Electrochemical Impedance Spectroscopy of Unitized Reversible Fuel Cells (URFC)

International Workshop on Impedance Spectroscopy (IS 2009)

22.10.2009, Chemnitz, Germany

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in der Helmholtz-Gemeinschaft

Content

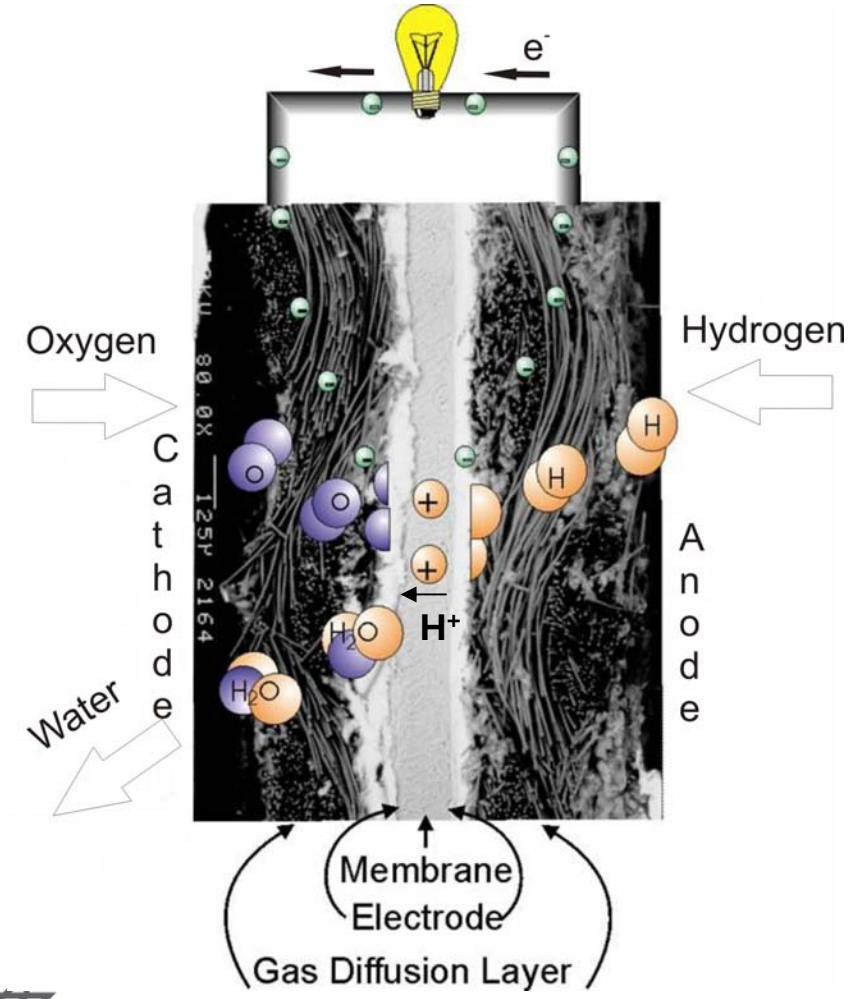
Introduction

- Advantages to secondary batteries
  - specific energy and energy density are higher then secondary batteries
  - modular
  - easy integration in existing systems (e.g. Ariane 5)
  - fast “recharging” option

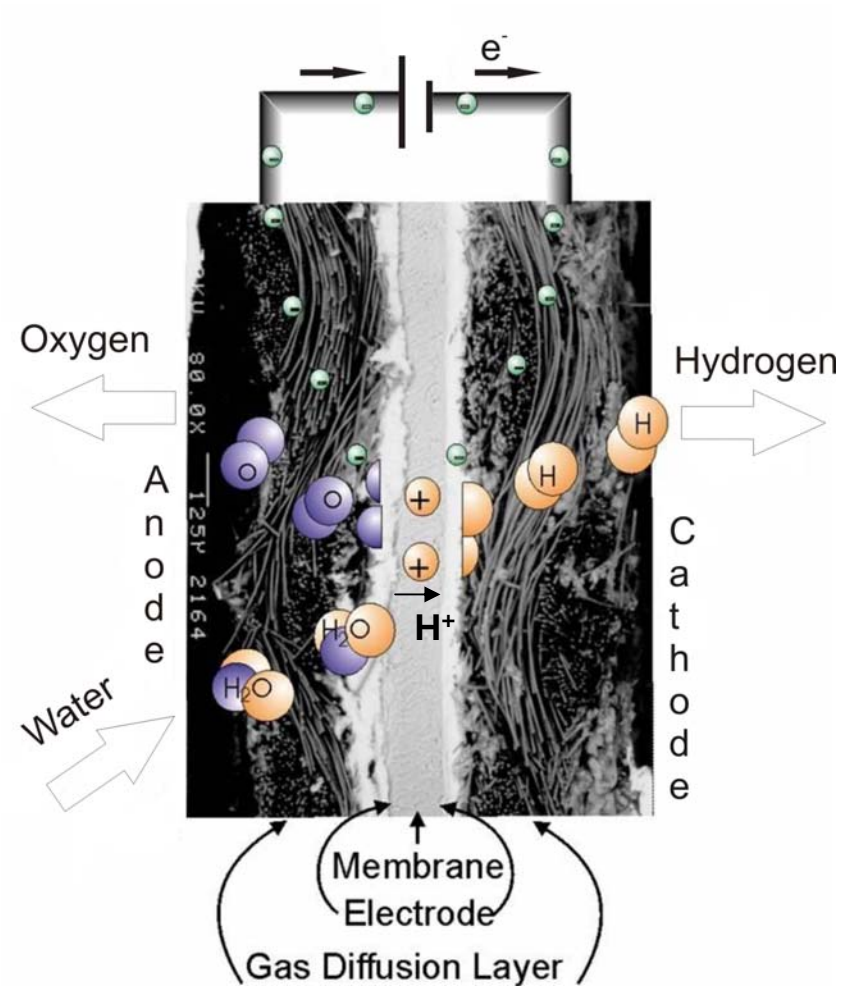
- Stand-alone systems without grid connection
  - manned (long-term) space missions
  - UAV (unmanned air vehicle)
  - local stationary energy supply

Introduction

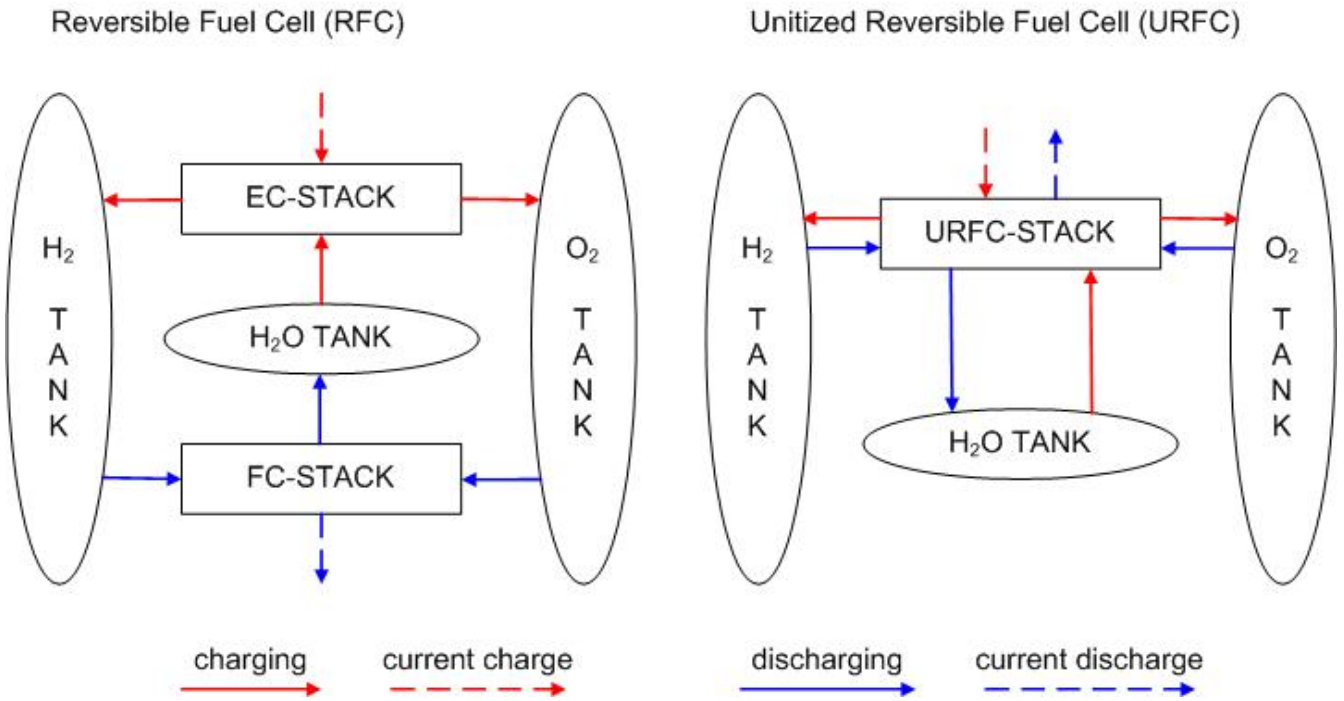
Fuel Cell



Electrolysis



Reversible Fuel Cell



☺ - optimized catalysts
- changing operation mode more easier (e.g. no time delay)

☹ - high mass
- high volume

☺ - reduced mass and volume
- cost reduction
- increased reliability (less components)

☹ - different catalyst on one electrode
- changing conditions at MEA

Preparation

- Dry-Spraying-technique by DLR

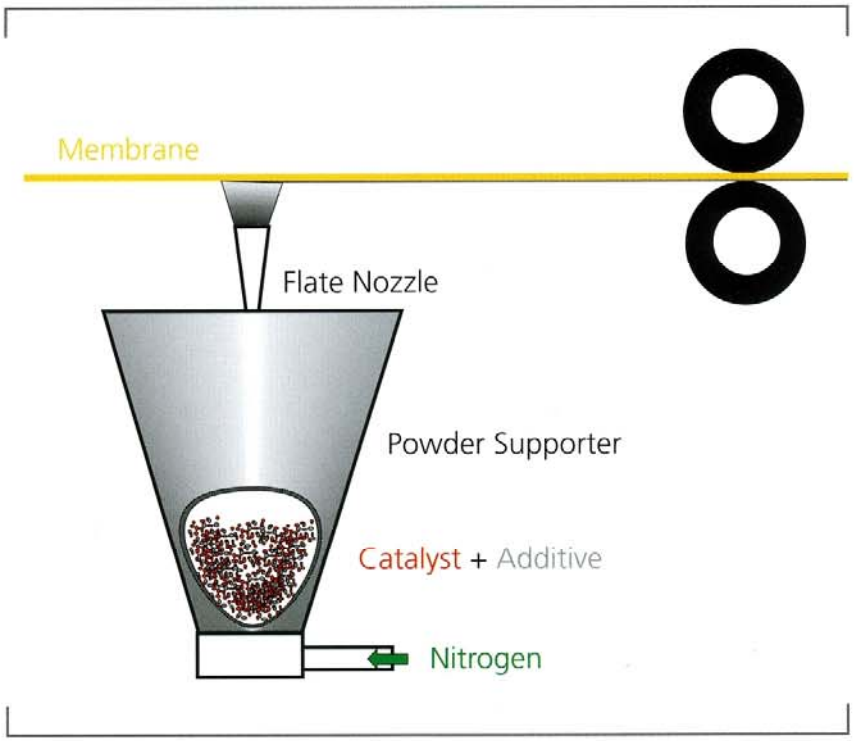


Figure 1: Principle of dry coating method for electrode production

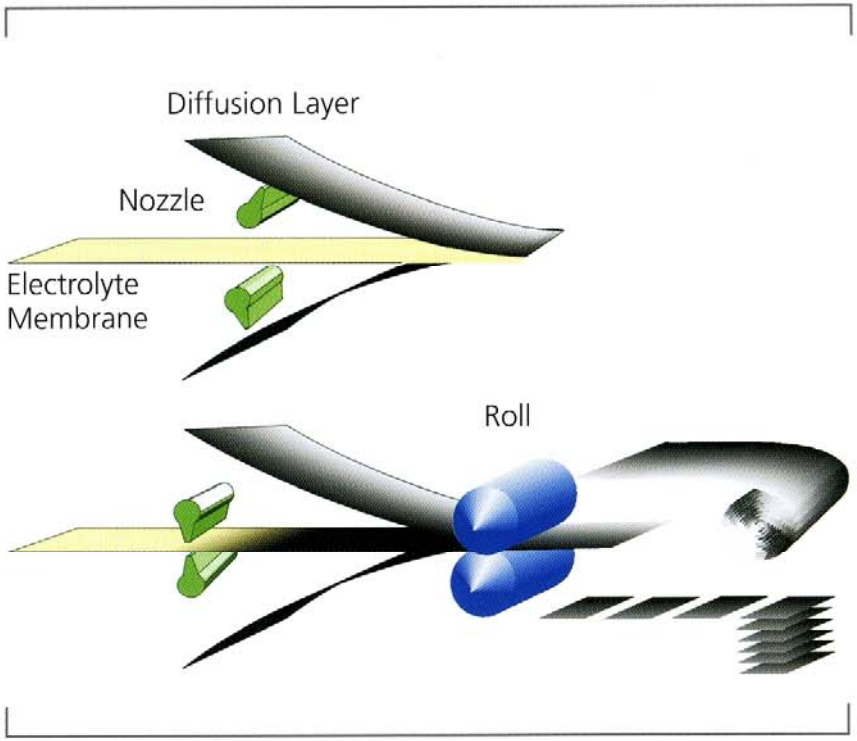


Figure 2: Production of membrane electrode assemblies by dry spray coating. Two alternative methods are shown.

Preparation

- fast (no evaporation of solvent, no ink preparation)
- simple (few steps in preparation)
- flexible
  - several mixture of catalysts and additives
  - different kind of electrodes (DMFC, PEFC,…)
  - various thickness
  - different loadings
  - various geometries of the electrodes
  - coating directly on membrane

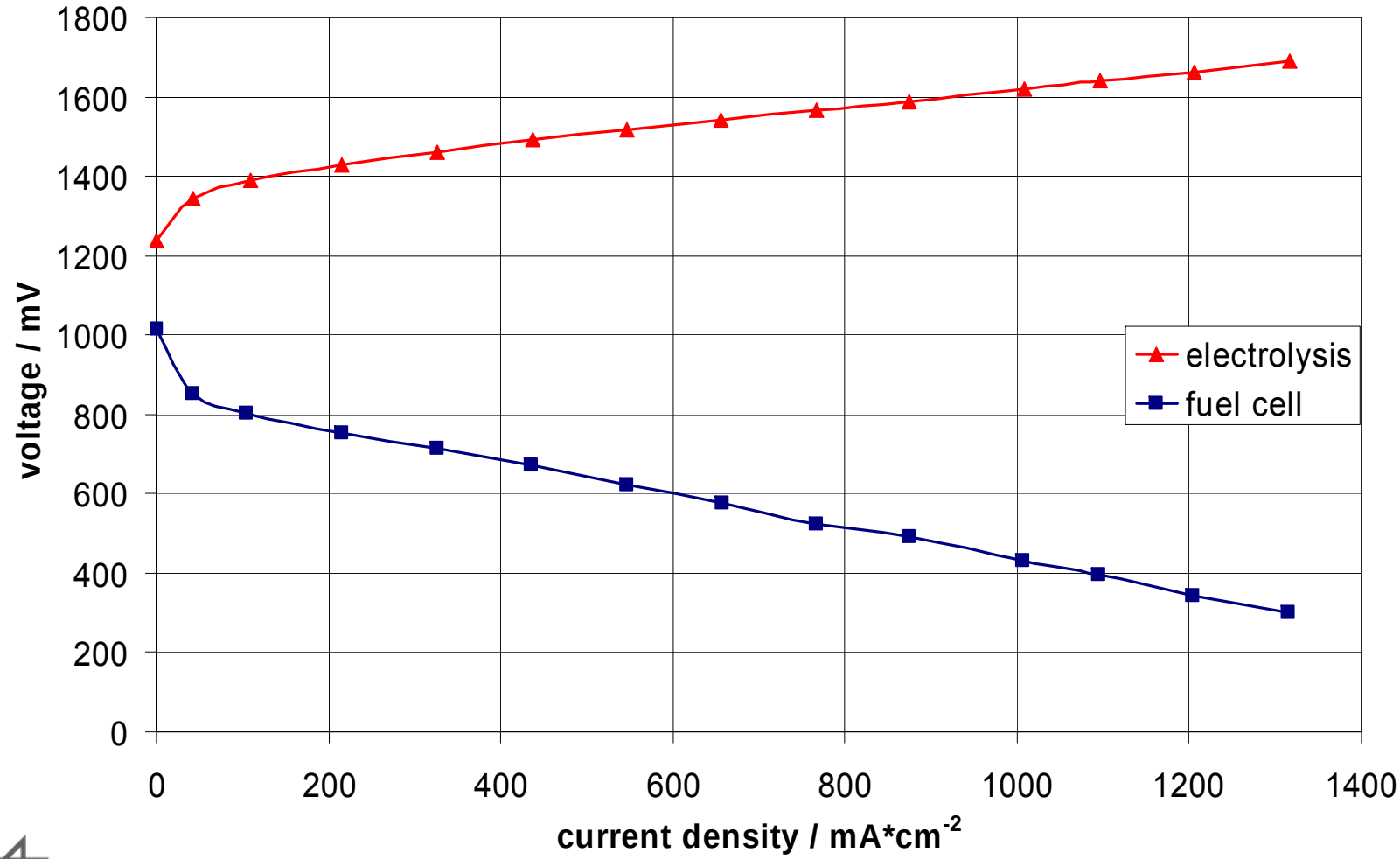
Experimental setup

Conditions

- catalysts
  - H_2 electrode: Pt black + 30wt% Nafion
loading ~ 1,56 mg/cm²
  - O_2 electrode: Pt black + IrO_2 (1:1) + 30wt% Nafion
loading ~ 2,08 mg/cm²
- membrane: Nafion 1135
- backing: SGL 35 DC
- active area: 23 cm²
- cell temperature: ~ 80°C (FC) / ~ 95°C (EC)
- pressure: ambient
- gas flow
  - H_2: 250 sccm (fully humidified)
  - O_2: 400 sccm (fully humidified)

Experimental setup

Polarization curves



Experimental Setup

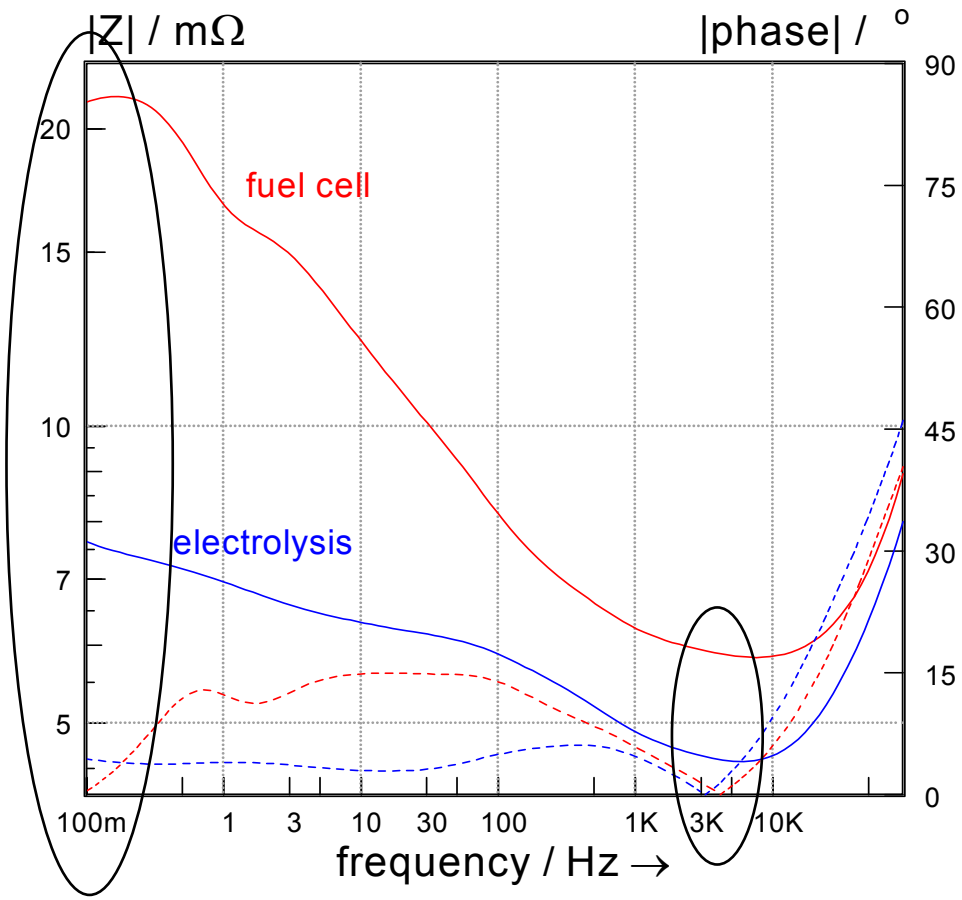
EIS

- Zahner IM 6 + PP 240
- frequencies: 30 mHz -> 100 kHz
- simulation: 100 mHz -> 20 kHz
- <u>fuel cell mode</u>
  - potentiostatic
  - at 500 mV
  - amplitude: 10 mV

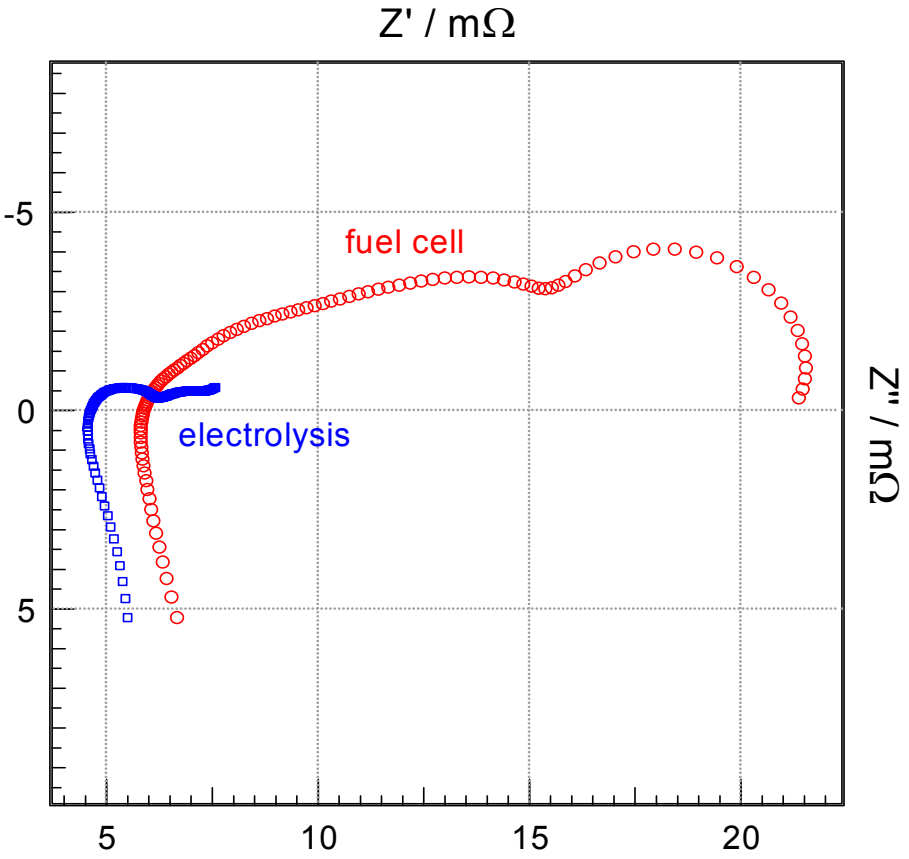
- <u>electrolysis mode</u>
  - galvanostatic
  - at 1 A/cm² (=> 23 A)
  - amplitude: 2 A

Experimental Setup

EIS

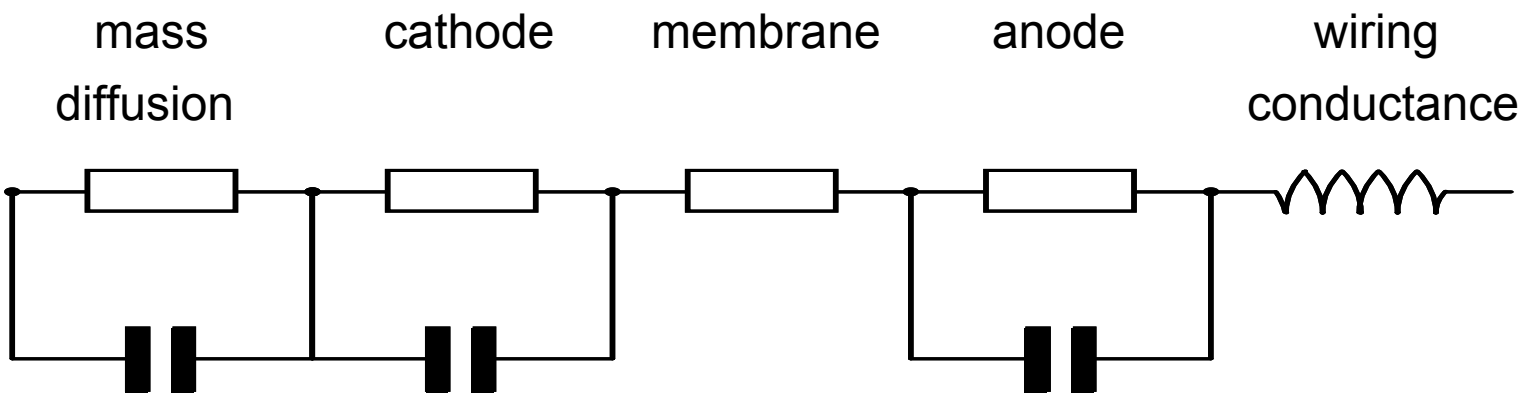


Bode plot



Nyquist plot

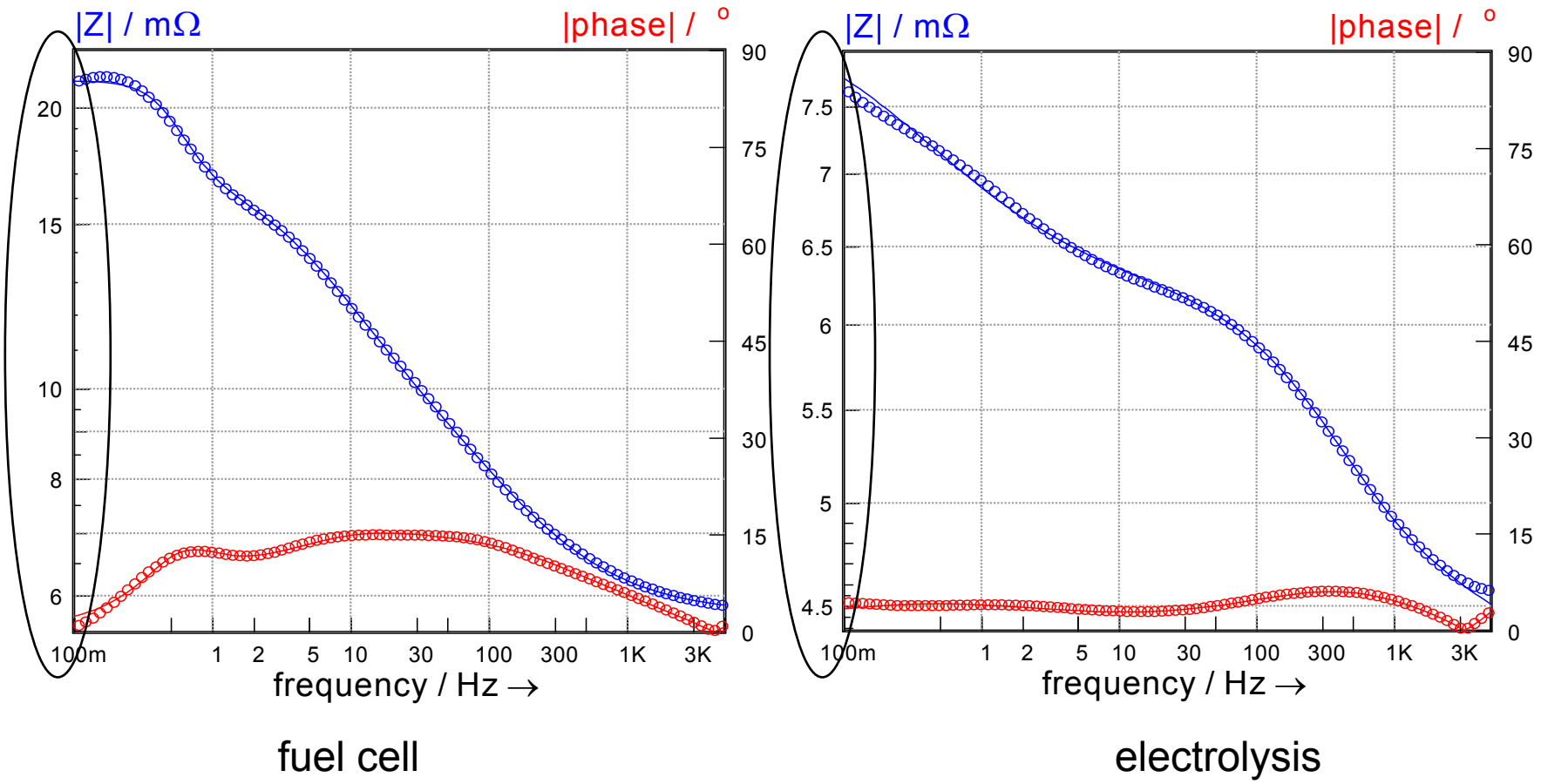
Model



limitations in gas flows because of porous structure (electrode, backing)	ohmic and ionic resistance of electrode (double layer, bulk), backing and bipolar-plate	ohmic resistance of membrane	ohmic and ionic resistance of electrode (double layer, bulk), backing and bipolar-plate	inductance through wires and Setup
< 1 Hz	1 – 100 Hz	~ 5 kHz	0,1 – 5 kHz	> 10 kHz

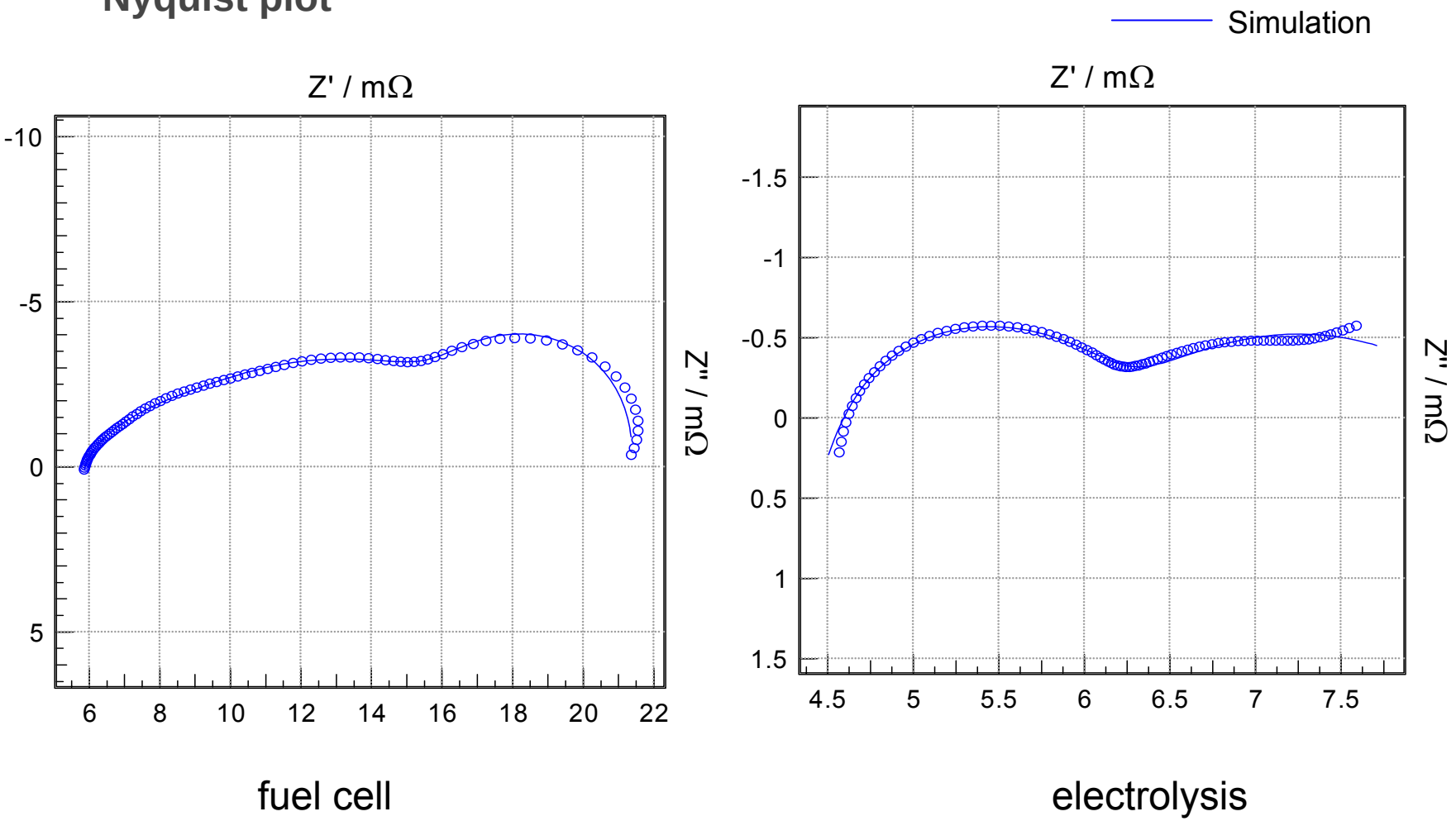
Simulation

Bode plot



Simulation

Nyquist plot

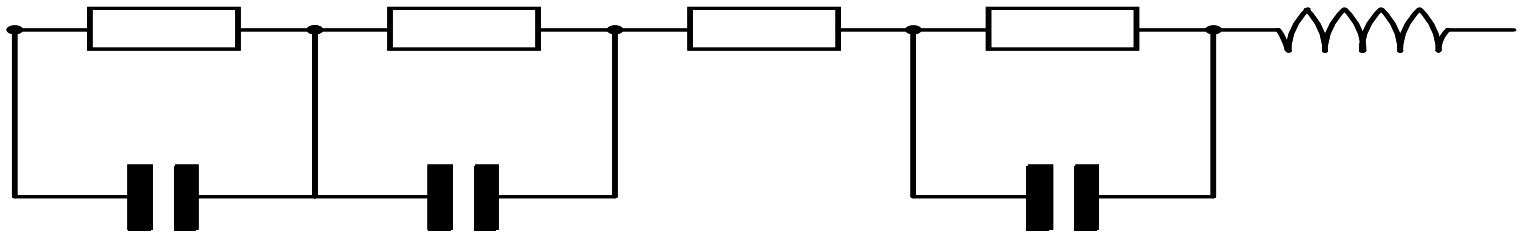


fuel cell

electrolysis

Simulation

element	fuel cell		electrolysis	
1	3,822 mΩ		2,165 mΩ	
2	413,8 F	1,224	6,712 F	0,563
3	8,552 mΩ		1,763 mΩ	
4	722,8 mF	0,715	198,1 mF	0,718
5	5,718 mΩ		3,912 mΩ	
6	3,373 mΩ		0,534 mΩ	
7	230,1 mF	0,682	23,83 mF	0,935
8	10,66 nH		18,88 nH	



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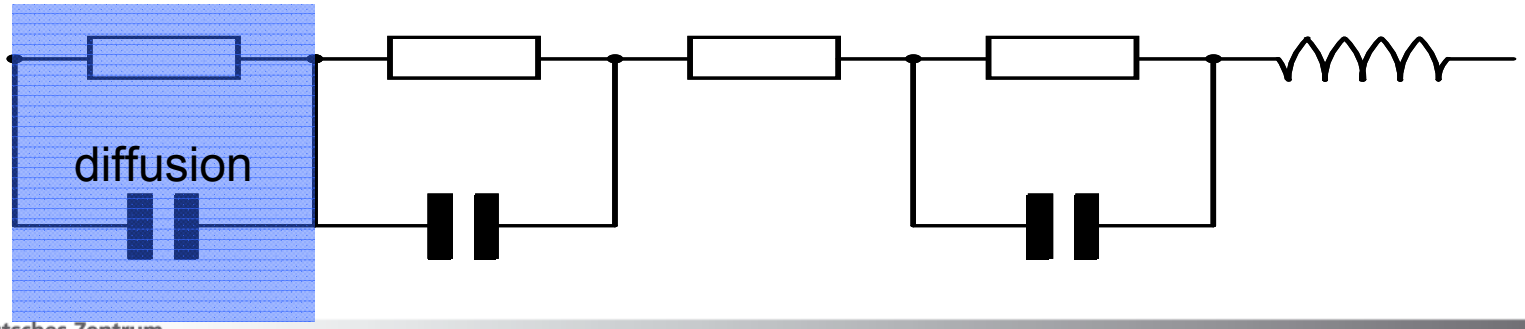

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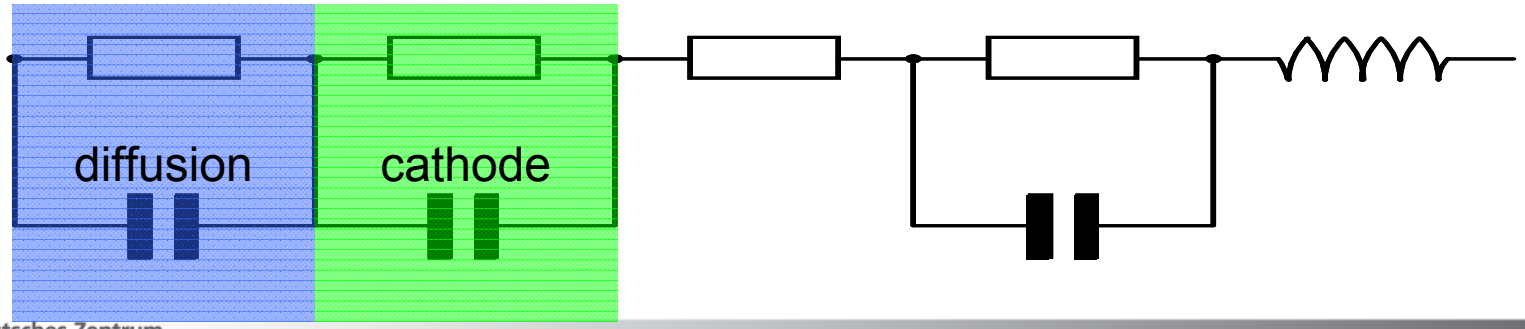

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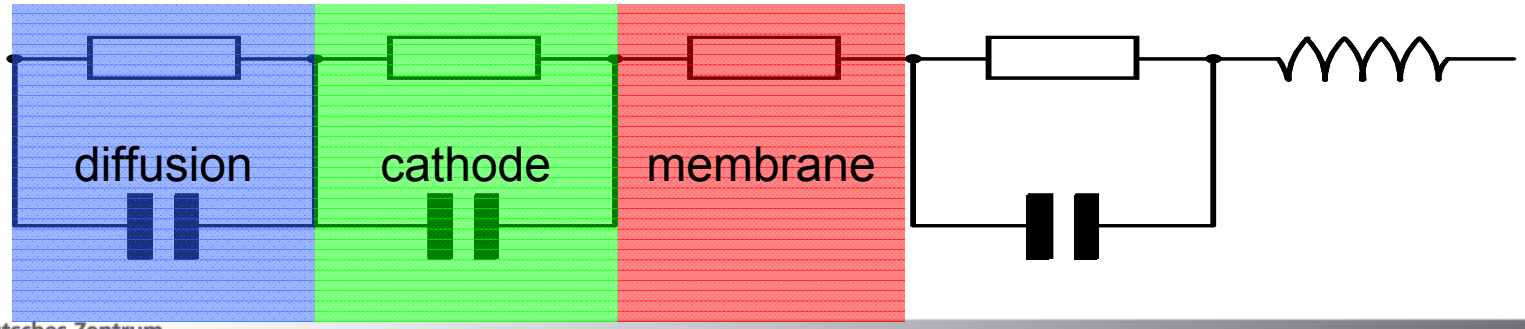

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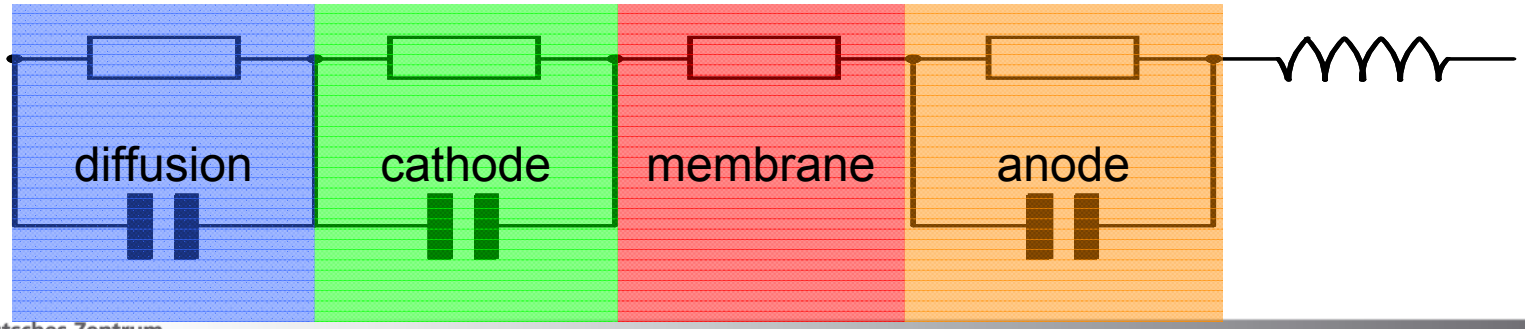

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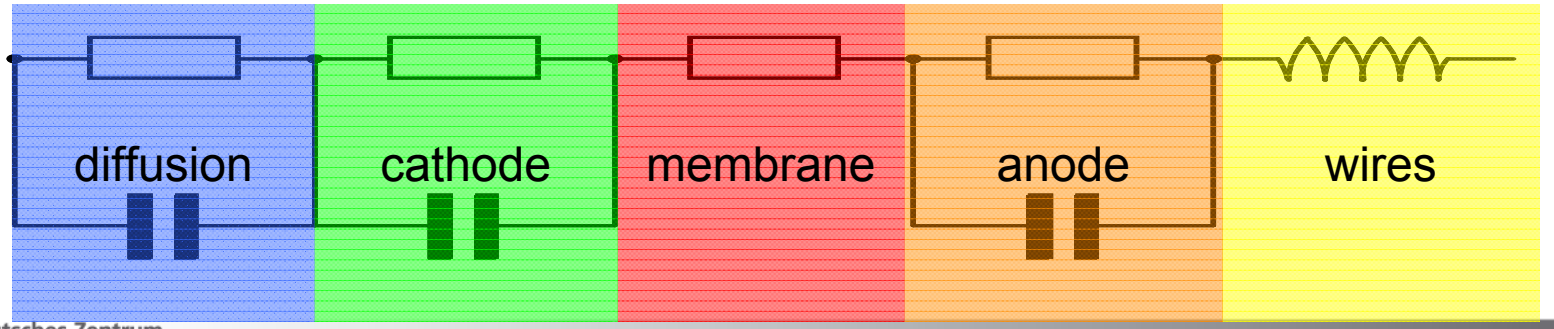
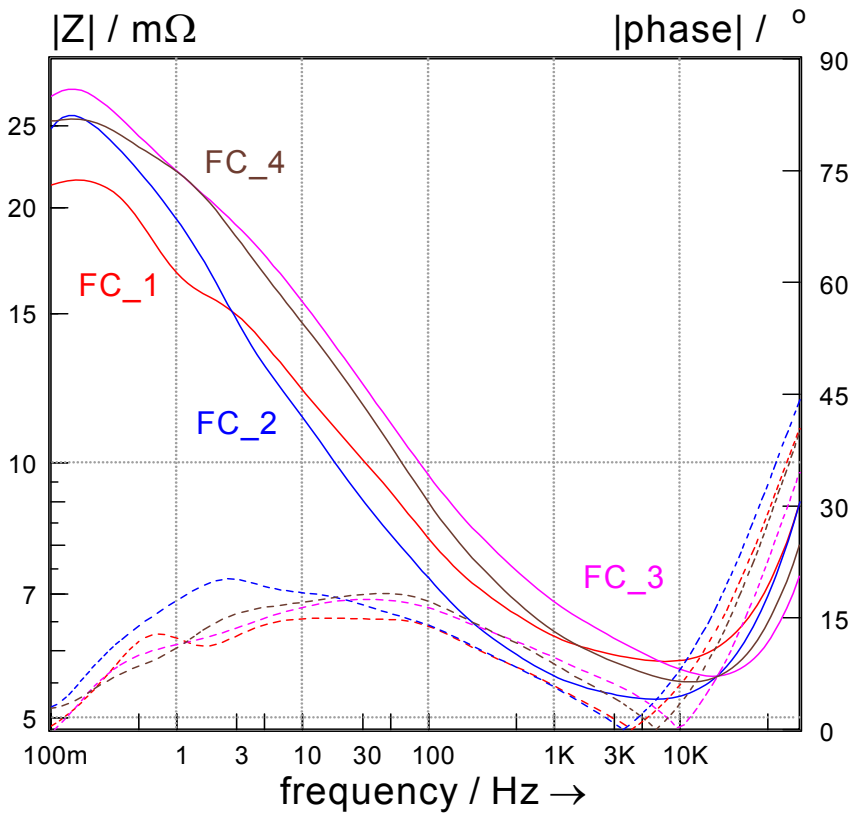
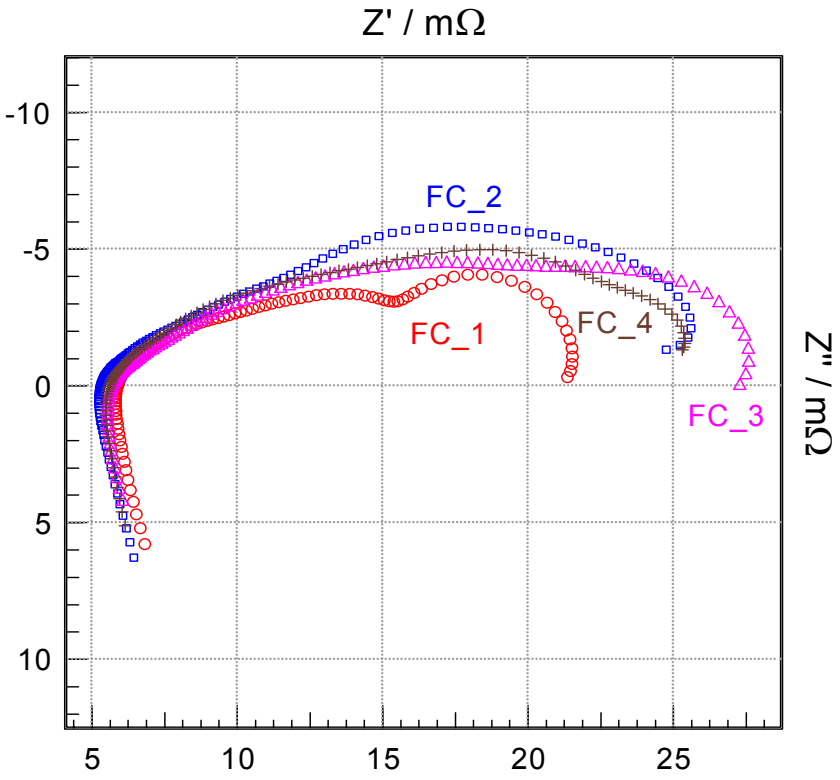


Cyclic stability

Fuel Cell





Cyclic stability

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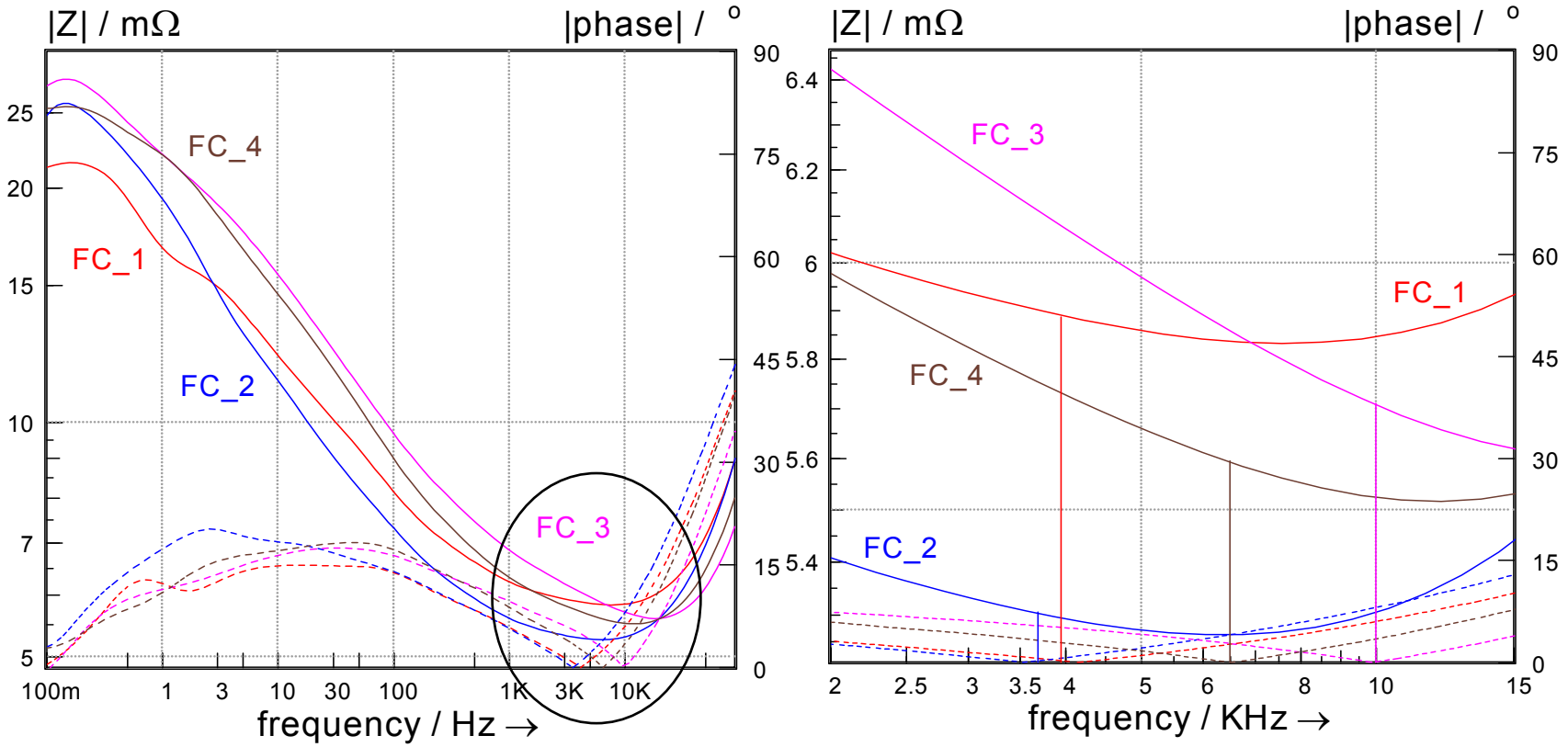
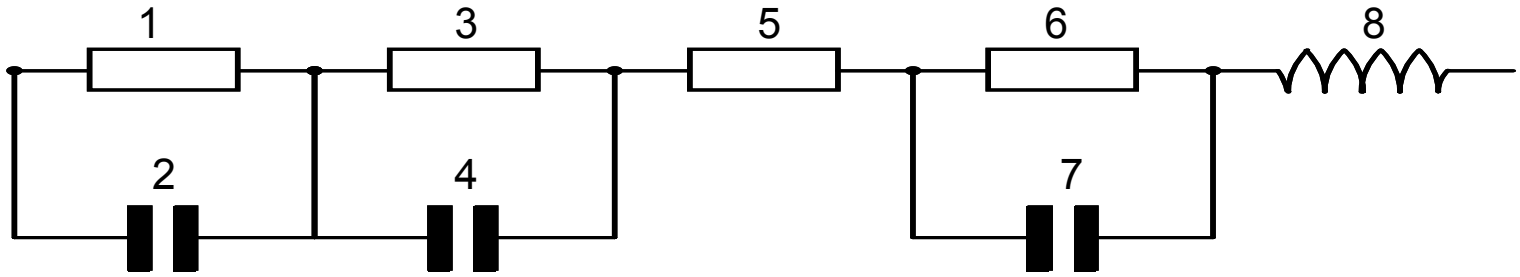


Cyclic stability

Fuel Cell

element	FC_1		FC_2		FC_3 (1)		FC_4 (1)		
1	2,873 mΩ		12,08 mΩ		8,351 mΩ		9,171 mΩ		diffusion
2	838,6 F	1,286	5,373 F	0,856	8,299 F	0,859	3,108 F	0,784	
3	13,59 mΩ		9,323 mΩ		11,01 mΩ		9,809 mΩ		cathode
4	156,1 mF	0,544	184,2 mF	0,559	258,3 mF	0,692	212,3 mF	0,636	
5	4,964 mΩ		4,525 mΩ		5,267 mΩ		5,222 mΩ		membrane
6	0,62 mΩ		0,528 mΩ		2,98 mΩ		2,246 mΩ		anode
7	3,261 µF	0,004	841,5 µF	0,234	72,89 mF	0,567	168,3 mF	0,536	
8	12,68 nH		14,18 nH		8,042 nH		10,53 nH		



(1) condition changed

Cyclic stability

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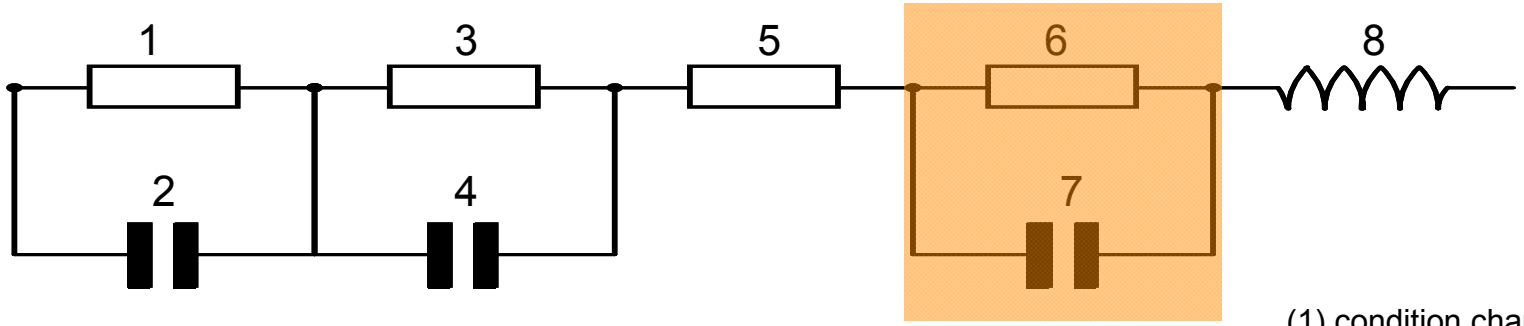

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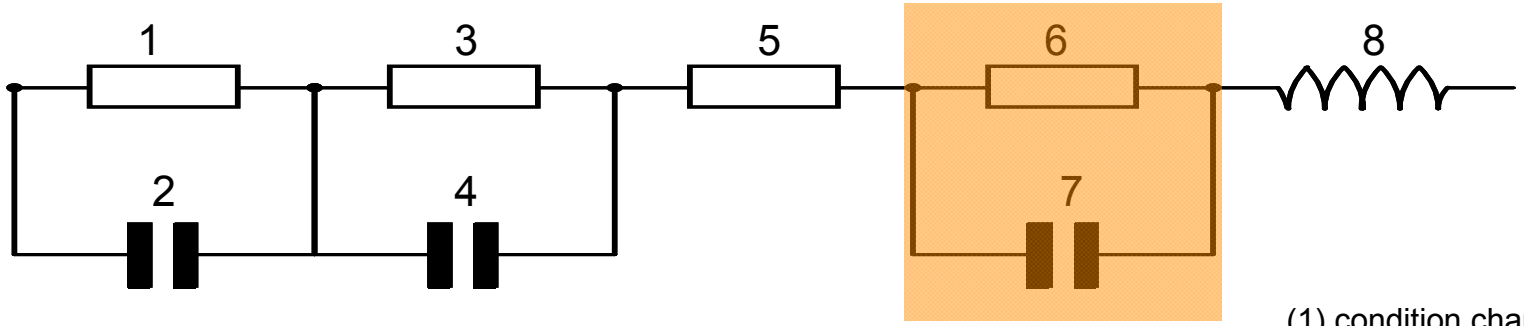

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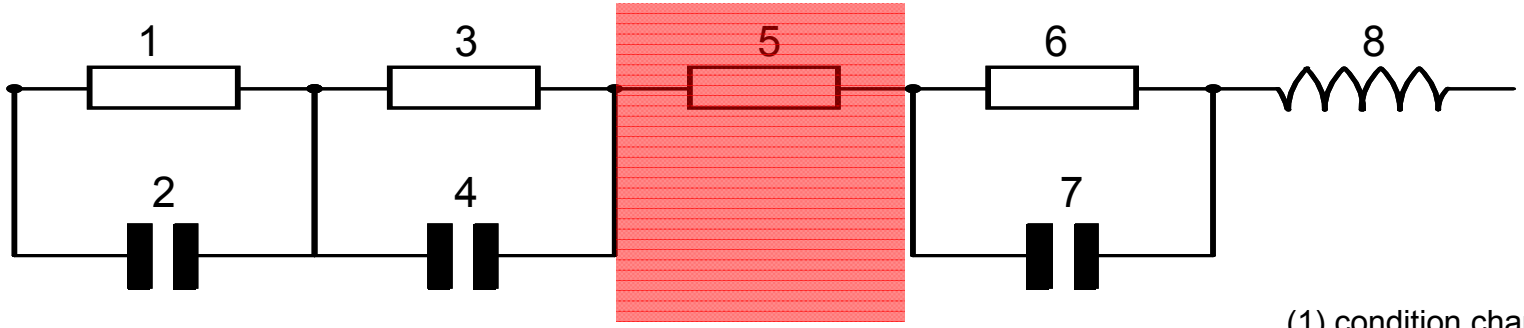

(1) condition changed

Cyclic stability

Fuel Cell

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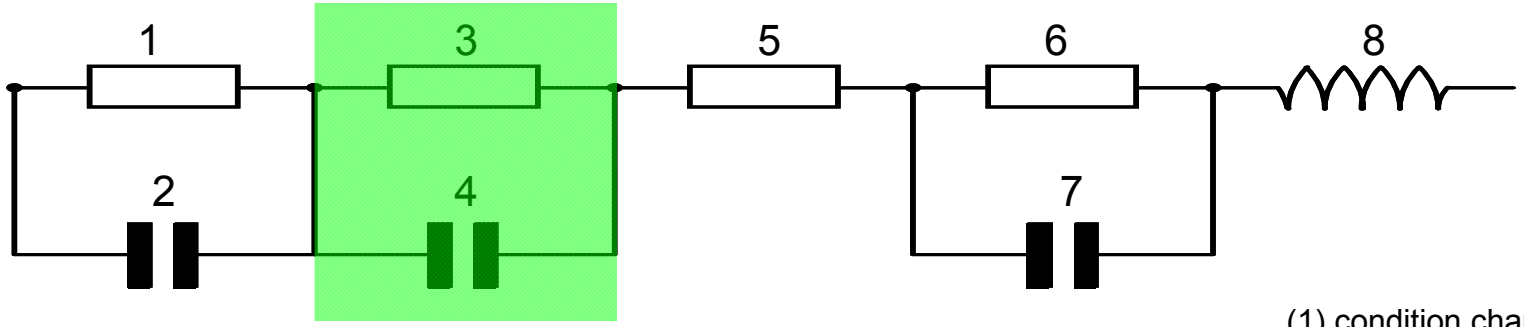
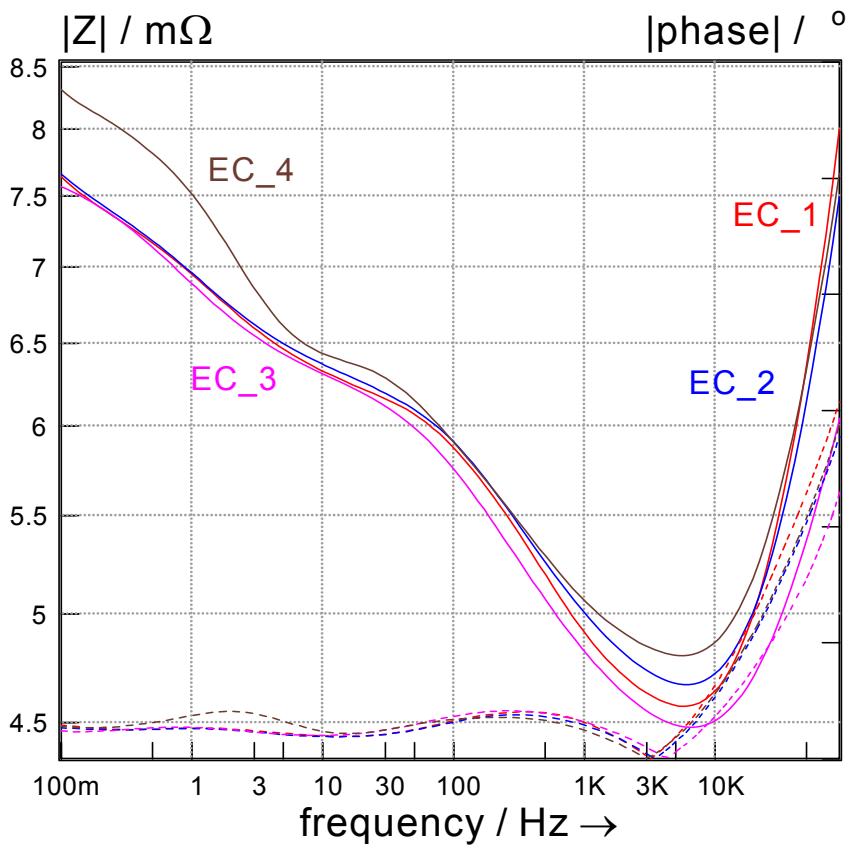
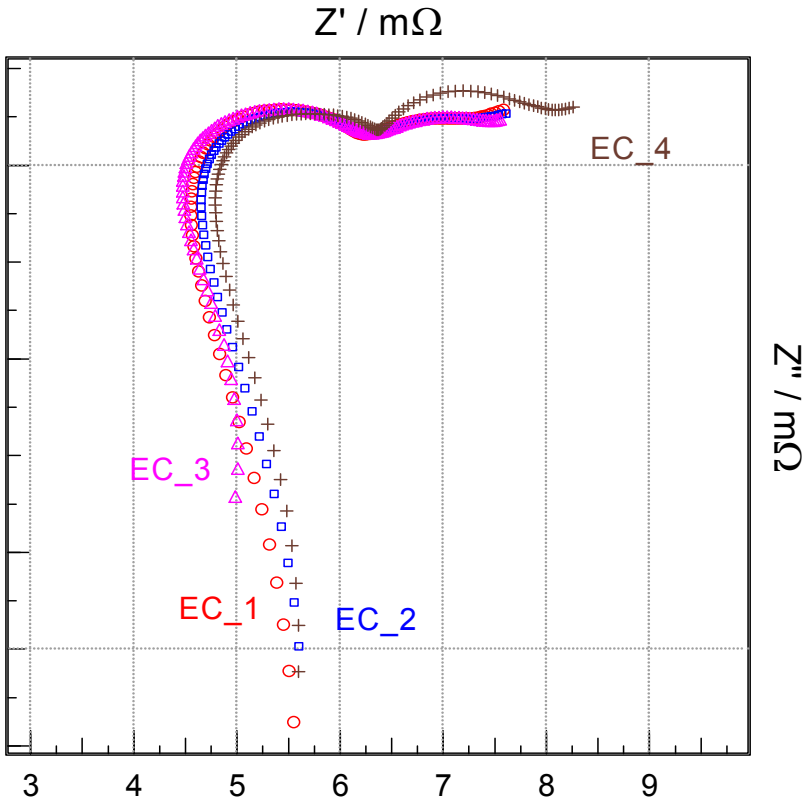


(1) condition changed

Cyclic stability

Electrolysis





Cyclic stability

Electrolysis

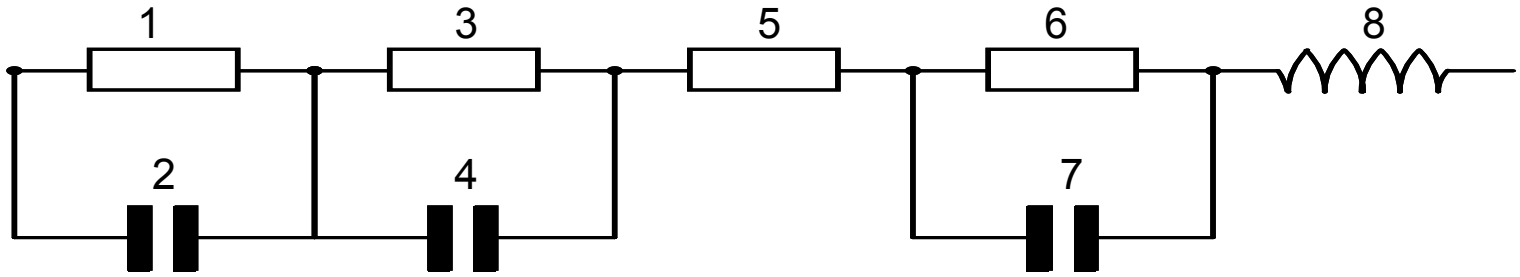
element	EC_1		EC_2		EC_3 (1)		EC_4	
1	2,262 mΩ		2,211 mΩ		1,985 mΩ		2,585 mΩ	
2	5,57 F	0,546	5,848 F	0,546	7,79 F	0,58	6,152 F	0,648
3	1,65 mΩ		1,614 mΩ		1,817 mΩ		1,455 mΩ	
4	225,4 mF	0,766	231,6 mF	0,741	226 mF	0,706	298,2 mF	0,768
5	4,322 mΩ		4,393 mΩ		4,188 mΩ		4,548 mΩ	
6	0,182 mΩ		0,206 mΩ		0,210 mΩ		0,207 mΩ	
7	2,623 mF	0,445	2,115 mF	0,564	1,526 mF	0,755	1,28 mF	0,491
8	13,3 nH		11,65 nH		8,347 nH		12,11 nH	

diffusion

cathode

membrane

anode



(1) after restart

Cyclic stability

Electrolysis

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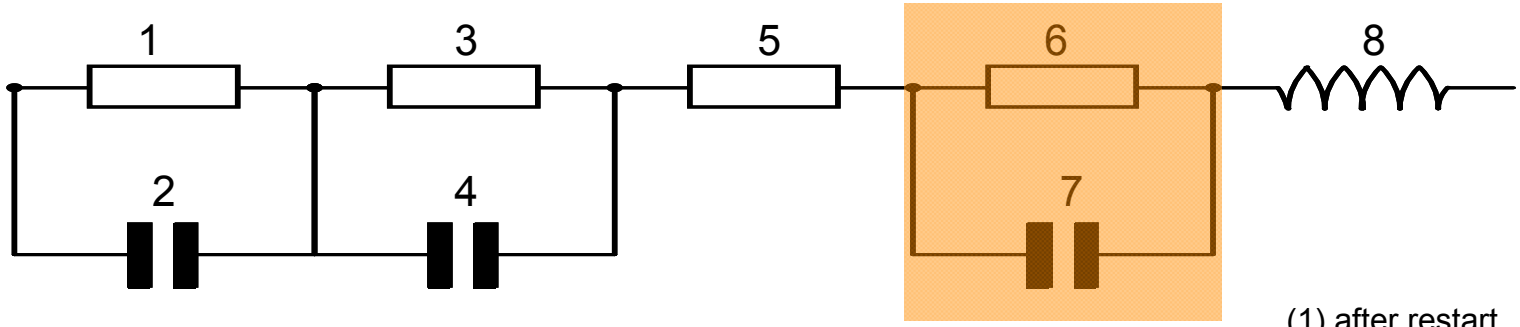
6	0,182 mΩ		0,206 mΩ		0,210 mΩ		0,207 mΩ		
7	2,623 mF	0,445	2,115 mF	0,564	1,526 mF	0,755	1,28 mF	0,491	anode
8	13,3 nH		11,65 nH		8,347 nH		12,11 nH		

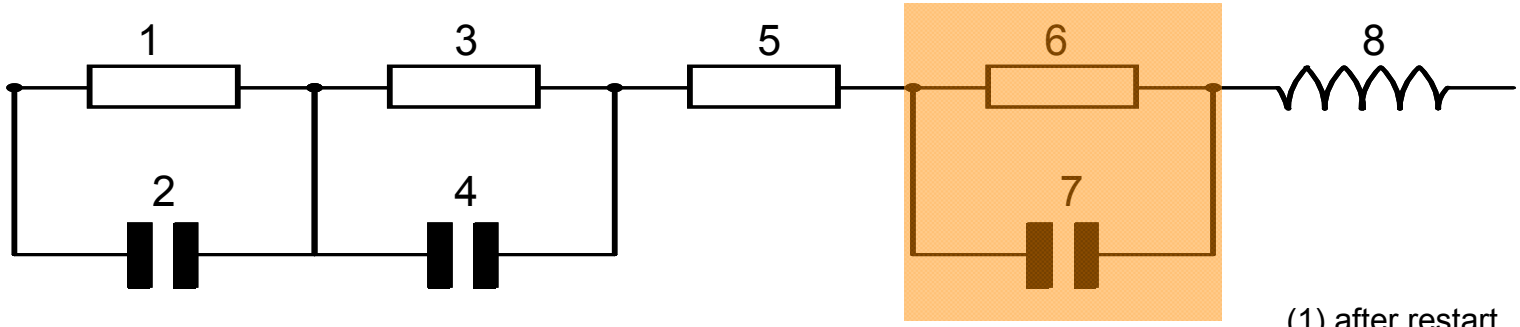


(1) after restart

Cyclic stability

Electrolysis

element	EC_1		EC_2		EC_3 (1)		EC_4		
1	2,262 mΩ		2,211 mΩ		1,985 mΩ		2,585 mΩ		diffusion
2	5,57 F	0,546	5,848 F	0,546	7,79 F	0,58	6,152 F	0,648	
3	1,65 mΩ		1,614 mΩ		1,817 mΩ		1,455 mΩ		cathode
4	225,4 mF	0,766	231,6 mF	0,741	226 mF	0,706	298,2 mF	0,768	
5	4,322 mΩ		4,393 mΩ		4,188 mΩ		4,548 mΩ		membrane
6	0,182 mΩ		0,206 mΩ		0,210 mΩ		0,207 mΩ		anode
7	2,623 mF	0,445	2,115 mF	0,564	1,526 mF	0,755	1,28 mF	0,491	
8	13,3 nH		11,65 nH		8,347 nH		12,11 nH		



(1) after restart

Cyclic stability

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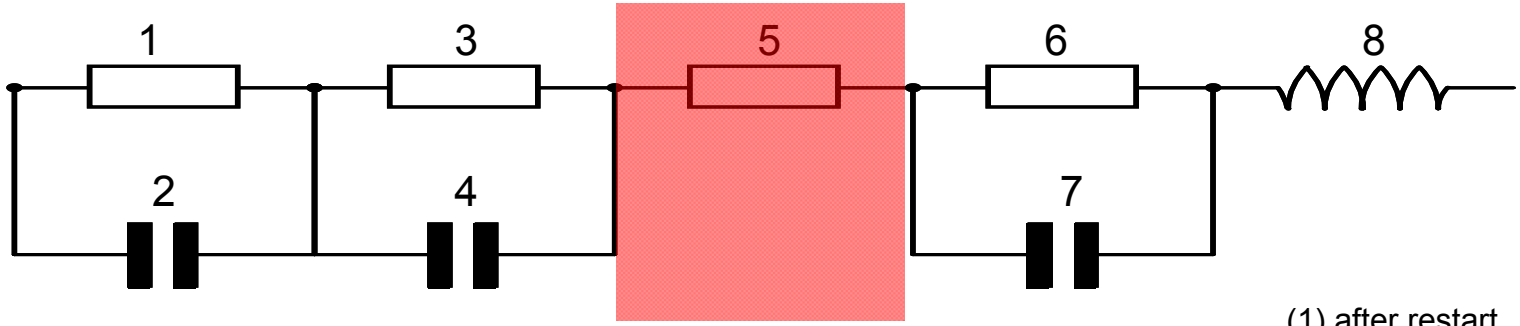

(1) after restart

Cyclic stability

Electrolysis

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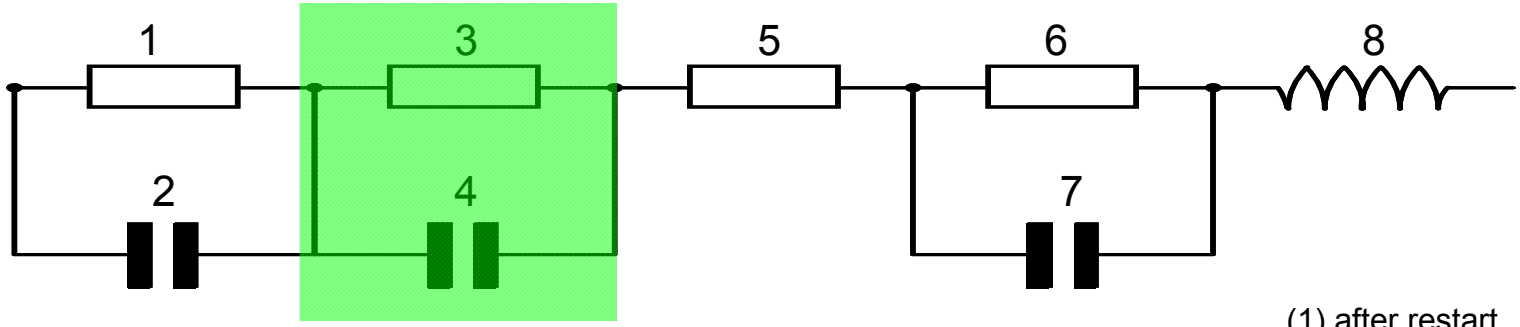

(1) after restart

Conclusion

- preparation of a unitized regenerative fuel cell
- EIS measurements in fuel cell and electrolysis mode
- simple model of URFC
  - anode
  - cathode
  - membrane
  - diffusion
- good correlation between model and experimental setup
- cyclic stability of membrane-electrode-assembly

Thank you for your attention!

Any questions?