SOFC-XV
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Evaluation of performance and degradation profiles of a metal supported solid oxide fuel cell under electrolysis operation

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SOFC-XV - July 26, 2017

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Outline

I. Metal-supported cell presentation

II. Performance study

III. Degradation study

IV. Conclusions - Prospects

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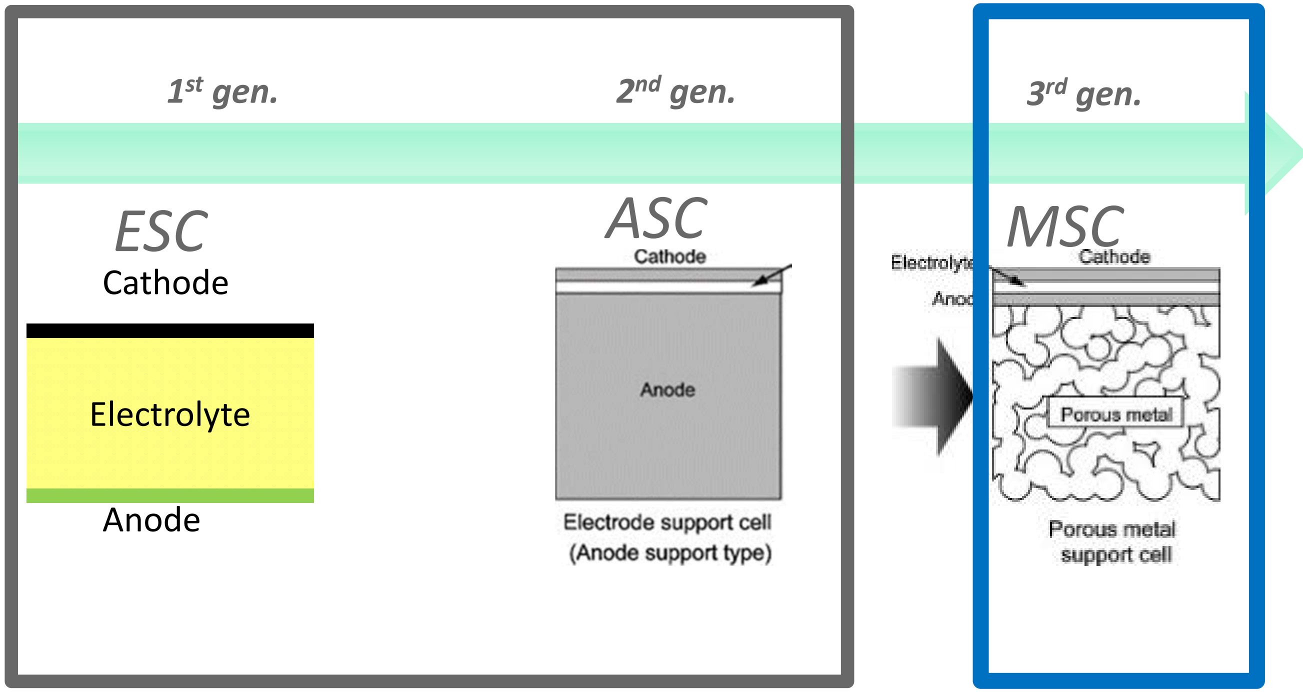
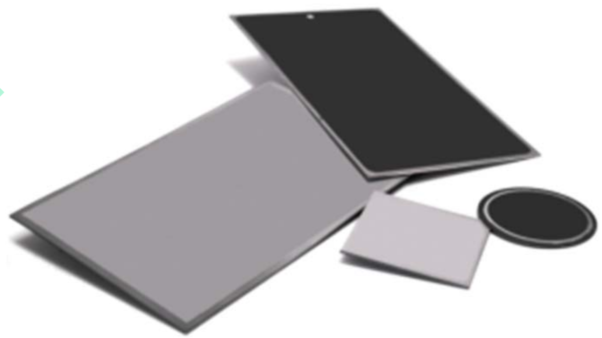
➢ Advantages of Metal Supported Cells





- ➢ To replace expensive ceramics by metals
- ➢ Reversible operation

Metal supported Cell (MSC):

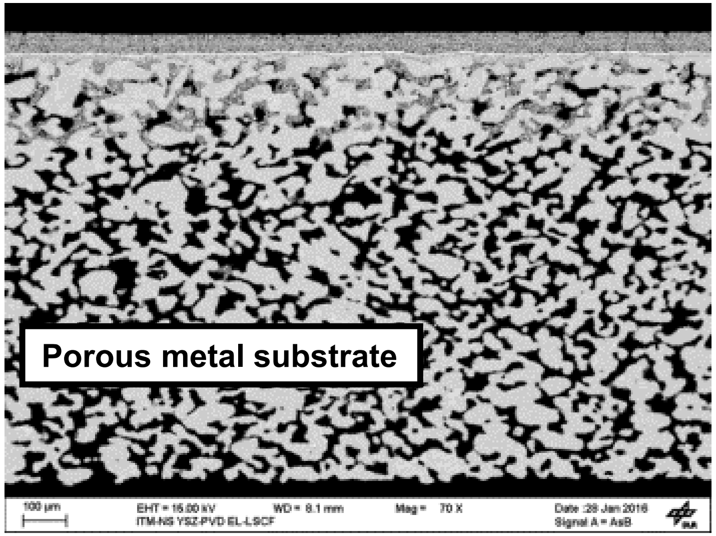
- High robustness
- High resistance against thermal and redox cycling
- Good integration into interconnects (bipolar plates) via brazing or welding
- Low cost of metal support and cell materials (thin layers)
- High electronic and thermal conductivity
- Fast start-up, etc.

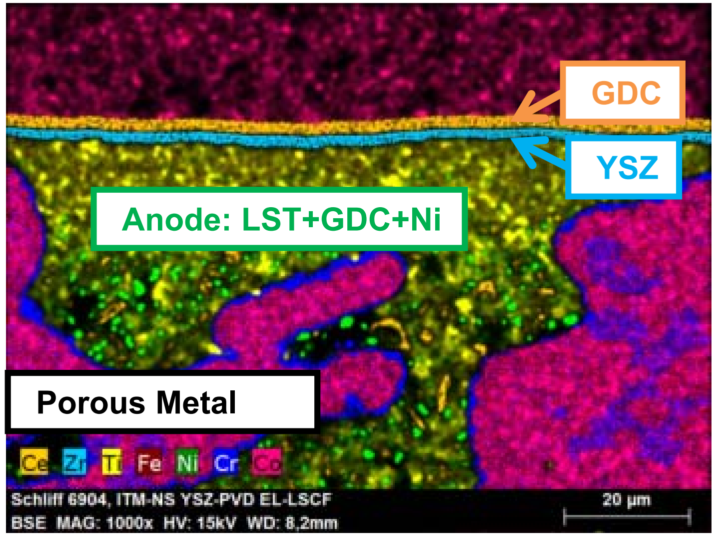
- **Objectives**

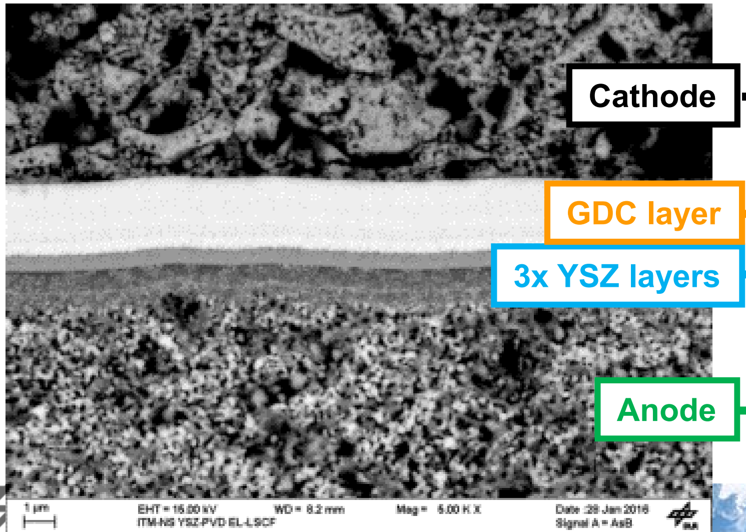
  - Development of metal supported SOCs for HTE application
  - Optimization of electrodes and functional layers for SOEC operation
  - Improving cells' power density and durability
  - Characterization and testing of metal supported SOECs

I. Metal-supported cell presentation

➢ Architecture of Metal Supported Cells





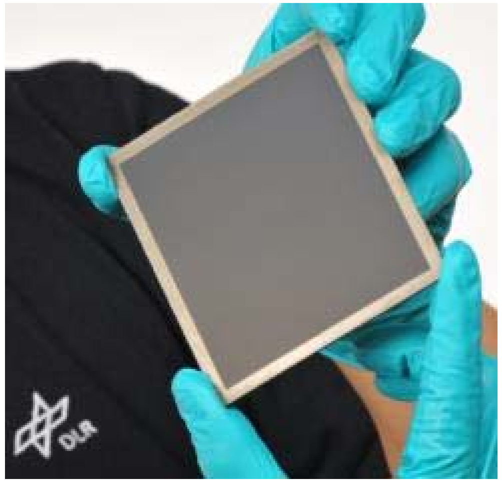


Cathode → $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)

GDC layer → $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO)

3x YSZ layers → 8mol% Y_2O_3-ZrO_2 (8YSZ)

Anode → $La_{0.1}Sr_{0.9}TiO_{3-\alpha}$ (LST) -GDC composite with Ni catalysts



Single cell up to 100mmx90mm

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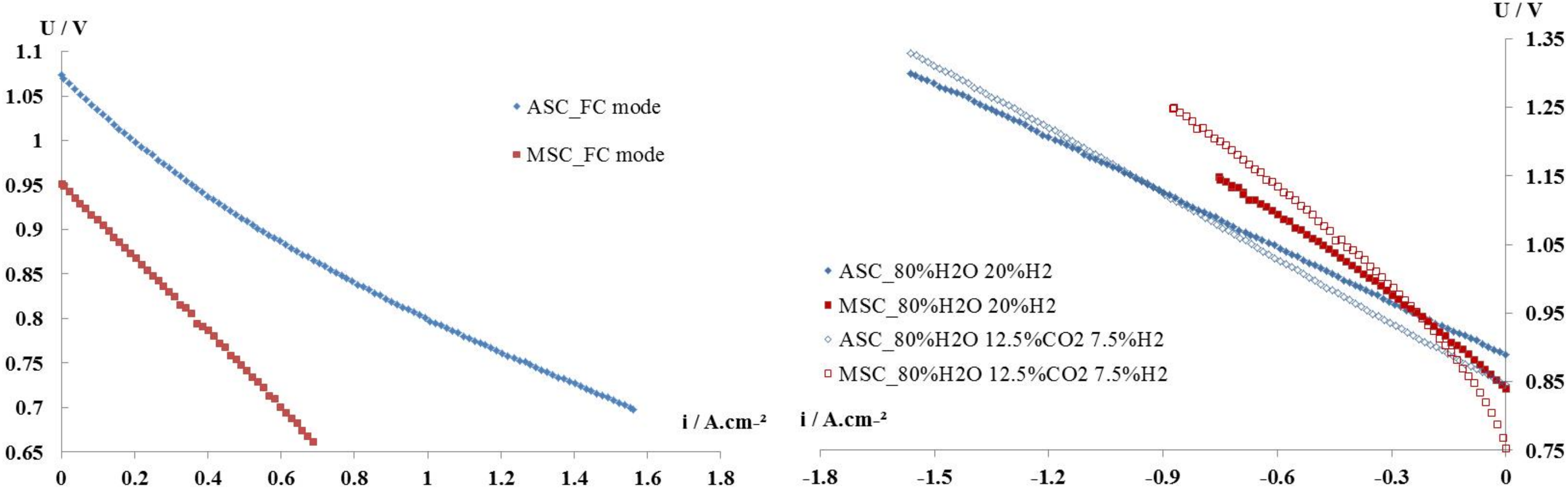
IV. Conclusions - Prospects

II. Performance study

- i-U curves



- **FC mode ➔ OCV_{ASC} = 1074 mV while OCV_{MSC} = 953 mV**
- **EL mode ➔ OCV_{ASC} = 890 mV while OCV_{MSC} = 840 mV**
- **co-EL mode ➔ OCV_{ASC} = 846 mV while OCV_{MSC} = 753 mV**

leakage issues with MSC ➔ Pinhole defects

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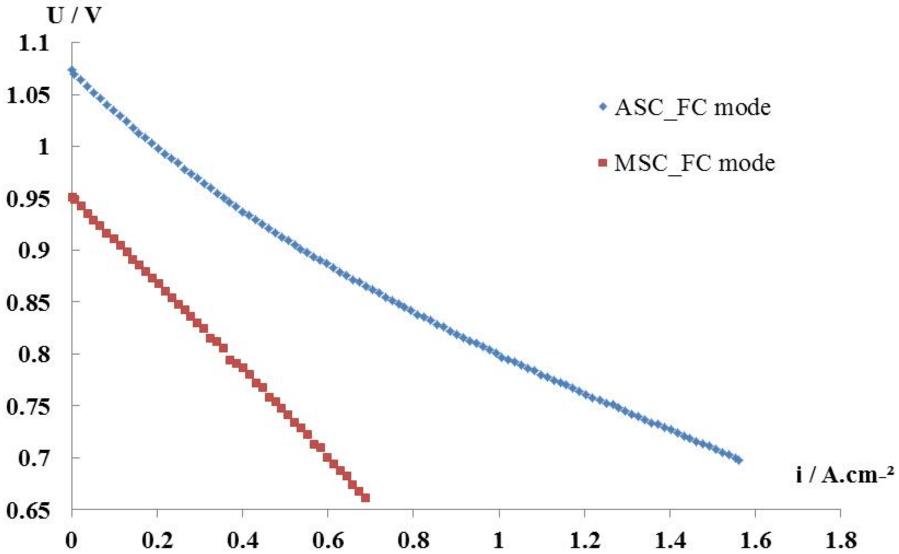
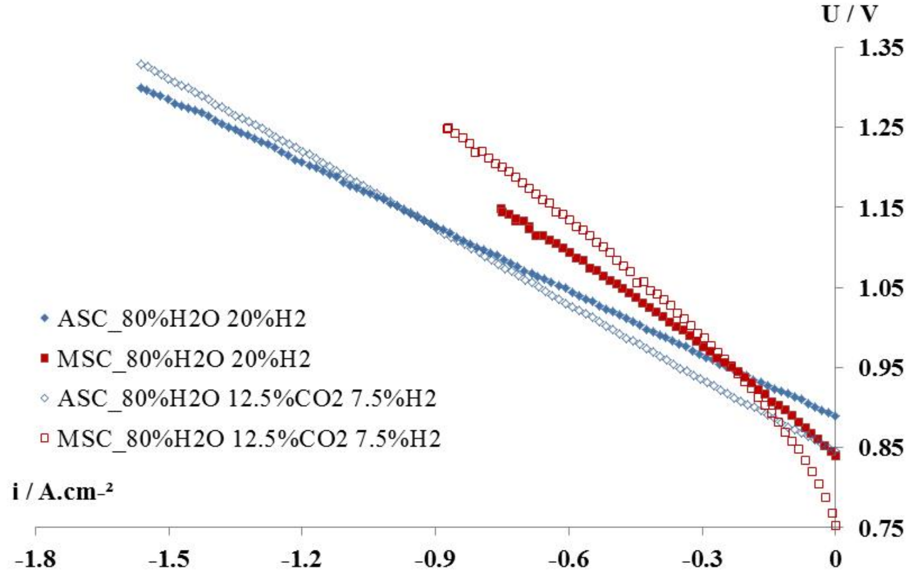
II. Performance study

➢ i-U curves





- FC mode : - **no activation part observed for the MSC** ➔ the MSC works directly at a minimum resistance
  - **no mass transport limitation observed for the MSC**

- EL and co-EL modes : - **activation part at lower currents observed for the MSC**, **<u>especially in co-EL mode</u>**
  - **no mass transport limitation observed for the MSC**

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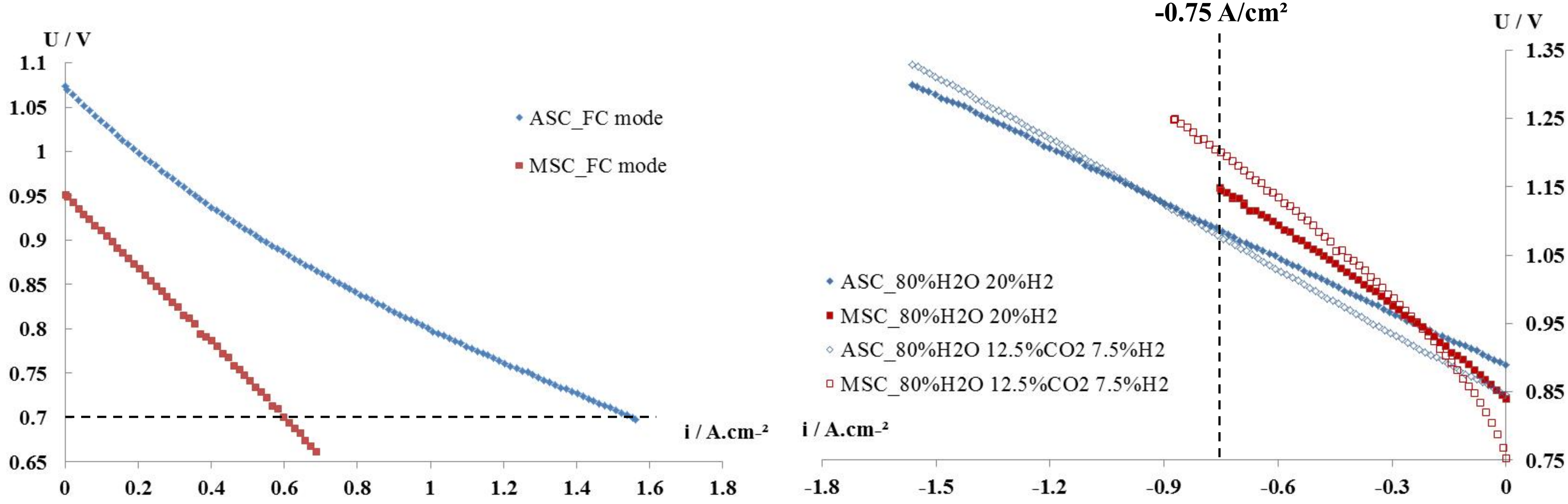
II. Performance study

➢ i-U curves

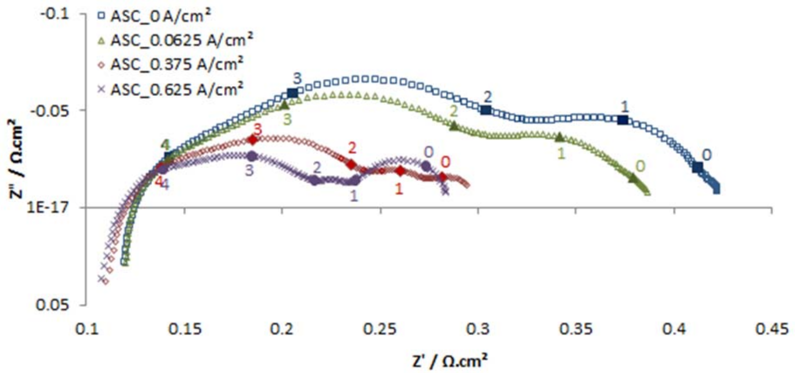


	FC mode (0.7 V)	EL mode (-0.75 A/cm²)	co-EL mode (-0.75 A/cm²)
P_{ASC} (W/cm²)	1.085	-0.815	-0.807
P_{MSC} (W/cm²)	0.448	-0.863	-0.901

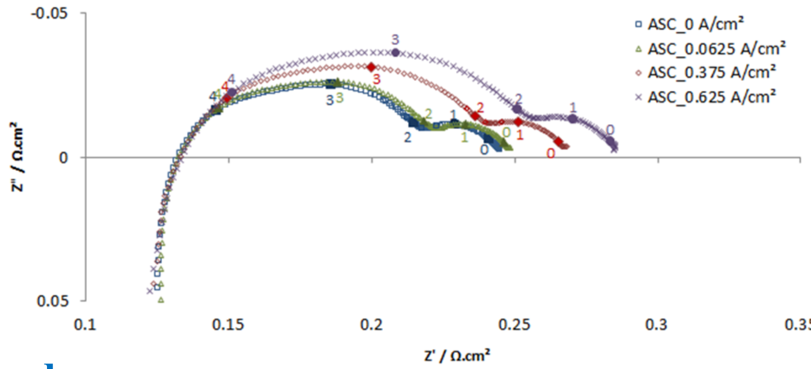
II. Performance study

➢ EIS - ASC

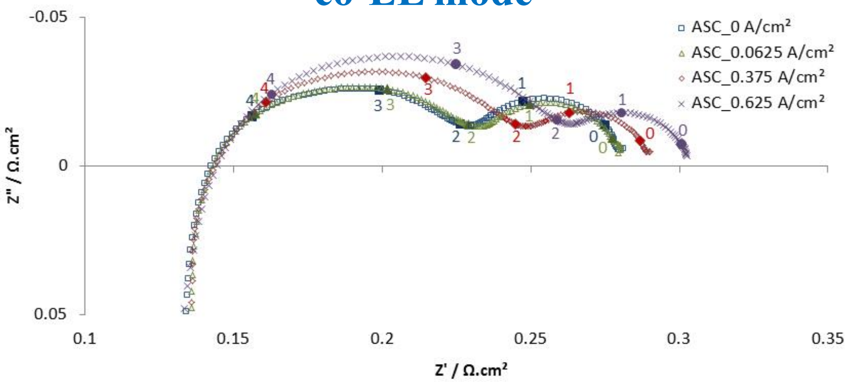
FC mode



EL mode



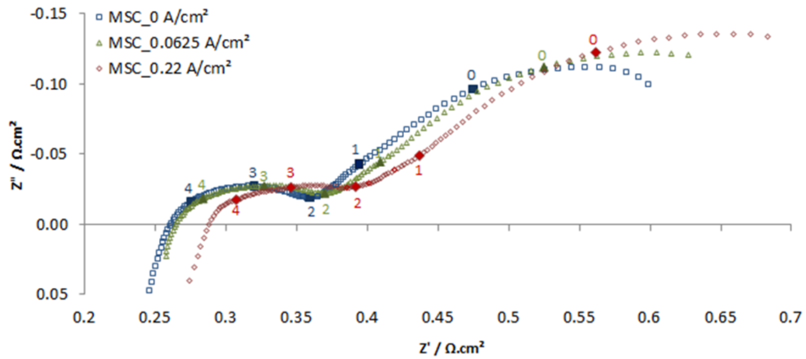
co-EL mode



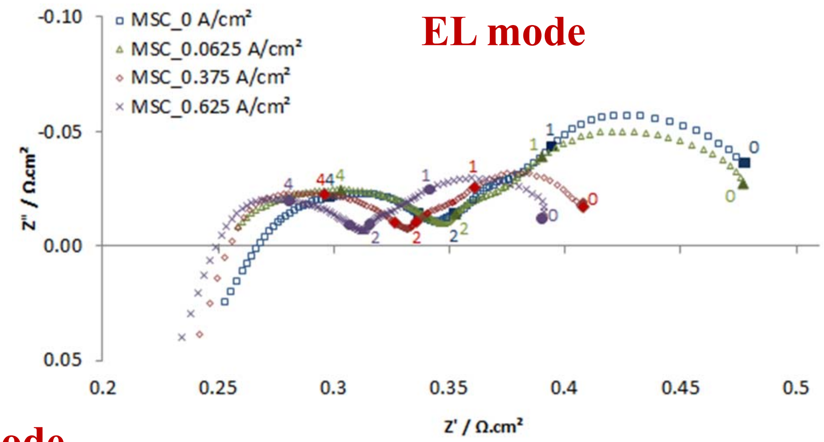
- **R_{ohm} = 115-145 mΩ.cm²** stable with i applied
- FC mode ➔ **Significant R_{pol}** ↘ ➔ All main electrochemical processes activated with i ↗
- EL and co-EL modes ➔ **R_{pol}** ↗ **with i** ➔ **mainly HF impedance** involved
  ➔ contrary to FC mode, cell activation **in EL and co-EL modes before optimum performances can be achieved**

➢ EIS - MSC

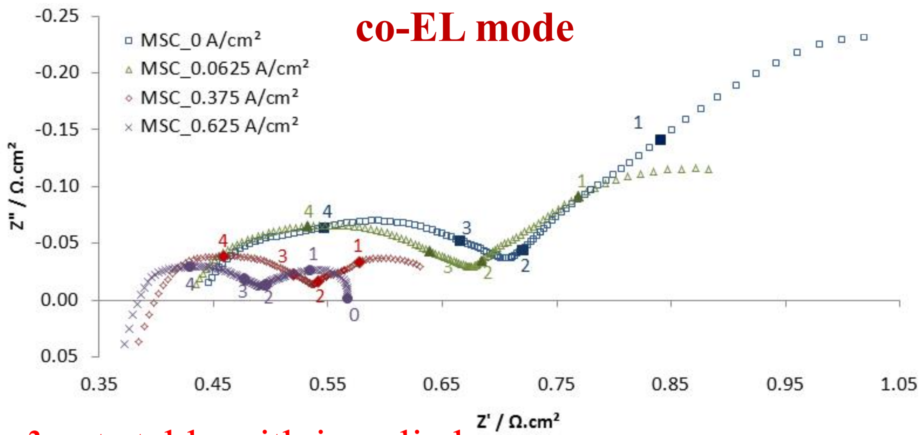
FC mode



EL mode



co-EL mode



- **R_{ohm} = 232-450 mΩ.cm²** not stable with i applied
- FC mode ➔ **very slight R_{pol}** ↗ ➔ expected from i-U curve trends
- EL and co-EL modes ➔ **R_{pol} ↘ with i ↗ ➔ decrease of the whole impedance diagram**
  ➔ all main electrochemical processes activated with i

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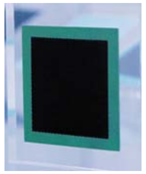
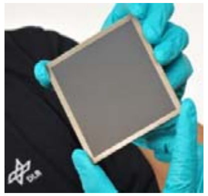
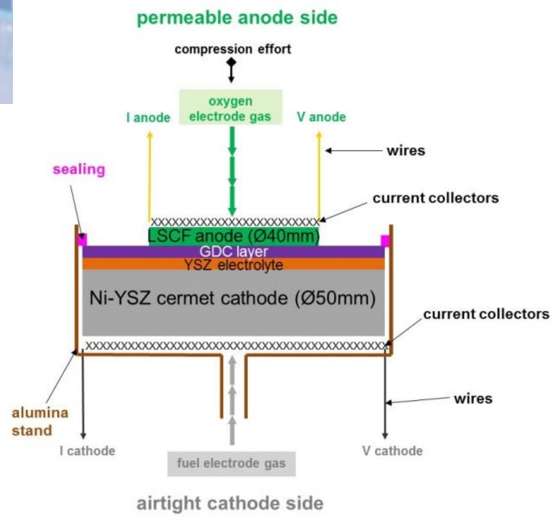
III. Degradation study

➢ Experimentals



- Cell 1 : CeramCell ASC-LSCF (Ceramtec, Germany) ➔ ASC
- Cell 2 : MSC (DLR, Germany) ➔ MSC
- Active area S = 16 cm²





- T = 750°C
- air (O_2 electrode), O_2 electrode flow rate = 2.0 SL/min/cell
- H_2 electrode flow rate = 2.0 SL/min/cell

	H_2 electrode gas composition	current applied	duration
Experiment 1	80% H_2O + 20% H_2	-0.25 A/cm²	120 h
Experiment 2	80% H_2O + 12.5% CO_2 + 7.5% H_2	-0.25 A/cm²	480 h
Experiment 3	90% H_2O + 10% H_2	-0.25 A/cm²	456 h
Experiment 4	90% H_2O + 10% H_2	-0.5 A/cm²	1176 h

- Total degradation test duration of **2232 hours** (~13 weeks)

- **U vs time**

	H_2 electrode gas composition	current applied	duration
Experiment 1	80% H_2O + 20% H_2	-0.25 A/cm²	120 h
Experiment 2	80% H_2O + 12.5% CO_2 + 7.5% H_2	-0.25 A/cm²	480 h
Experiment 3	90% H_2O + 10% H_2	-0.25 A/cm²	456 h
Experiment 4	90% H_2O + 10% H_2	-0.5 A/cm²	1176 h

	Exp. 1		Exp. 2		Exp. 3		Exp. 4	
	ASC	MSC	ASC	MSC	ASC	MSC	ASC	MSC
ΔV (mV/1000 h)	40	120	6.3	290	11	21.9	43.4	26.4
%/1000 h	4.2	11.4	0.7	30.2	1.2	2.0	4.3	2.0

III. Degradation study

➢ **U vs time**

	H_2 electrode gas composition	current applied	duration
Experiment 1	80% H_2O + 20% H_2	-0.25 A/cm²	120 h
Experiment 2	80% H_2O + 12.5% CO_2 + 7.5% H_2	-0.25 A/cm²	480 h
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	ASC	MSC	ASC	MSC	ASC	MSC	ASC	MSC
ΔV (mV/1000 h)	40	120	6.3	290	11	21.9	43.4	26.4
%/1000 h	**4.2**	11.4	**0.7**	30.2	**1.2**	2.0	**4.3**	2.0

ASC

low degradation, even for co-EL

significant degradation
➔ cell activation

significant degradation
➔ time + higher i applied

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III. Degradation study

➢ U vs time

	H_2 electrode gas composition	current applied	duration
Experiment 1	80% H_2O + 20% H_2	-0.25 A/cm²	120 h
Experiment 2	80% H_2O + 12.5% CO_2 + 7.5% H_2	-0.25 A/cm²	480 h
Experiment 3	90% H_2O + 10% H_2	-0.25 A/cm²	456 h
Experiment 4	90% H_2O + 10% H_2	-0.5 A/cm²	1176 h

	Exp. 1		Exp. 2		Exp. 3		Exp. 4	
	ASC	MSC	ASC	MSC	ASC	MSC	ASC	MSC
ΔV (mV/1000 h)	40	120	6.3	290	11	21.9	43.4	26.4
%/1000 h	4.2	**11.4**	0.7	**30.2**	1.2	**2.0**	4.3	**2.0**

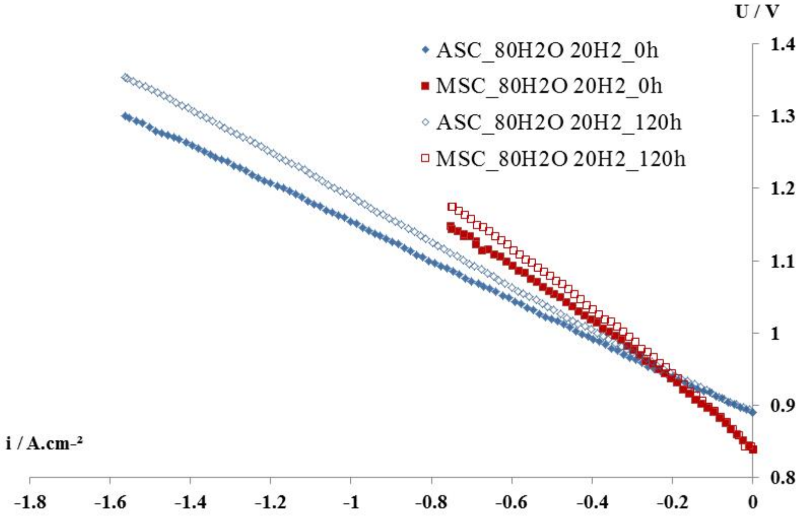
MSC

huge degradation !!!
(especially co-EL)

much lower degradation
➔ partial cell reactivation/recovery under EL

III. Degradation study

- **i-U vs time**



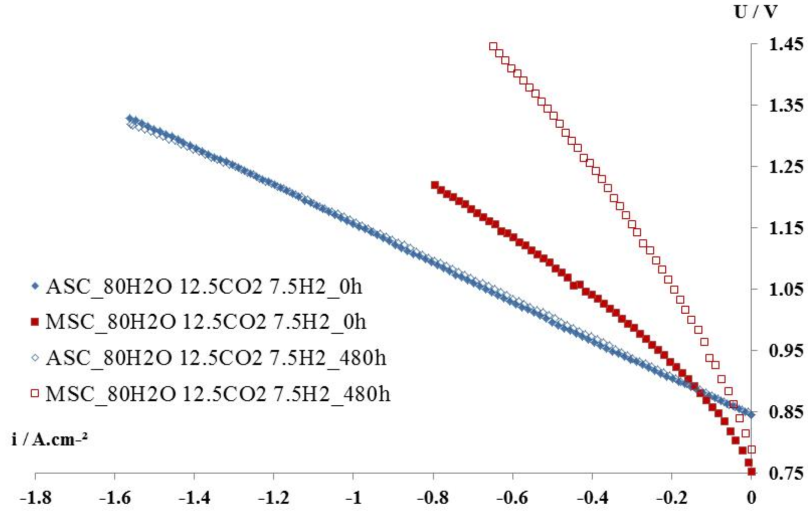
Exp.1 (80% H_2O + 20% H_2)

ASC and MSC

- OCV stable over time

- effect of degradation over time not visible at lower i applied

visible at higher i applied



Exp.2 (80% H_2O + 12.5% CO_2 + 7.5% H_2)

ASC → - OCV stable over time

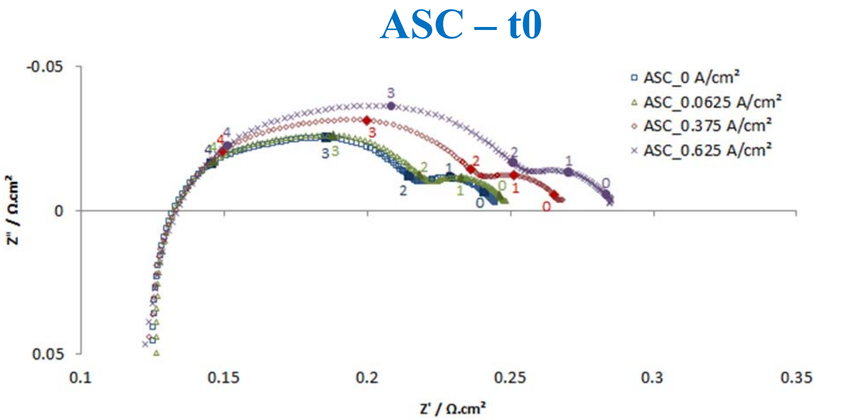
- **almost no degradation over time**

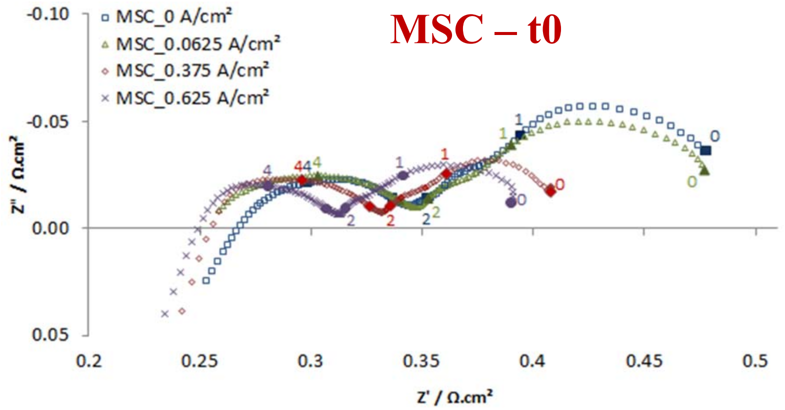
MSC → - OCV increase over time (leakage + defects)

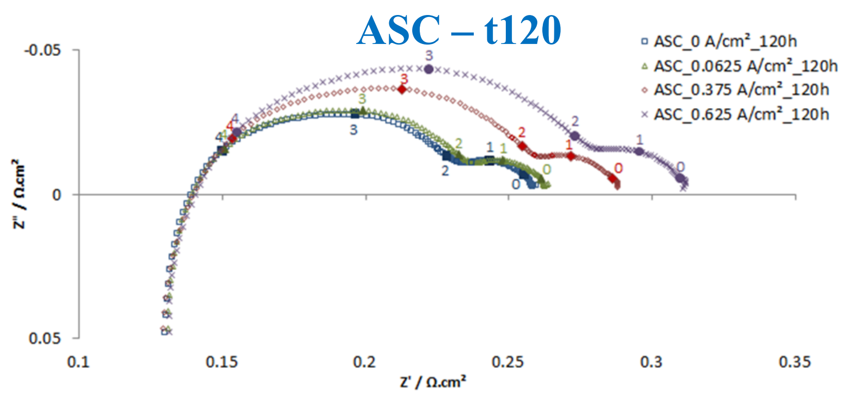
- effect of degradation over time visible from lower i applied

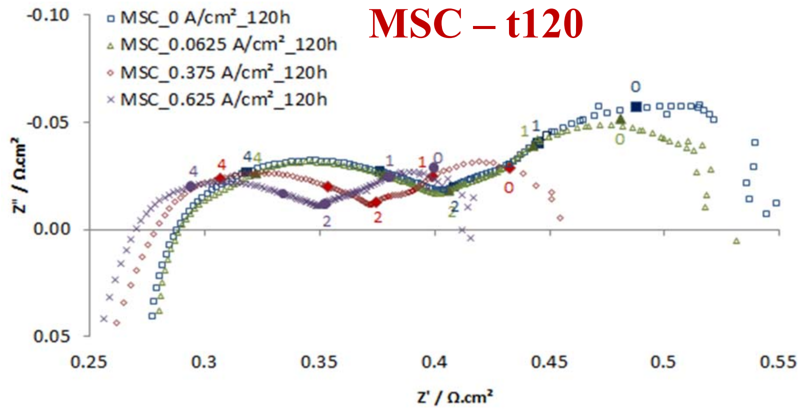
III. Degradation study

- EIS vs time – EL mode 80%H_2O + 20%H_2 (i = -0.25 A/cm²)









MSC R_{ohm} ↘ when i ↗ ➔ not stable

➔ electrode/electrolyte interface behavior changing with i ?!

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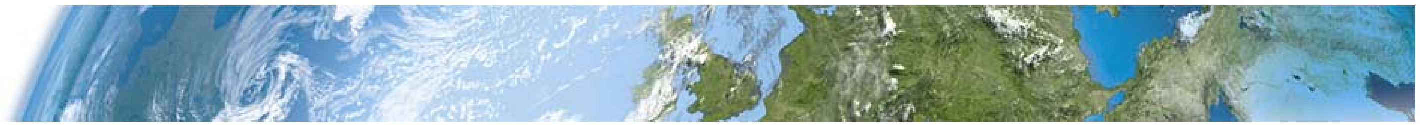
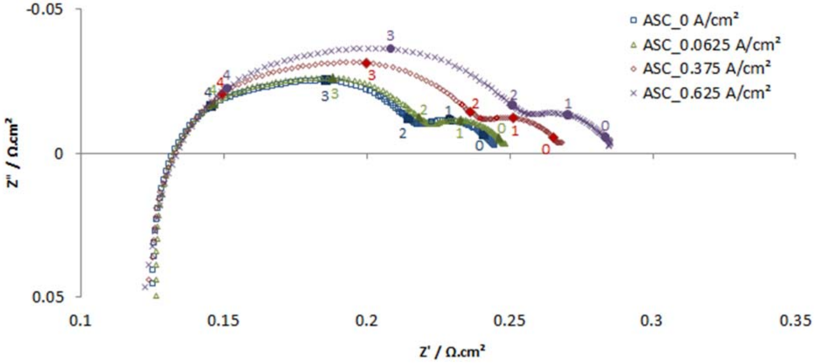
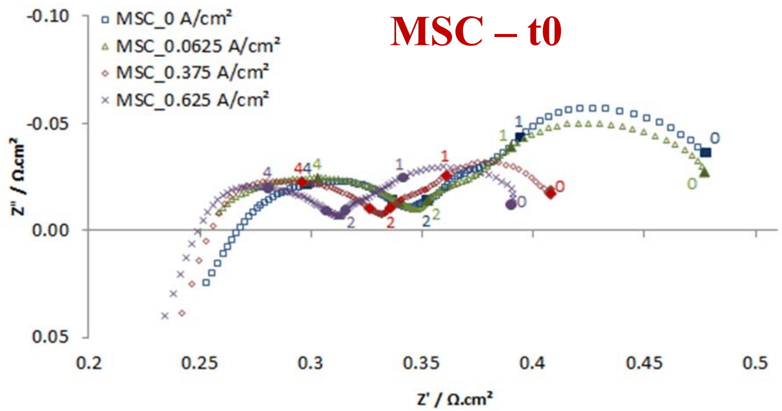


- **EIS vs time – EL mode 80%H_2O + 20%H_2 (i = -0.25 A/cm²)**

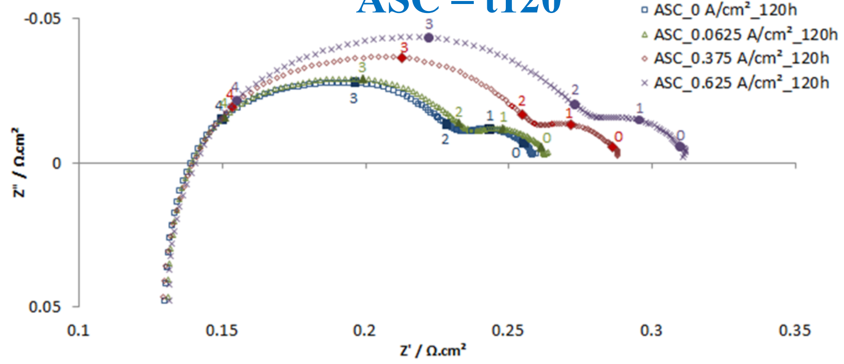
ASC – t0



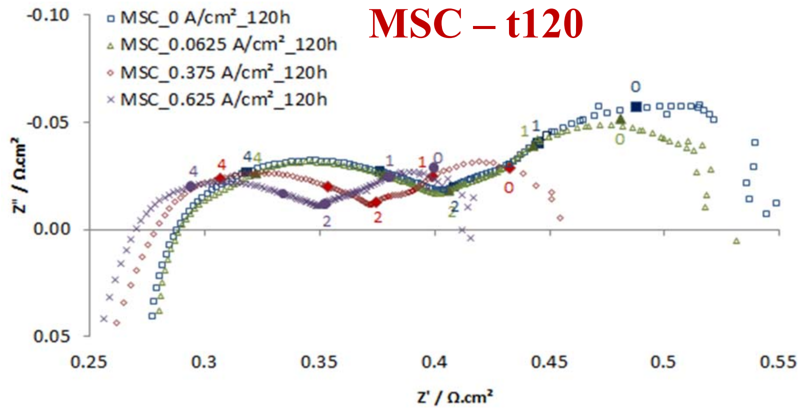
MSC – t0



ASC – t120



MSC – t120



MSC [10^5 Hz – 10^3 Hz] ➔ **frequency shift + R_{pol} ↗ over time** whatever i applied

➔ **H_2 electrode charge transfer related phenomena [1-3] affected** over time from lower i applied

[1] A. Leonide, V. Sonn, A. Weber, E. Ivers-Tiffée, J. Electrochem. Soc., 155 (2008) B36-B41
[2] A. Nechache, B.A. Boukamp, M. Cassir, A. Ringuedé, Electrochim. Acta 210 (2016) 596-605
[3] A. Hauch, K. Brodersen, M. Chen, M.B. Mogensen, Solid State Ionics 293 (2016) 27-36

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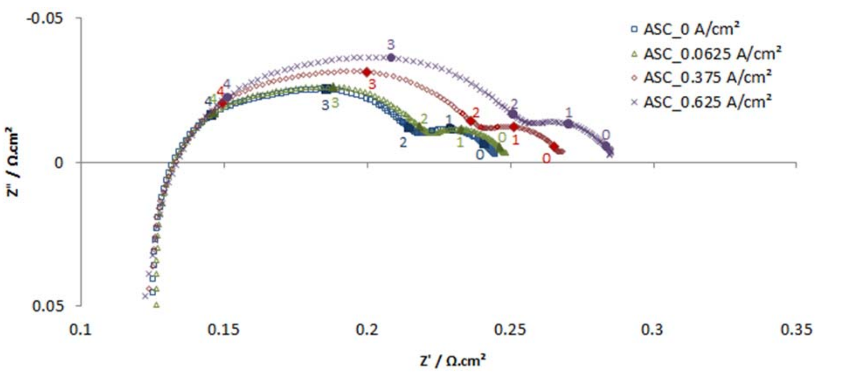
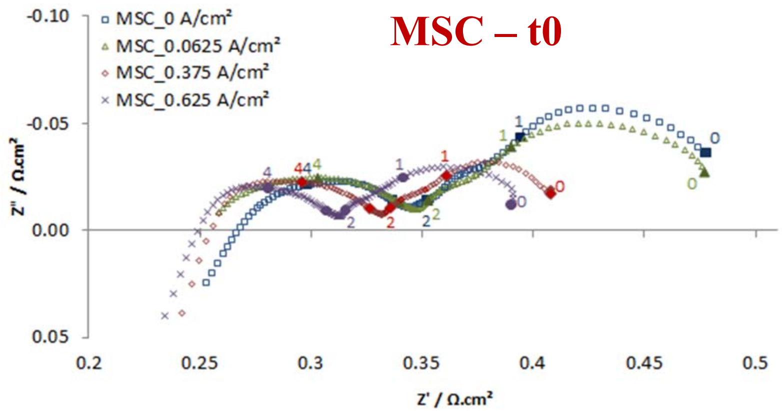
➢ **EIS vs time – EL mode 80%H_2O + 20%H_2 (i = -0.25 A/cm²)**

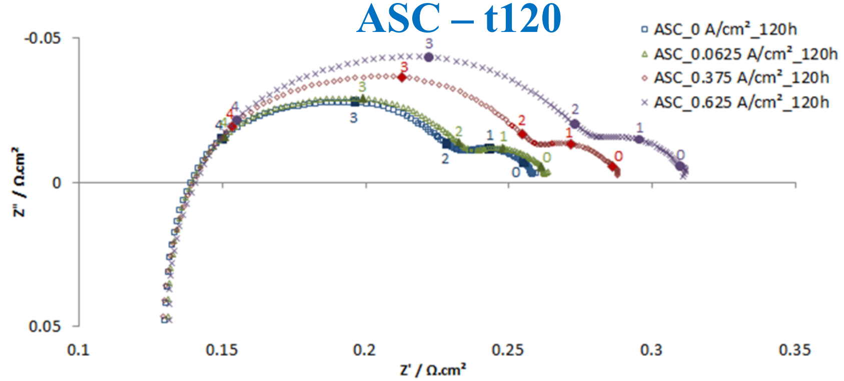
ASC – t0



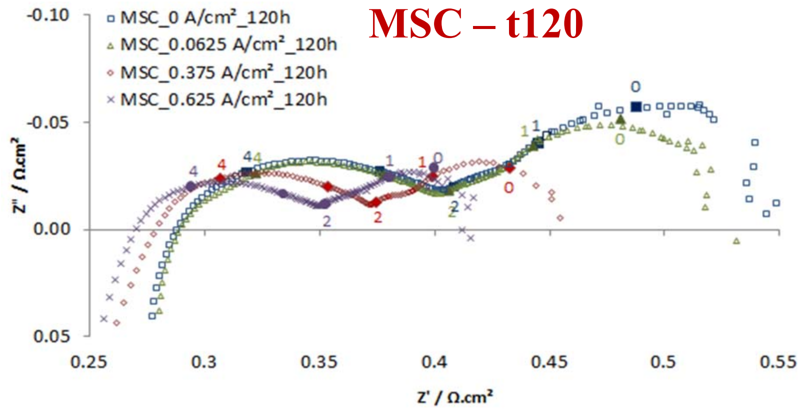
MSC – t0



ASC – t120



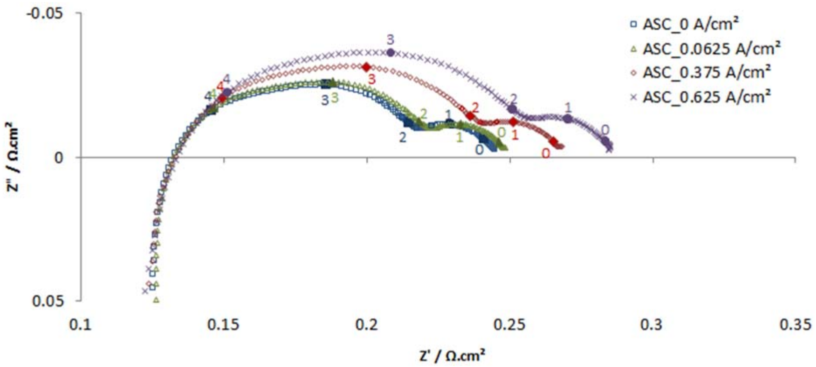
MSC – t120



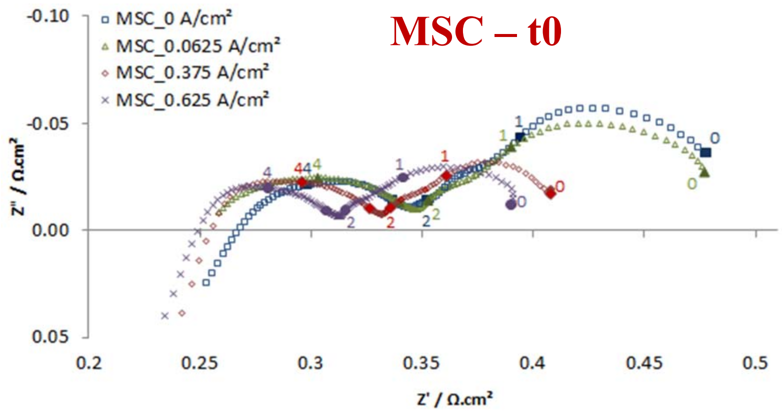
MSC **[10^3 Hz – 0.5 Hz] ➔ R_{pol} ↗ for [10^3 Hz – 10^2 Hz] and [10 Hz – 0.5 Hz]**
whatever i applied

- **EIS vs time – EL mode 80%H_2O + 20%H_2 (i = -0.25 A/cm²)**

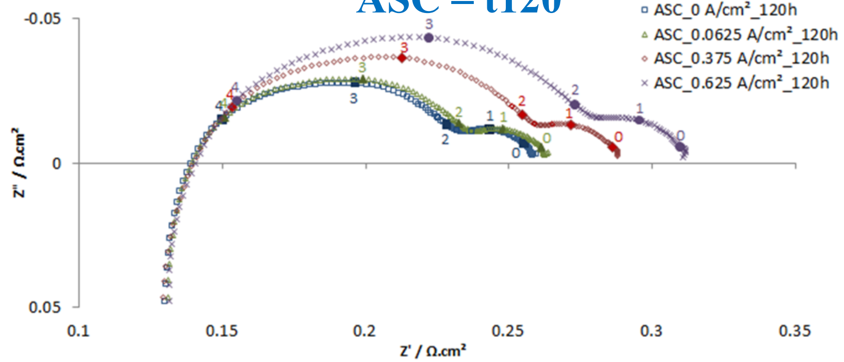
ASC – t0



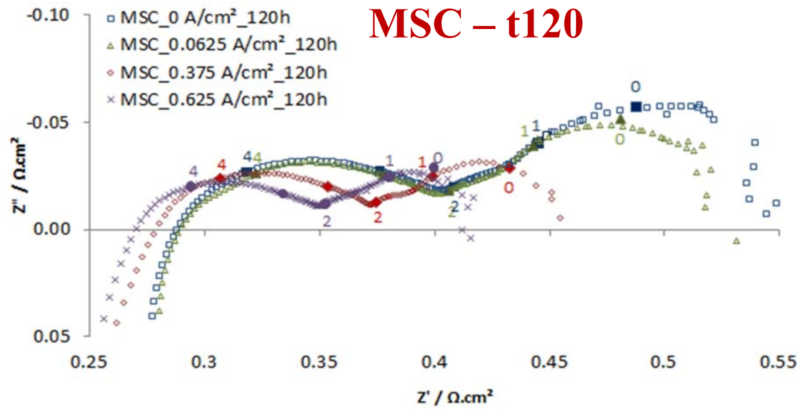
MSC – t0



ASC – t120



MSC – t120



MSC **[10^3 Hz – 0.5 Hz] ➔ H_2 electrode charge transfer** ([10^3 Hz – 10^2 Hz]) **and H_2 electrode diffusion + conversion** ([10 Hz – 0.5 Hz]) **affected [1-3]** over time from lower i applied

[1] A. Leonide, V. Sonn, A. Weber, E. Ivers-Tiffée, J. Electrochem. Soc., 155 (2008) B36-B41
[2] A. Nechache, B.A. Boukamp, M. Cassir, A. Ringuedé, Electrochim. Acta 210 (2016) 596-605
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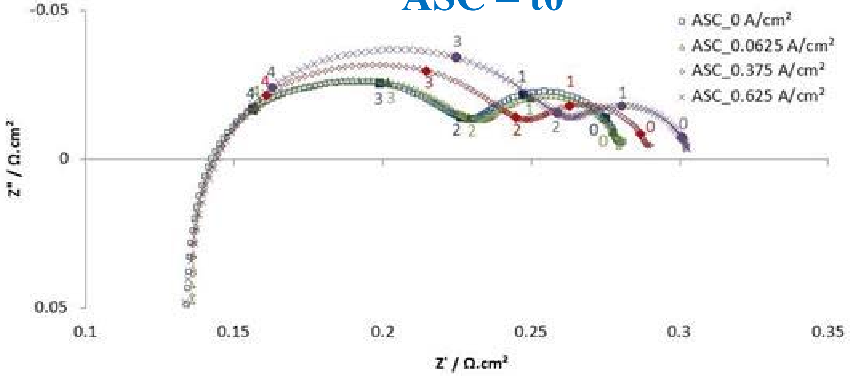
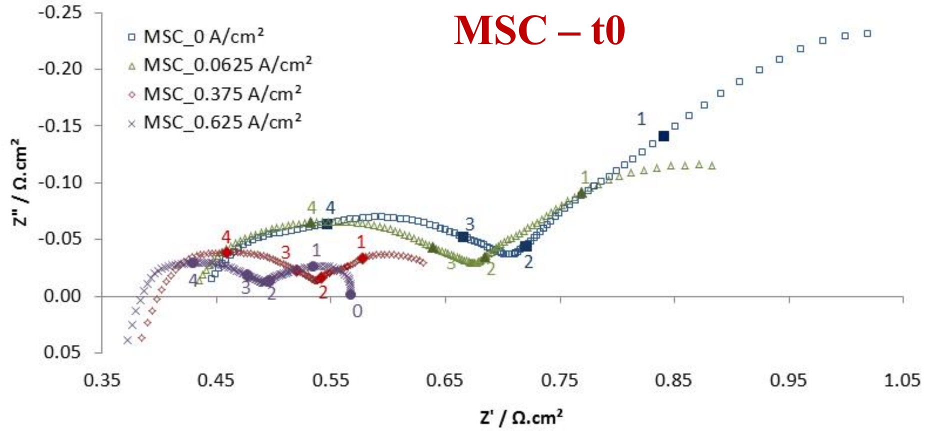
III. Degradation study

- **EIS vs time – co-EL mode 80%H_2O + 12.5%CO_2 + 7.5%H_2 (i = -0.25 A/cm²)**

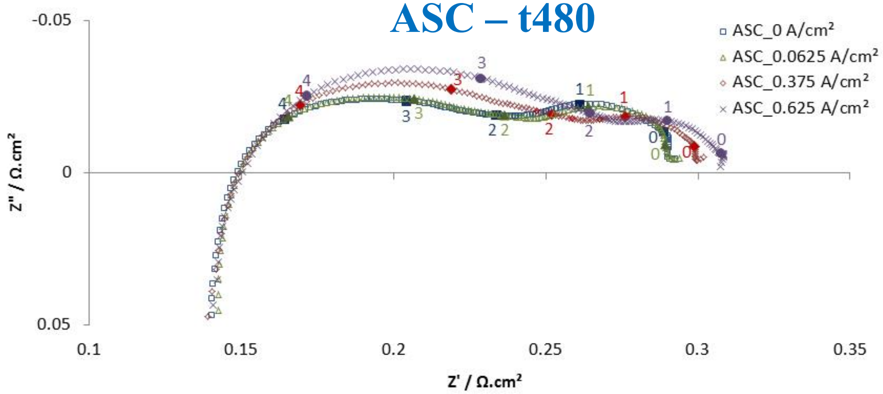
ASC – t0



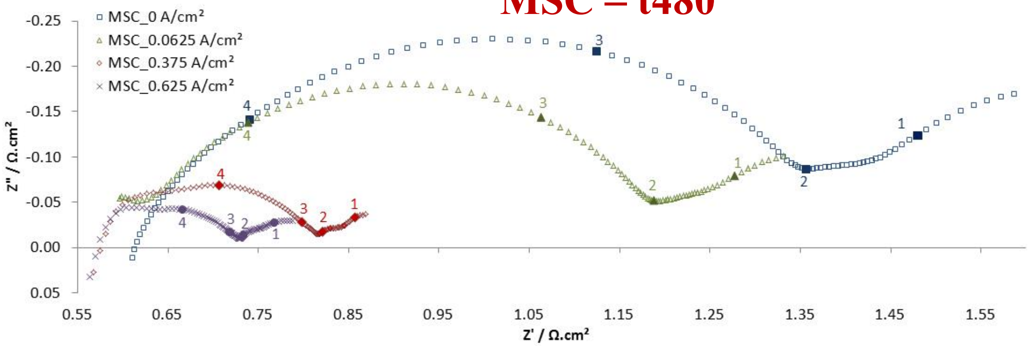
MSC – t0



ASC – t480



MSC – t480



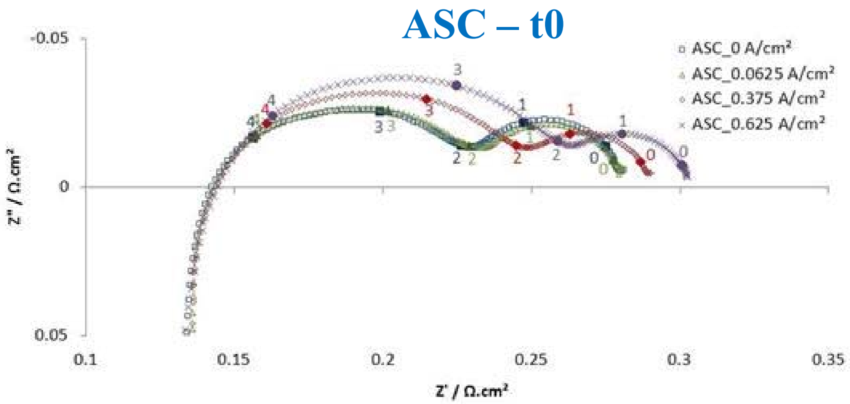
MSC **R_{ohm} ↘ when i ↗ ➔ not stable**

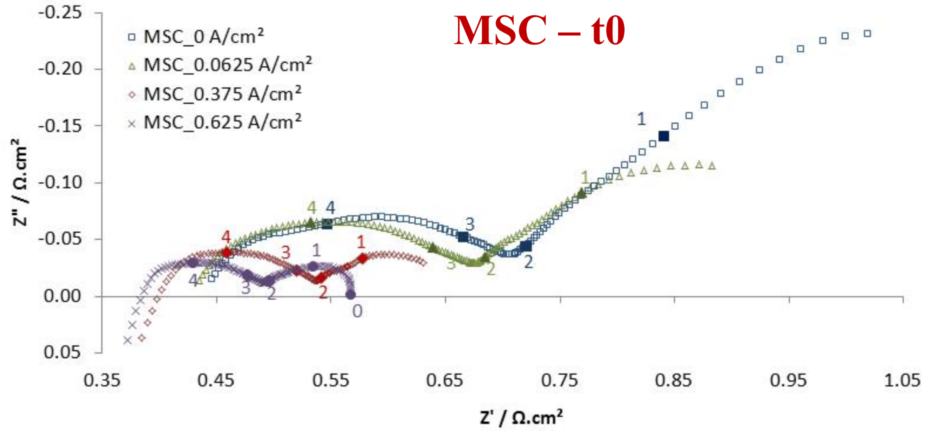
➔ electrode/electrolyte interface behavior changing with i ?!

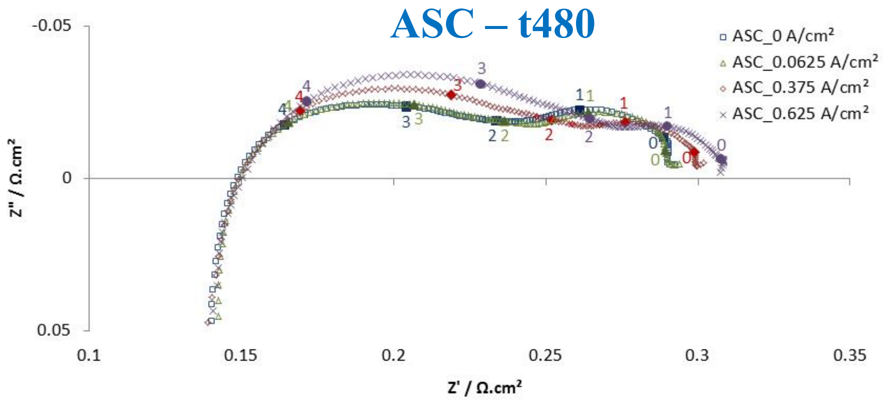
DLR

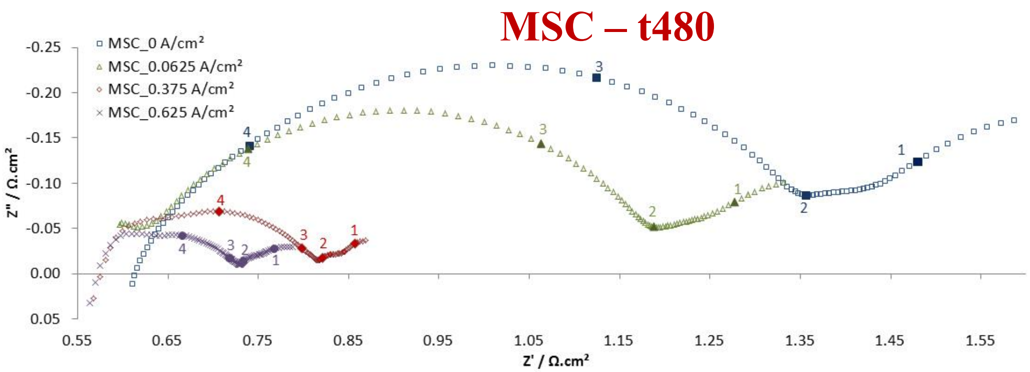
III. Degradation study

- **EIS vs time – co-EL mode 80%H_2O + 12.5%CO_2 + 7.5%H_2 (i = -0.25 A/cm²)**









MSC [10^5 Hz – 10^3 Hz] ➔ **frequency shift + R_{pol} ↗ over time** whatever i applied

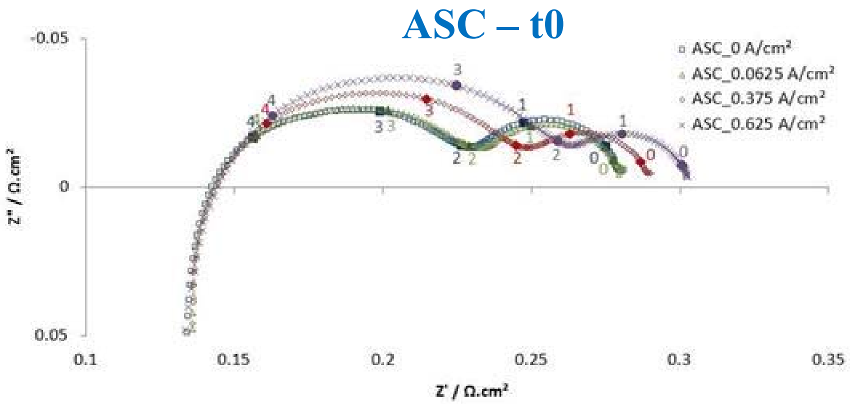
➔ **H_2 electrode charge transfer related phenomena [1-3] affected** over time from lower i applied

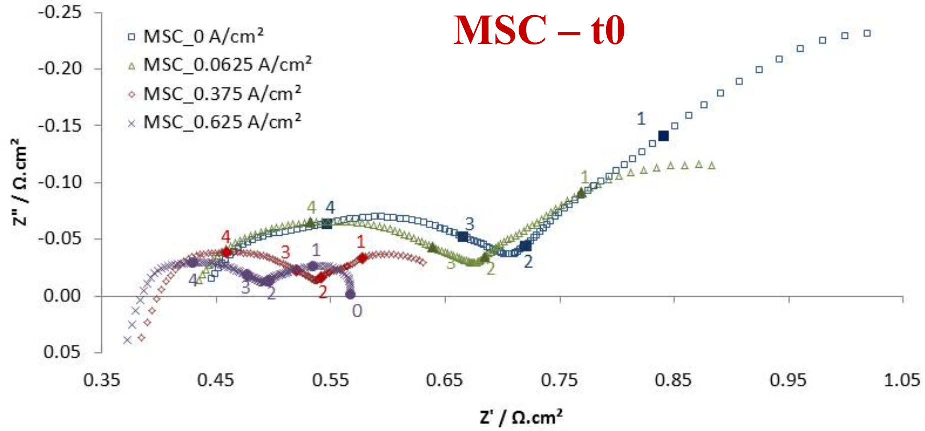
[1] A. Leonide, V. Sonn, A. Weber, E. Ivers-Tiffée, J. Electrochem. Soc., 155 (2008) B36-B41
[2] A. Nechache, B.A. Boukamp, M. Cassir, A. Ringuedé, Electrochim. Acta 210 (2016) 596-605
[3] A. Hauch, K. Brodersen, M. Chen, M.B. Mogensen, Solid State Ionics 293 (2016) 27-36

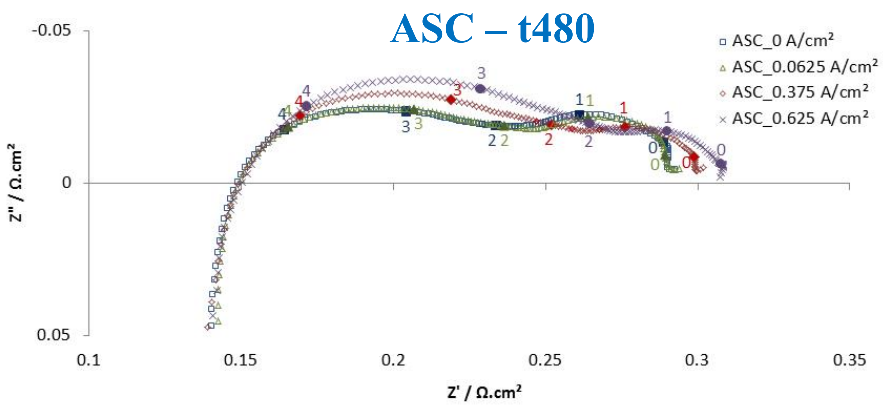
DLR

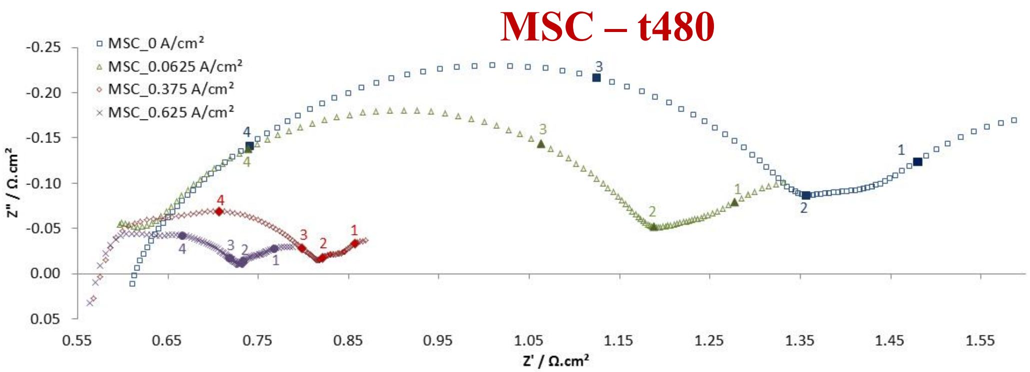
III. Degradation study

- **EIS vs time – co-EL mode 80%H_2O + 12.5%CO_2 + 7.5%H_2 (i = -0.25 A/cm²)**









MSC [10^3 Hz – 1 Hz] ➔ **significant R_{pol} ↗** **for [10^3 Hz – 10^2 Hz] and [10 Hz – 1 Hz]** at lower i applied

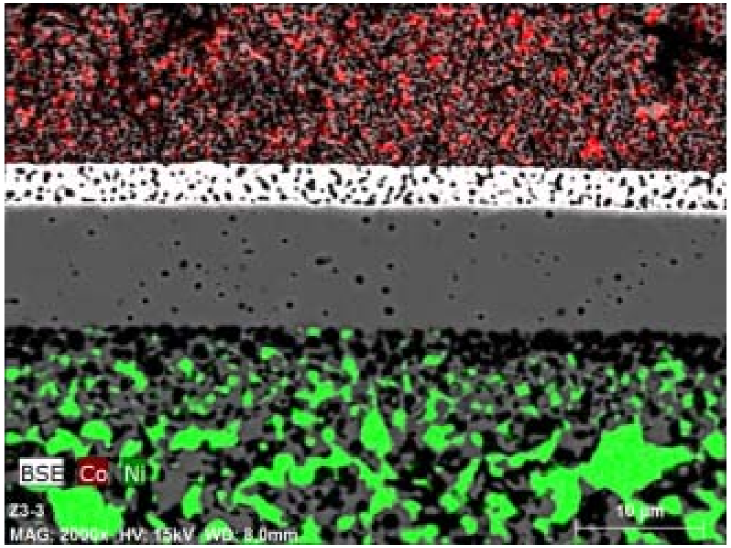
➔ **no significant freq. shift + R_{pol} increase** at higher i applied

➔ **effect of co-EL work not clear yet…**

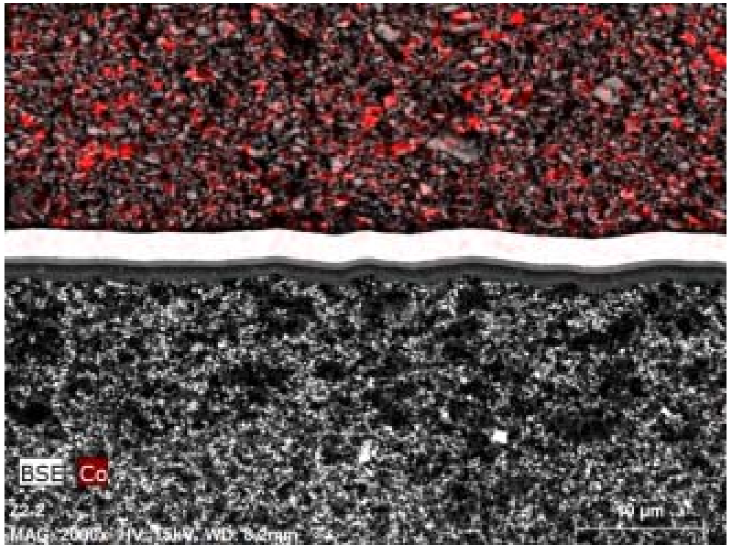
DLR

III. Degradation study

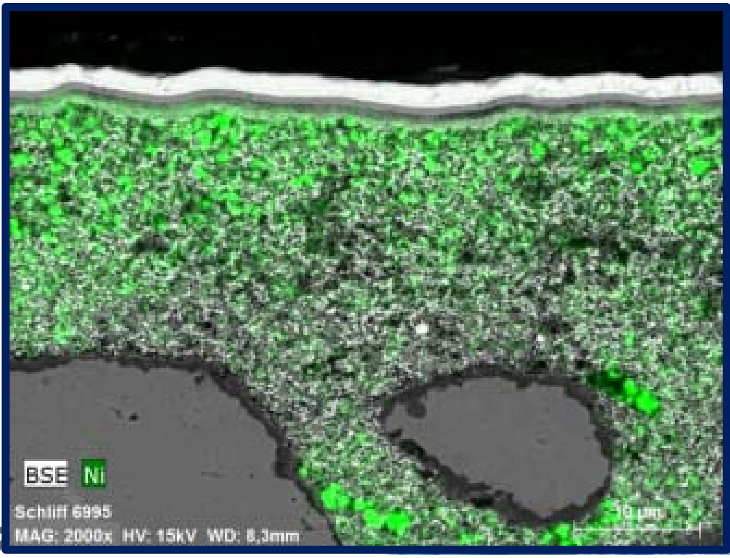
- **SEM cross section of tested MSC**



Anode supported cell



Metal supported cell, no Ni infiltration / no current load

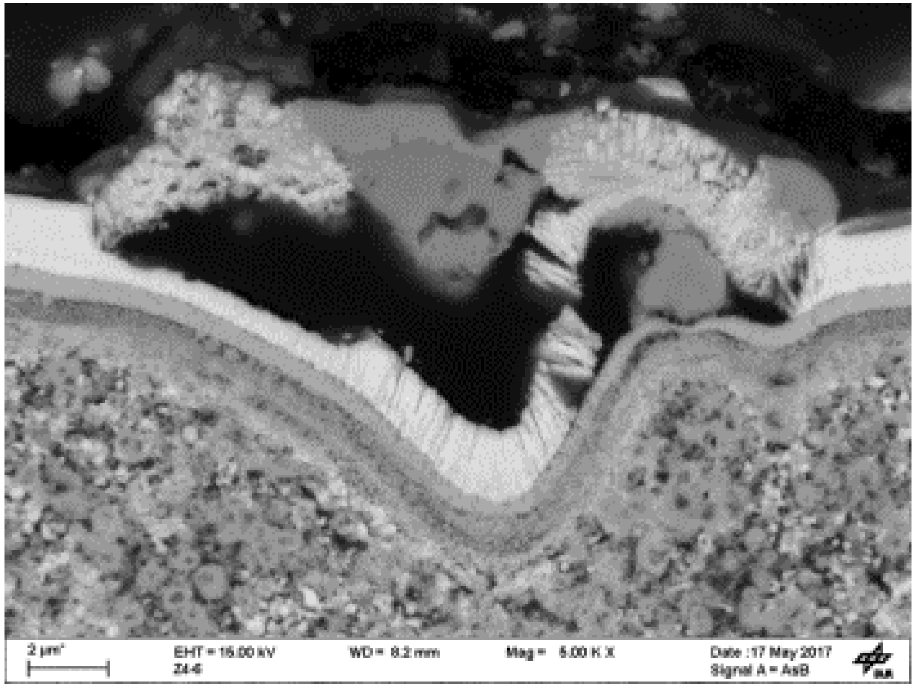


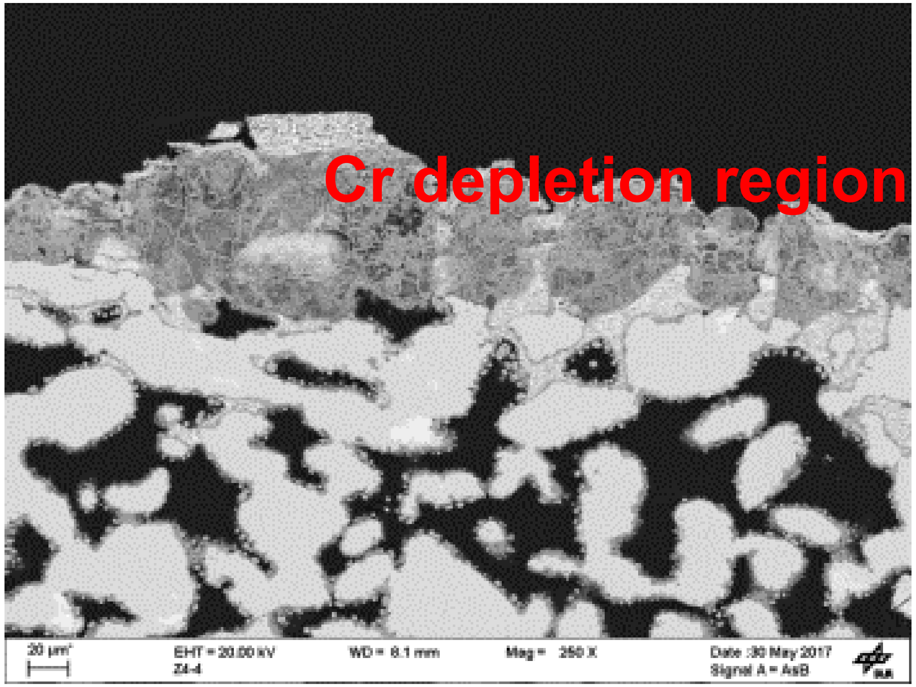
Metal supported cell

- **No Ni depletion / significant Ni coarsening in AFL**
- **Electrolyte with good mechanical stability**
- **Pores are rarely found in the thin-film electrolyte layer after SOEC operation**
- **Delamination of LSCF Air electrode**

III. Degradation study

- **Defects in thin film electrolyte**

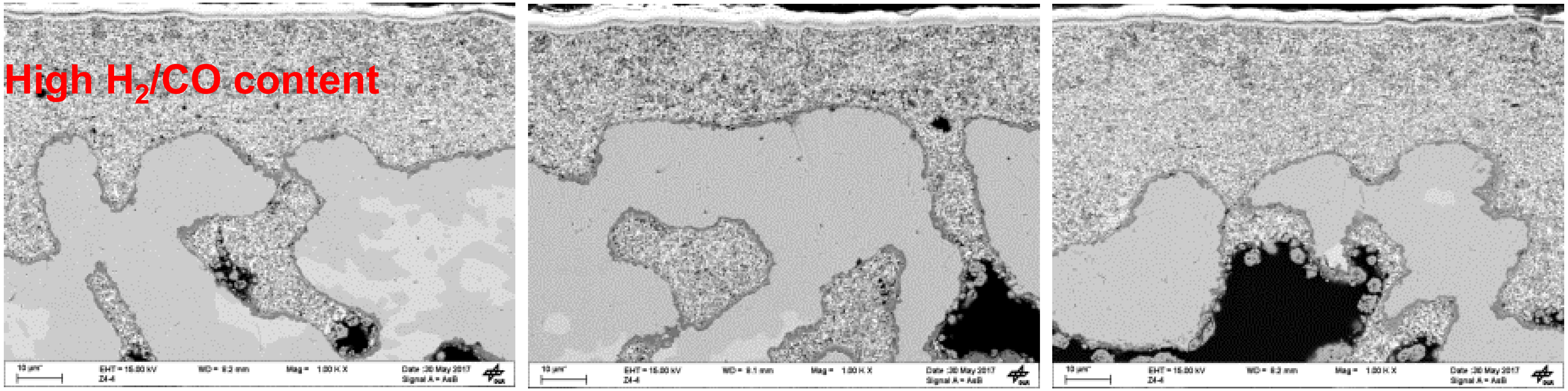


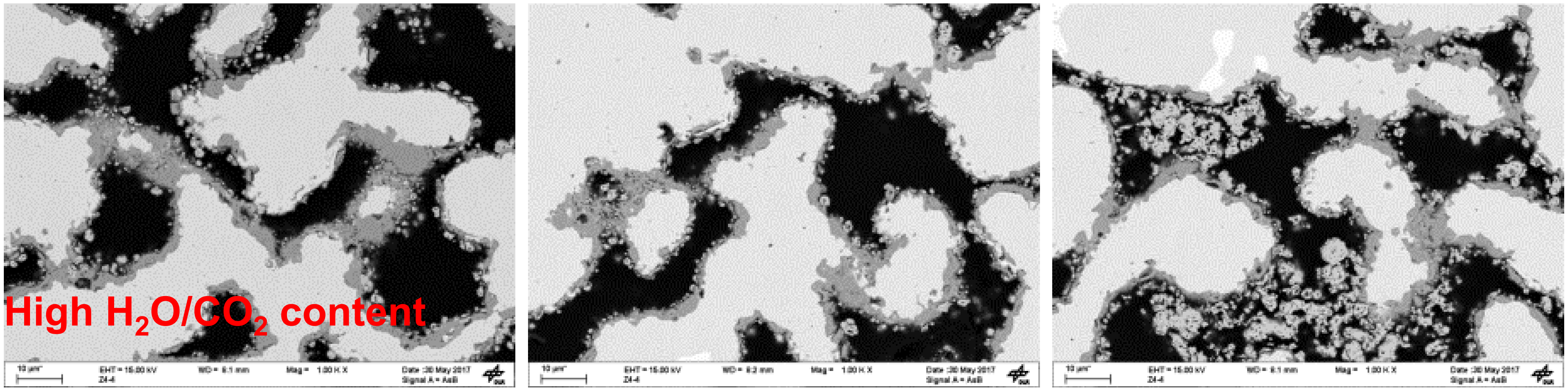


III. Degradation study

➢ **Chromia scale and nickel particle in MSC**

Internal interface: thin chromia scale and fine nickel particles





External Interface: thick chromia scale and coarsened nickel particles

Outline

I. Metal-supported cell presentation

II. Performance study

III. Degradation study

IV. Conclusions - Prospects

IV. Conclusions - Prospects

➢ Conclusions

- over 2500 h performance + degradation study of MSC
- **promising performances** shown in FC, EL and co-EL modes
- **huge MSC degradation** over time during electrolysis work, especially in co-EL mode
- **H_2 electrode charge transfer and H_2 electrode diffusion + conversion affected**
- influence of i applied not clear yet

➢ Prospects

- thorough parametric study in FC, EL and co-EL modes
- perform more degradation studies (≠ i and gas comp.) in EL and co-EL modes
- better understanding of reaction mechanisms influencing perf. + deg.

Acknowledgements

Part of this work was supported by the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n°303429.

Thank you for your attention!
Questions/Comments?