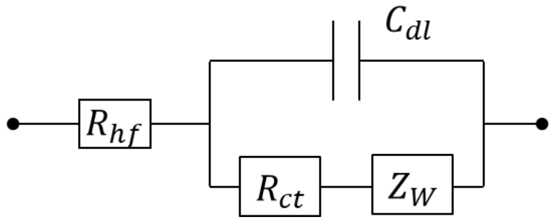
❑ H_2/air operation (in operando) – thin electrodes

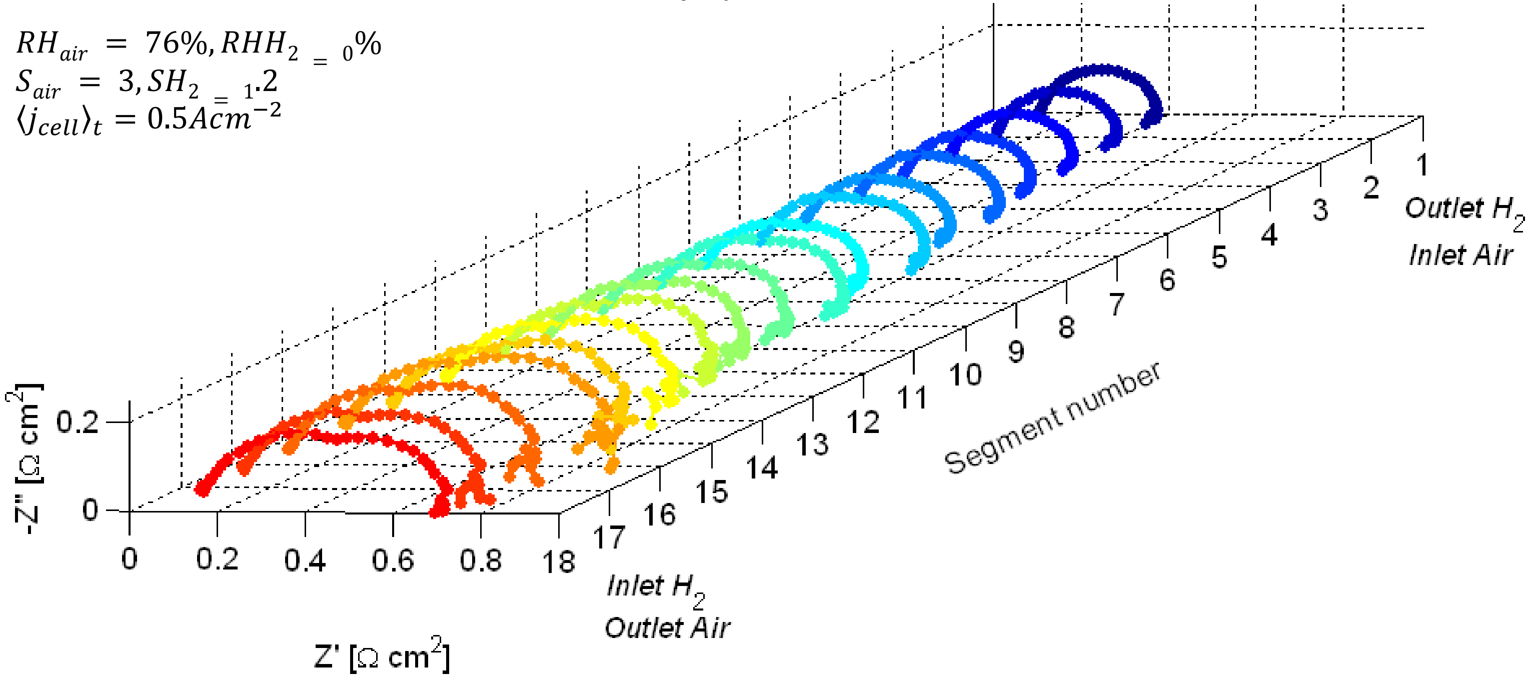
Application : local EIS analysis – Randles circuit [1]



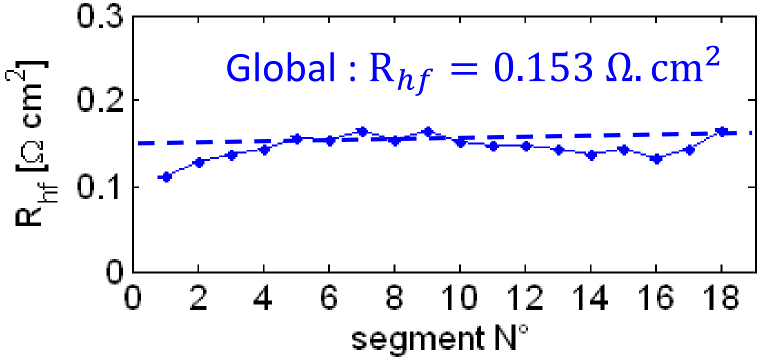
$RH_{air} = 76\%, RHH_2 = 0\%$
$S_{air} = 3, SH_2 = 1.2$
$\langle j_{cell} \rangle_t = 0.5 A cm^{-2}$



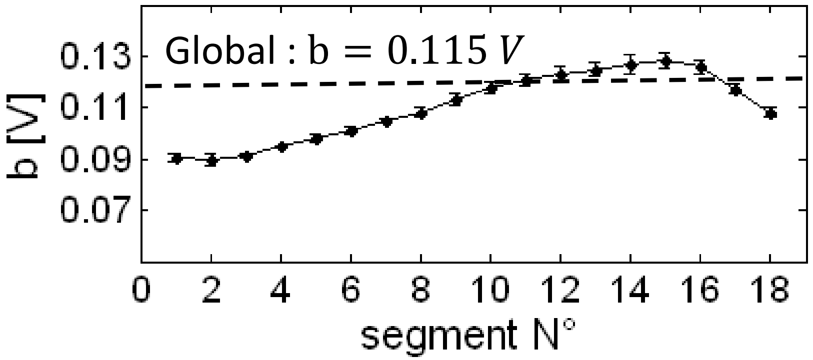




High frequency resistance R_{hf}



Tafel slope $b = R_{ct} \times j$



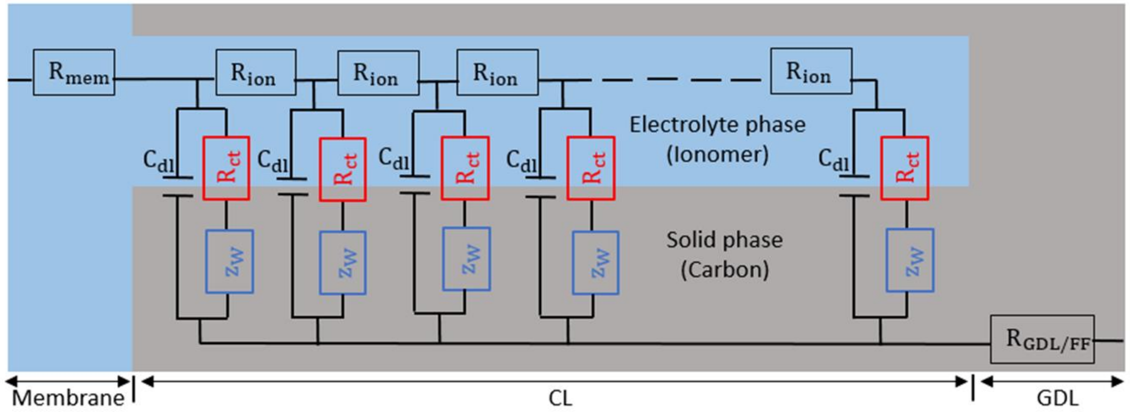
[1] Mainka et al., J. Pow. Sources (2014)

4. PEMFC modeling – Electrode EECs

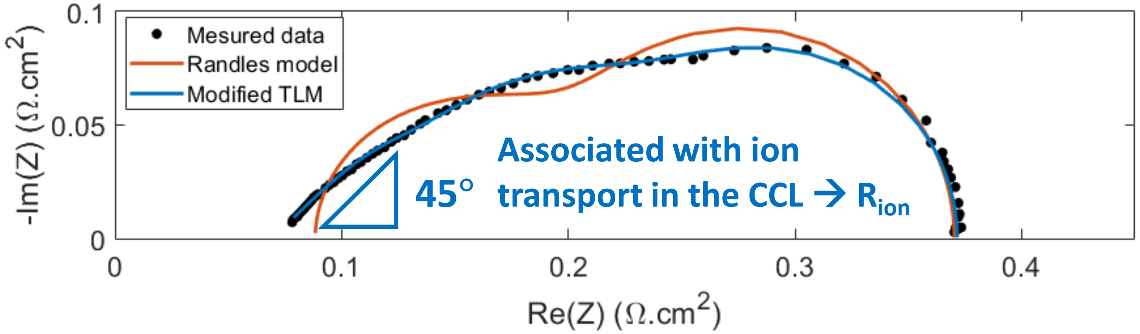
❑ H_2/air operation (in operando) – thick electrodes [1]

Modified Transmission Line Model (M-TLM) circuit with oxygen transport limitations [1-2]

- **PEMFC EEC** → thick electrodes



Cell B (hot-pressed GDE) – thick electrode



- No satisfying fit quality with Randles EEC
- Good fit quality with the modified TLM
  → **More adapted for thick electrodes (45° slope)**

- **PEMFC impedance** (anode neglected)

$$Z_{Cell}(\omega) = R_{hf} + Z_{M-TLM}(\omega)$$

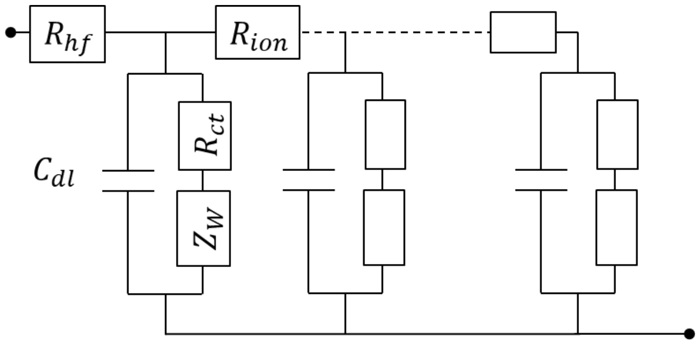
$$= R_{hf} + \frac{\sqrt{R_{ion}}}{\sqrt{i\omega C_{dl} + (1/(R_{ct} + Z_W(\omega)))}} \coth\left(\sqrt{iR_{ion}C_{dl} + (R_{ion}/(R_{ct} + Z_W(\omega)))}\right)$$

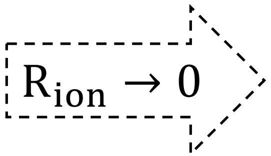
[1] S. Touhami et al, *J. Electrochem. Soc.* (2019)
[2] S. Cruz-Manzov and R. Chen, J. electroanal. Chem. (2013)

4. PEMFC modeling – Electrode EECs

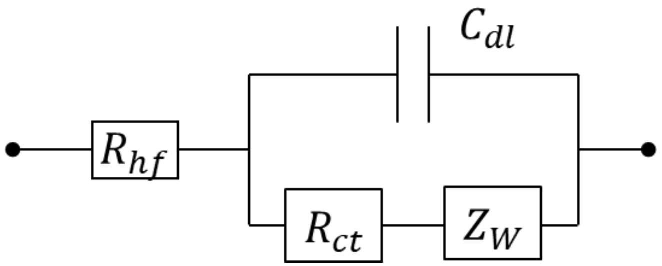
- H_2/air operation (in operando) – from thick to thin electrodes [1]
  - **PEMFC EEC**

M-TLM EEC → thick electrodes





Randles EEC → interfacial (thin) electrodes

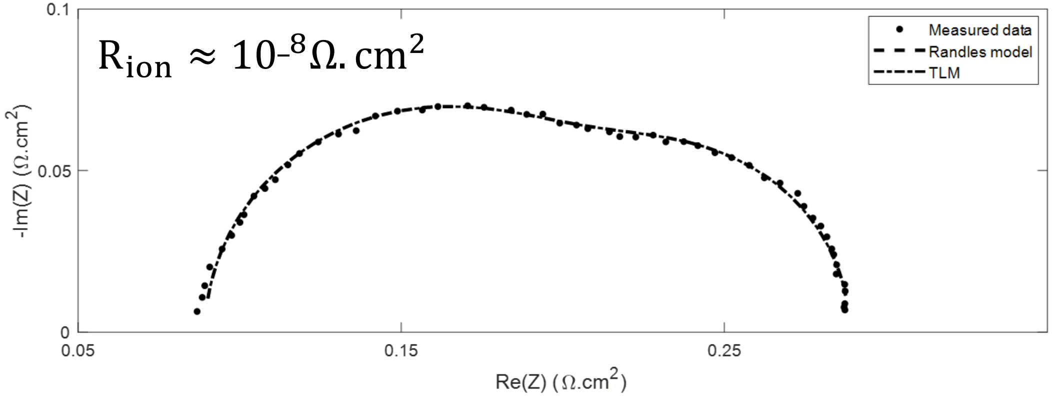


  - **PEMFC impedance** (anode neglected) : asymptotic study for low values of R_{ion}

$$\lim_{R_{ion}\to 0} Z_{M-TLM}(\omega) = \frac{1}{\frac{1}{R_{ct}+Z_W} + i\omega C_{dl}} = Z_{Randles}(\omega)$$

→ **Modified TLM as a generalization of Randles EEC** (thin and thick electrodes)

Cell A (CCM - SolviCore) – thin electrode

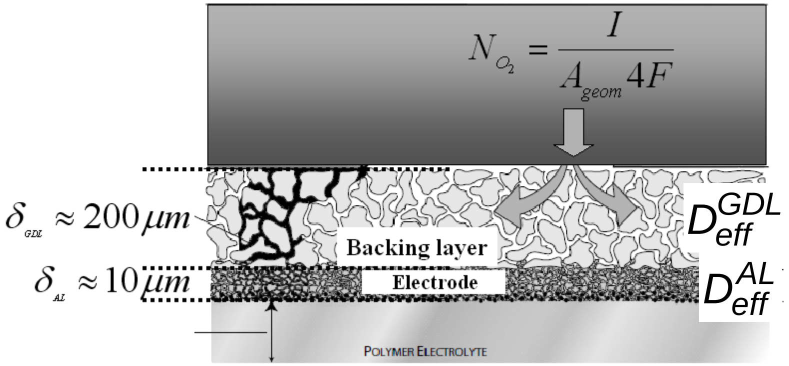


[1] S. Touhami et al, *J. Electrochem. Soc.* (2019)

4. PEMFC modeling – Focus on O_2 diffusion impedance

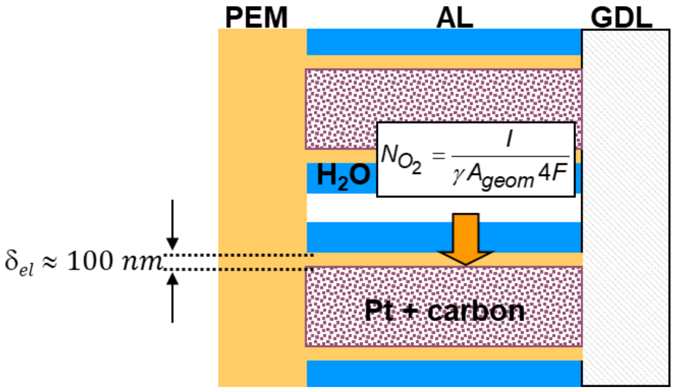
- **Application: O_2 diffusion limiting layer identification [1-3]**
  - **Three stages of O_2 diffusion**

Pores of GDL and CCL → Gas diffusion



M. Reum, Ph.D thesis, 2008

Ionomer film in CCL → Liquid diffusion



→ **Which layer is at the origin of the oxygen transport impedance?**

- **EIS diffusion parameters**

From the Warburg diffusion impedance: $Z_w(R_d, \tau_d) = R_d \frac{\tanh\sqrt{i\omega\tau_d}}{\sqrt{i\omega\tau_d}}$

Diffusion resistance: $R_d = \lim_{\omega\to 0} Z_w = \frac{b\delta}{4FD_{eff}\langle c_{O_2}(0)\rangle_t}$

Characteristic diffusion time: $\tau_d = \frac{\delta^2}{D_{eff}}$

Characteristic diffusion length: $\boxed{\delta = \left(1 + \frac{R_{ct}}{R_d}\right) \times \frac{j_{cell}\,\tau}{4FC_{O_2}}}$

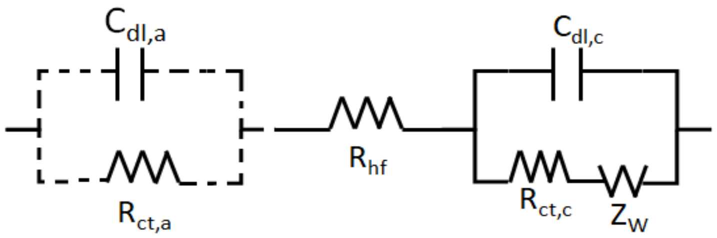
Effective diffusion coefficient: $\boxed{D_{eff} = \frac{\delta^2}{\tau_d}}$

[1] Mainka et al., J. Pow. Sources (2014)
[2] S. Touhami et al, *J. Electrochem. Soc.* (2019)
[3] Aït-Idir et al., IEEE (2021)

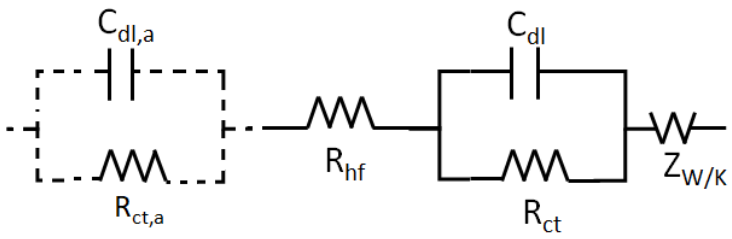
4. PEMFC modeling – Focus on O_2 diffusion impedance

- **Application: O_2 diffusion limiting layer identification [1,2]**
  - **PEMFC EECs** (with anode)

Diffusion impedance in CCL – Randles EEC



Diffusion impedance in GDL – Modified Randles



  - **PEMFC impedance** (with anode)

Diffusion impedance in CCL:

$$\boxed{Z_{cell\_CCL} = Z_{anode} + \boldsymbol{Z_{Randles}} = \left(\frac{1}{R_{ct,a}} + i\omega C_{dl,a}\right)^{-1} + R_{hf} + \left(\frac{1}{R_{ct} + \boldsymbol{Z_w}} + i\omega C_{dl}\right)^{-1}}$$

Warburg diffusion impedance: $Z_w = R_d \frac{\tanh\sqrt{i\omega\tau_d}}{\sqrt{i\omega\tau_d}}$

Diffusion impedance in GDL:

$$\boxed{Z_{cell\_GDL} = Z_{anode} + \boldsymbol{Z_{M-Randles}} = \left(\frac{1}{R_{ct,a}} + i\omega C_{dl,a}\right)^{-1} + R_{hf} + \left(\frac{1}{R_{ct}} + i\omega C_{dl}\right)^{-1} + \boldsymbol{Z_{w/K}}}$$

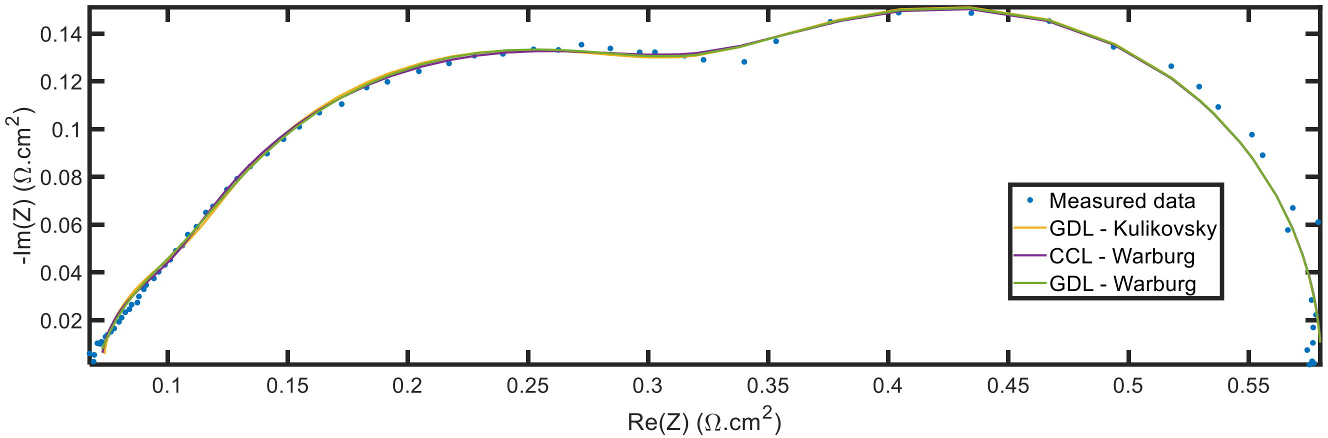
Warburg or Kulikovsky diffusion impedance [3]: $Z_K = \frac{Z_w}{1+i\omega C_{dl} R_{ct}}$

[1] Aït-Idir et al., IEEE (2021)
[2] S. Touhami et al, J. Electrochem. Soc. (2019)
[3] A. Kulikovsky, Electrochem. Comm. (2017)

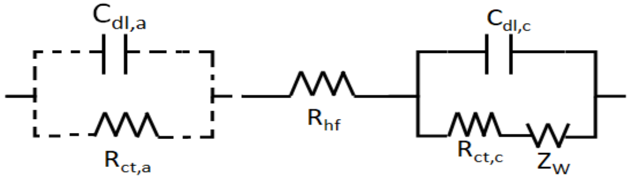
4. PEMFC modeling – Focus on O_2 diffusion impedance

- **Application: O_2 diffusion limiting layer identification [1,2]**
  - **PEMFC impedance spectrum (H_2/air)** @ 0.5 A/cm², f = 20 mHz-10 kHz

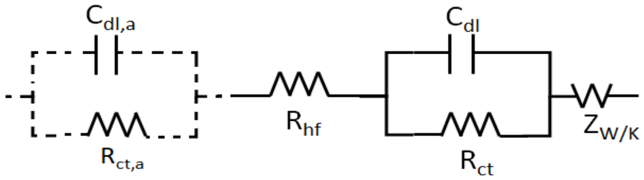
$T_{FC} = 60$ °C
$HR_{H2,air} = 50\%$
$S_{air} = 3, SH_2 = 1.2$



Randles EEC – Z_W in CCL



M-Randles EEC – Z_W/Z_K in GDL

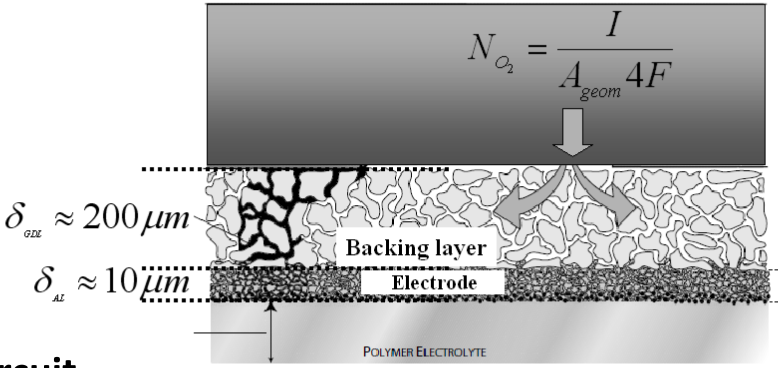


  - **Identified diffusion parameters**

Model	Warburg CCL	Warburg GDL	Kulikovsky GDL
δ [μm]	308	359	302
D_{eff} [10^{-6}m^2.s^{-1}]	1.35	1.92	1.25

→ δ and D_{eff} of the order **gaseous O_2 diffusion through the GDL** for all EECs

- **GDL main contribution to oxygen transport impedance**
- In contradiction with Randles circuit (interfacial electrode) → **Modified Randles circuit**



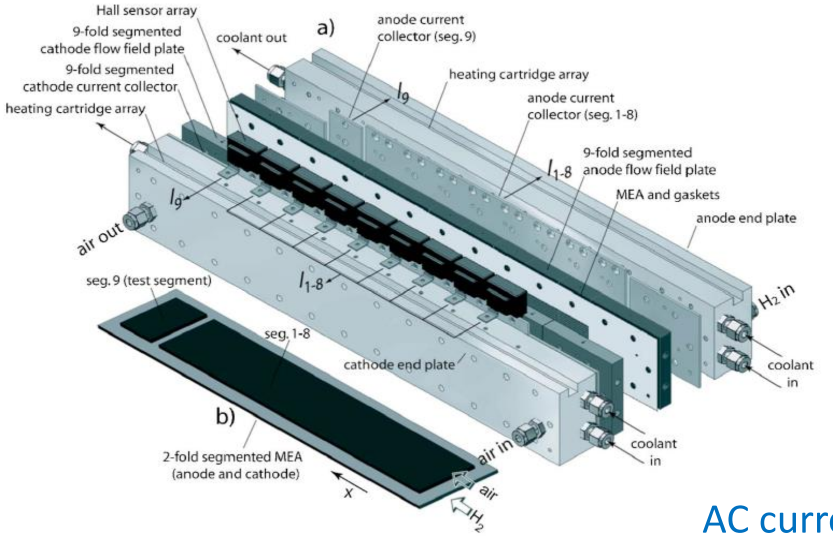
M. Reum, Ph.D thesis, 2008

[1] Mainka et al., J. Pow. Sources (2014)
[2] S. Touhami et al, *J. Electrochem. Soc*. (2019)
[3] Aït-Idir et al., IEEE (2021)

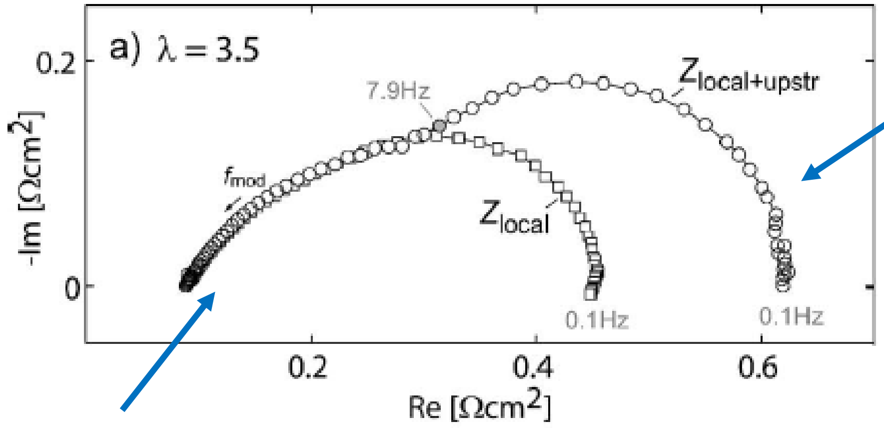
4. PEMFC modeling – Focus on O_2 diffusion impedance

❑ Difficulties with EIS at low frequencies

- **Oxygen oscillation propagation** along the gas channels → Measuring artefacts [1-3]



Impedance spectra of the last segment



AC current applied to the **cell**

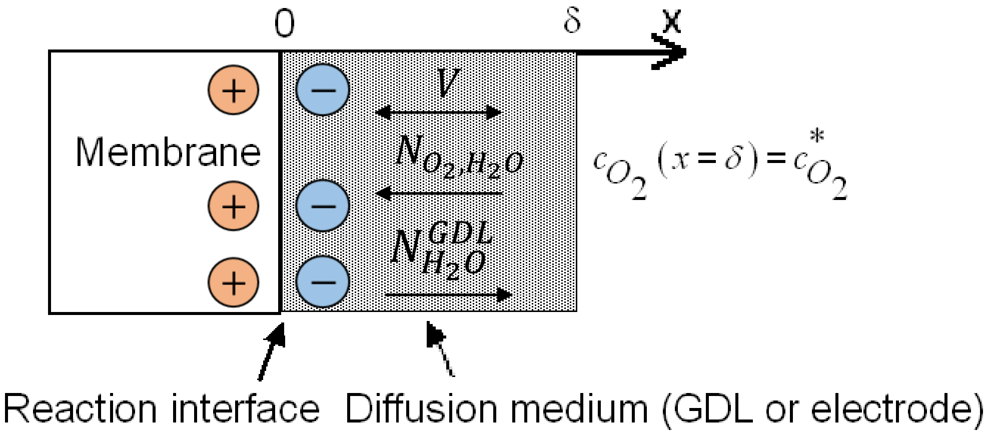
AC current applied to the **last segment**

- **Limits of Warburg diffusion impedance**: **constant oxygen concentration** along the GDL/flow field interface [2,4] and oxygen transport by **1D Fickian diffusion** instead of **Stefan-Maxwell equations** [5 -7]

[1] I. A. Schneider et al., J. Electrochem. Soc. 154 (2007)
[2] G. Maranzana et al., Electrochimica Acta 83 (2012)
[3] P. Guillemet et al., ECS Transactions 50 (2012)
[4] J. Mainka et al., J. Electrochem. Soc. 157 (2010)
[5] J. Mainka et al., Fuel cells 12 (2012)
[6] T.E. Springer et al., J. Electrochem. Soc. 138 (1991)
[7] O. Lottin et al., Int. J. Therm. Sci. 48 (2009)

4. PEMFC modeling – Focus on O_2 diffusion impedance

- **Example** of alternative to Warburg impedance: **1D convecto-diffusive impedance [1]**



Hypothesis: convective flux through the GDL (vapor evacuation)

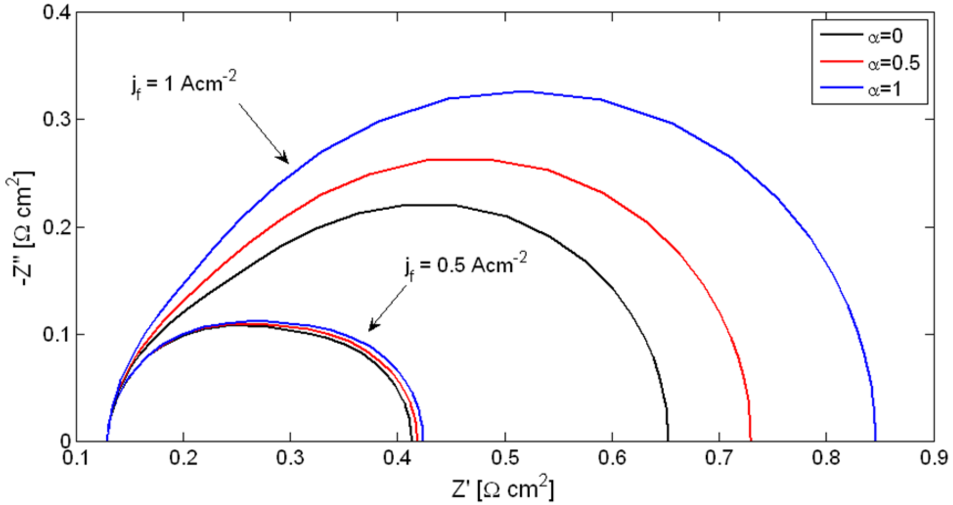
$N_{H_2O}^{GDL} = \alpha N_{H_2O}^{prod}$ with α - **water transport coefficient**

- **α = 0**: convection and diffusion in the same direction
- **α = 0.5**: O_2 diffusion only
- **α = 1**: convection opposite to diffusion

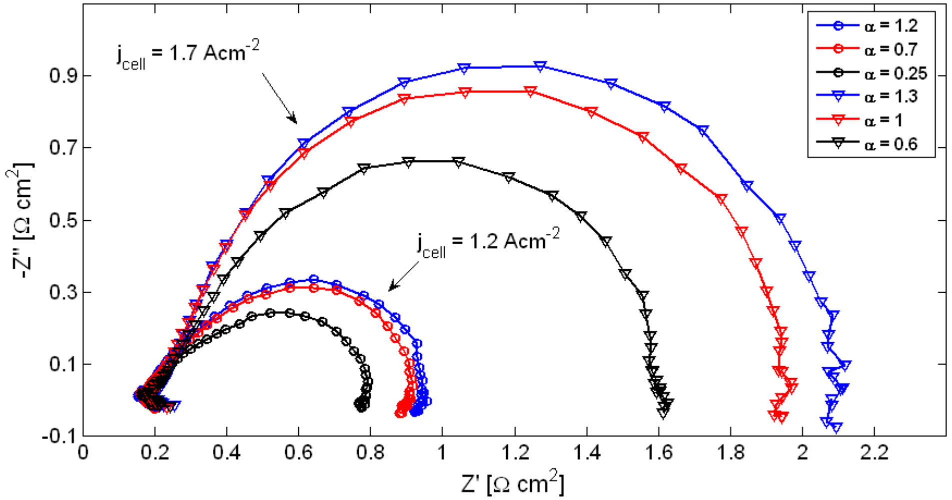
$\boxed{Z_{conv,diff}^{1D}(\delta, D_{eff}, V)}$ with $V = (2\alpha - 1)\frac{j_f}{4F}\frac{RT}{P}$ - convective flux velocitiy

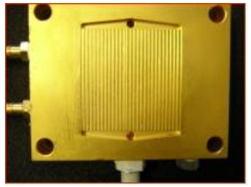
Simulated PEMFC spectra

Model conditions	
R_{hf} [Ωcm²]	0.13
R_{ct} [Ωcm²]	0.19
C_{dl} [Fcm⁻²]	0.02
δ [µm]	200
D_{eff} [m²s⁻¹]	10^{-6}
j_f [Acm⁻²]	0.5
T_{cell} [°C]	60
P [bar]	1



Experimental PEMFC specta (CCM - Johnson Matthey)





$T_{FC} = 60$ °C
$HR_{H2,air} = 60\%$
$S_{air} = 3, SH_2 = 1.4$

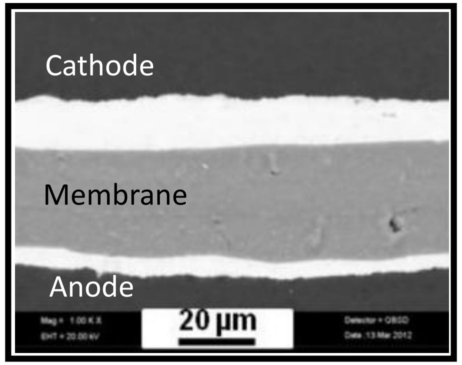
[1] J. Mainka et al., *Fuel cells* (2012)

4. PEMFC modeling – Application to PEMFC ageing

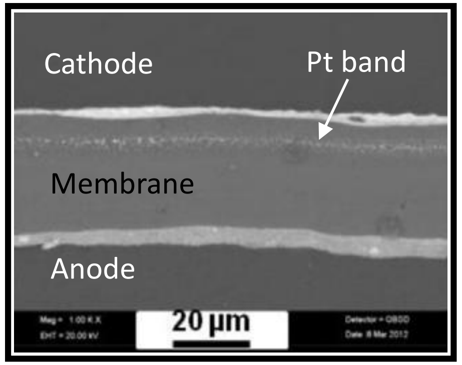
❑ PEMFC ageing

Active layer [1,2]

Fresh MEA(a)

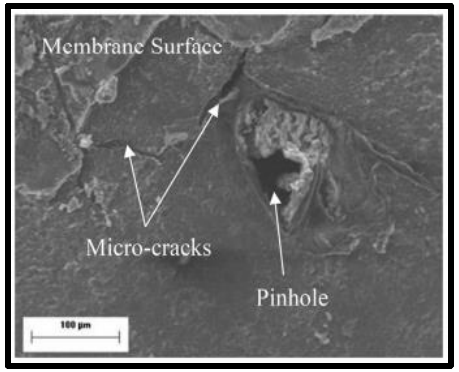


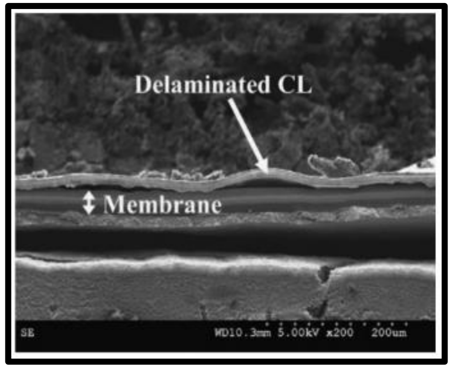
Aged MEA



→ Carbon corrosion and Pt dissolution and redeposition

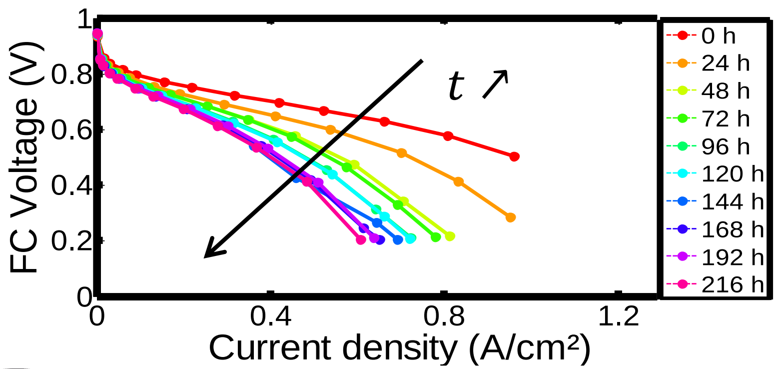
Membrane and membrane-electrode interface [3,4]





→ Chemical, mechanical and thermal stresses

→ **Decrease of FC performance [5]**



→ **Insufficient lifetime** to meet the DOE targets for 2050 [6]

Light duty vehicles: +8000 h

Heavy duty vehicles: +20000 h

[1] Durst et al., *Appl. Catalysis B : Env*. (2013)
[2] Macauley et al., *J. Electrochem. Soc*. (2018)
[3] Lim C et al., J. Pow. Sources. (2014
[4] Kim S et al., *J. Pow. Sources*. (2008)
[5] S. Abbou, *Ph.D Thesis*, UL (2015)
[6] M. Whiston, PNAS (2019)

4. PEMFC modeling – Application to PEMFC ageing

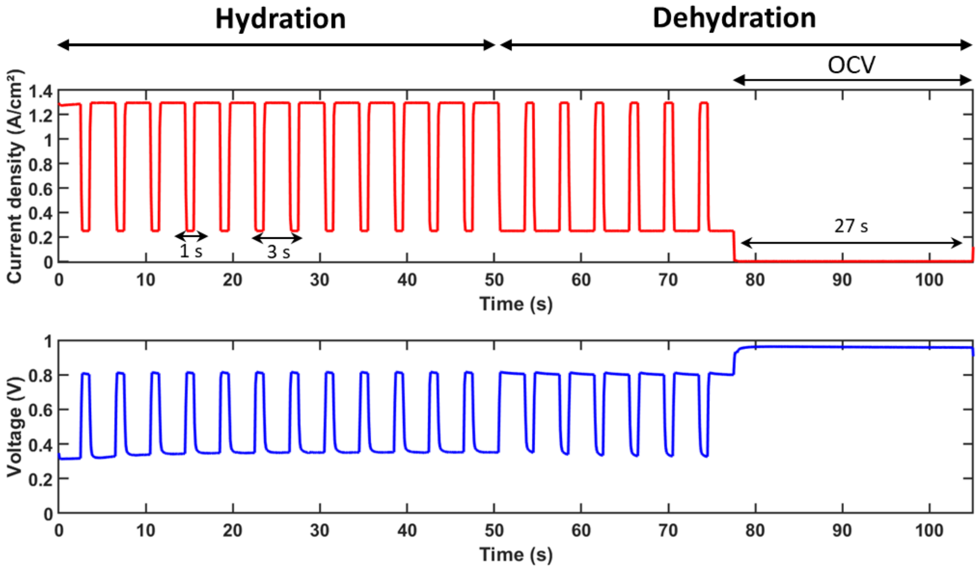
❑ Accelerated Stress Test (AST)

PEMFC durability testing under realistic conditions is expensive and tedious → AST

Applied AST [1]

- Potential cycling
- Open circuit voltage (OCV)
- (Load induced) humidity cycling [2 - 4]

(constant gas flow rates ↔ I_{max} = 1.3 A/cm^2)



Experimental Protocol

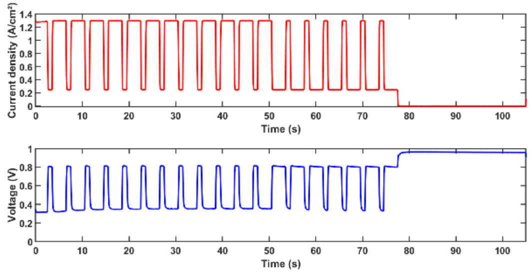
Conditioning (2h)

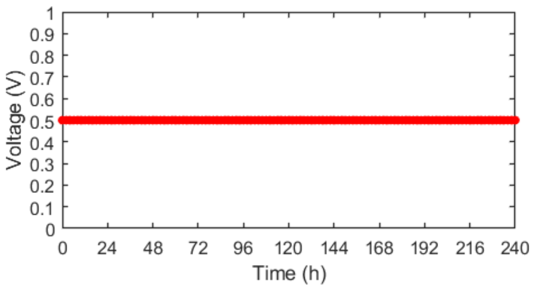
Characterization stage

- Current and voltage @ 0.5 A/cm^2
- **EIS @ 0.5 A/cm^2**
- Polarization curve
- Cathode H_2 permeation
- Cathode CV @ 50 mV/s sweeping rate
- Anode H_2 permeation
- Anode CV @ 50 mV/s sweeping rate

AST/constant current during 24h

×10



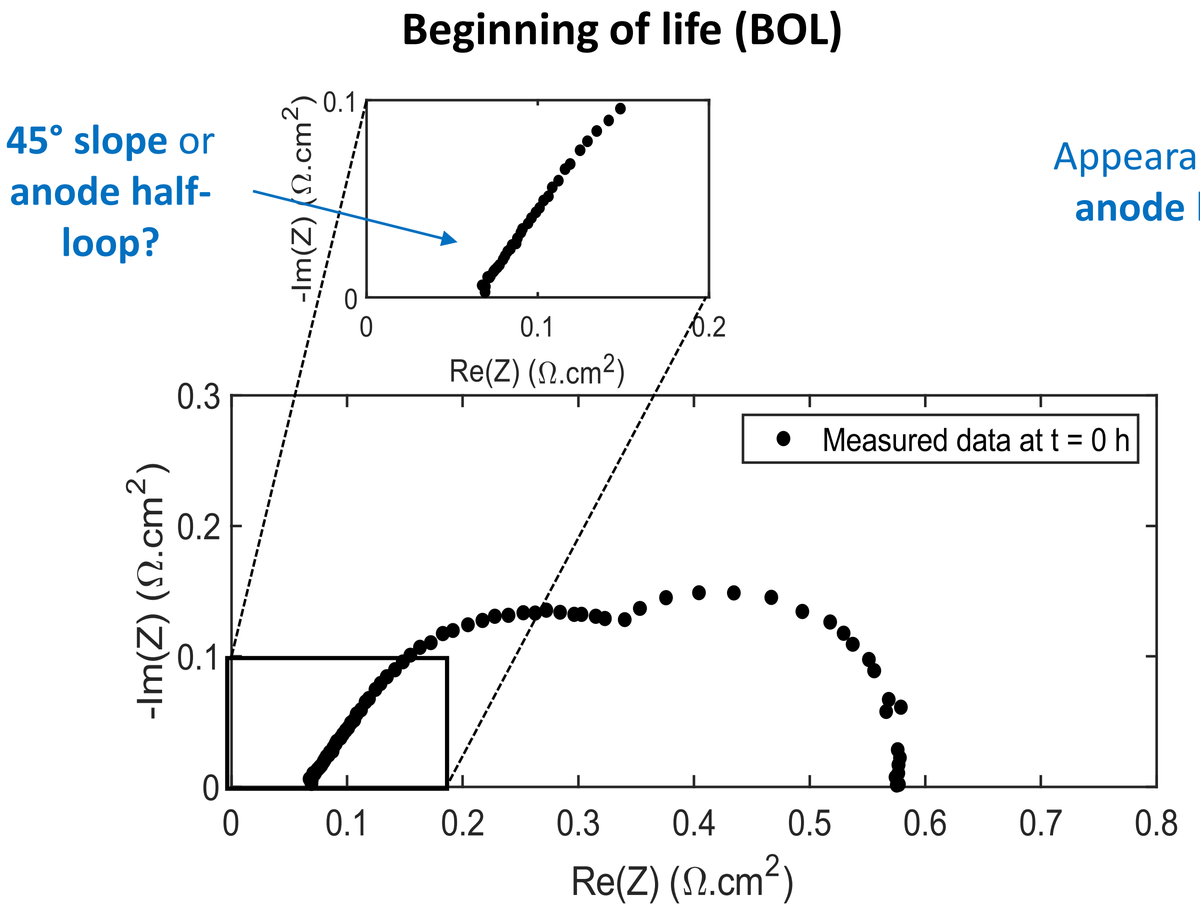


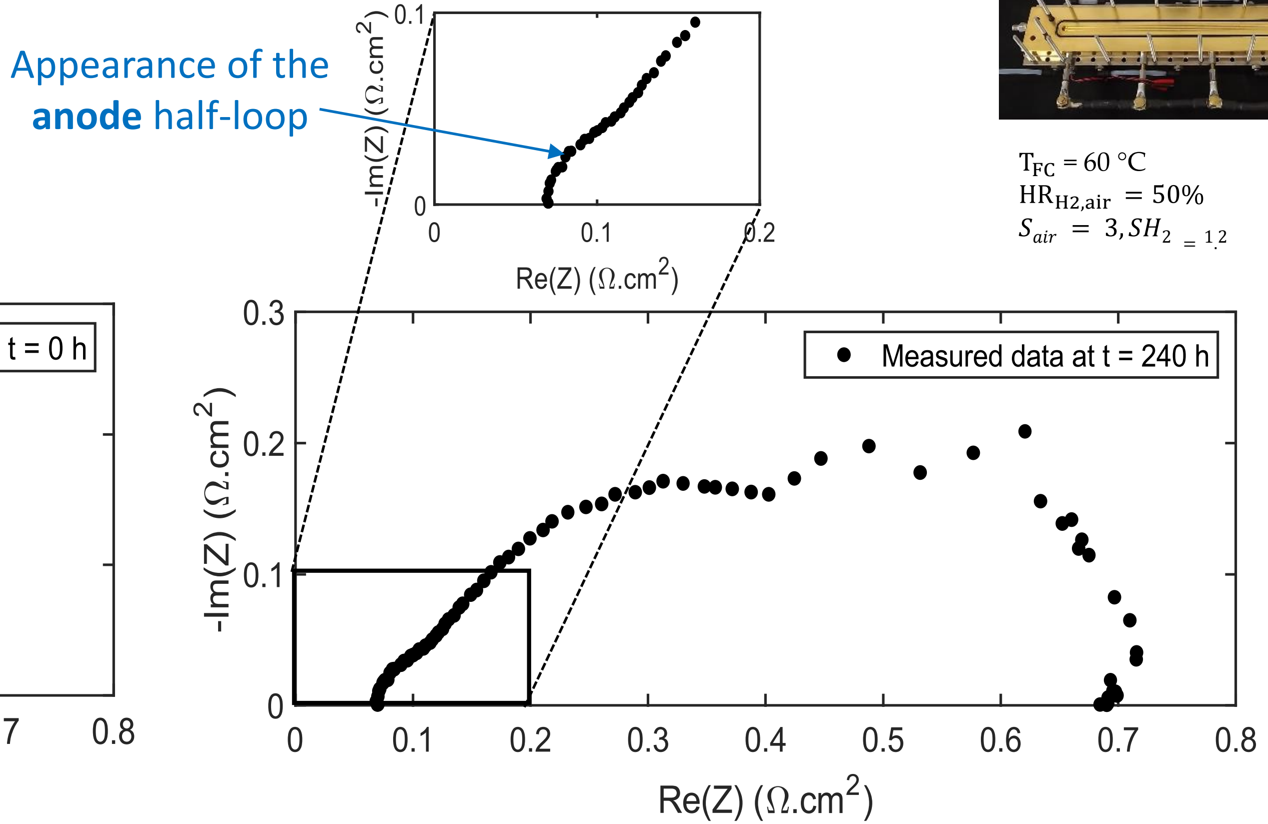
Characterization stage

[1] S. Touhami et al., J. Pow. Sources. (2021)
[2] Yeh-Hung Lai et al., J. Electrochem. Soc. (2018)
[3] T.C. Jao et al., Int. J. Hydrogen Energy. (2010)
[4] M. Marrony et al., J. Pow. Sources. (2008)

4. PEMFC modeling – Application to PEMFC ageing

- **Experimental results [1] - EIS**
  - **PEMFC impedance spectra** @ 0.5 A/cm² (IRD MEA) → **BOL** and **AST**





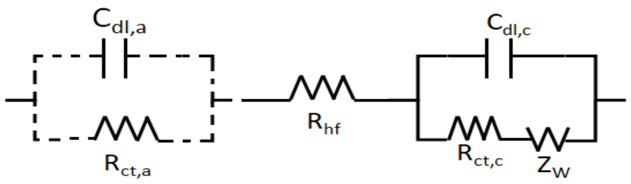
T_{FC} = 60 °C
$HR_{H2,air}$ = 50%
S_{air} = 3, SH_2 = 1.2

[1] S. Touhami et al., J. Pow. Sources (2021)

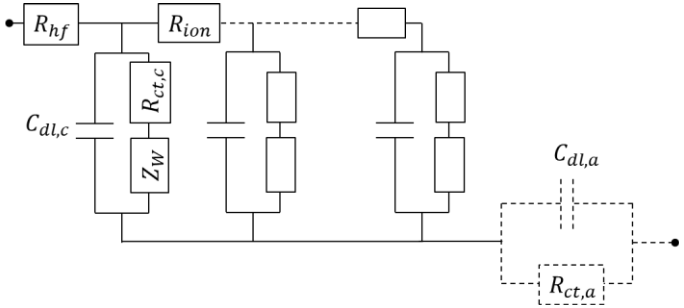
4. PEMFC modeling – Application to PEMFC ageing

- **Experimental results [1] - EIS → BOL**
  - **PEMFC EECs** (with and without anode)

Randles EEC + Anode

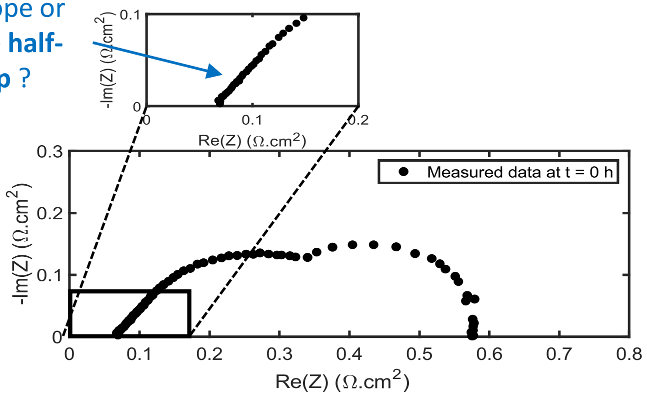


M-TLM + Anode



Beginning of life (BOL)

45° slope or anode half-loop ?



  - **Identified parameters** without and with **anode**

EEC	R_{hf} [Ω.cm²]	τ [s]	R_d [Ω.cm²]	R_{ion} [Ω.cm²]	$C_{dl,c}$ [Ω.cm⁻²]	$R_{ct,c}$ [Ω.cm²]	$C_{dl,a}$ [Ω.cm⁻²]	$R_{ct,a}$ [Ω.cm²]
Randles (cathode only) Residue = 5.8×10⁻³	0.084	0.122	0.286	-	0.015	0.209	-	-
M-TLM (cathode only) Residue = 1.7×10⁻³	0.055	0.128	0.266	0.141	0.018	0.213	-	-
Randles + anode Residue = 1.1×10⁻³	0.073	0.129	0.262	-	0.019	0.212	0.016	0.033
M-TLM + anode Residue = 1.1×10⁻³	0.073	0.129	0.262	1×10^{-5}	0.019	0.212	0.016	0.033

→ **The anode must be taken into account** no matter the EEC (Randles of M-TLM)

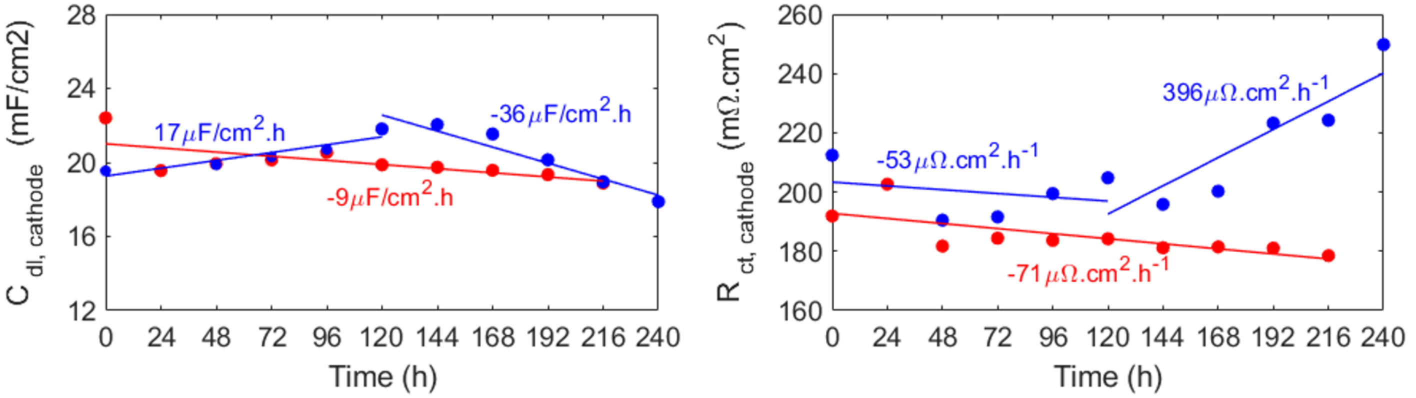
[1] S. Touhami et al., J. Pow. Sources (2021)

4. PEMFC modeling – Application to PEMFC ageing

❑ Experimental results [1] - EIS

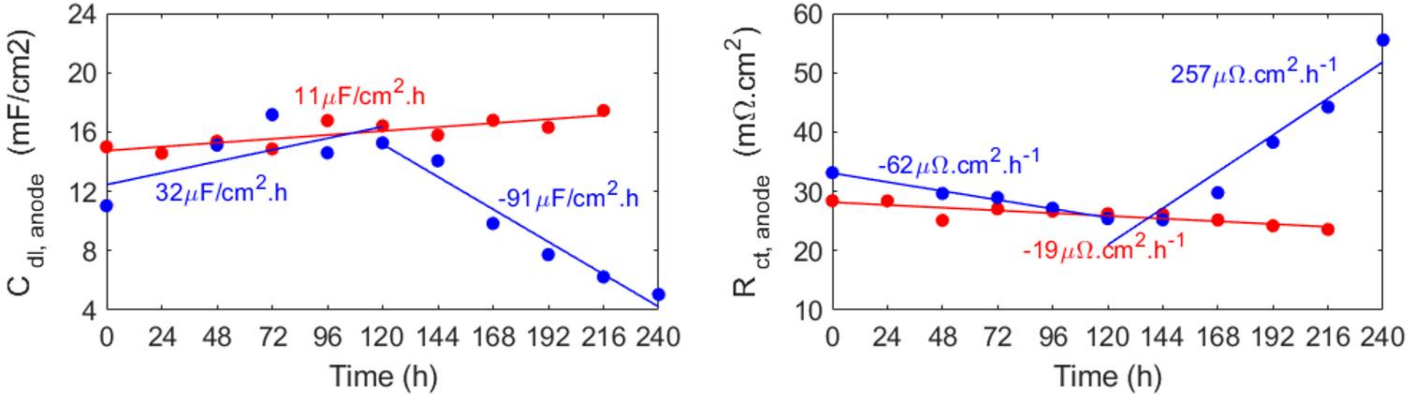
- **EIS measurements** (@ 0.5 A/cm²) → electrode kinetic parameters: constant current vs. AST

Cathode

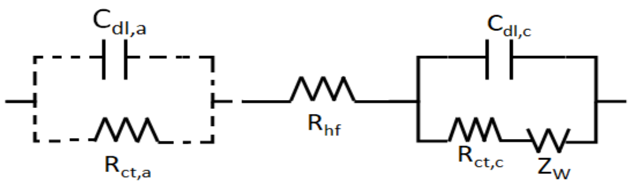


- ● Constant current test
- ● Accelerated stress test

Anode



Randles EEC + Anode



- **Constant current:** no evidence of ageing
- **AST: ageing of both electrodes**

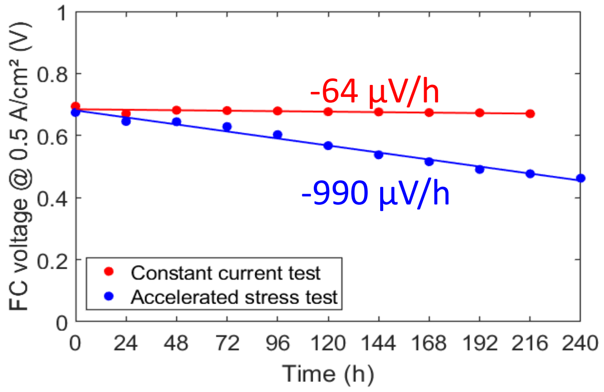
[1] S. Touhami et al., J. Pow. Sources (2021)

4. PEMFC modeling – Application to PEMFC ageing

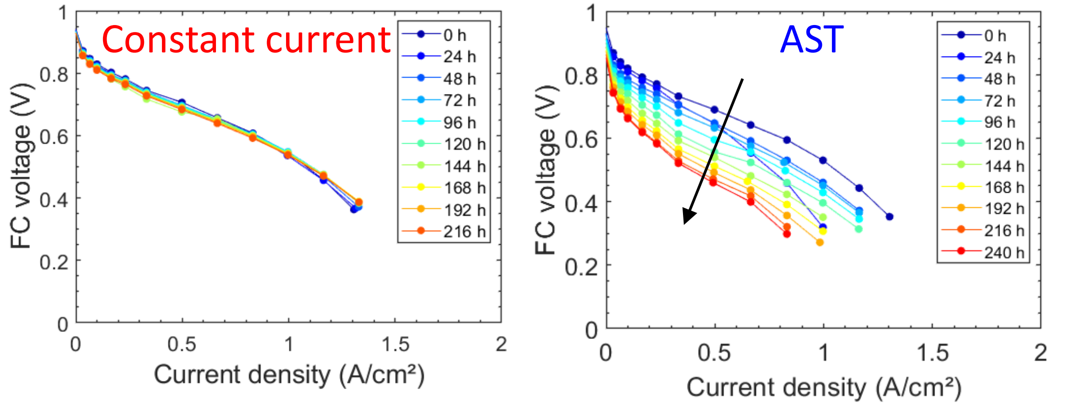
❑ Experimental results [1] - complementary analyses

- **Cell performance:** constant current vs. AST

Voltage at 0.5 A/cm²

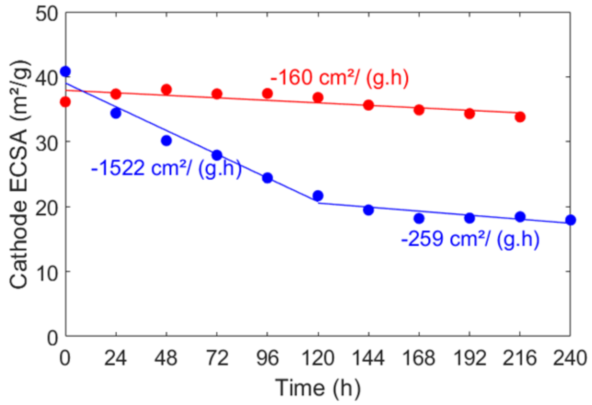


Polarization curves

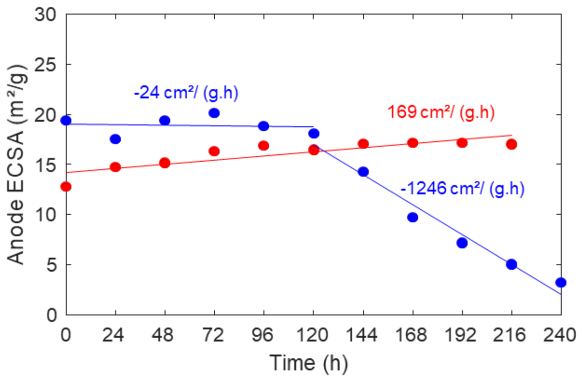


- **ElectroChemical Surface Area (ECSA):** constant current vs. AST

Cathode



Anode



- **Constant current:** no evidence of ageing
- **AST: ageing of both electrodes**
  Cathode : -57%
  Anode: -83%

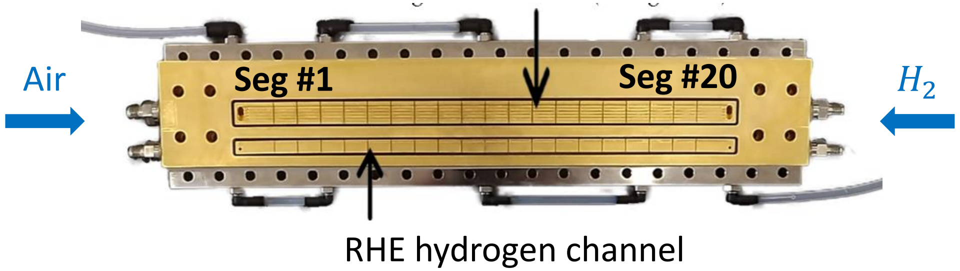
→ **Confirmation of results obtained by EIS**

[1] S. Touhami et al., J. Pow. Sources (2021)

4. PEMFC modeling – Application to PEMFC ageing

❑ Experimental results [1] - complementary analyses → AST

- **Local electrode potentials**



Cathode

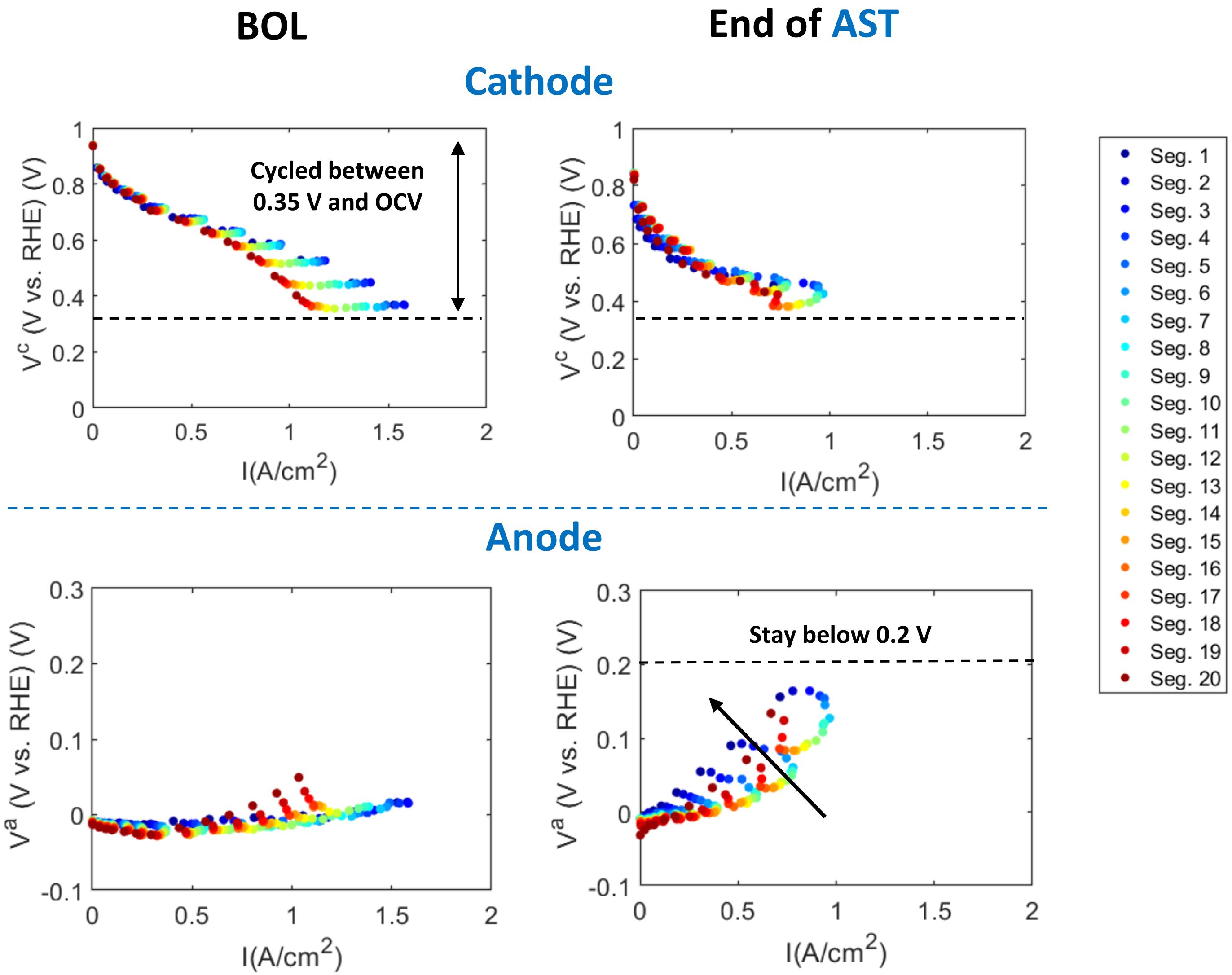
Cathode local potentials cycled between 0.25V and OCV

→ **Electrochemical mechanisms at the origin of cathode degradation** [2]

Anode

Anode local potentials below 0.2V

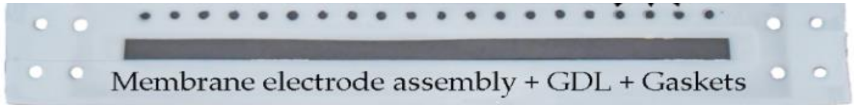
→ **Electrochemical mechanisms (high potentials) are not responsible for anode degradation**



[1] S. Touhami et al., J. Pow. Sources (2021)
[2] L. Dubau et al., Wiley Interdiscip. Rev. Energy Environ (2014)

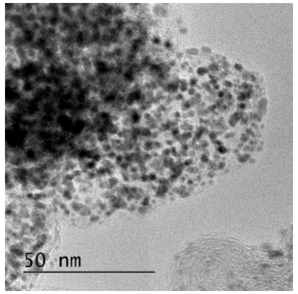
4. PEMFC modeling – Application to PEMFC ageing

- ❑ **Experimental results [1] - complementary analyses** → **AST**
  - ▪ **Post-mortem Transmission Electron Microscopy (TEM)** @ 50 and 200k

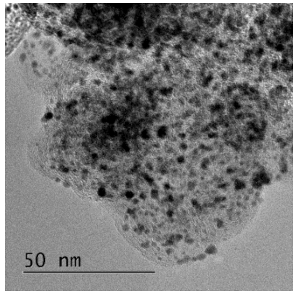


Pristine MEA

Anode



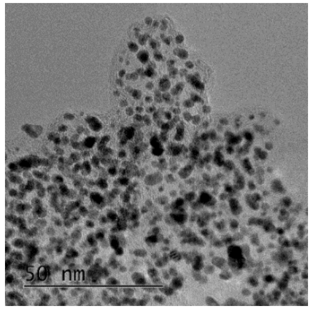
Cathode



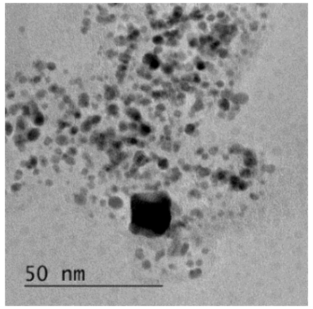
Aged MEA

Anode

Inlet

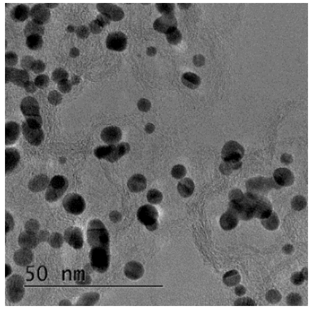


Outlet

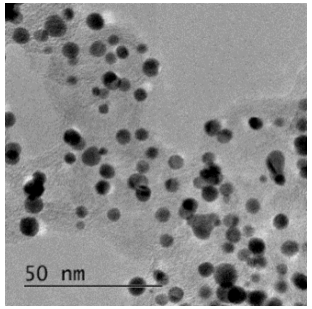


Cathode

Inlet



Outlet



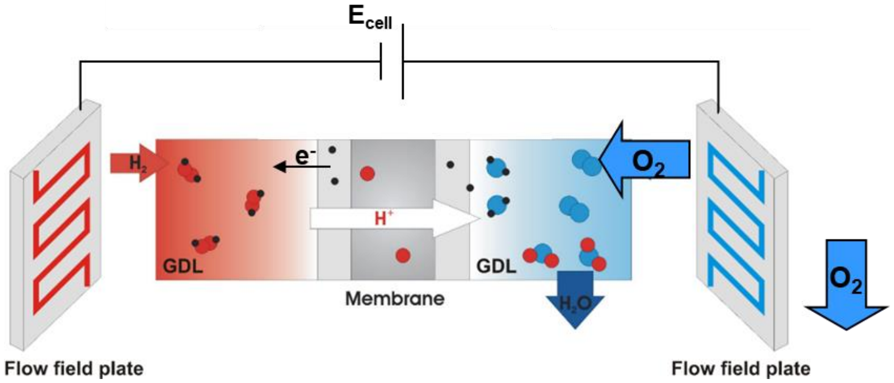
→ **Pt particle agglomeration** primarily a the **cathode**
→ Confirmation of results obtained by other techniques (EIS, potential measurements…)

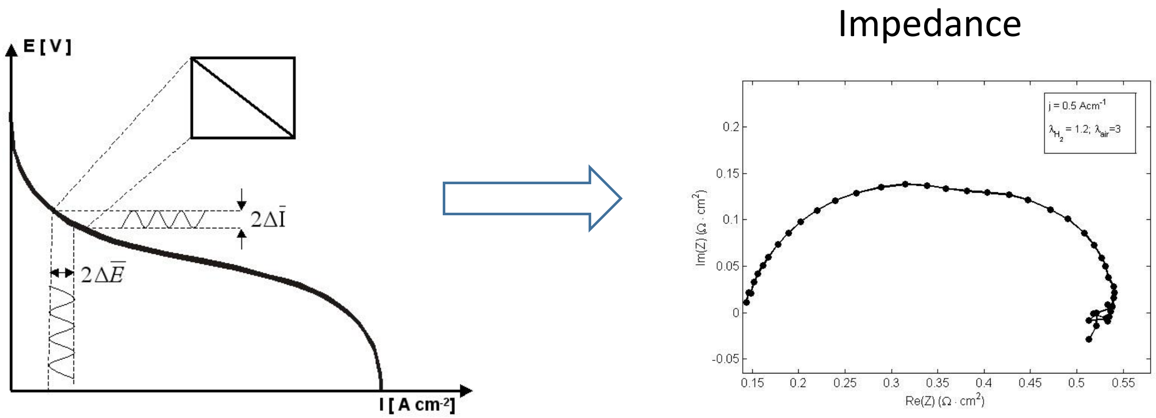
[1] S. Touhami et al., J. Pow. Sources (2021)

Outline

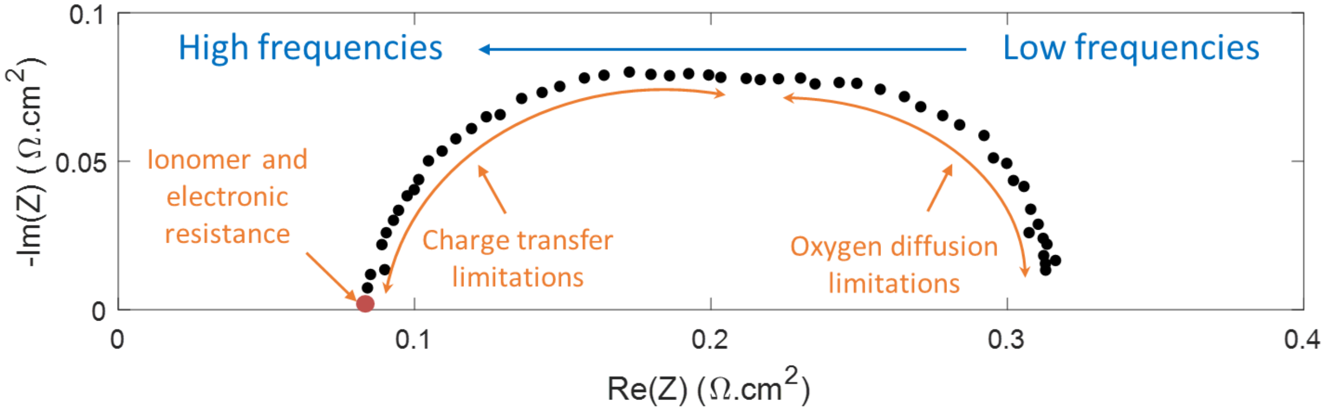
5. Concluding remarks

- **Electrochemical Impedance Spectroscopy (EIS)** is a common technique used to **analyze the performance** of electrochemical systems such as fuel cells and supercapacitors during operation.



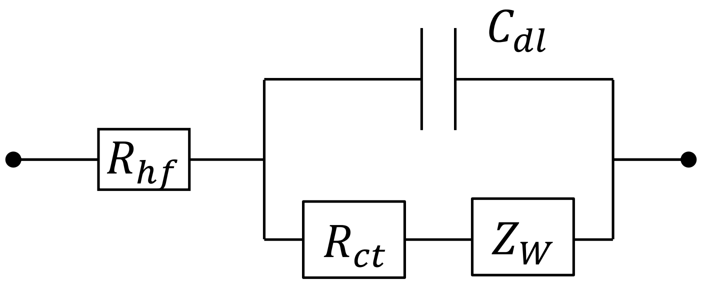


- The main advantage of EIS is that **microscopic phenomena** with different time constants can be **considered separately** in the frequency domain.

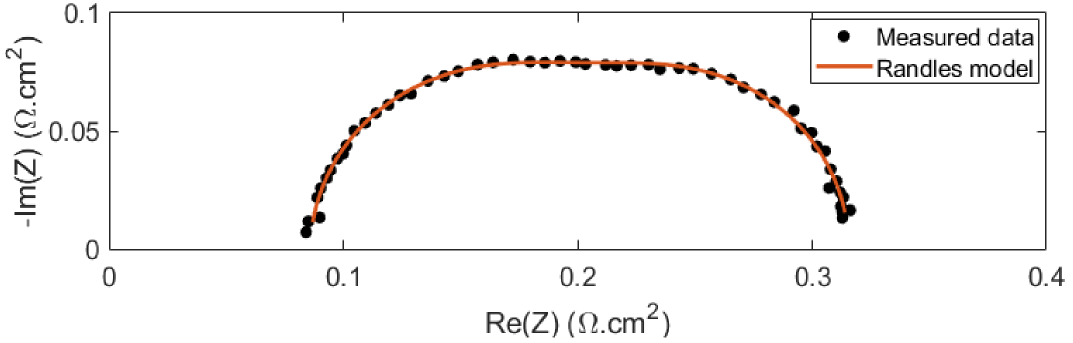


5. Concluding remarks

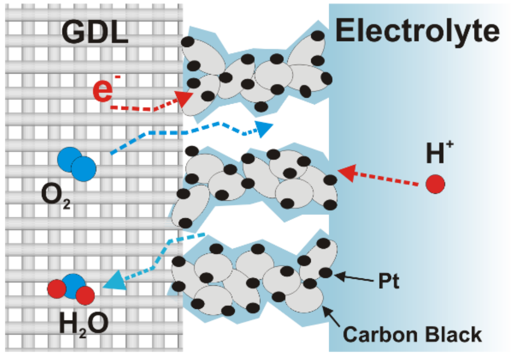
- **Equivalent Electrical Circuit (EEC)** models allow to **reproduce EIS spectra** of an electrochemical system.



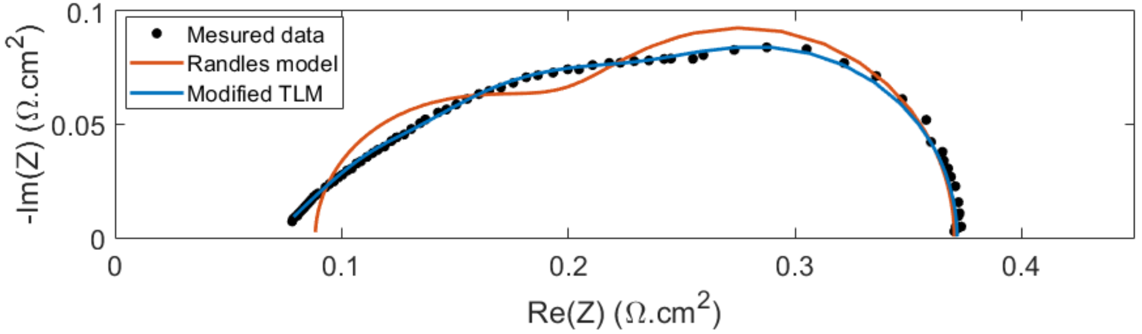
CCM MEA - thin electrodes



- For a reliable **interpretation**
  - The parameters have to be **related to the microscopic phenomena** at the origin of the electrical output.
  - The circuit has to be **adapted to the operating conditions and the composition** of the system.



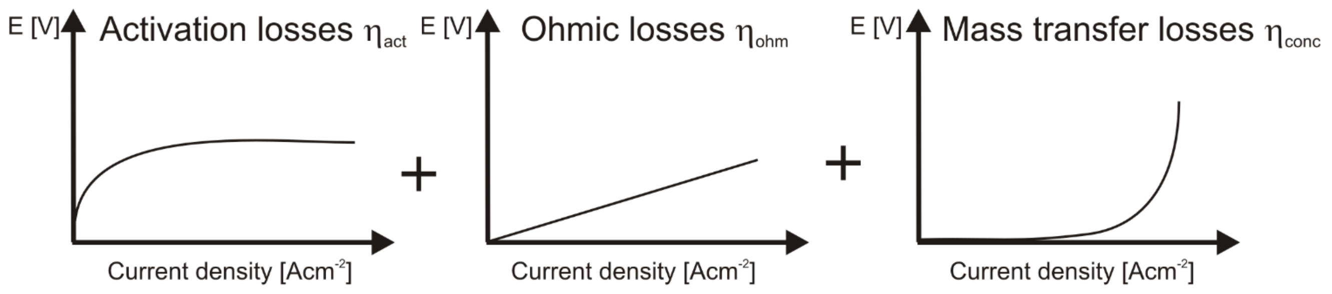
GDE MEA - thick electrodes

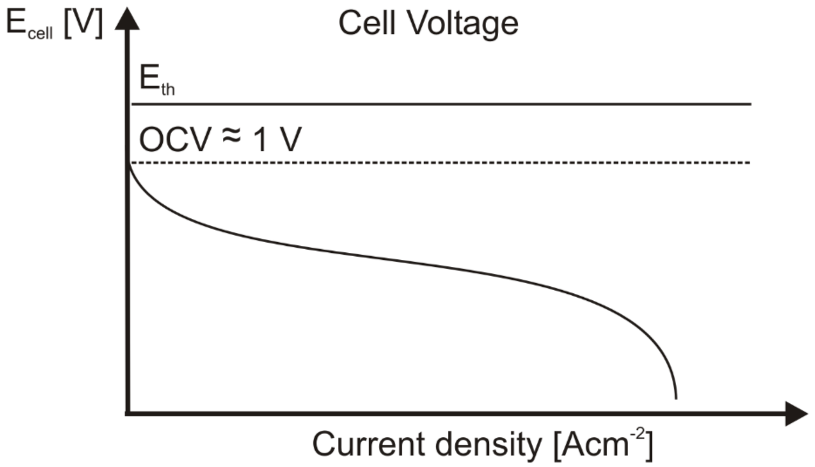


Thank you for your attention

2. PEMFC modeling – Cell performance

- **Polarization curve** - Additional voltage losses during operation





- Kinetic overpotential (ORR at cathode limiting):

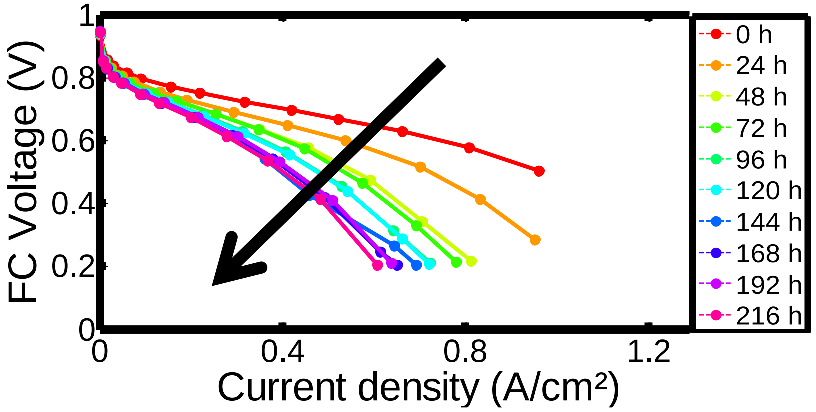
$$\eta_{act} = b \ln \frac{j}{j_0} \frac{c^*_{O_2}}{c_{O_2}} \quad \text{(Tafel law)}$$

- Ionic conduction (membrane) and other contact resistances:

$$\eta_{ohm} = R_{hf} j \quad \text{(Ohmic law)}$$

→ Total cell voltage: $\boxed{E_{cell}(j) = E^0 - \eta_{act}(j) - \eta_{ohm}(j) - \eta_{conc}(j)}$

+ Ageing (Pt coarsening, carbon corrosion,...)[1]



Main aims of R&D:

- Minimize voltage losses
- Enhance lifetime

[1] S. Abbou, Ph.D Thesis, UL (2015)

2. PEMFC modeling – Application to PEMFC ageing

❑ Segmented cell with Reference Hydrogen Electrodes (RHEs)

Instrumented cell [1-3]

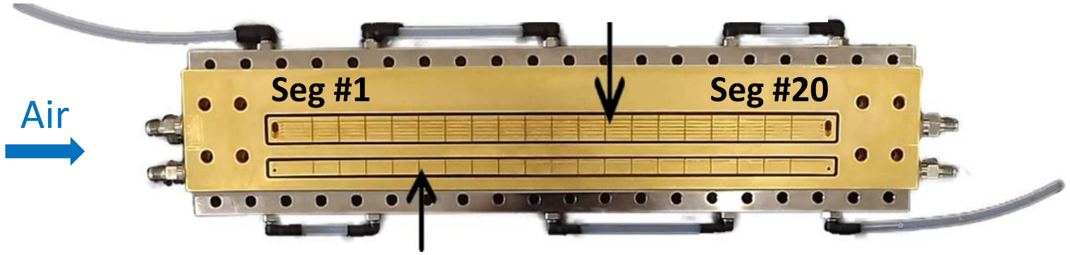
- Linear cell (316 stainless steel)
- Cathode flow field plate (20 segments)
  - Current collection
  - RHE
- 5 parallel channels (L x H x W = 300 x 0.7 x 1 mm)
- MEA: 30 cm²
- Gas supply: counter-current

→ **Measurements (local and global):** currents and electrode potentials
→ **Electrochemical characterization (local and global)**: EIS, CV (ECSA) ....

Heating /cooling water circuit

Cathode flow field plate (20 segments)

Air



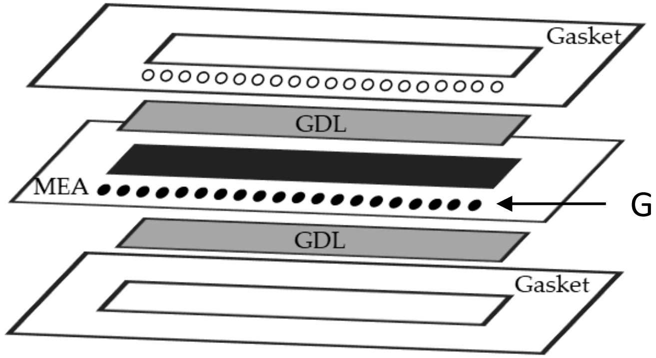
RHE hydrogen channel

Anode flow field plate

H_2

MEA (IRD)

- Membrane: Nafion XL 100
- Platinum loading:
  - Anode 0.1 mg_{pt}/cm^2
  - Cathode 0.3 mg_{pt}/cm^2
- HSA carbon: 800 m²/g both electrodes
- GDL: Sigracet 28 BC



GDE for RHE

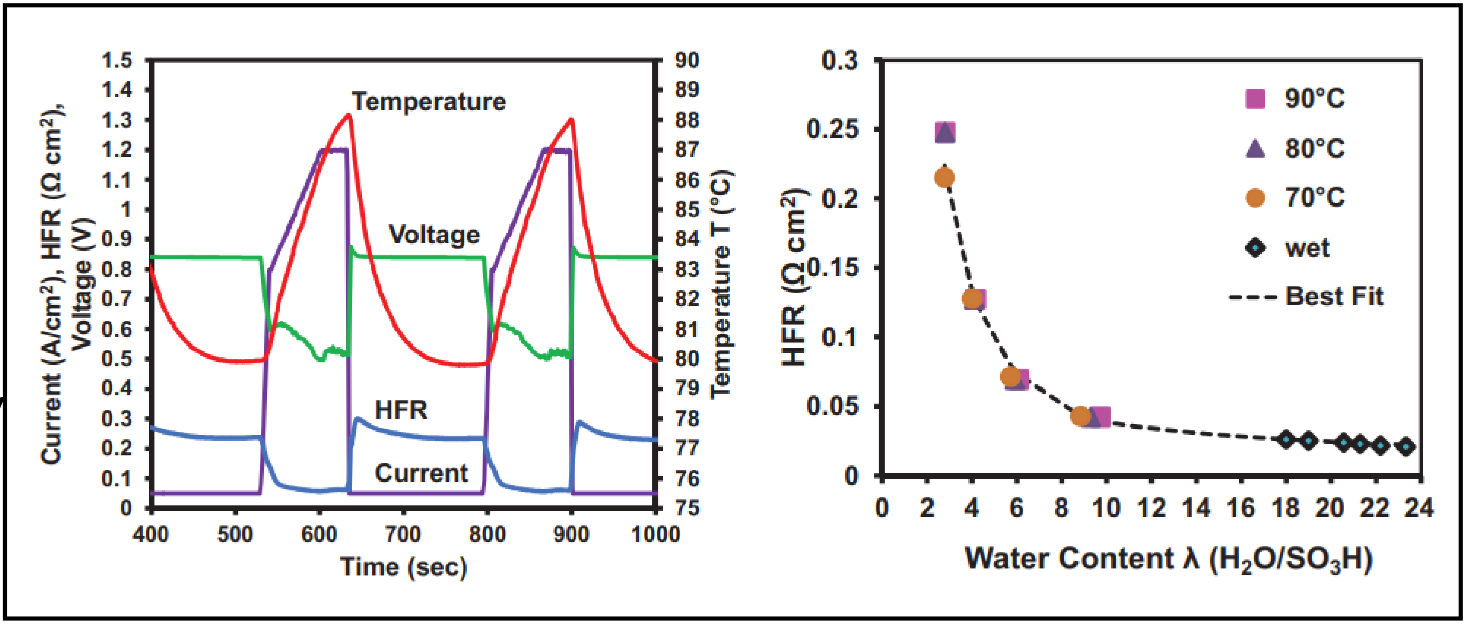
[1] Abbou et al., *J. Pow. Sources*, 340 (**2017**)
[2] A. Lamibrac et al., *J. Pow. Sources*, 196 (**2011**)
[3] Abbou et al., *ECS Transactions*, **2013**

Accelerated stress tests (AST)

PEMFC durability testing under **realistic conditions** is **expensive** and **tedious** ➔ AST

Harmful FC operation conditions

- Start-up/shut-down cycles [1]
- Open circuit voltage (OCV) [2,3]
- Load/potential cycling [2,4]…
- … and constant load [7]
- Fuel depletion [5-7]…
- Potentiostatic cycling and hold under H_2/N_2 [8]
- Load induced humidity cycling [9]



➔ **Our AST: potential cycling + load-induced humidity cycling + OCV**

[1] Maranzana et al., *J. Electrochem. Soc.*, 162 (**2015**)
[2] Gaumont et al., *J. Electrochem. Soc.*, 164 (**2017**)
[3] Mukundan et al., *J. Electrochem. Soc.*, 165 (**2018**)
[4] Macauley et al., *J. Electrochem. Soc.*, 165 (**2018**)
[5] Abbou et al., *J. Pow. Sources*, 340 (**2017**)
[6] Abbou et al., *ECS Transactions*, 58 (**2015**)
[7] Enz et al., *J. Pow. Sources,* 274 (**2015**)
[8] Fairweather et al., *J. Electrochem. Soc.* 160 (**2013**)
[9] Yeh-Hung Lai et al., *J. Electrochem. Soc.*, 165 (**2018**)