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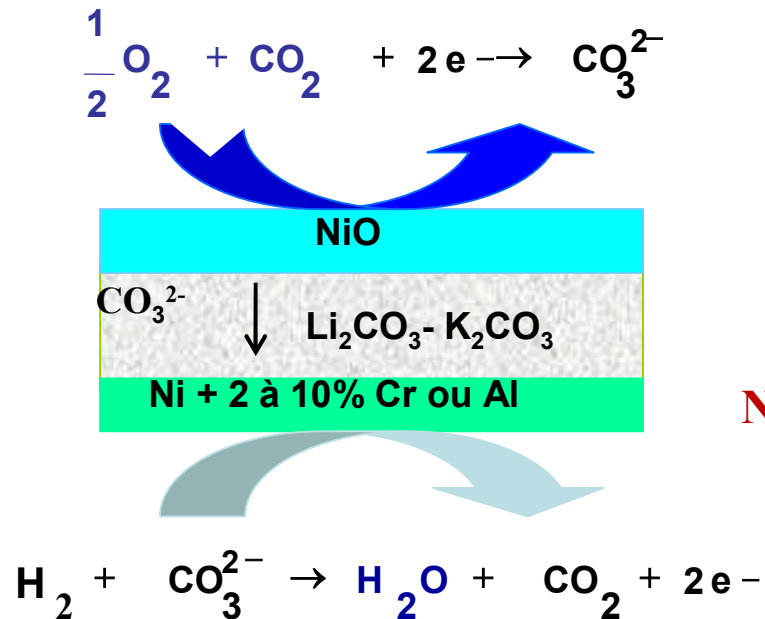
EIS diagnosis tool for high temperature devices from fuel cells to electrolyzers

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France*

High-temperature fuel cells & electrolyzers

MCFC 600-650°C



MCFC/SOFC

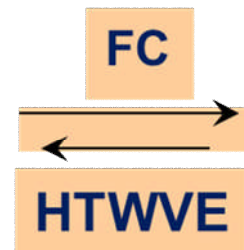
*Composite
carbonate/oxide*

↑ Lifetime &
performance:

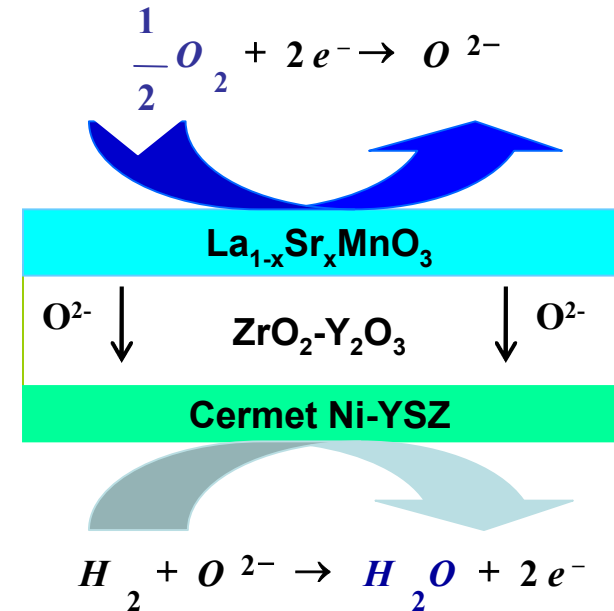
Nanostruct./electrochem.

→ half-cells

→ single cells

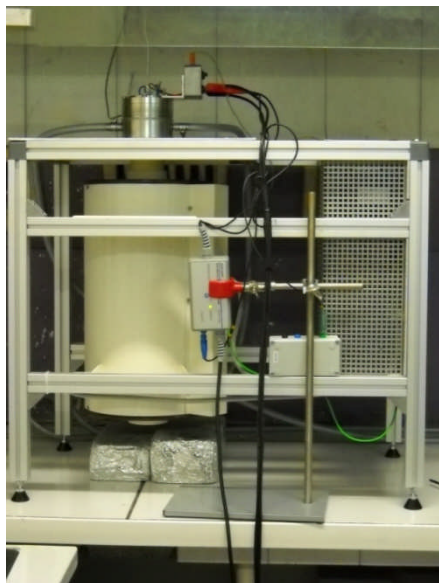


SOFC 600-700°C

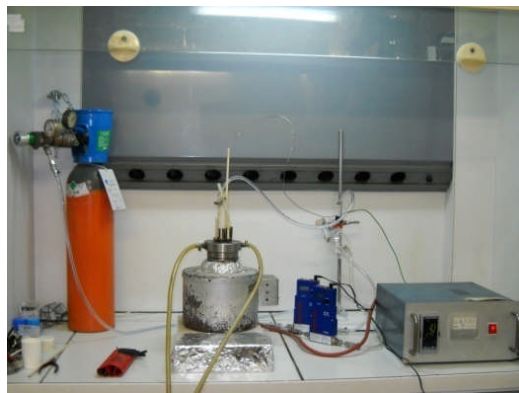


High-temperature electrochemical platform

SOFC, anode under H_2



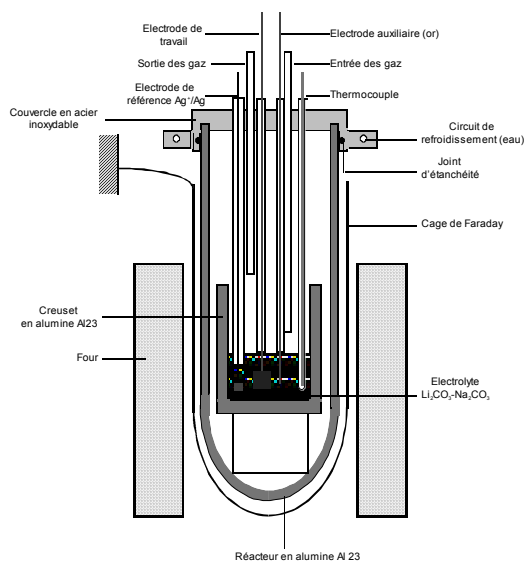
MCFC, cathode, $P(O_2) + P(CO_2)$
or anode H_2



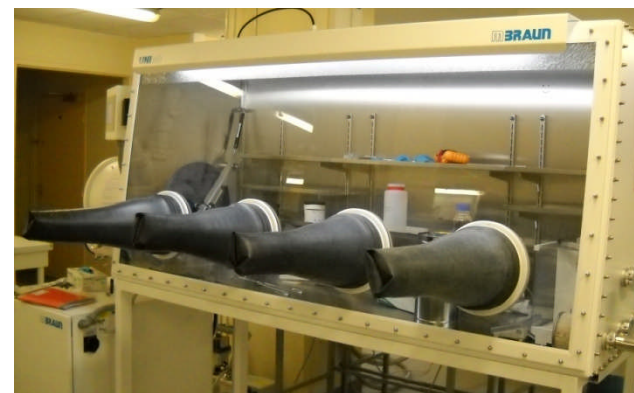
Single cell for HT-electrolysis of water



SOFC, cathode, $P(O_2)$ controlled



Lithium battery



Methods for EIS analysis

1- ELECTRICAL EQUIVALENT CIRCUIT (EEC)

Nyquist & Bode diagrams, fitted by combining ideal (resistor, capacitor, inductor, etc...) and non-ideal (constant phase element or CPE, Warburg, etc...) electrical elements in series and/or in parallel. Deconvolution of the impedance diagram: main contributions governing the system, each associated to a **f range**, a **relaxation f** and the **electrical element value**.

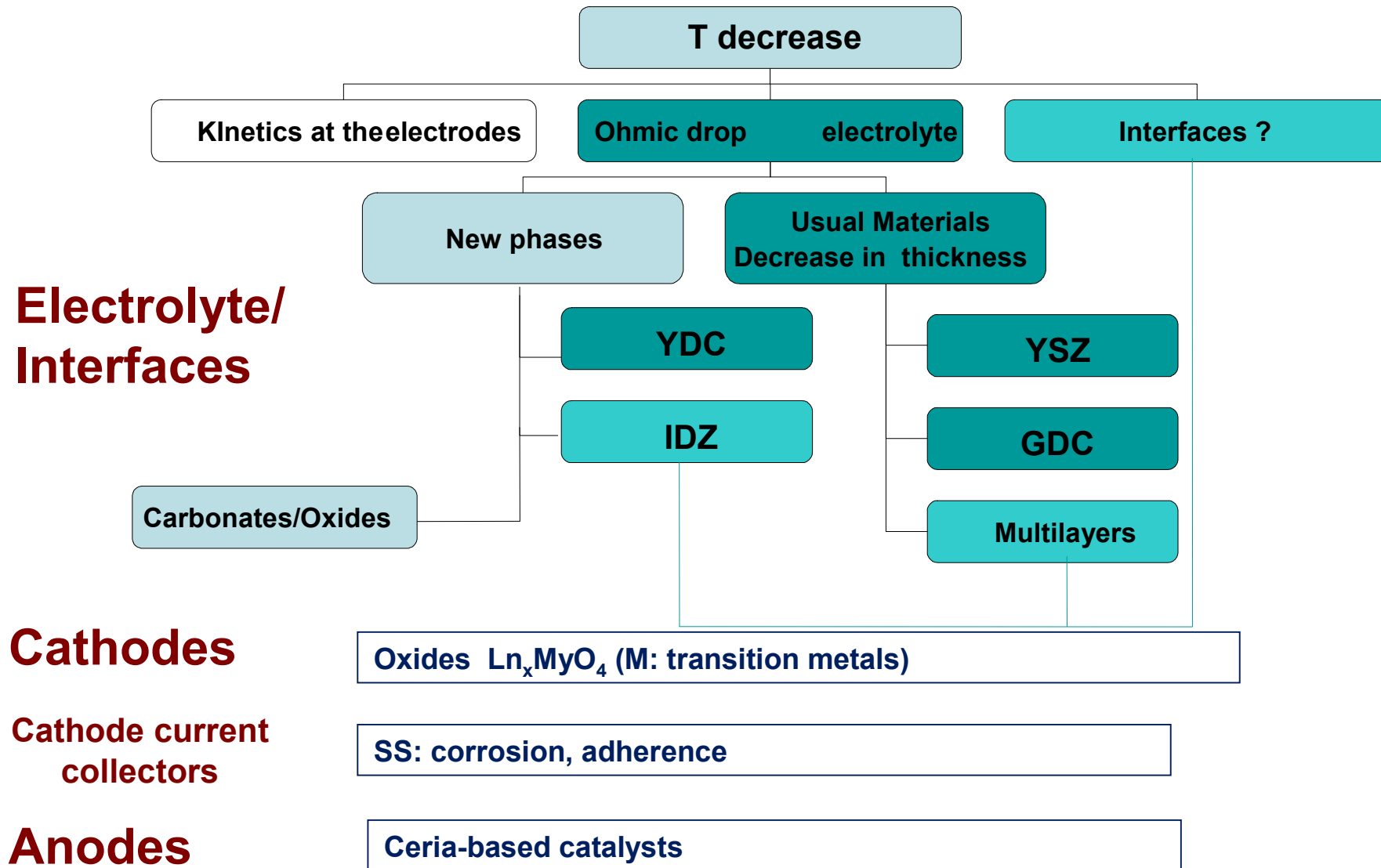
2- ANALYSIS OF THE DIFFERENCE IN IMPEDANCE SPECTTRA (ADIS)

Change in an impedance spectrum when an operation parameter is changed (P, T...), recording it before and after such a change. Real and imaginary parts differentiated with respect to $\ln(f)$: **$\Delta Z' = g(\partial \ln f)$ or $\Delta Z'' = k(\partial \ln f)$** .

3- DISTRIBUTION OF RELAXATION TIME (DRT)

Deconvolution method allowing calculation of a distribution function of relaxation times and amplitudes of impedance-related processes from experimental data. Direct access to kinetic parameters of underlying processes. No *a priori* choice of EEC model.

Research strategy in the field of SOFCs



Nano-scaled layers for SOFC, i.e. CeO_2 or ZrO_2 -based

* As SOFC electrolytes: μ -SOFC

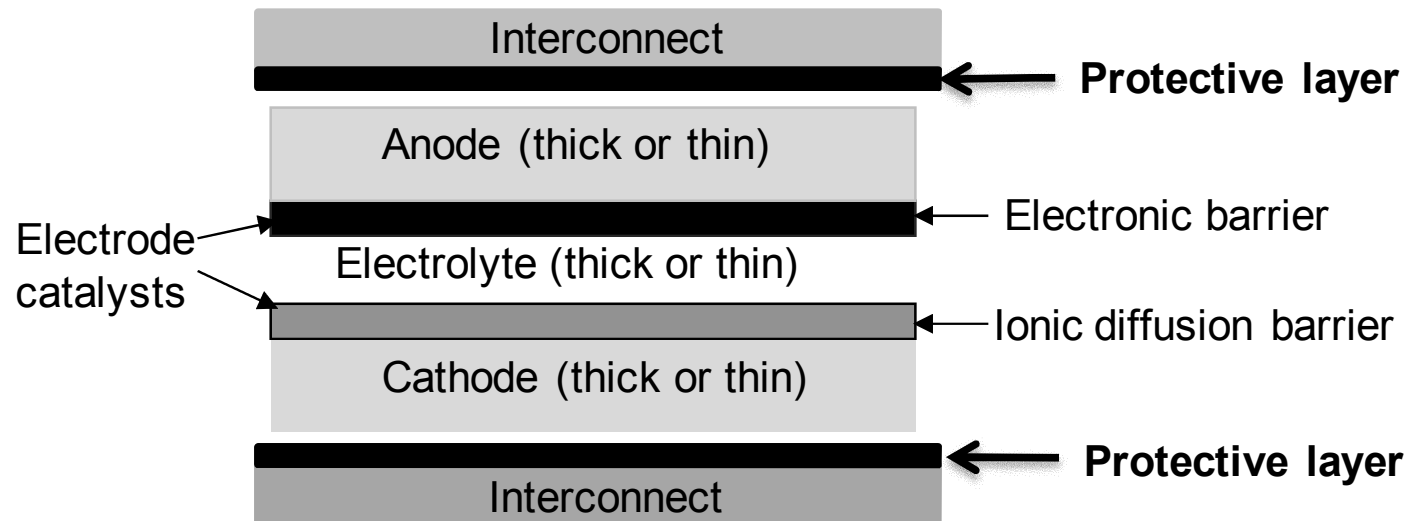
Charge transfer enhancement, resistance $\downarrow$ conductivity $\uparrow$?

* Interfacial layers

- *Chemical diffusion barrier (cathode/electrolyte interface)*
- *Electronic barrier (anode/electrolyte interface)*
- *Catalyst/electrode (at both interfaces)*
- *Bond layer*

* As corrosion protective layers for interconnects

* As active layer at the cathode interface



Thin layers platform

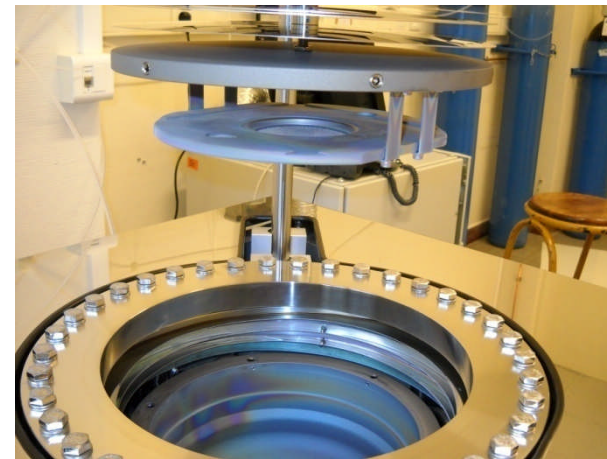
ALD (*Atomic layer deposition*)
SOFC, batteries, photovoltaic,
corrosion protection

Electrodeposition
SOFC, MCFC, batteries

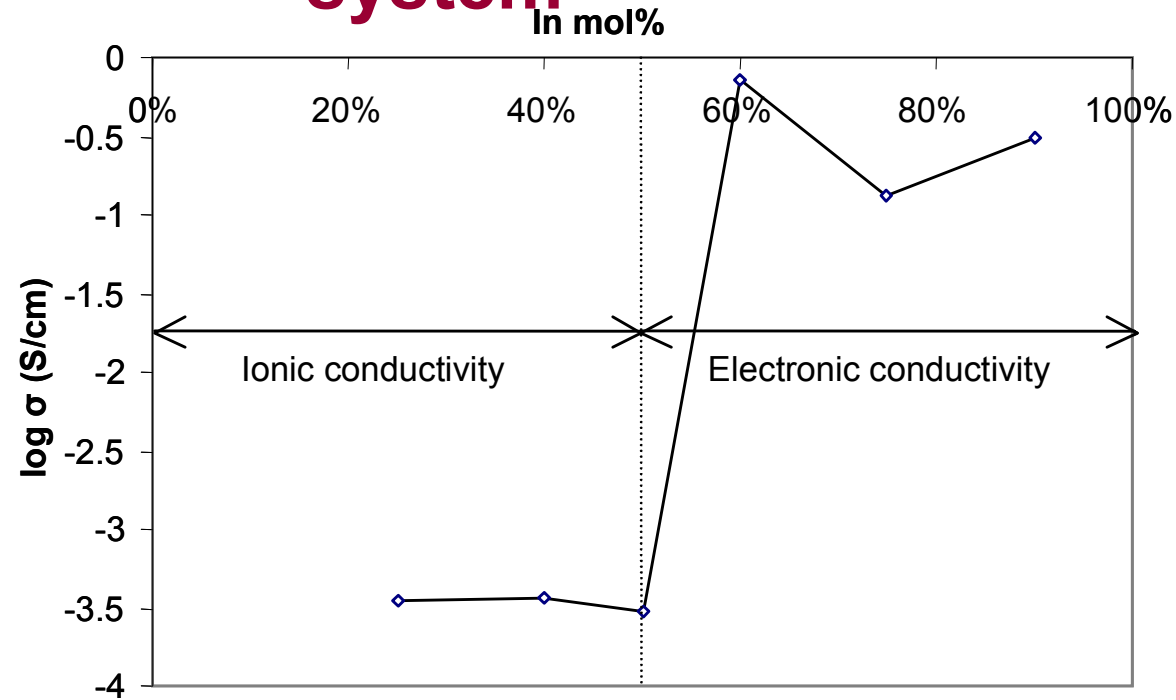
CBD (*Chemical bath deposition*)
SOFC, MCFC

Sol gel
Cathodes SOFC

Hydrothermal deposits
Catalysts



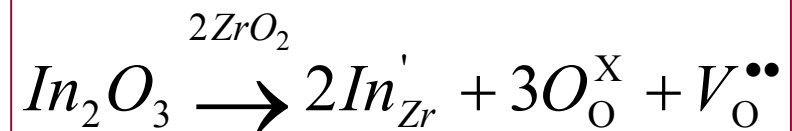
ZrO₂-In₂O₃ system



A. Ringuedé, P. Mouro, C. Alvarez Lugano, J-C. Badot and M. Cassir,
J. New Mat. for Electrochem. Syst. 9 (2006) 201-208

➤ Ionic & electronic conductivity = f(In³⁺ ratio)

- In³⁺ size close to Zr⁴⁺
 - $r(\text{In}^{3+}) = 0.80 \text{ \AA}$
 - $r(\text{Zr}^{4+}) = 0.84 \text{ \AA}$

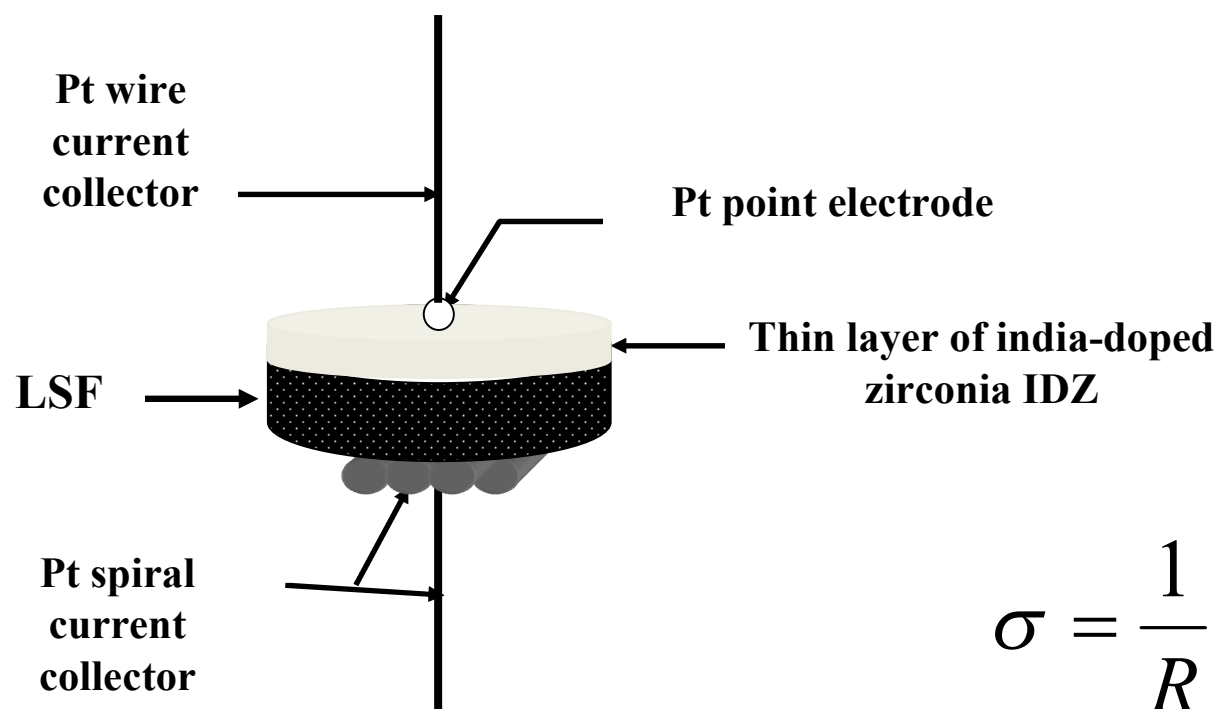


Measurement device for EIS

Transverse configuration

Electrodes of different surface and nature $\Rightarrow$

Asymmetric configurations: $R \rightarrow \sigma$



1 MHz à 10⁻² Hz

11 points per frequency decade

DV = 50 mV

Atmospheric pressure: $T \leq 700^\circ\text{C}$

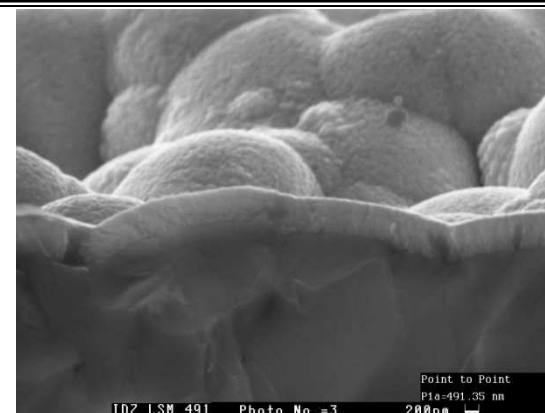
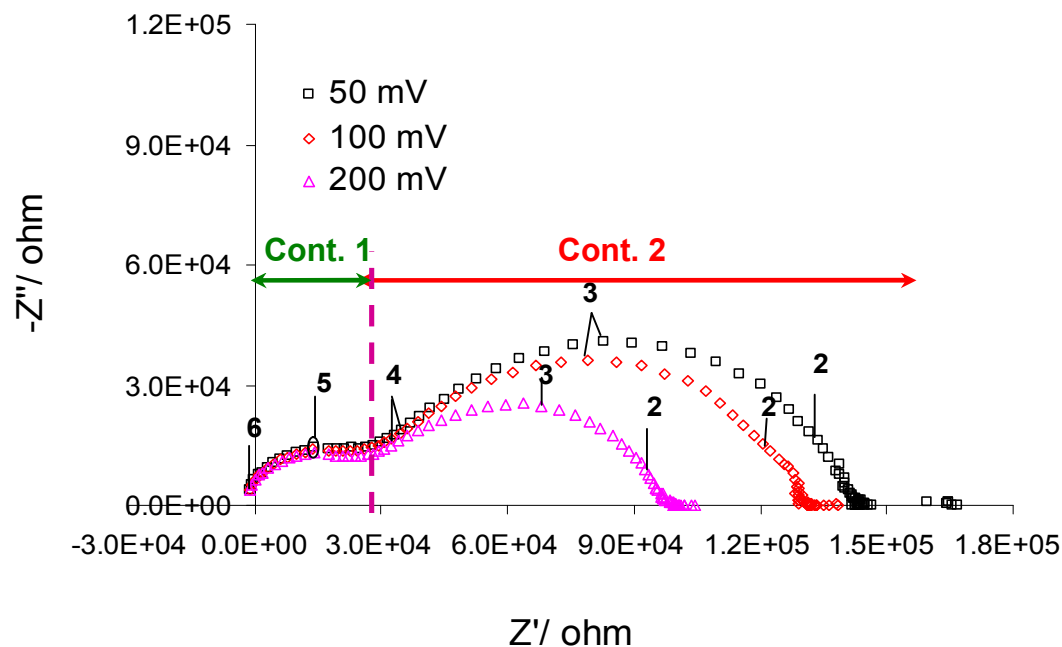
Autolab PGSTAT20

$$\sigma = \frac{1}{R} \frac{\ell}{S}$$

*Messaoud Benamira, Ph.D. thesis,
ENSCP, Paris VI, (2009)*

IDZ ionic conductor thin layer (31,4 mol%)

T = 480°C, under air



480 nm of IDZ (26 mol%) / LSM
Deposition at 300 °C

⇒ no annealing treatment

Well-covering, dense and uniform
cubic-structured deposits

Contribution 1 ≥ 50 kHz

Contribution 2

R = cte when ΔV varies

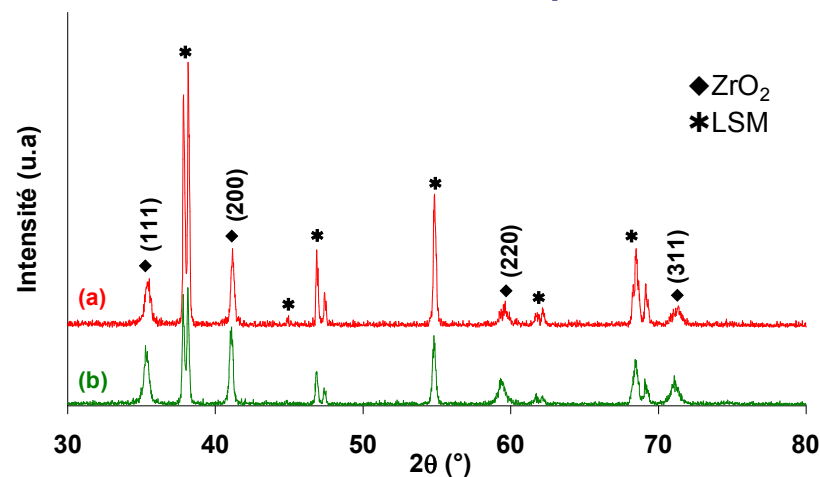
R varies with ΔV



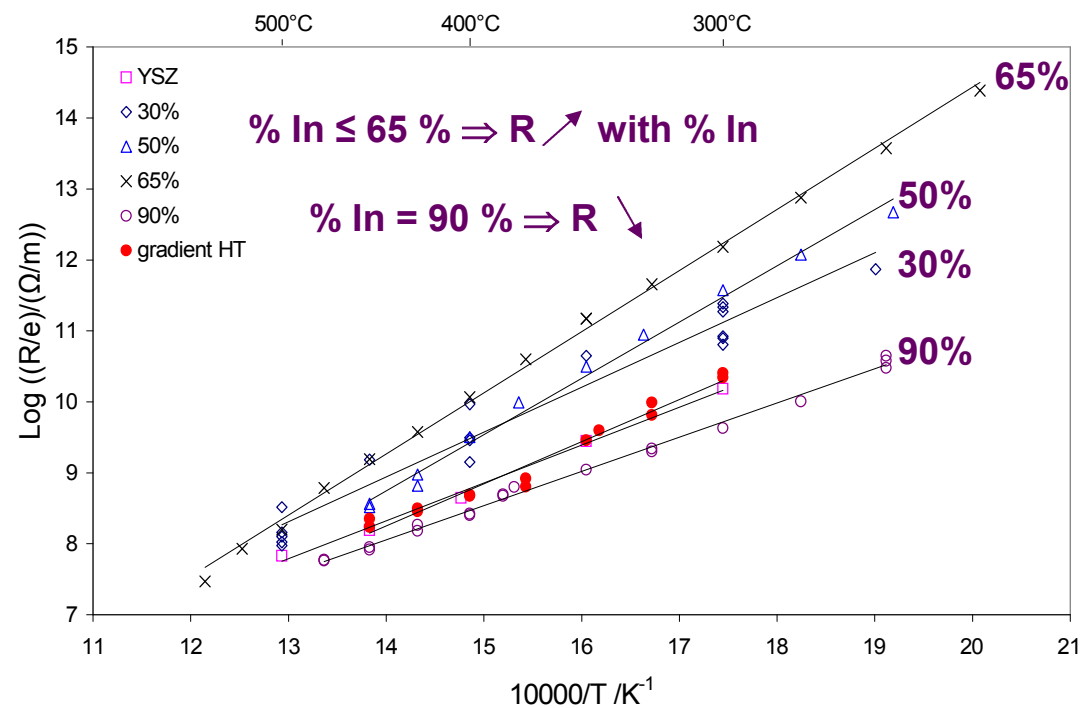
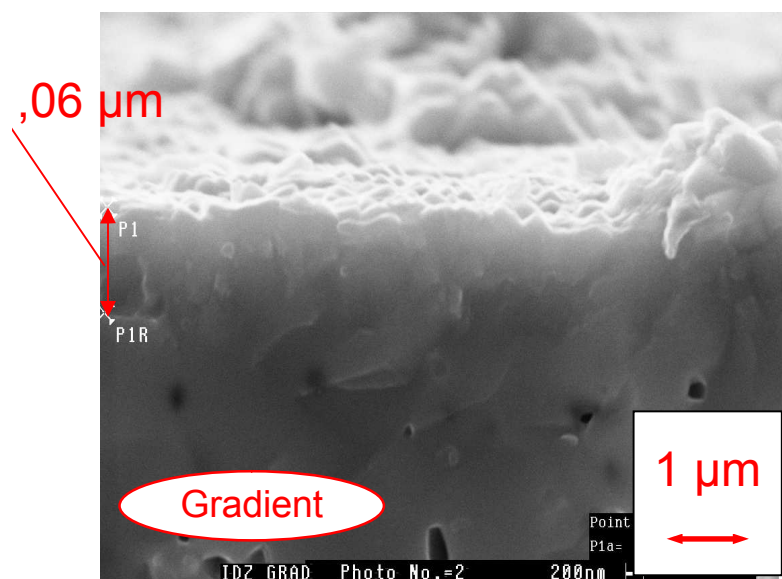
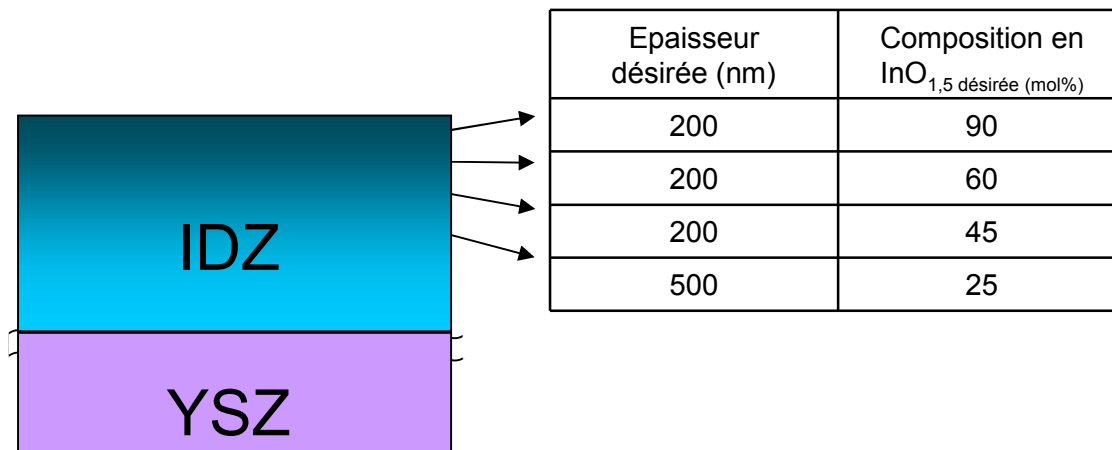
IDZ electrolyte



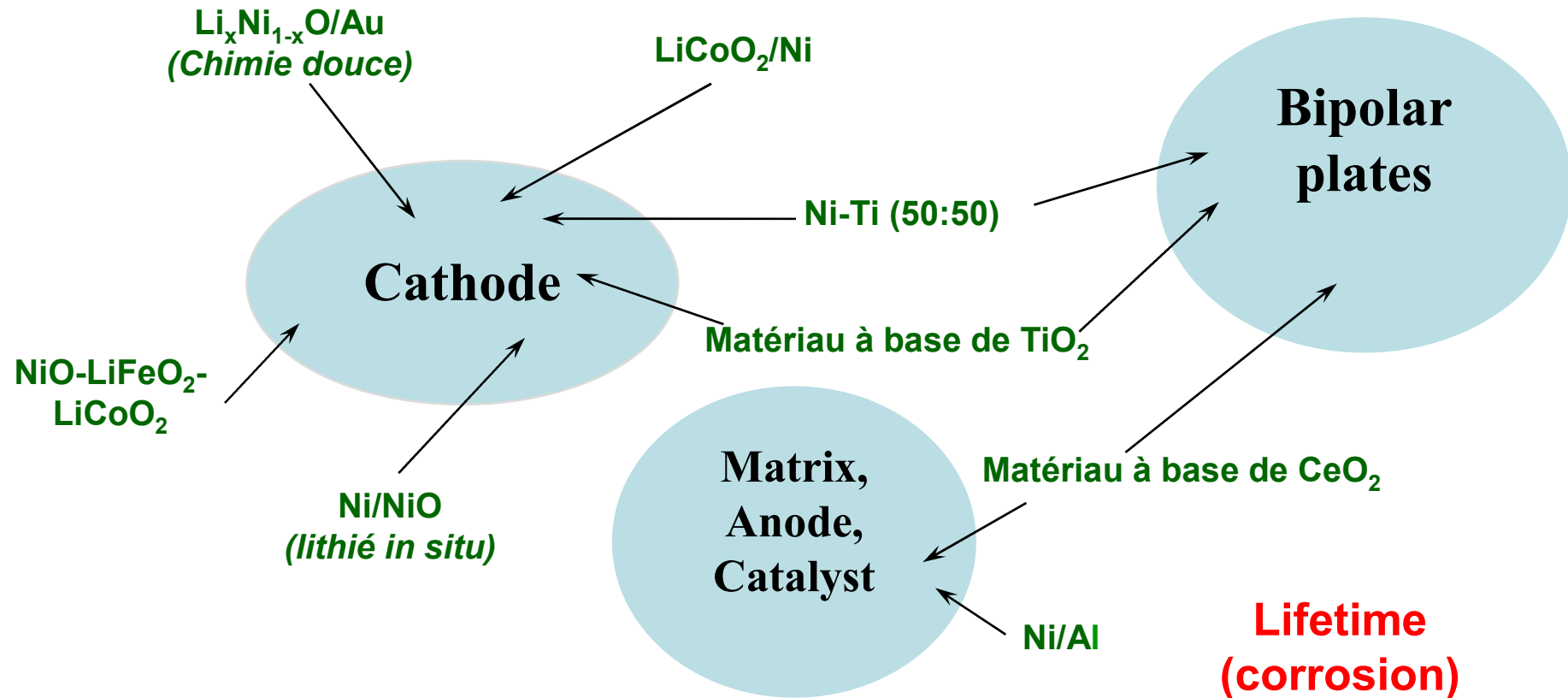
Electrode phenomena



ZrO₂-In₂O₃ (gradient) / YSZ

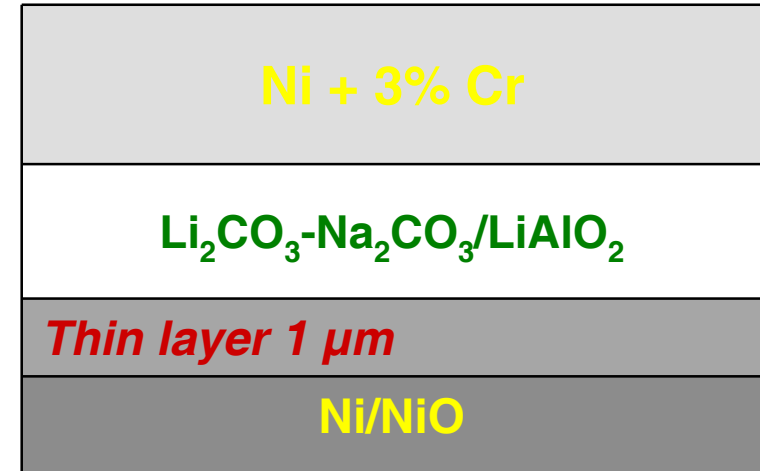
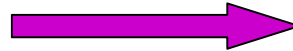
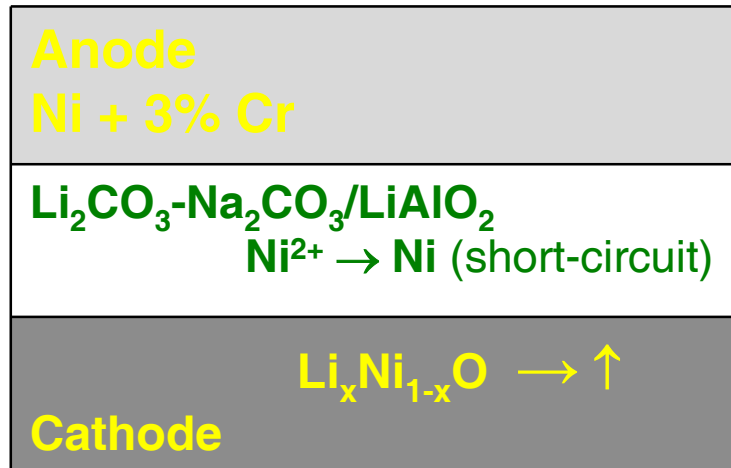


Molten carbonates (MCFC 650°C): scientific & technological challenges

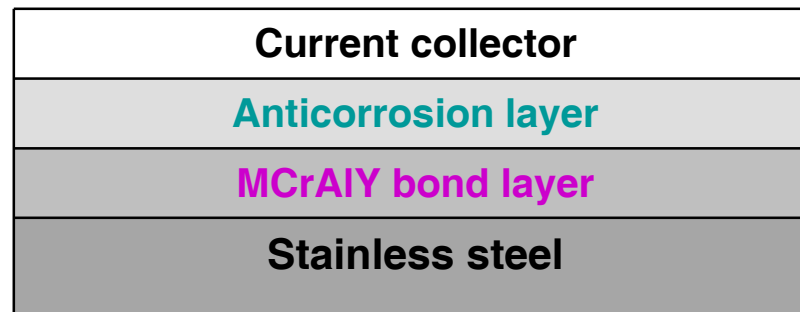


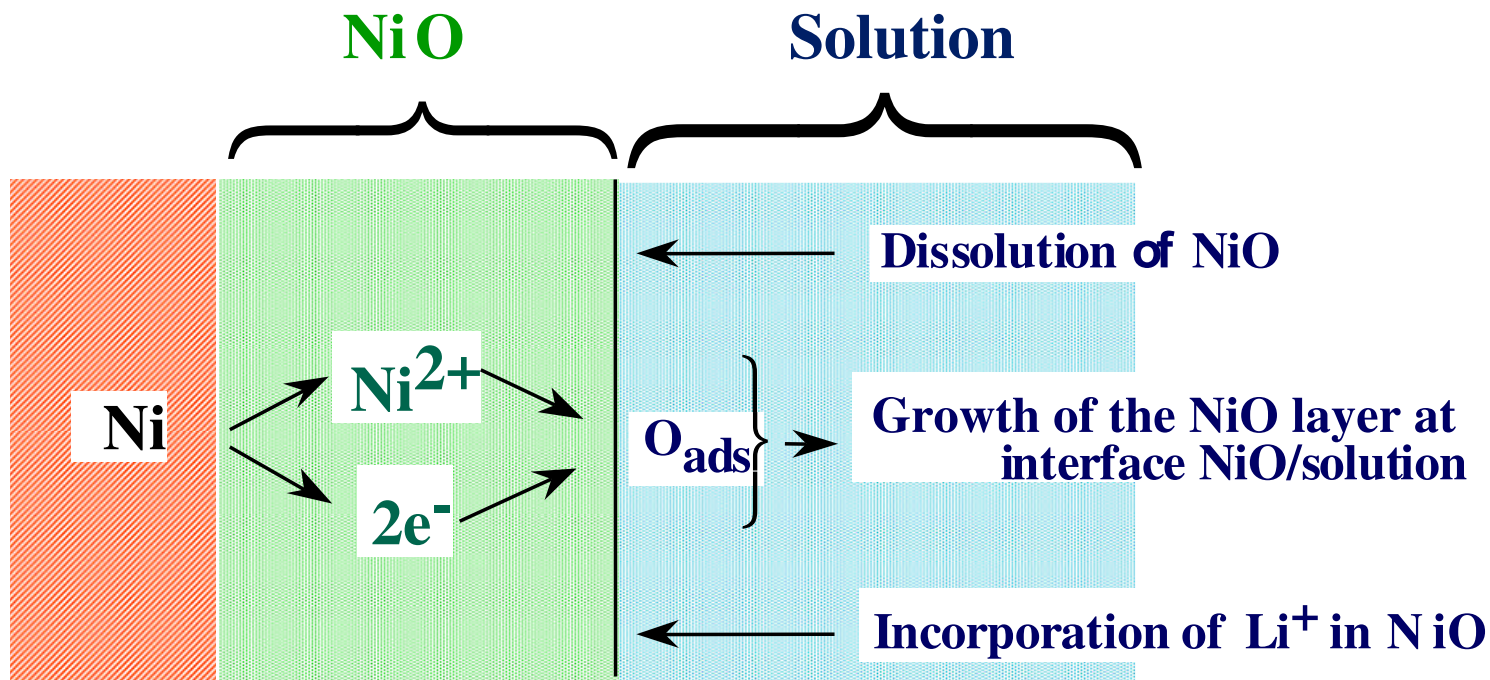
Thin layers for MCFC

Protection of the cathode cathode



Protection of MCFC separator plates





MCFC cathode

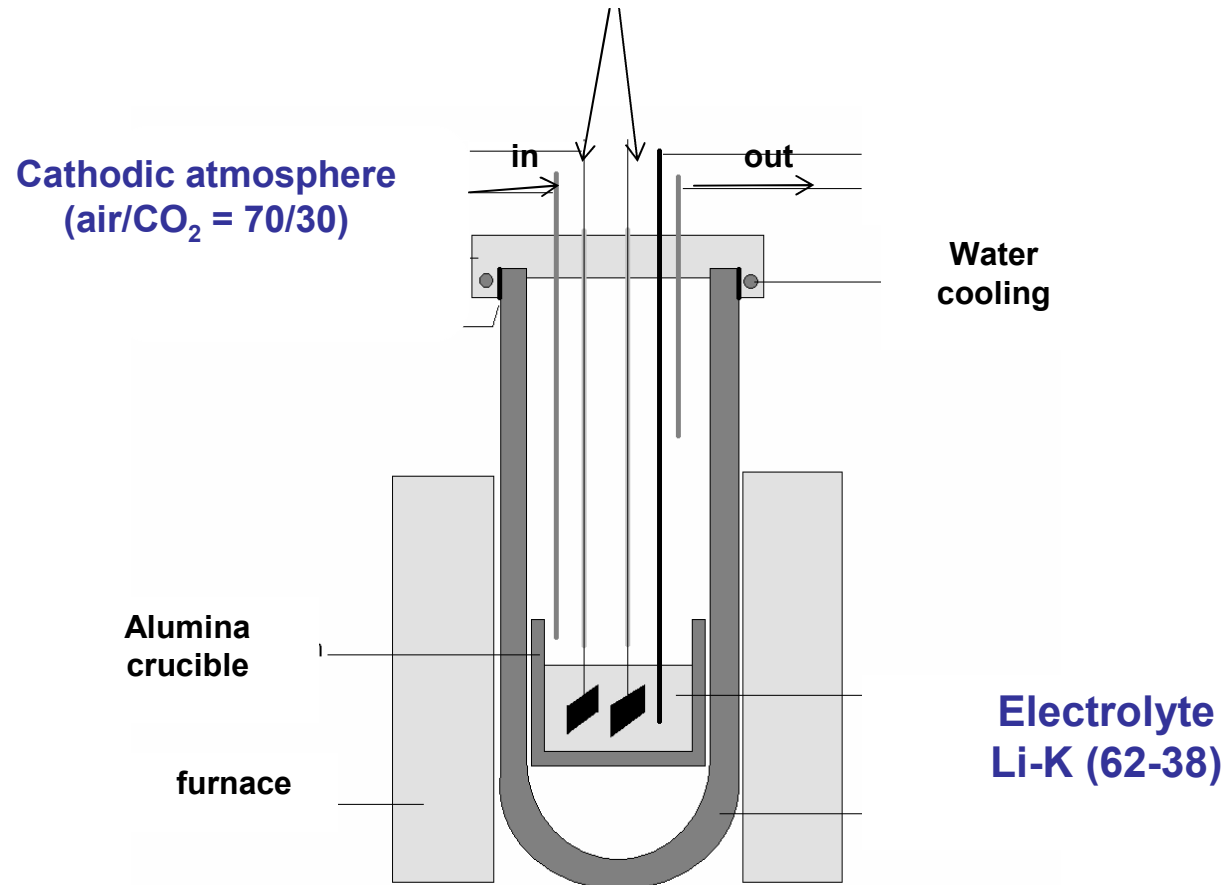
1. $\text{Ni} + \text{CO}_3^{2-} \rightarrow \text{NiO} + \text{CO}_2 + 2e^{-}$
2. $\text{NiO} + \text{CO}_2 \rightarrow \text{Ni}^{2+} + \text{CO}_3^{2-}$
3. $\text{Ni}^{2+} + \text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{Ni} + \text{CO}_2 + \text{H}_2\text{O} \Rightarrow \text{Short-circuit}$



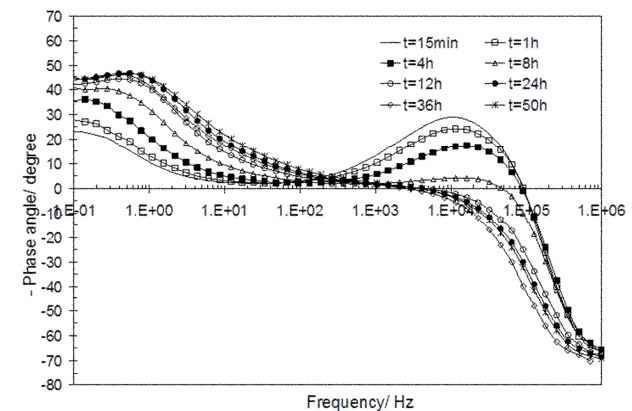
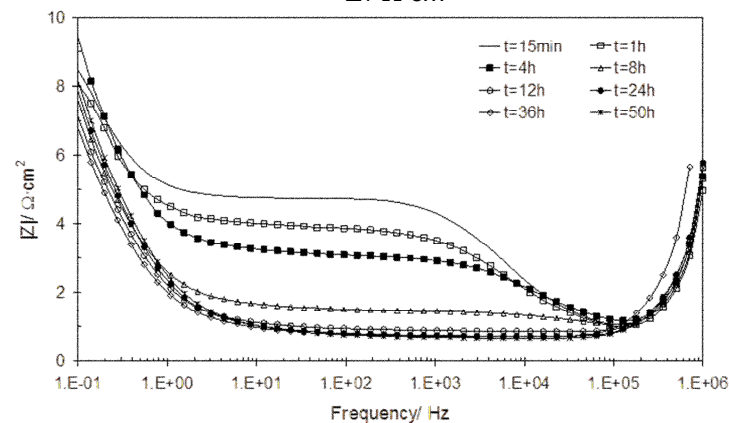
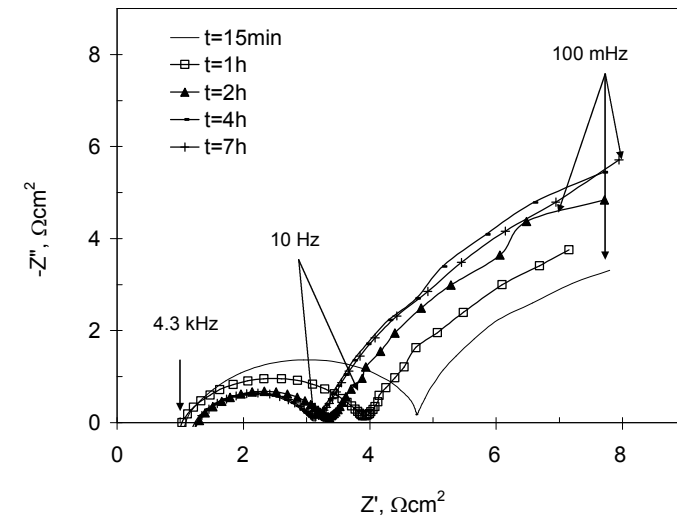
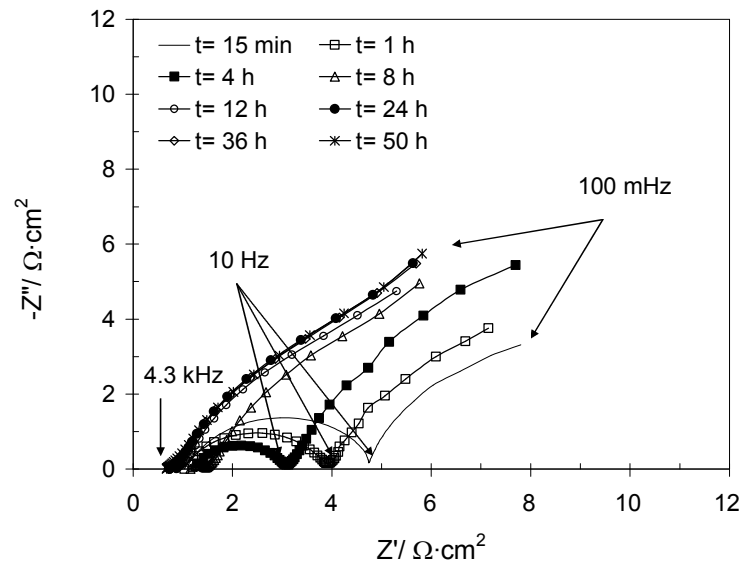
➤ *Lifetime decrease*

Bare $\text{Li}_x\text{Ni}_{1-x}\text{O}$ cathode or coated with LiCoO_2 EIS measurements in molten carbonates

2 Ni or Co-coated electrodes



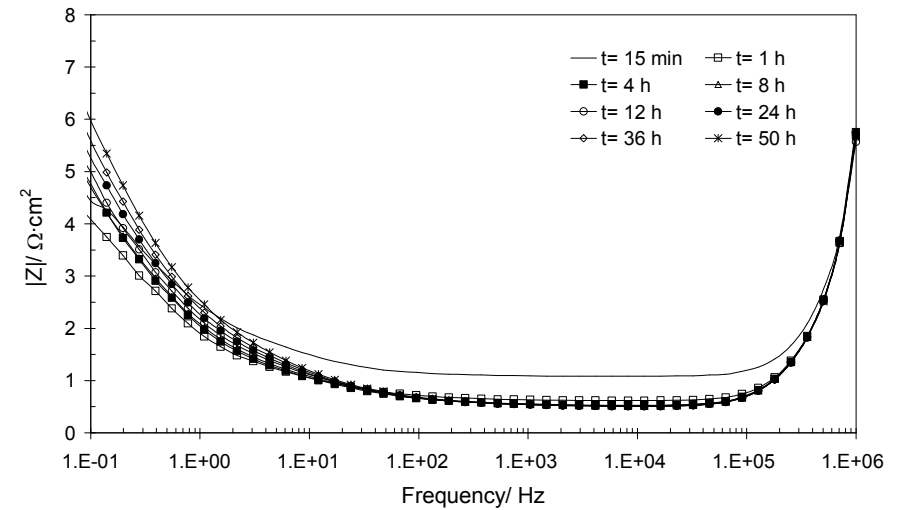
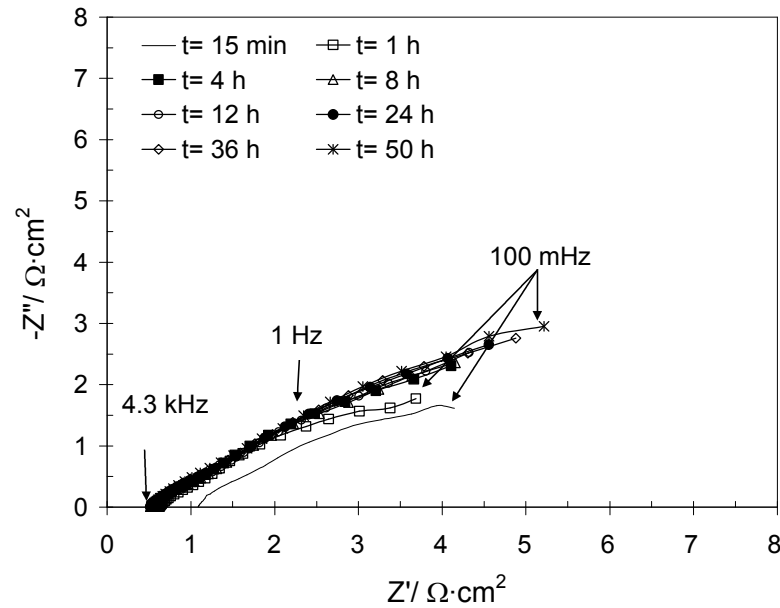
Nyquist and Bode diagrams of NiO cathode in Li-Na carbonate eutectic at 650° C



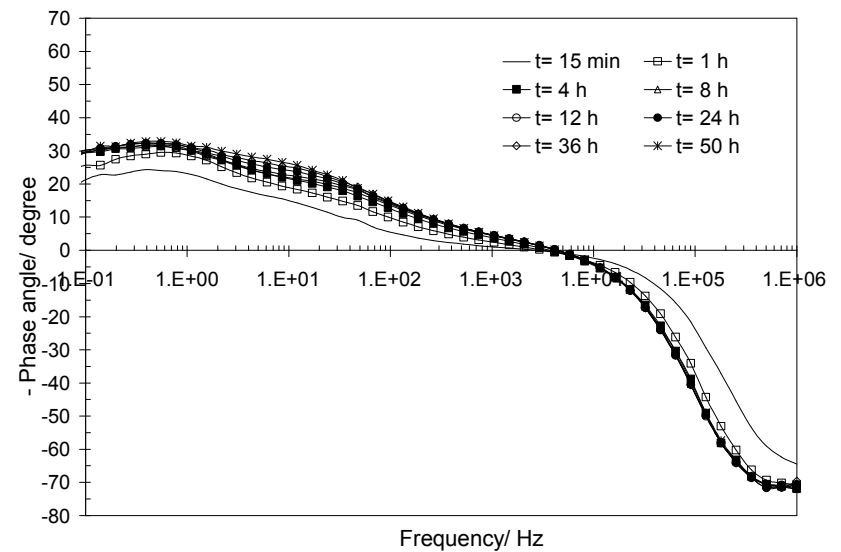
- 2 arcs until 8 h, the first decreasing with t , then only 1 with increasing amplitude
- Bode confirms that after 12 h both module & phase angle stable

HF arc due to charge transfer and during the first eight hours to the formation of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ (oxidation and lithiation)

Nyquist and Bode diagrams of Co_3O_4 -coated NiO cathode in Li-Na carbonate at 650°C

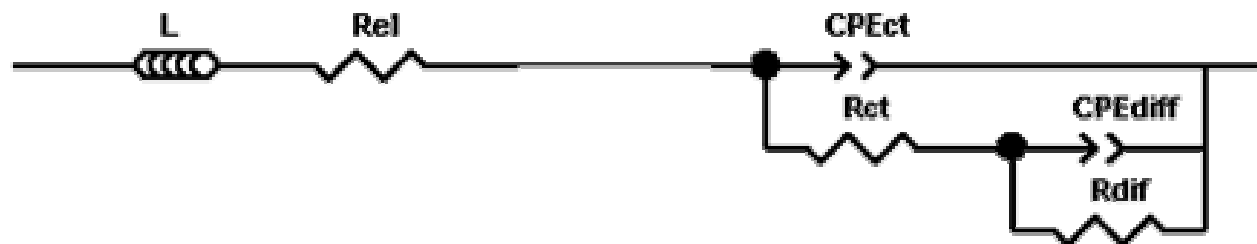


- 1 dominant semi-circle & the other less visible increases up to 4h
- Bode diagram shows a 3rd phenomenon in MF

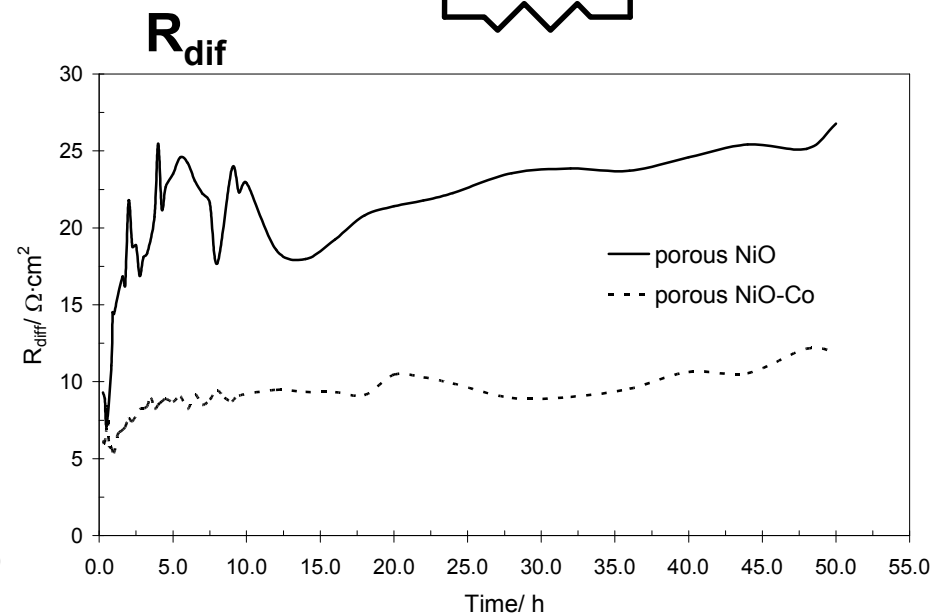
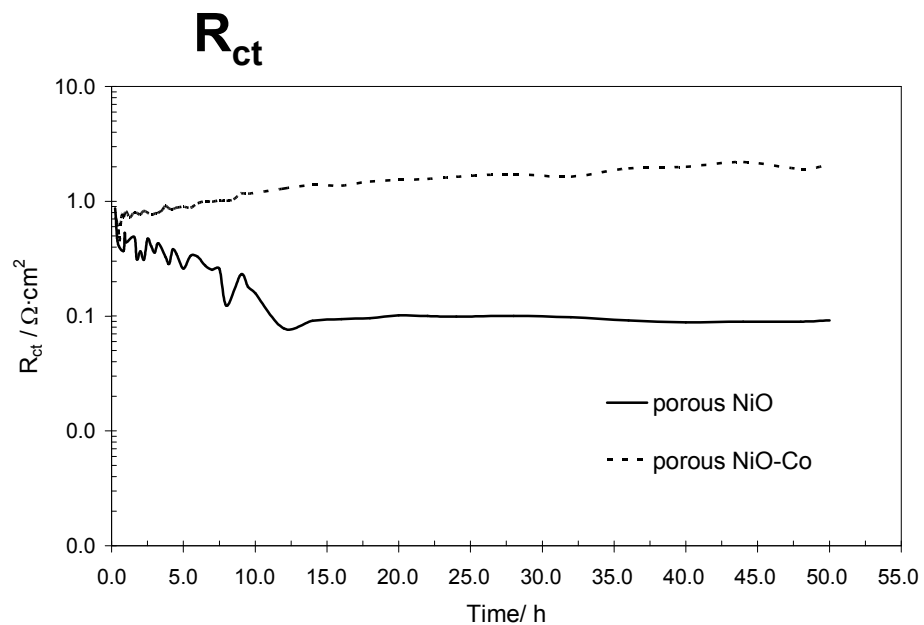
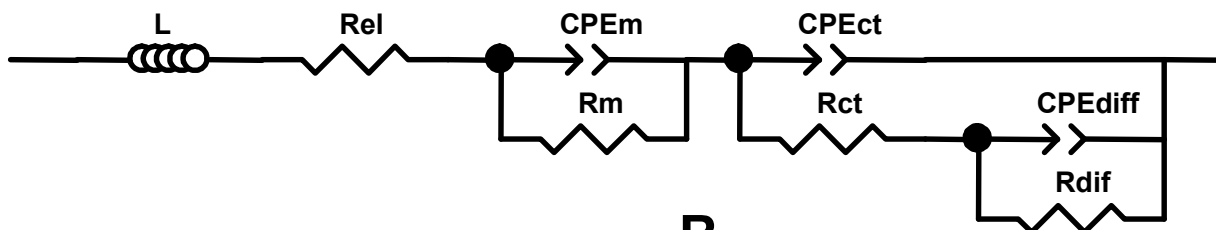


Equivalent circuits

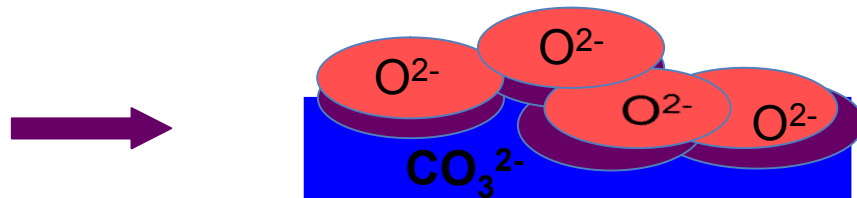
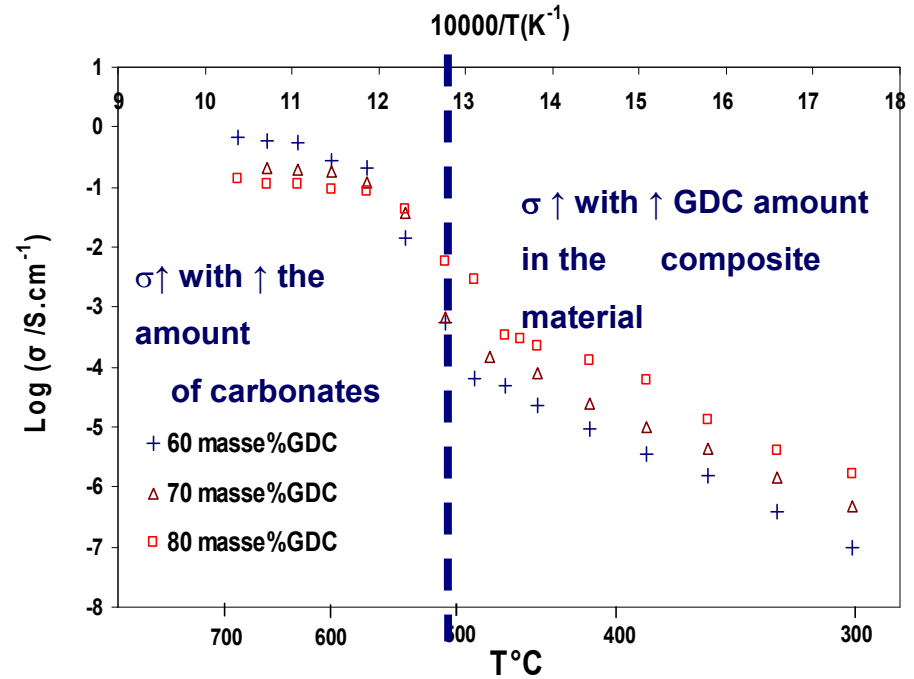
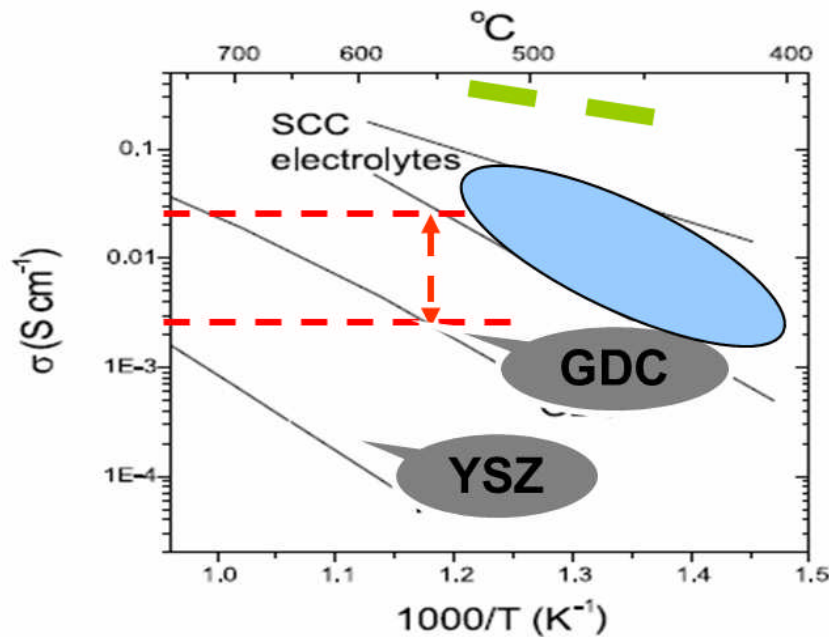
General



Ni short t



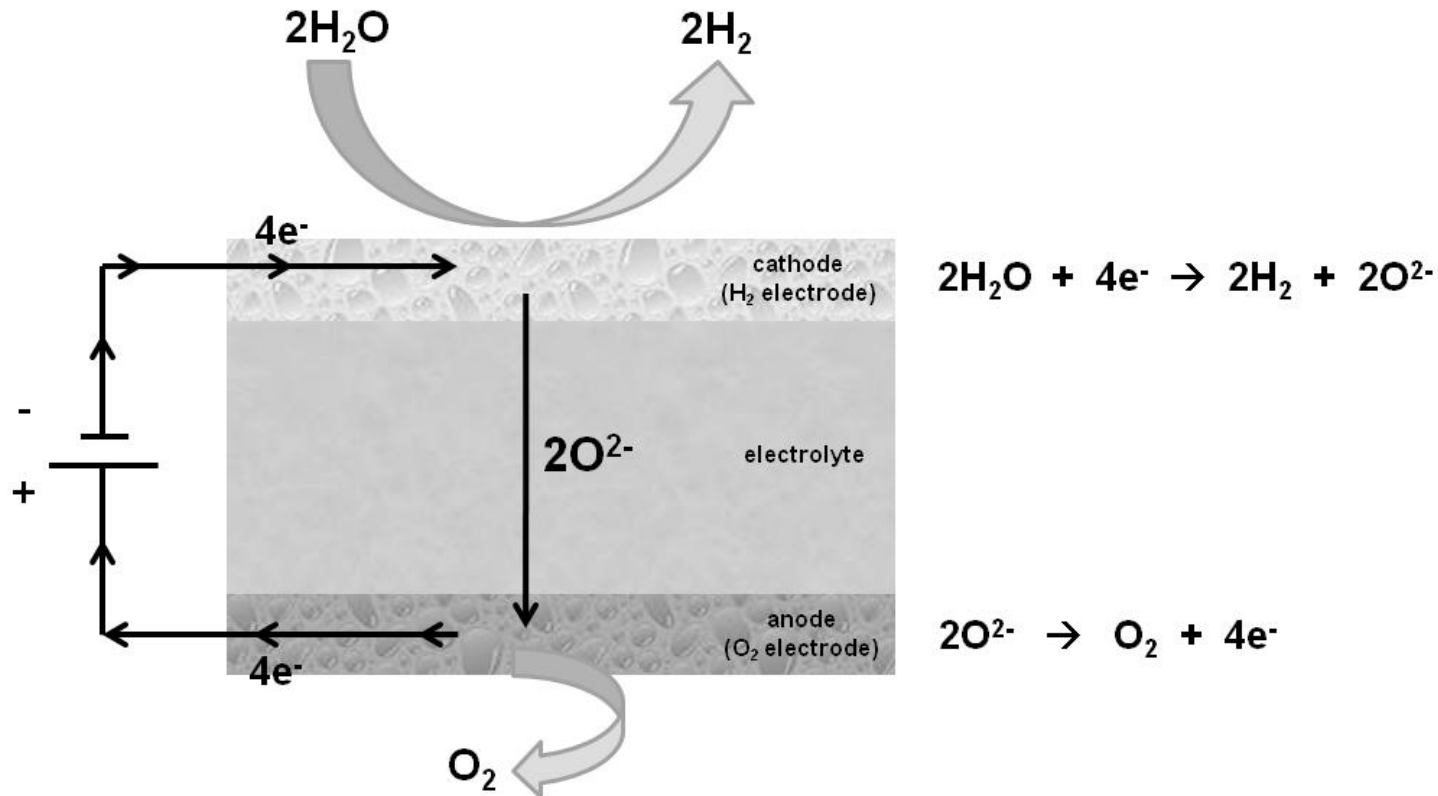
SOFC/MCFC electrolytes: composites YSZ or GDC/CO₃²⁻



- at lower T: σ controlled by O²⁻
- at higher T: control by CO₃²⁻
- at intermediate T: mixed control
- Interfacial enhanced σ : complex phenomenon

“Superionic conduction highway” “Space-charge region”

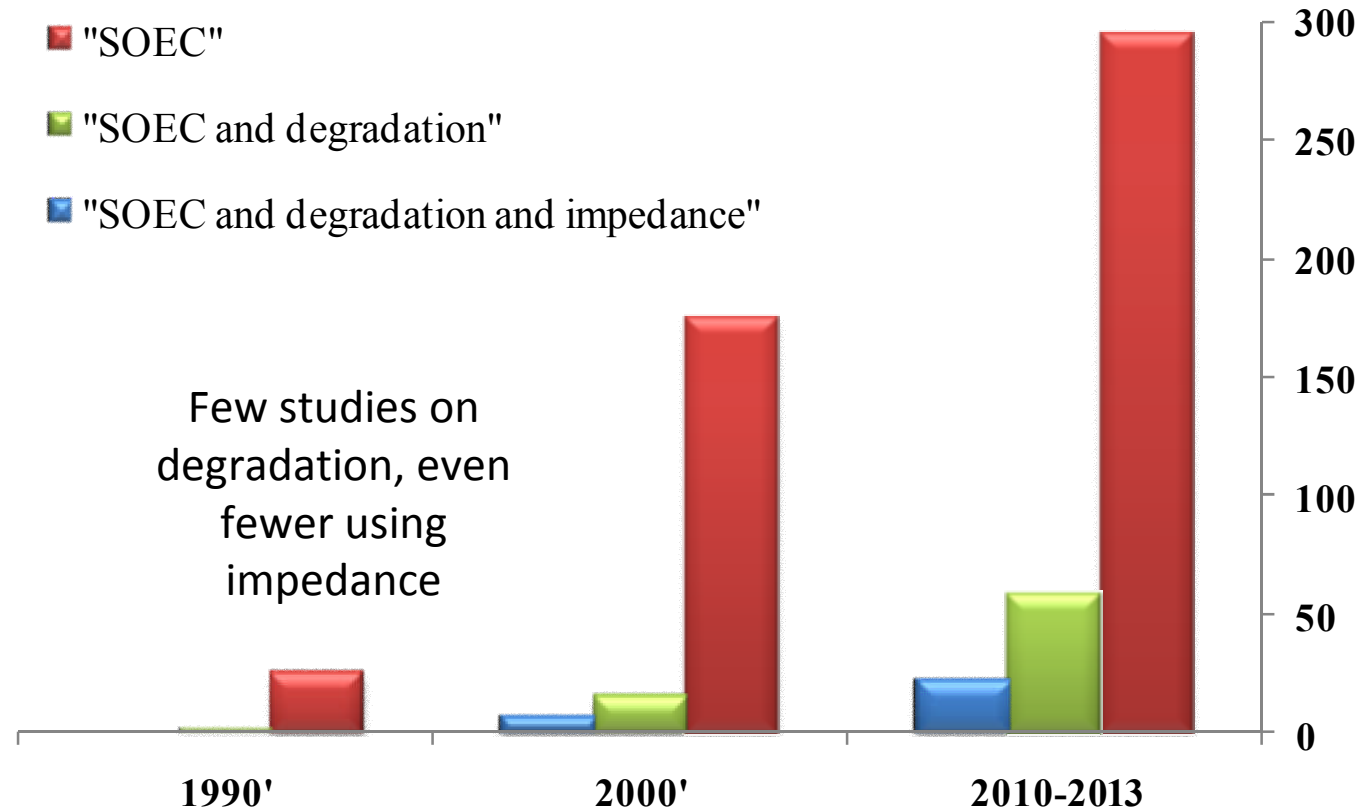
Solid oxide electrolysis cell, SOEC



➤ Why high T?

- ✚ Avoiding expensive catalyst (Pt,...)
- ✚ Using less electrical energy balanced by more thermal energy (partly wasted otherwise) ➔ less expensive
- ✚ Generating important quantities of directly pure H₂
- ✖ Degradation facilitated (interfacial delamination, interconnectors corrosion,...)

➤ Web of Science literature search (sept. 2013)



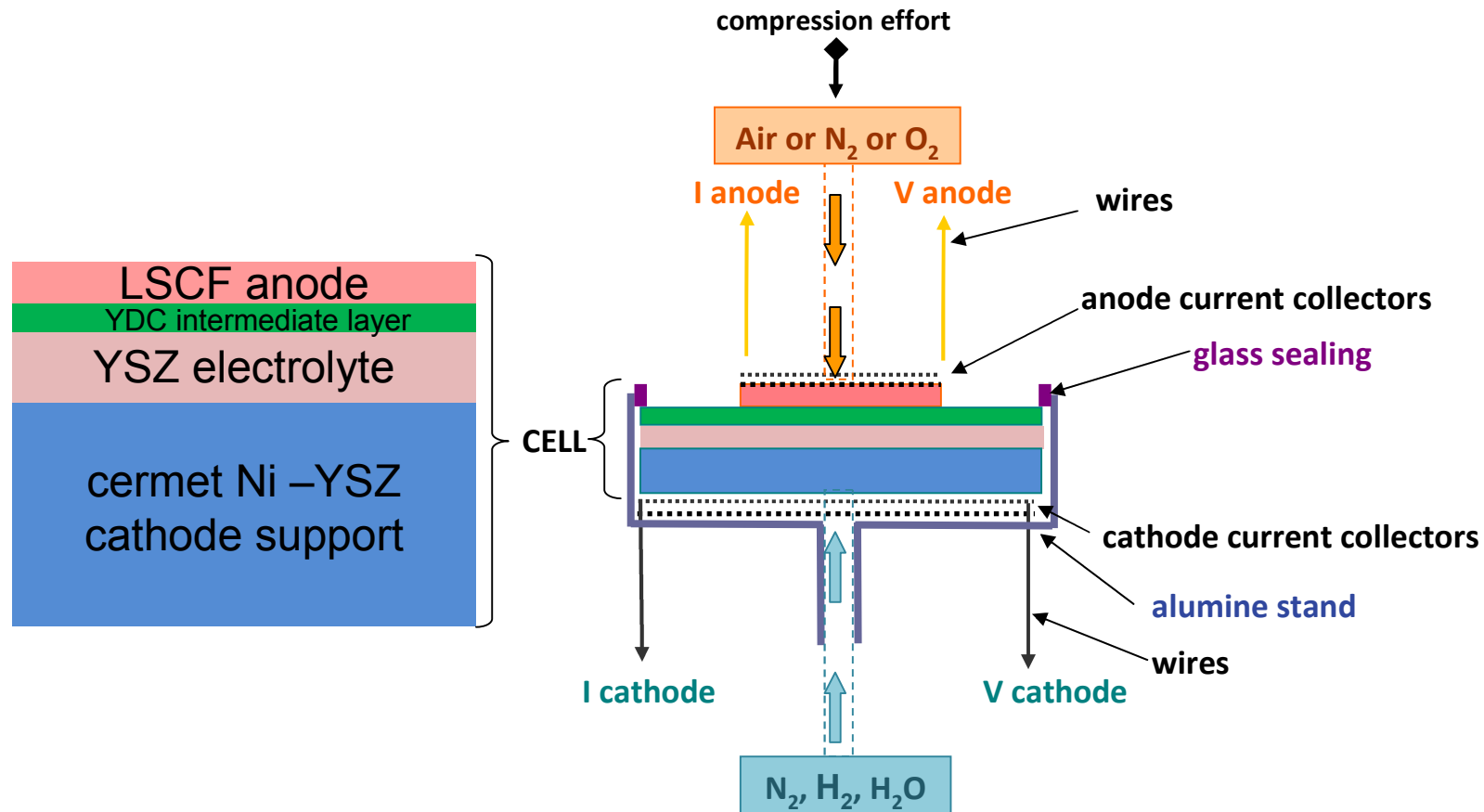
➡ Growing research interest for SOEC

➡ Few studies on degradation, even fewer using impedance

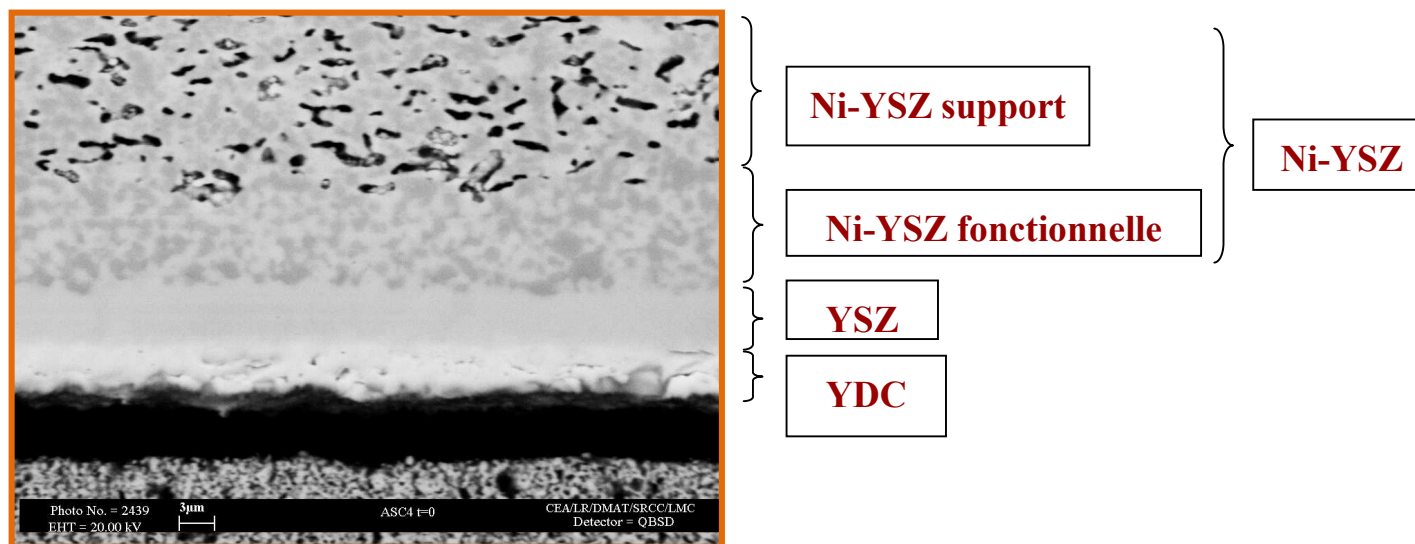
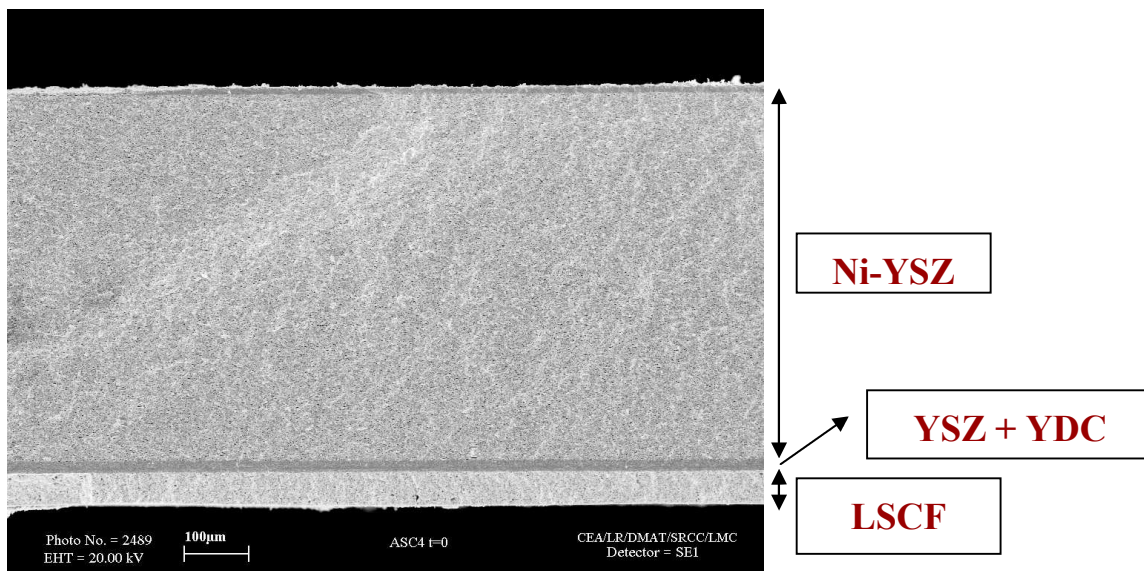
Experimental set-up (single cell, towards *SRU, stack*)

Cathode-supported SOEC

unsealed anode compartment



sealed cathode compartment



Experimental set-up

- EIS measurement conditions  dc current with a 30 mA amplitude perturbation, from 10 kHz to 0.01 Hz (10 points per decade)

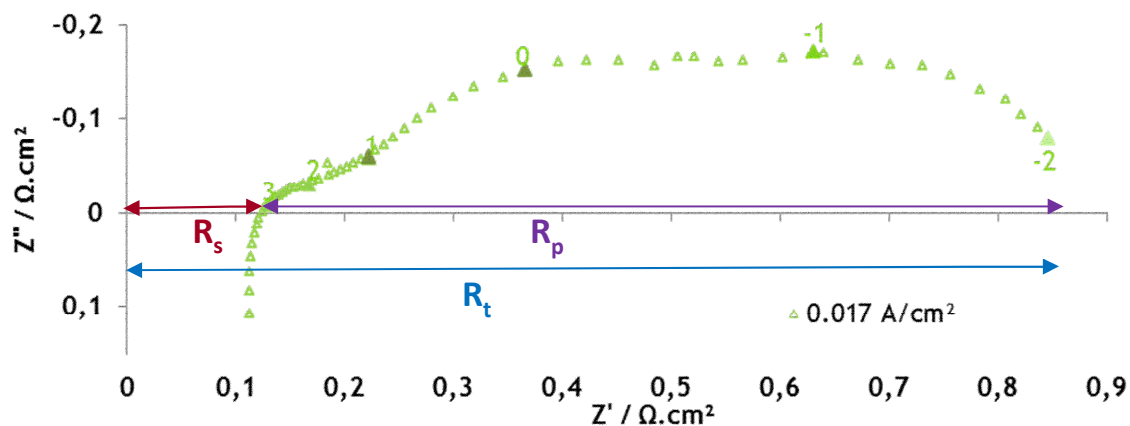
- Studied parameters:

- Temperature  650°C, 700°C, 750°C, 800°C
- $\text{PH}_2\text{O}/\text{PH}_2$ ratio, cathode side (air) > 1
> 5
> 9
- PO_2 , anode side ($\text{PH}_2\text{O}/\text{PH}_2 = 9$) > N_2 (10^{-5})
> air (0.2)
> O_2 (0.8)
- Cathode gas flow rate ($\text{PH}_2\text{O}/\text{PH}_2 = 9$, air) > standard flow* x1
> standard flow* x1,5
> standard flow* x2

* 1.88 NL.h⁻¹ H₂O

Experimental data analysis

Basic decomposition of an impedance diagram



polarisation
(electrode mechanisms)

$$R_t = R_s + R_p$$

ohmic
(electrolyte + current collectors)

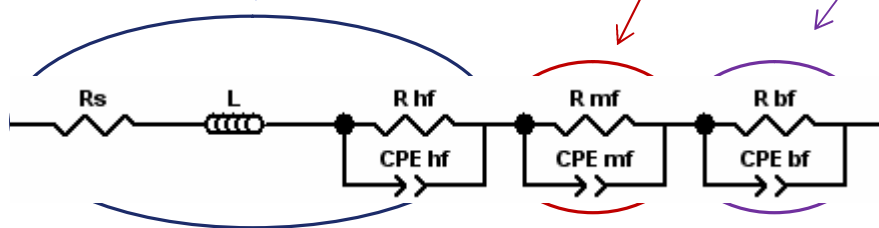
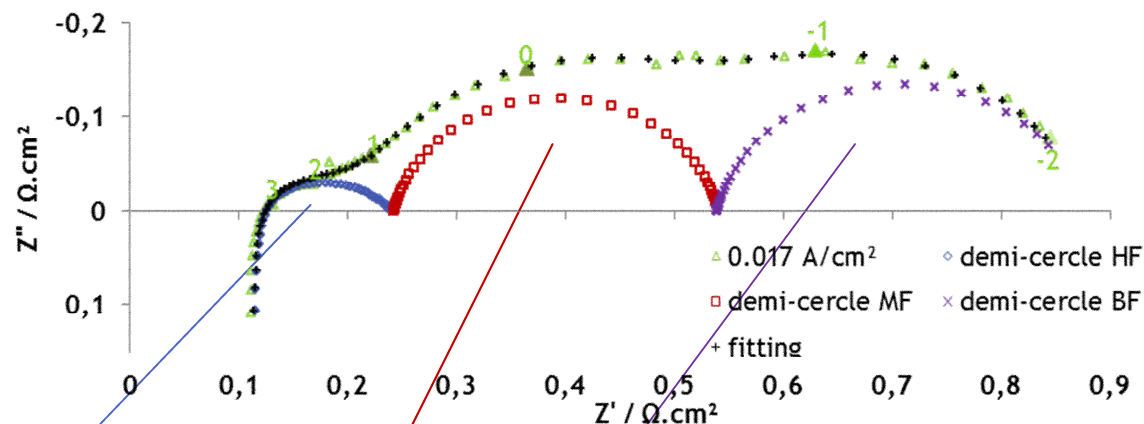
$T = 800^\circ\text{C}$, 90% H_2O (cathode), Air (anode), cathode gas flow rate x1,

$i = 0.017 \text{ A/cm}^2$

Decomposition with electrical equivalent circuit (EEC)

$T = 800^{\circ}\text{C}$, 90% H_2O (cathode), Air (anode), cathode gas flow rate x1,

$$i = 0.017 \text{ A/cm}^2$$



➤ possible EEC for fitting

Calculation of characteristic parameters C and f_0

$$Z_{\text{CPE}} = R / (1 + RY_0(j\omega)^n)$$

Mean capacitance

$$C = R^{((1-n)/n)} Y_0^{(1/n)}$$

Relaxation frequency

$$f_0 = 1 / (2\pi (RY_0)^{(1/n)})$$

Calculation of characteristic parameters C and f_0

I (A/cm ²)	C_{HF} (F/cm ²)	C_{MF} (F/cm ²)	C_{BF} (F/cm ²)	f_{HF} (Hz)	f_{MF} (Hz)	f_{BF} (Hz)
0,015	0,0195	0,64	9,0	62	0,81	0,052
0,127	0,0185	0,78	9,3	93	1,63	0,099
0,318	0,0137	0,71	13,7	135	2,10	0,129
0,500	0,0086	0,52	11,3	201	2,69	0,152
0,732	0,0061	0,26	8,8	176	2,16	0,132
	0.013	0.59	10.5	134	1.88	0.113

we can clearly distinguish the frequency ranges of the impedance diagram



Attribution of each frequency range to one/several phenomena

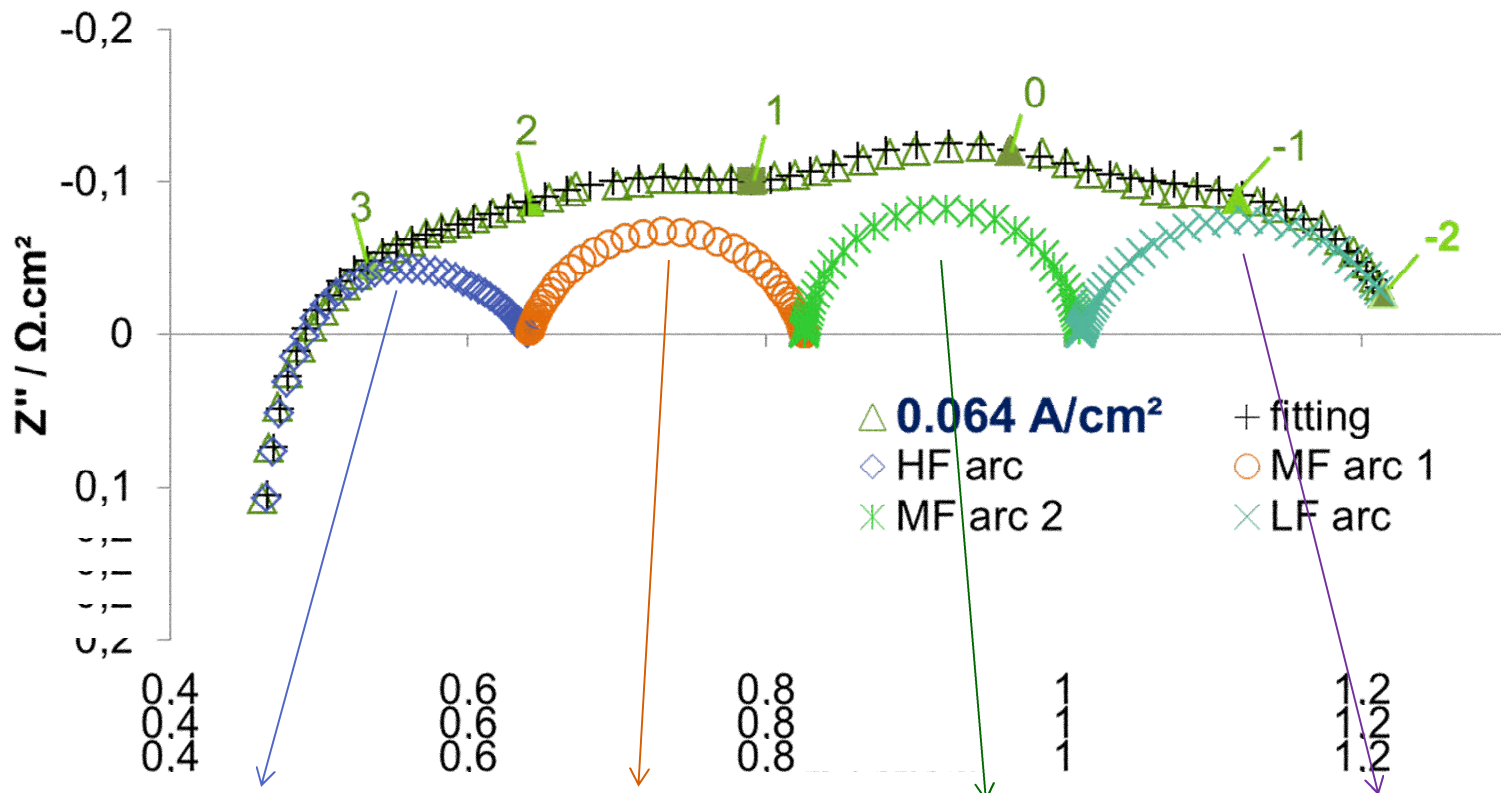
Extension to all parameters: i , T , $\text{PH}_2\text{O}/\text{PH}_2$, PO_2 , cathode gas flow rate

Experimental conditions		C_{HF} (F/cm ²)	C_{MF} (F/cm ²)		C_{BF} (F/cm ²)	f_{HF} (Hz)	f_{MF} (Hz)		f_{BF} (Hz)
			C_{MF1} (F/cm ²)	C_{MF2} (F/cm ²)			f_{MF1} (Hz)	f_{MF2} (Hz)	
$T = 800^\circ\text{C}$, $\text{PH}_2\text{O}/\text{PH}_2=9$ (cathode), air (anode), cathodic flow x1		0,004	0,062	0,68	7	394	19	1,1	0,17
$i = 0.5 \text{ A/cm}^2$, cathode: $\text{PH}_2\text{O}/\text{PH}_2=9$, anode: N_2 or air or O_2 , cathodic flow x1	air	0,004	0,68		14	259	1,9		0,16
	O_2	0,004	0,77		13,6	265	1,8		0,15
	N_2	0,004	0,64		11,8	281	2		0,16
$T = 650^\circ\text{C}$, $\text{PH}_2\text{O}/\text{PH}_2=9$ (cathode), air (anode), cathodic flow x1	0,016 A/cm ²	0,0014	0,026	0,25	8,7	442	16	0,8	0,05
	0,064 A/cm ²	0,0013	0,021	0,21	11,2	577	20	1,5	0,06
	0,127 A/cm ²	0,0009	0,011	0,26	7,5	811	33	2,3	0,09
	0,35 A/cm ²	0,0006	0,006	0,53	9,9	799	129	1,5	0,13
$T = 650^\circ\text{C}$, $\text{PH}_2\text{O}/\text{PH}_2=9$ (cathode), $i = 0.175 \text{ A.cm-2}$, cathodic flow x1		0,001	0,014	0,67	17,1	472	43	1	0,07
$T = 800^\circ\text{C}$, $\text{PH}_2\text{O}/\text{PH}_2=9$ (cathode), air (anode)	0,016 A/cm ²	0,004	0,058	0,44	13,9	475	28	1,3	0,17
	0,064 A/cm ²	0,004	0,056	0,46	11,6	559	27	1,7	0,15
	0,127 A/cm ²	0,004	0,052	0,47	9,8	649	31	2,2	0,26
	0,446 A/cm ²	0,003	0,032	0,29	13,3	1012	70	3,8	0,58
	0,924 A/cm ²	0,002	0,016	0,20	1,2	776	73	3,8	1,3
	1,21 A/cm ²	0,003	0,024	0,09	1	477	34	4,1	1,1
		1 mF/cm ²	1 F/cm ²		10 F/cm ²	100 Hz	1 Hz		0,1 Hz
			0,05 F/cm ²	0,5 F/cm ²			10 Hz	1 Hz	



orders of magnitude clearly different

Extension to all parameters: i , T , $\text{PH}_2\text{O}/\text{PH}_2$, PO_2 , cathode gas flow rate



[100 Hz, 1000 Hz]

~ 1

HF arc $\Leftrightarrow$ related to charge transfer at the electrode/electrolyte interface ^{1,2}

~ 10

Hz

MF arc(s) $\Leftrightarrow$ associated to gas diffusion (anode) and/or O^{2-} ions transport (anode) and/or gas conversion (cathode) ³

~ 1

Hz

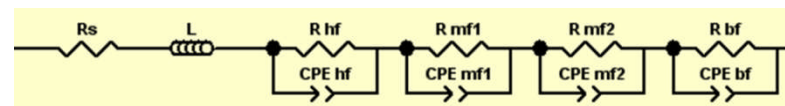
$\sim 0,1$ Hz

LF arc $\Leftrightarrow$ related to gas diffusion at the cathode ^{1,2}

¹ A. Brisse, J. Schefold, and M. Zahid, *Int. J. Hydrogen Energy*, 33 (2008) 5375

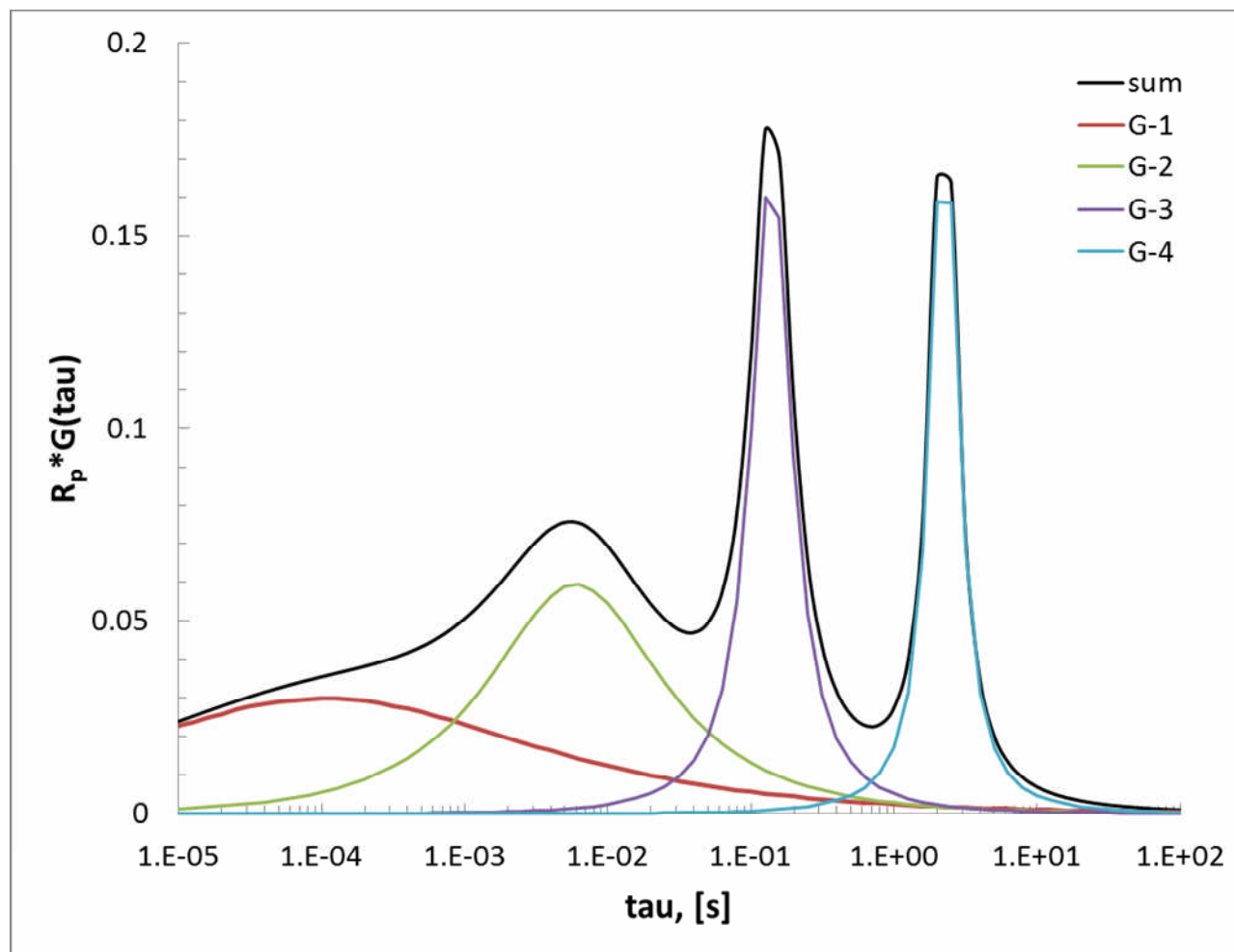
² J. Schefold, M.J. García, A. Brisse, D. Perednis and M. Zahid, *Electrolysis and Proton Conductors*, (2008) A1101

³ R. Knibbe, M. L. Traulsen, A. Hauch, S. D. Ebbesen, and M. Mogensen, *J. Electrochem. Soc.*, 157 (2010) B1209



DRT at $i = -0.064 \text{ A/cm}^2$ and $T = 650^\circ\text{C}$

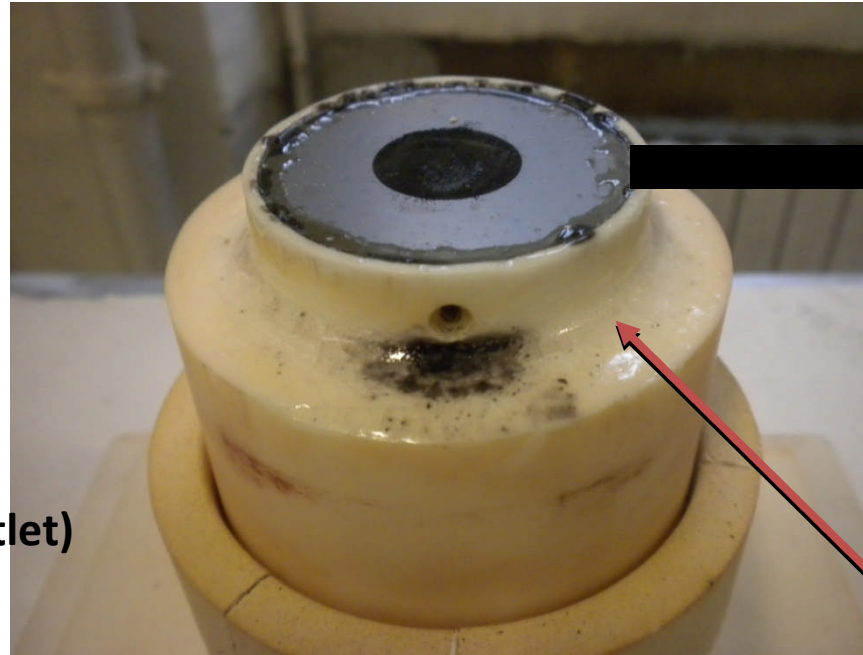
$\text{PH}_2\text{O}/\text{PH}_2 = 9$ (H_2 electrode), air (O_2 electrode), H_2 electrode gas flow rate x1.



Premature/early cell degradation!!!

Alumina cell
support

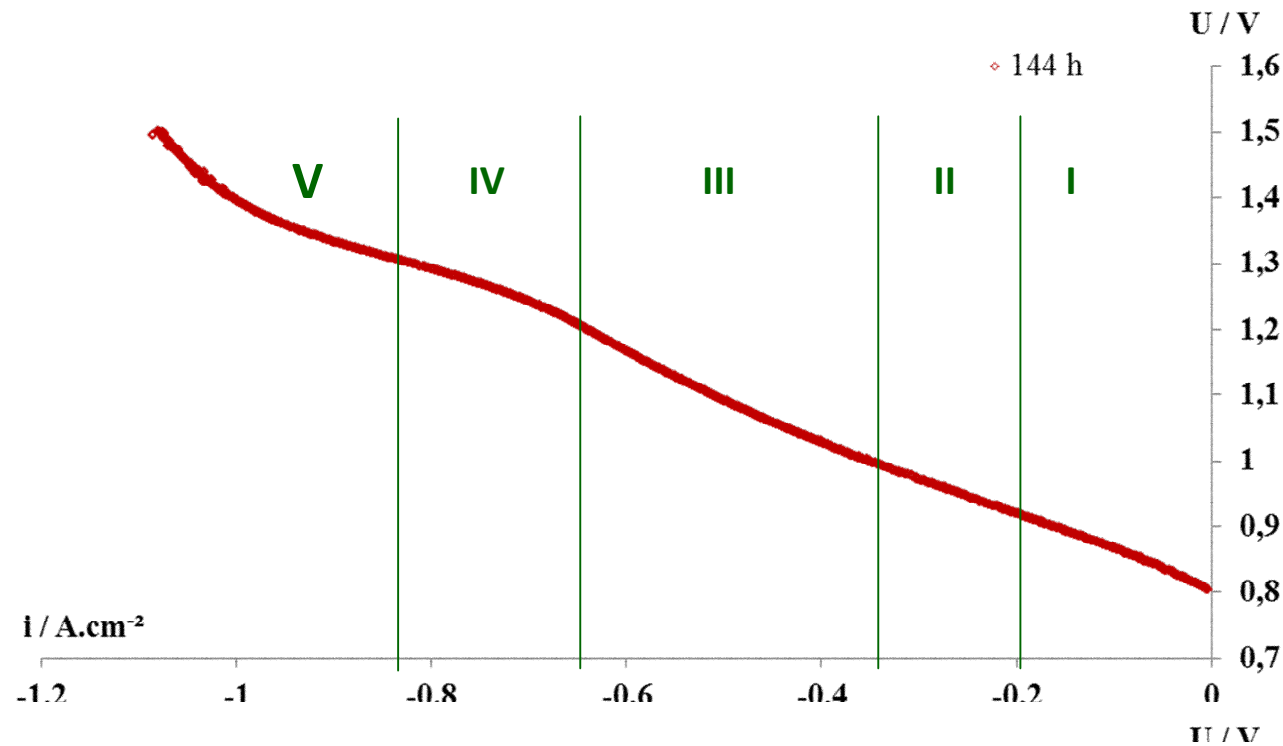
Alumina support
(cathode gas inlet + outlet)



Glass sealing
→ → anode and
cathode atmospheres
separation

Glass sealing
→ → preventing gas leaking
between alumina cell support
and alumina support

Current-tension behaviour



I: Cell activation

II : "optimal" utilization

III : "partial" gas transport lim.

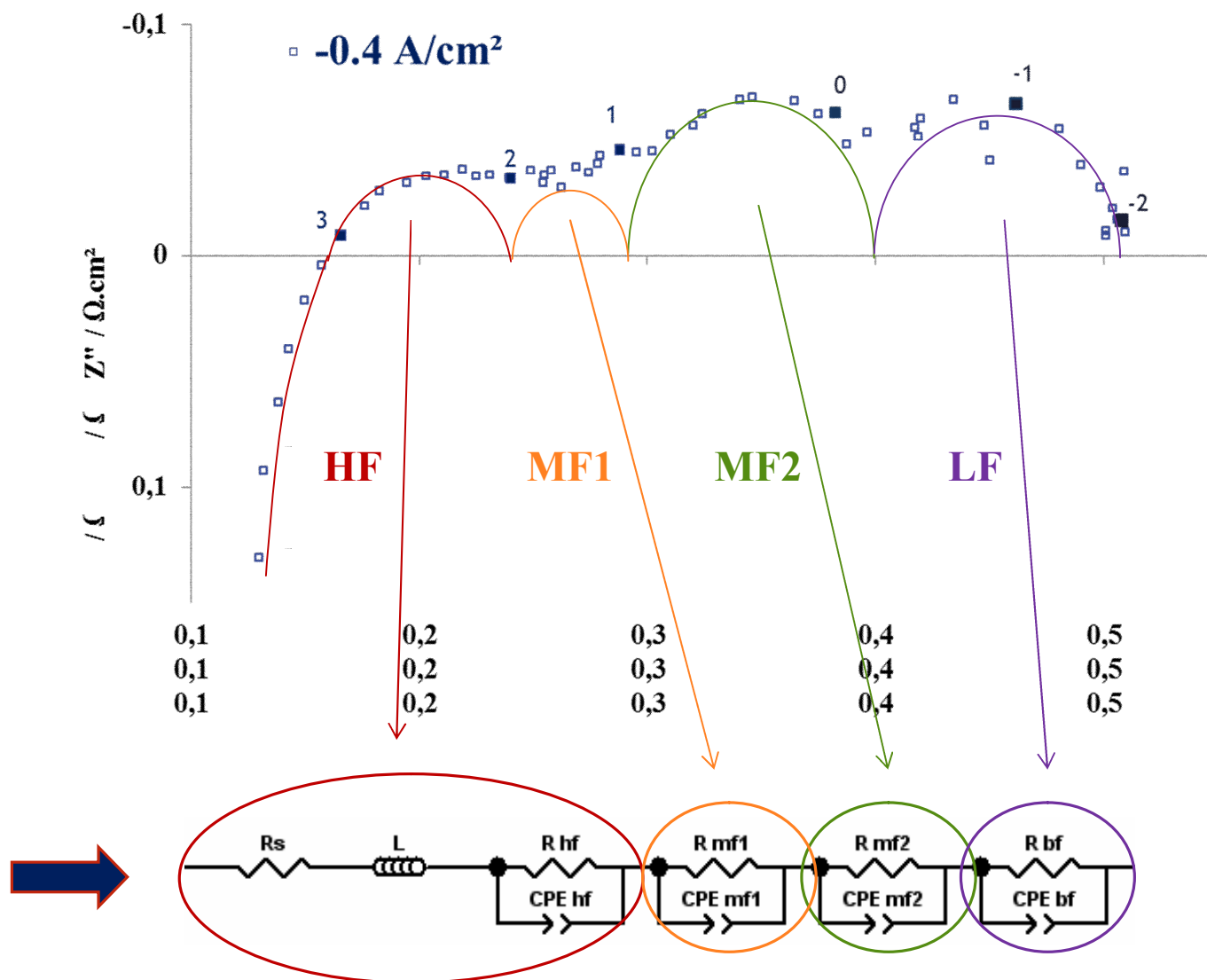
Usual

IV : cell reactivation

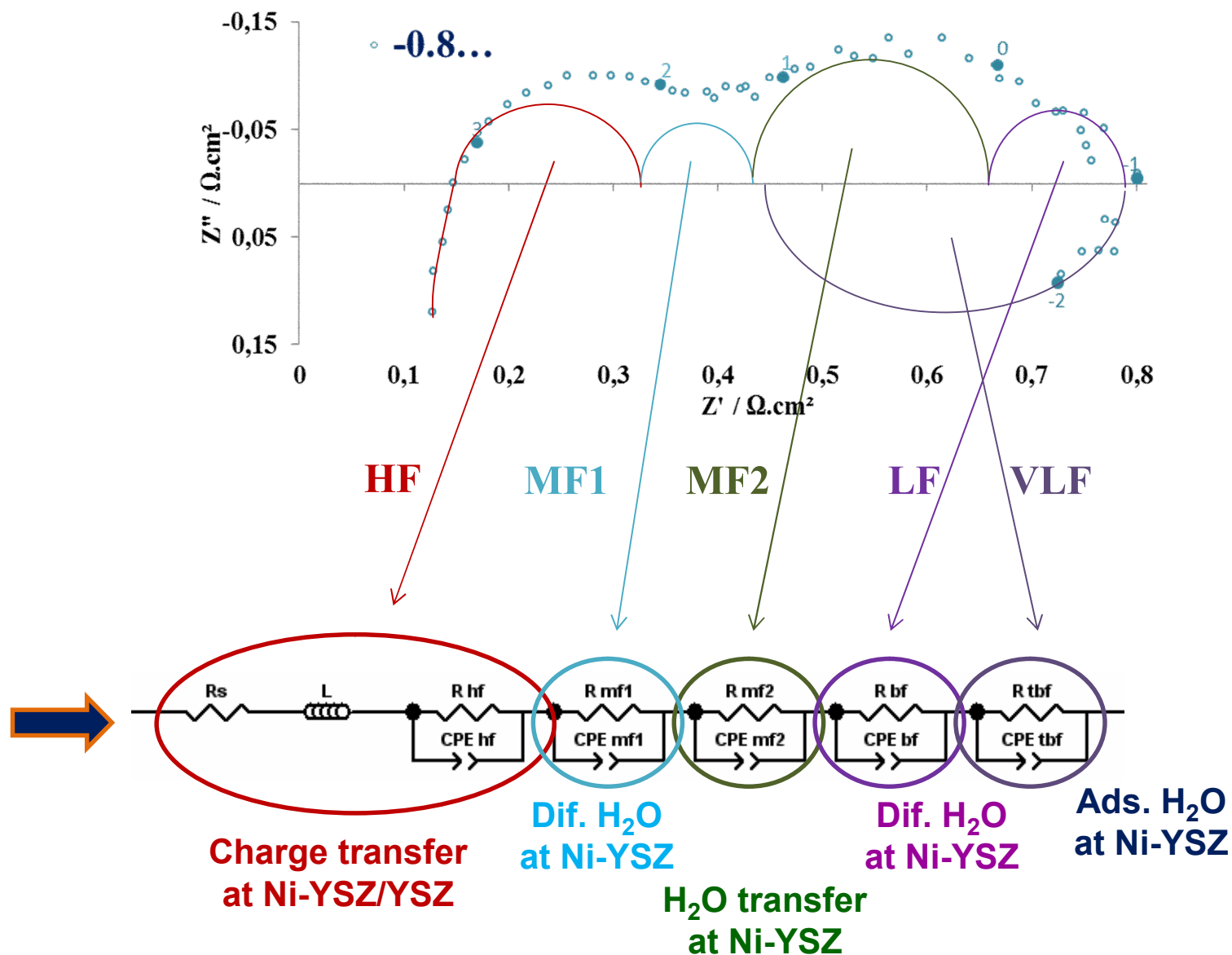
V : "final" gas transport lim.

Unusual

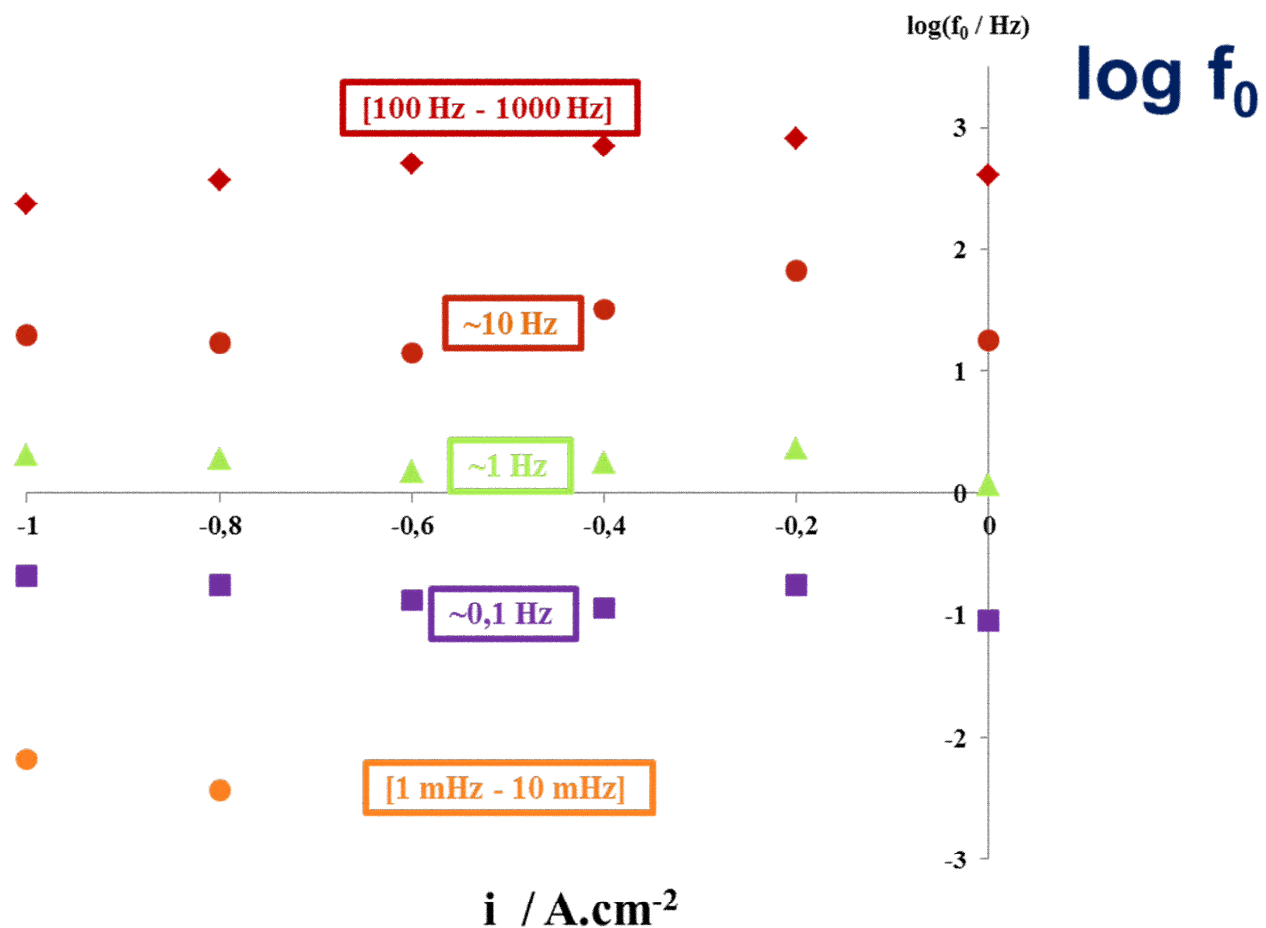
Regions I to III [0 A/cm^2 ; -0.6 A/cm^2]

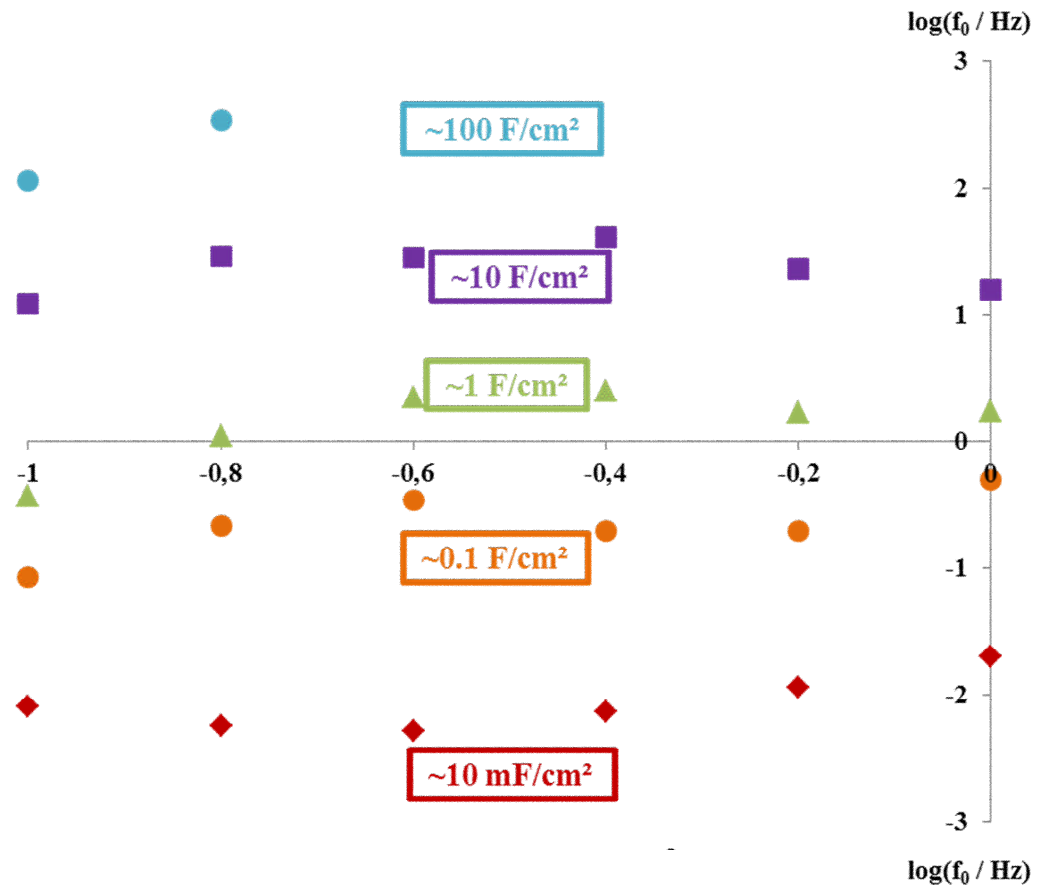


Regions IV to V [-0.6 A/cm²; -1.1 A/cm²]



Regions I to V [0 A/cm²; -1.1 A/cm²]

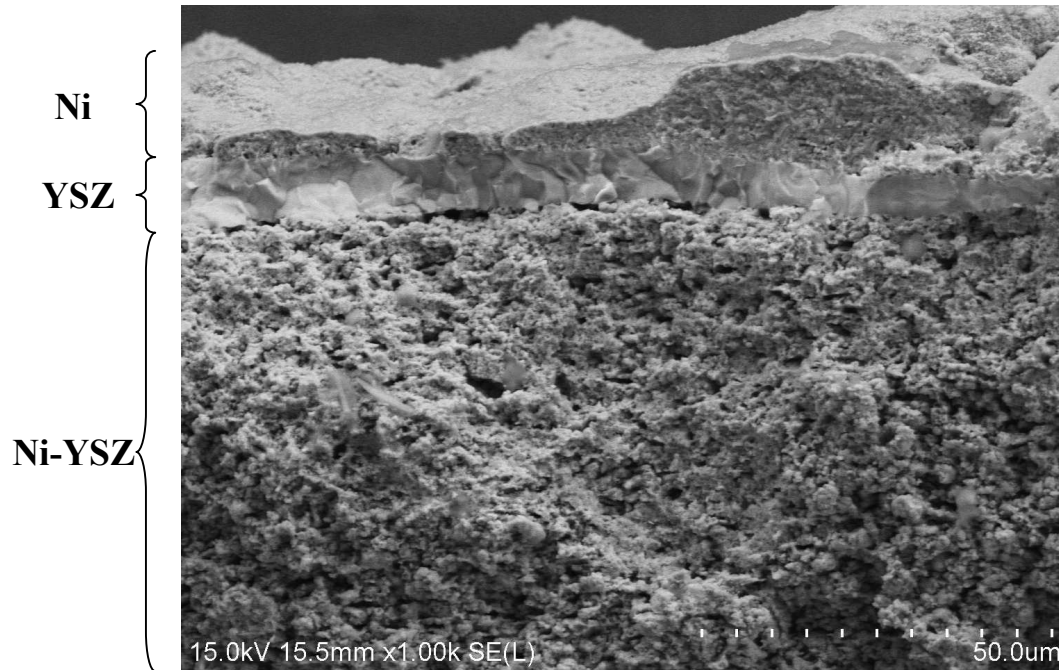




$\log C$

Degradation origins

Ni-YSZ electrode outmost



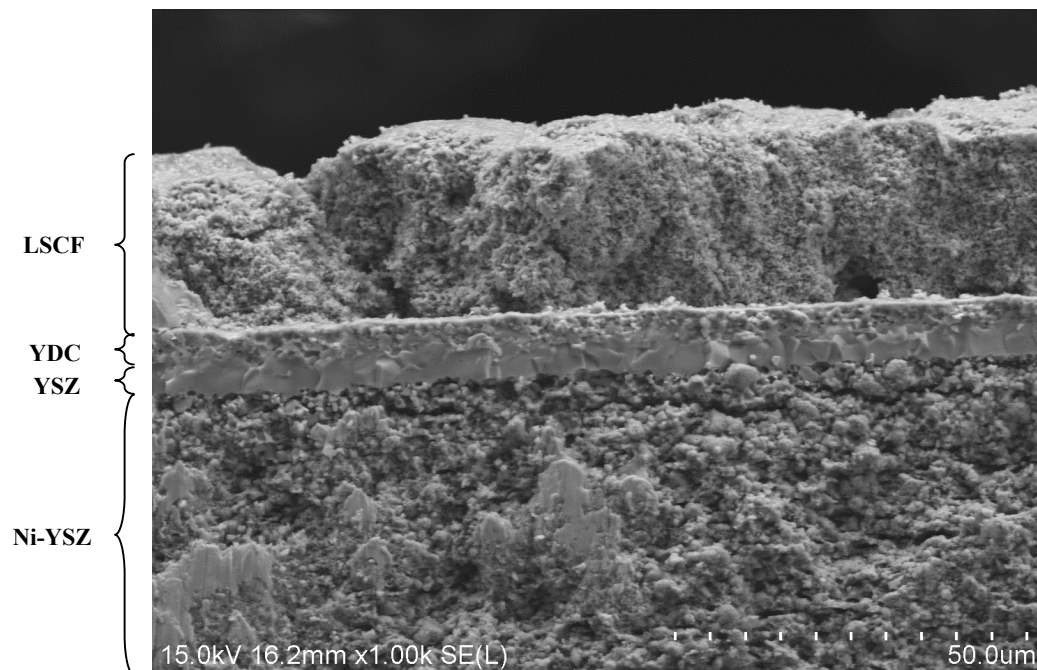
	O	Na	Al	Si	K	Ca	Fe	Ni	Y	Zr	Ce
Ni	65.0	1.9	1.3	0.5	0.7	0.8	0.4	25.7	0.4	3.0	0.3
	58.0	0.1	1.0	0.1	0.3	0.5	0.0	39.2	0.1	0.7	0.0
YSZ	42.8	0.6	1.8	2.3	0.2	0.1	0.3	49.5	0.1	2.4	0.0
	53.8	0.3	0.3	0.1	0.3	0.5	0.0	42.7	0.3	1.7	0.1
Ni-YSZ	65.5	0.5	0.3	0.0	0.2	0.6	0.1	2.1	4.0	26.3	0.5
	57.8	0.0	0.2	0.0	0.1	0.1	0.1	1.6	5.4	34.6	0.2
	59.1	0.0	0.2	0.0	0.0	0.0	0.0	1.5	5.7	33.5	0.0
	60.5	0.0	0.2	0.0	0.2	0.0	0.0	2.3	5.0	31.9	0.0
	64.2	1.1	0.6	1.2	0.1	0.0	0.0	17.3	0.5	14.8	0.0
	51.2	0.1	0.3	0.0	0.0	0.0	0.0	27.5	0.9	20.0	0.0
	57.1	0.0	0.3	0.1	0.0	0.1	0.0	25.1	0.7	16.6	0.0
	66.1	0.7	3.2	0.3	0.2	0.3	0.0	18.0	0.2	11.1	0.0
	57.8	0.0	0.2	0.0	0.1	0.0	0.0	20.7	0.8	20.4	0.0
	45.6	0.1	0.1	0.0	0.0	0.0	0.0	37.0	0.6	16.2	0.0
	52.2	0.3	0.3	0.0	0.1	0.1	0.0	25.7	0.8	20.6	0.0
	41.5	0.1	0.8	0.6	0.3	0.0	0.0	34.4	0.6	21.6	0.1
	60.2	0.0	0.2	0.0	0.0	0.0	0.0	18.5	0.7	20.4	0.0

➡ Si deposits at the outmost Ni layer

➡ Si deposits at the first 12 μm in Ni-YSZ electrode volume

+ Na, Al, K and Ca

LSCF/YDC/YSZ/Ni-YSZ



	O	Al	Si	Cr	Fe	Co	Ni	Sr	Y	Zr	La	Ce
LSCF	56.1	0.2	4.9	0.0	13.7	3.3	2.5	6.9	0.3	0.4	11.6	0.0
	59.5	0.1	4.8	0.0	12.9	3.4	1.1	7.3	0.2	0.1	10.7	0.0
	55.2	0.2	3.9	0.0	14.8	3.4	2.3	6.9	0.1	0.7	12.3	0.2
YDC	66.6	0.1	0.0	0.0	0.1	0.0	0.6	0.0	4.1	20.0	0.1	8.4
	70.2	0.0	2.2	0.1	0.1	0.1	0.6	2.5	3.3	16.1	0.1	4.8
	66.4	0.1	0.2	0.0	0.5	0.0	1.5	0.2	3.6	19.9	0.3	7.3
YSZ	75.9	0.3	0.0	0.0	1.4	0.1	2.7	0.0	2.3	14.9	0.1	2.2
	73.1	0.1	0.0	0.0	0.1	0.0	0.8	0.0	2.9	19.9	0.0	3.1
	70.4	0.6	0.0	0.0	2.9	0.2	3.9	0.0	2.5	16.3	0.1	3.1
Ni-YSZ	68.9	0.8	3.4	0.0	0.8	0.3	9.7	0.2	1.8	12.5	0.4	1.2
	34.2	0.3	0.0	0.0	0.0	0.8	42.7	0.0	1.5	14.6	0.3	5.7
	43.1	0.1	0.0	0.0	0.3	0.7	26.9	0.0	2.5	22.4	0.2	3.7
	46.9	0.1	0.1	0.0	0.1	0.6	50.1	0.0	0.0	1.9	0.0	0.1
	57.7	0.1	0.0	0.0	0.1	0.1	14.3	0.0	2.6	22.8	0.0	2.4
	63.7	0.1	0.0	0.0	0.1	0.4	19.0	0.0	1.1	14.6	0.1	0.9
	32.0	0.2	0.0	0.0	0.1	0.4	32.9	0.0	0.4	33.1	0.0	0.9
	55.6	0.3	0.0	0.0	0.2	0.3	25.0	0.0	0.1	18.2	0.0	0.3
	54.9	0.2	0.0	0.0	0.1	0.2	17.9	0.0	0.4	25.8	0.0	0.4

➡ Ponctual Si deposits near the Ni-YSZ/YSZ interface

➡ Si deposits at the YDC layer & the LSCF electrode

+ Al

Conclusion - Prospects

- Study influence of several parameters on cell behaviour
- Impedance diagrams decomposition with electrical equivalent circuit

- ➡ identification of different frequency ranges
- ➡ each frequency range associated to relaxation frequency + capacitance
- ➡ attribution of each frequency range to one/several phenomena
- ➡ understanding/monitoring cell degradation in real time

First important step for *in situ* diagnosis tool for SOEC degradation

- Identification phenomena related to MF ranges (combining with DRT & ASIS)
 - ➡ study other parameters (anode gas flow rate, ...)
 - ➡ study other cells (microstructure, thickness, materials,...)
- Applying this approach to a SRU and a stack