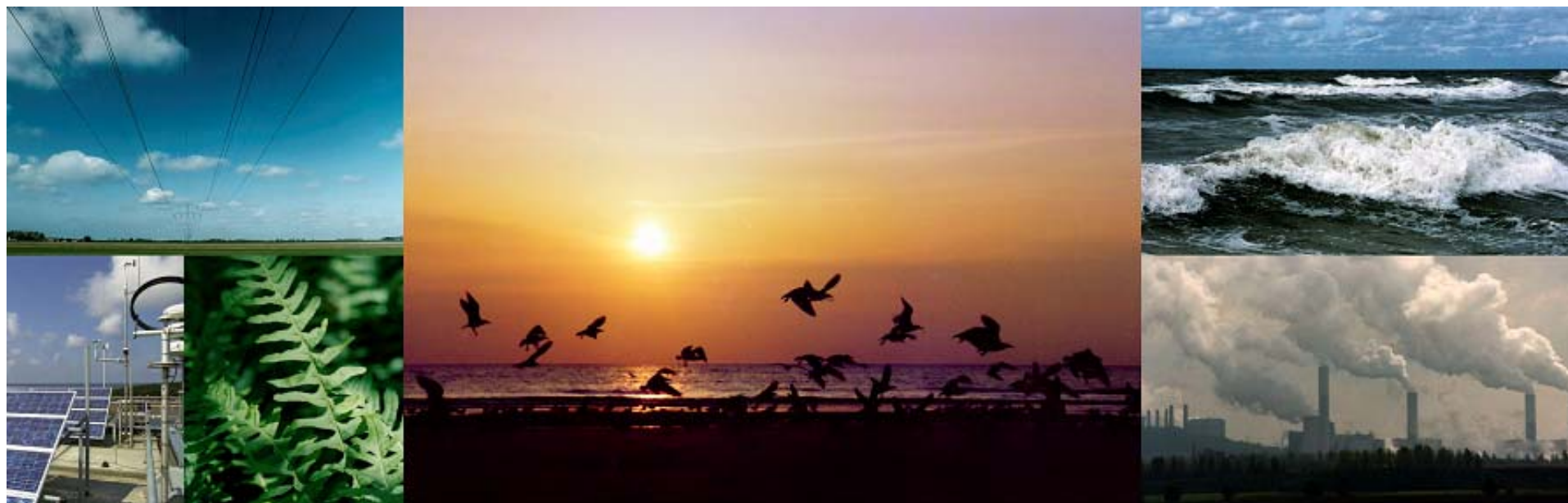




Energy research Centre of the Netherlands

Biosyngas Utilization in Solid Oxide Fuel Cells with Ni/GDC Anodes

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Acknowledgement

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Biomass Fuel Cell Utility System BIOCELLUS

Contract No. 502759

Power generation from biomass

Biomass is widely considered as sustainable primary energy source suitable for power generation

Economical conversion of biomass requires:

- 1/ Highly efficient centralized power plants, or
- 2/ Cheap decentralized combined heat and power plants (CHP)

Model studies indicate efficient small scale CHP systems when biomass gasifiers are used in combination with solid oxide fuel cell systems (Karl,2004):

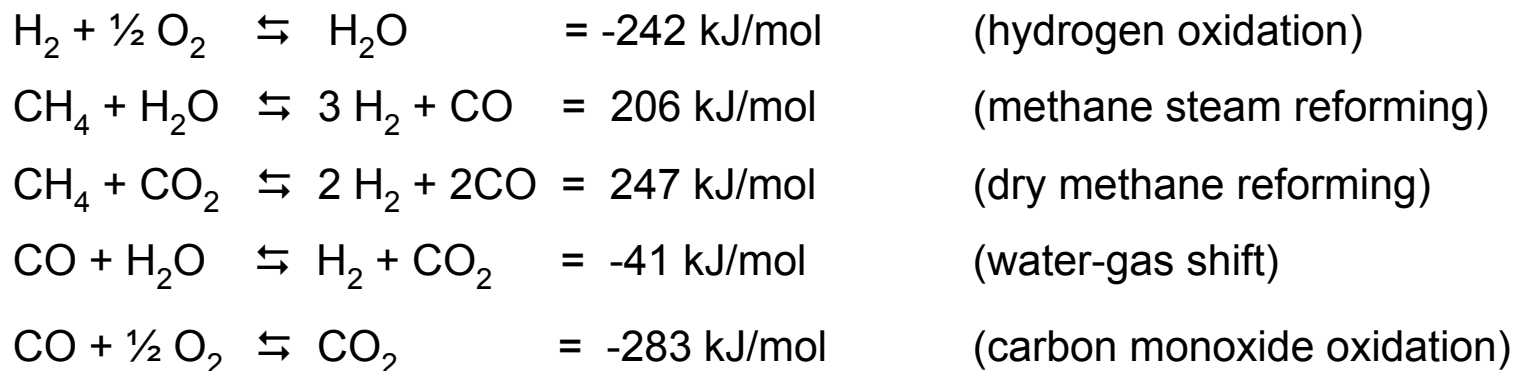
- Autothermal gasification: gasifying agent air, low calorific value, η_e 28%
- Allothermal gasification (indirect gasification): gasifying agent steam, high calorific value, external heat input from combustor, η_e 26%
- Allothermal gasification + thermal integration with SOFC system: gasifying agent steam, high calorific value, external heat input from SOFC, η_e 51%

Biosyngas usage in high temperature fuel cells

Examples of biosyngas compositions:

- Air blown gasification: 20% H₂, 20% CO, 12% CO₂, 2% CH₄, balance N₂
- Steam blown: 38% CO, 35% H₂, 12% CO₂, 10% CH₄, 5% other hydrocarbons
- Pollutants: dust, tars, alkali metals, halides, heavy metals, sulfur

Possible reactions:



Influence of other compounds and pollutants on the performance are unknown

Experiments

Aim:

Understanding the electrochemical performance of state-of-the-art SOFC membranes operated with biosyngas, in order to define strategies for further materials improvement

Approach:

- 1/ SOFC activity for the conversion of the main components in biosyngas
- 2/ Impact of gas pollutants on the anode activity: only sulfur investigated till now
- 3/ SOFC performance with biosyngas

Electrochemical characterisation at 850 and 920°C :

- Discharge behaviour
 - Open circuit voltage
 - Current limitation
- Impedance measurements
- Electrochemical performance at 80% fuel utilisation

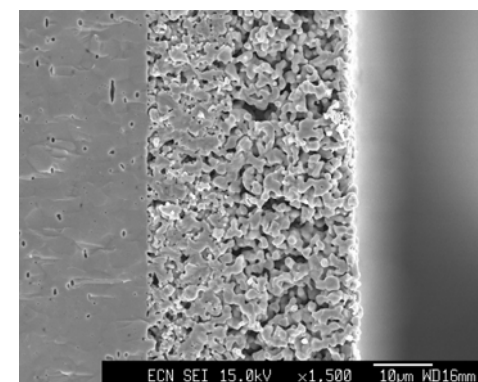
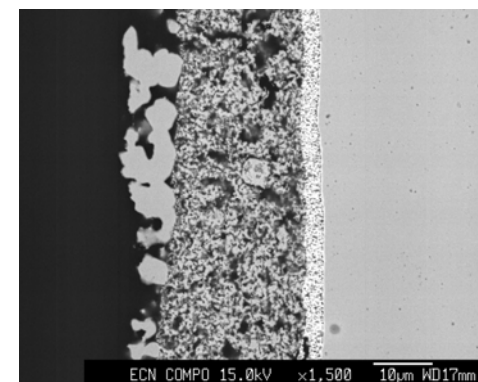
SOFC membranes

Membranes from InDEC Pilot Production B.V.

- Electrolyte: 3YSZ 90 μm
- Anode: Ni/GDC 50 μm , 3-layer structure
- Cathode: SLM/8YSZ 40 μm , 2-layer structure

Other specifications:

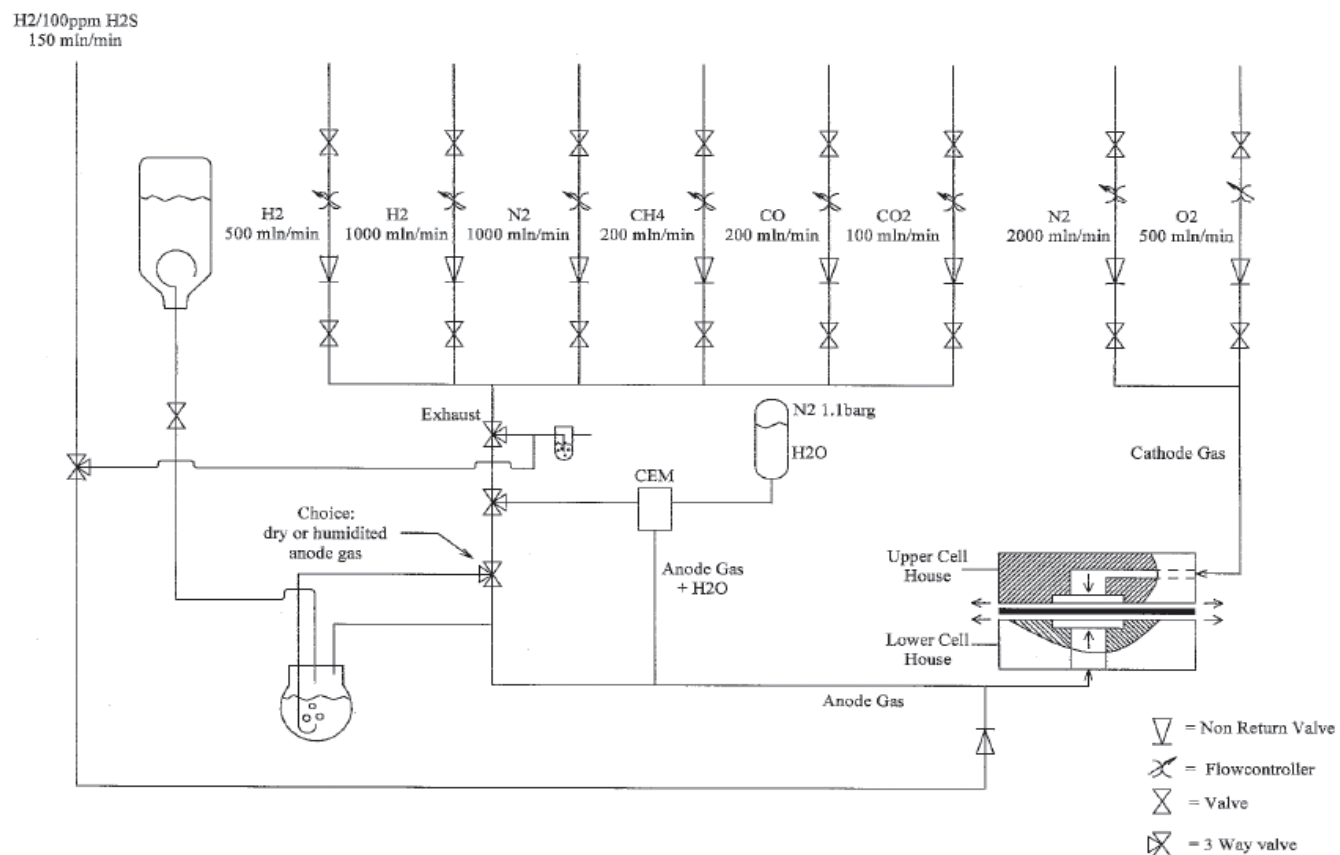
- Circular shaped, 120 mm diameter
- Electrode area 100 cm^2



Fuel cell test set-up



Gas mixing station



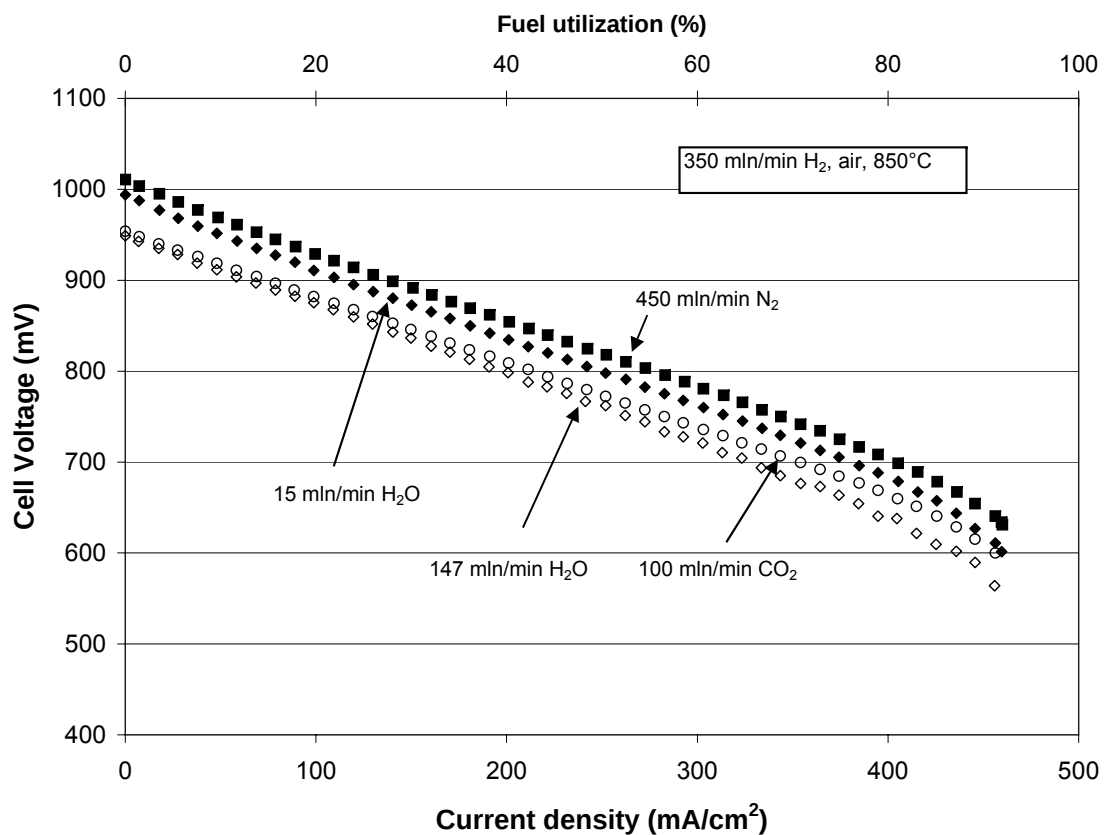
Fuel compositions for determination anode activity

Measurements at 850°C, sometimes also at 920°C, flows in mln/min:

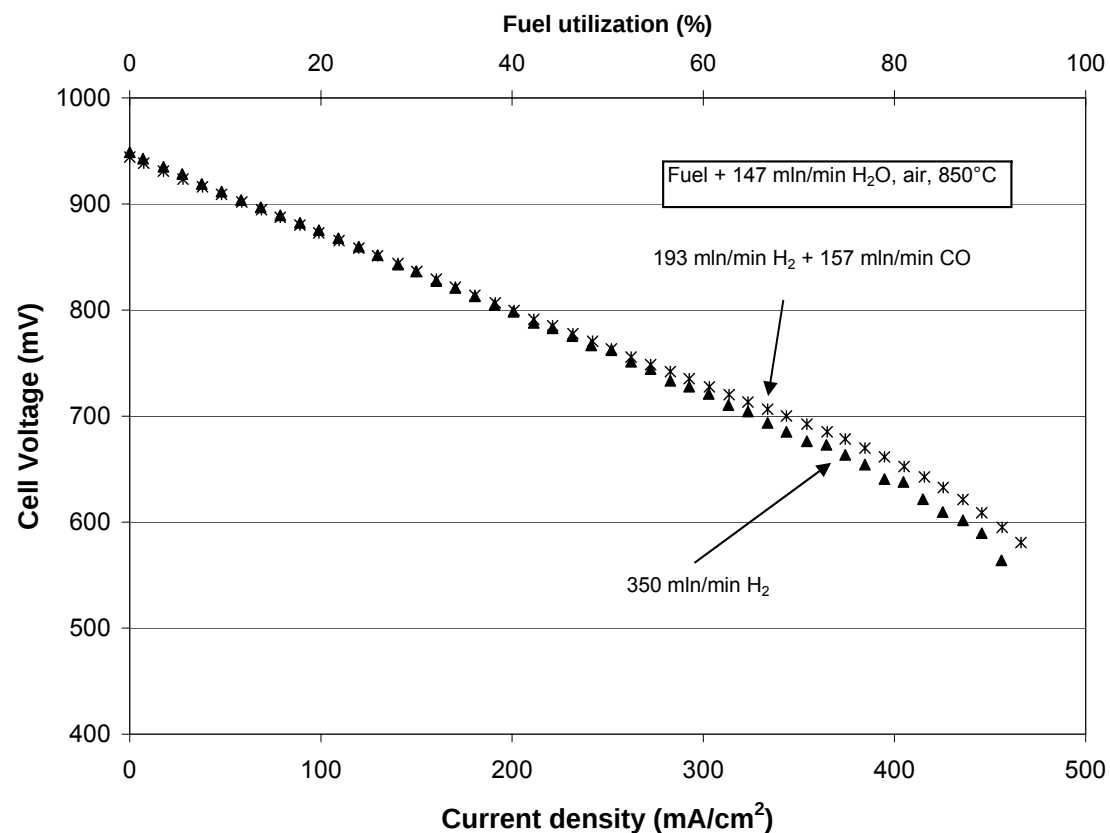
Fuel	H ₂	CO	CH ₄	CO ₂	N ₂	H ₂ O	H ₂ S ppm
1	350	-	-	-	450	34	0-9
2	350	-	-	-	-	15	
3	350	-	-	-	-	147	
4	-	-	87	-	-	147	
5	-	-	87	-	-	294	
6	350	-	-	100	-	20	
7	-	-	87	100	238	18	0-2
8	193	157	-	-	-	147	
9	256	-	23	44	238	44	0-2

➡ 100% fuel utilisation at 50 A

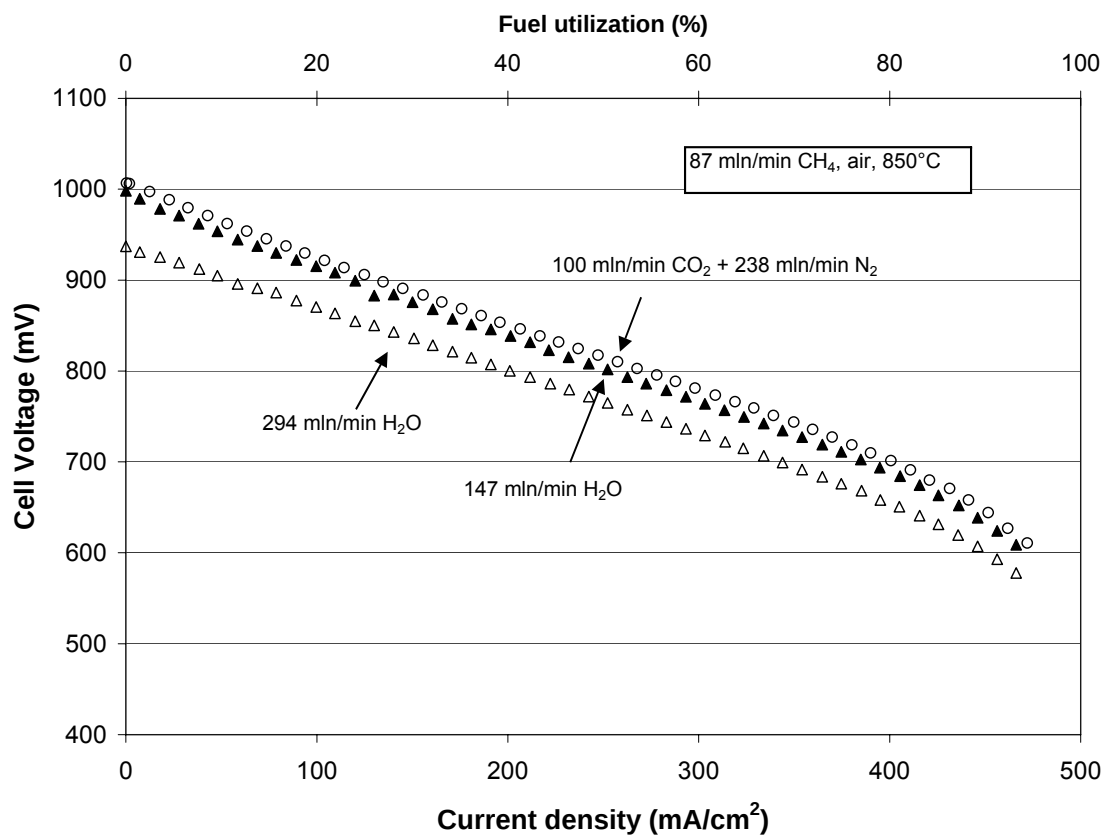
Impact of N₂, H₂O and CO₂ addition to H₂



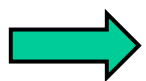
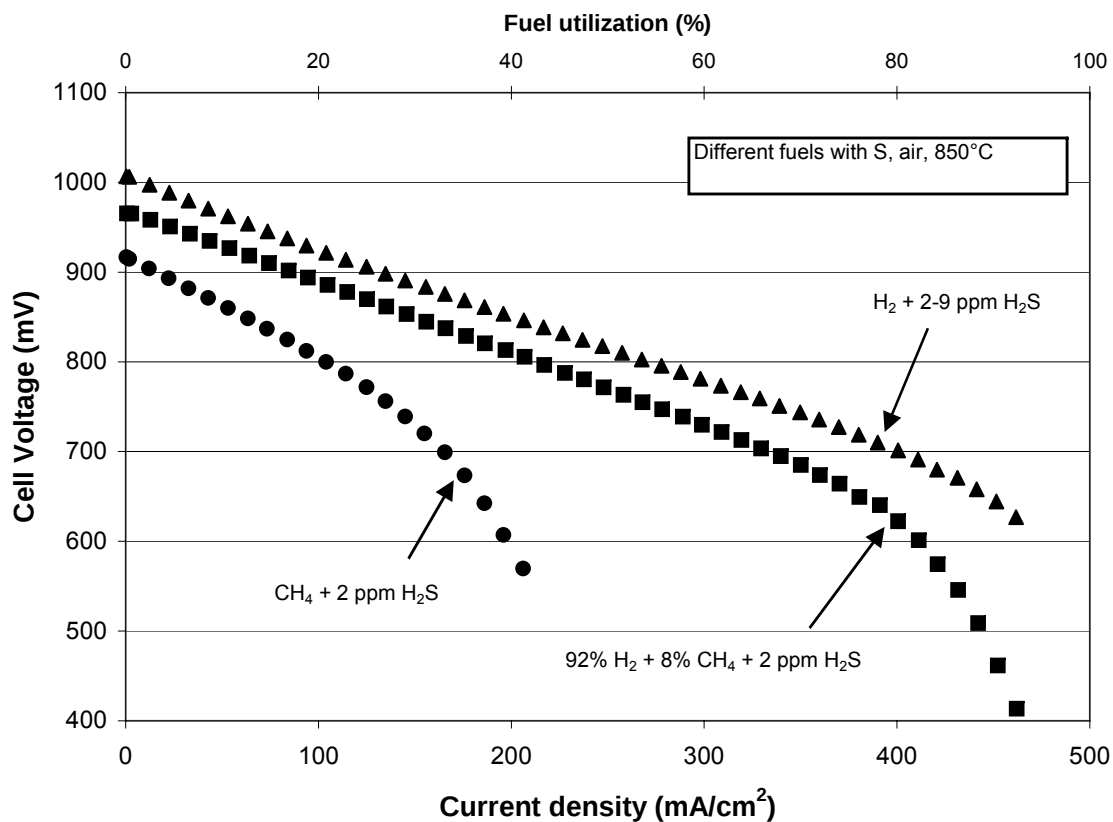
Partial substitution of H₂ with CO



Impact of CO₂ and H₂O addition to CH₄



Impact of sulfur

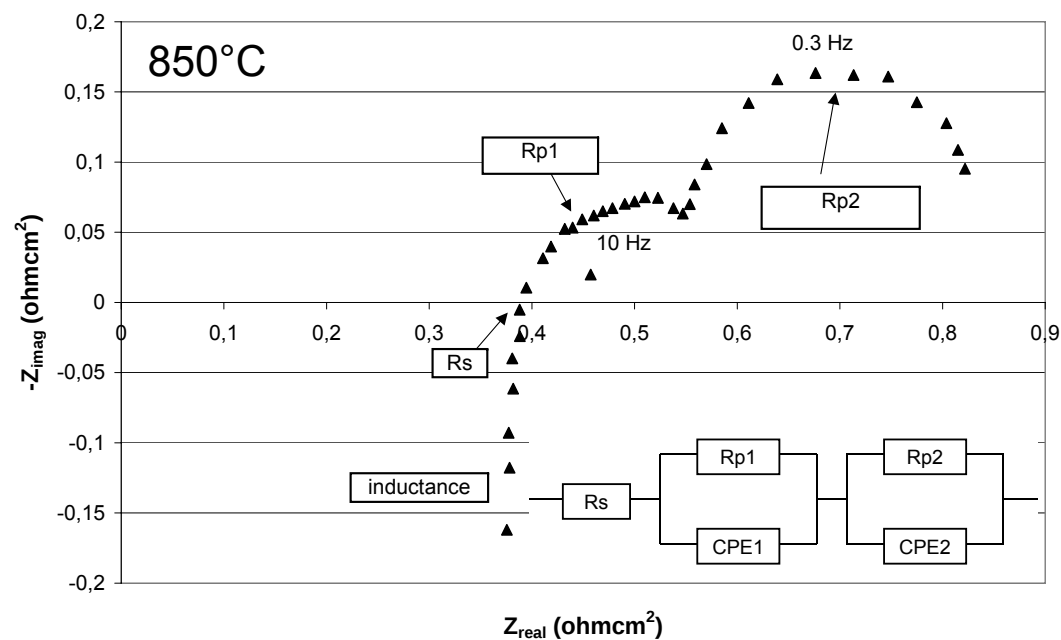


S-tolerance for H₂ oxidation, not for CH₄ reforming

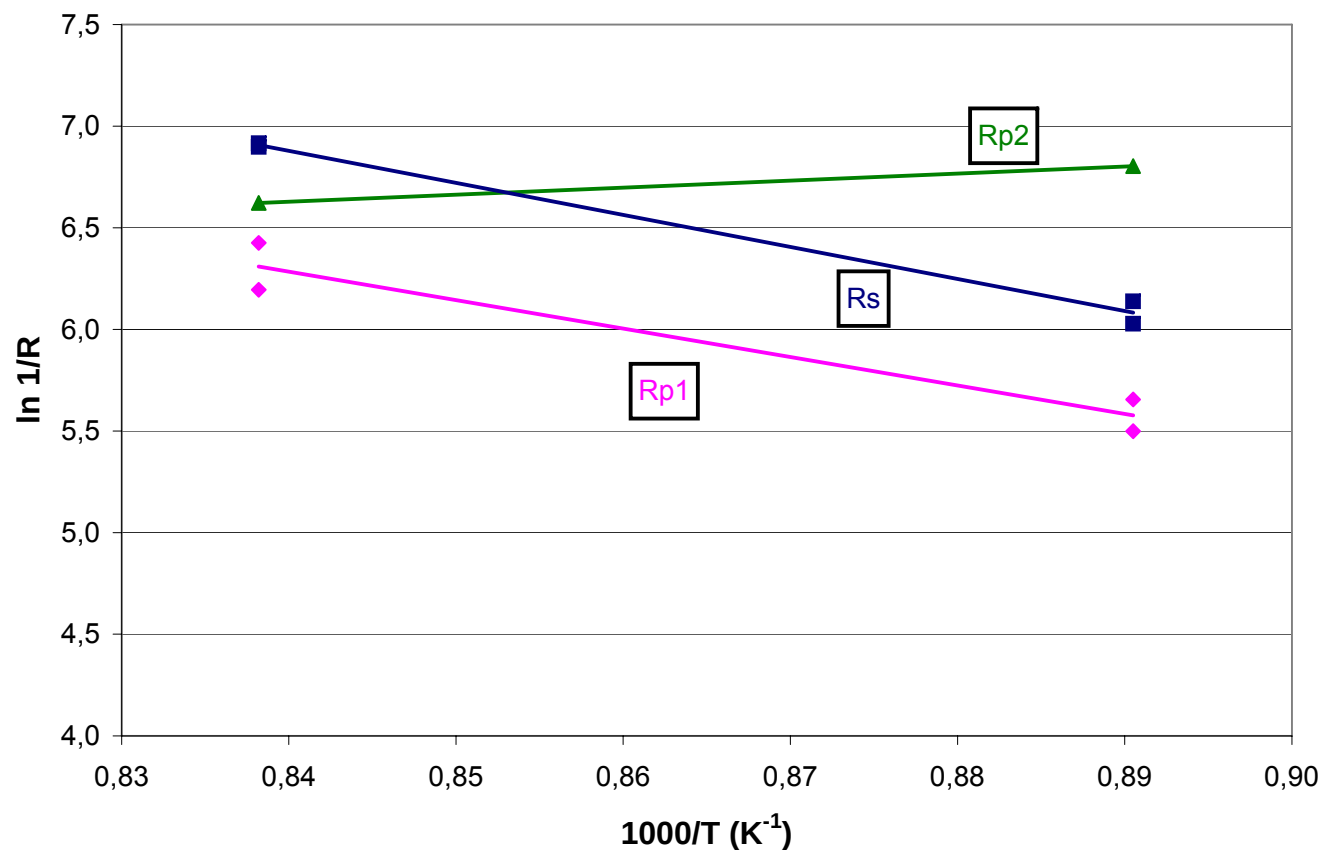
Impedance measurements

Methodology:

- Gamry FC500 connected to existing equipment
- AC Impedance measurements between 0.1 and 20000 Hz
- Equivalent circuit fitting



Temperature dependence



Rp2 is not thermally activated !

Results obtained at 850°C

Resistances in Ohmcm², only fuels without sulfur:

Fuel	Impedance at 10 A				Impedance at 40 A			
	Rs	Rp1	Rp2	Rtotal	Rs	Rp1	Rp2	Rtotal
1	0.28	0.24	0.24	0.75	0.28	0.29	0.30	0.88
2	0.33	0.25	0.23	0.81	0.31	0.35	0.29	0.95
3	0.36	0.25	0.15	0.77	0.37	0.26	0.30	0.94
4	0.33	0.25	0.17	0.76	0.28	0.44	0.26	0.98
5	0.32	0.27	0.10	0.69	0.27	0.55	0.25	1.07
6	0.34	0.24	0.14	0.72	0.33	0.27	0.28	0.87
8	0.35	0.26	0.14	0.75	0.36	0.22	0.28	0.86

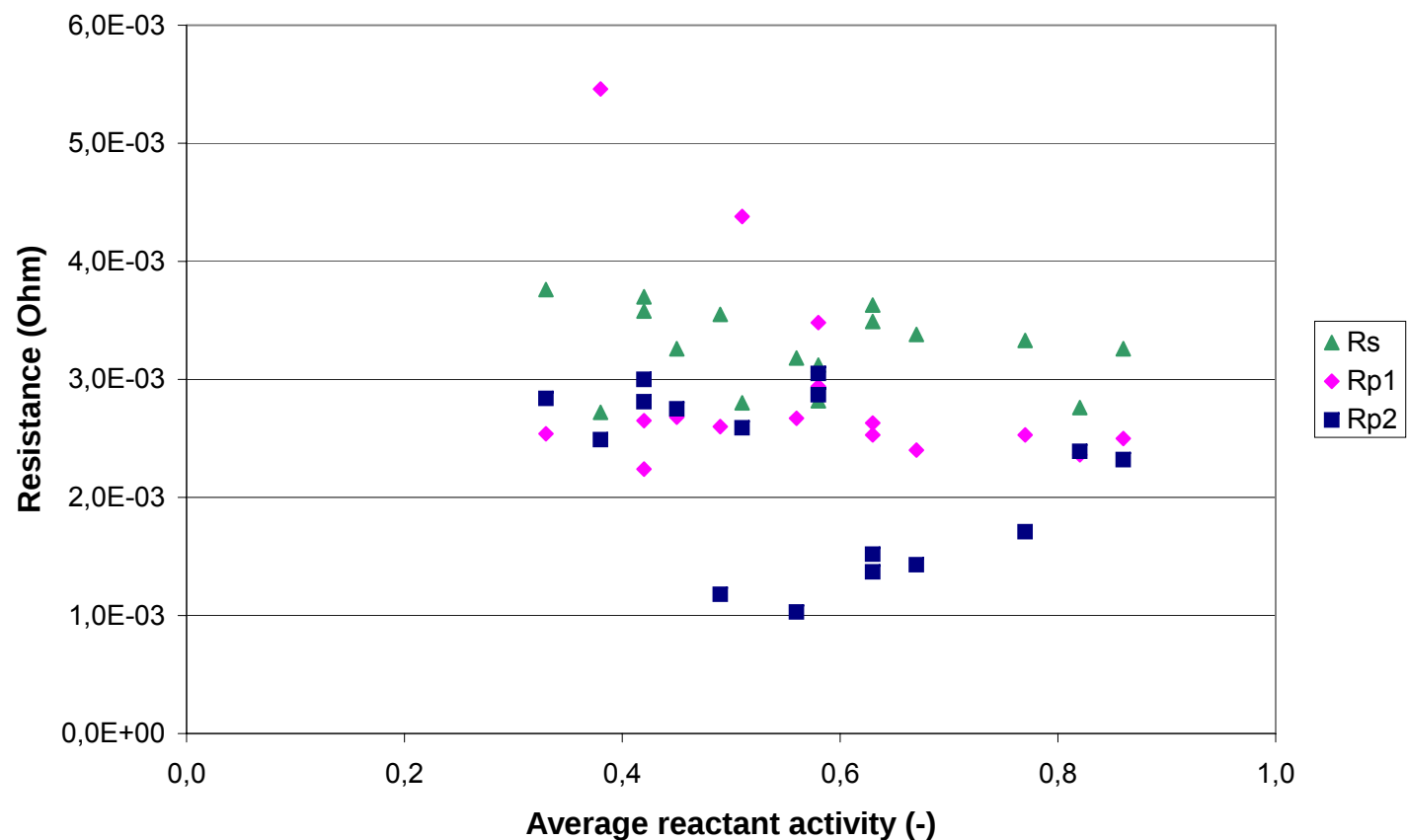


1/ Rs agrees with electrolyte conductivity

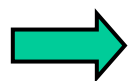
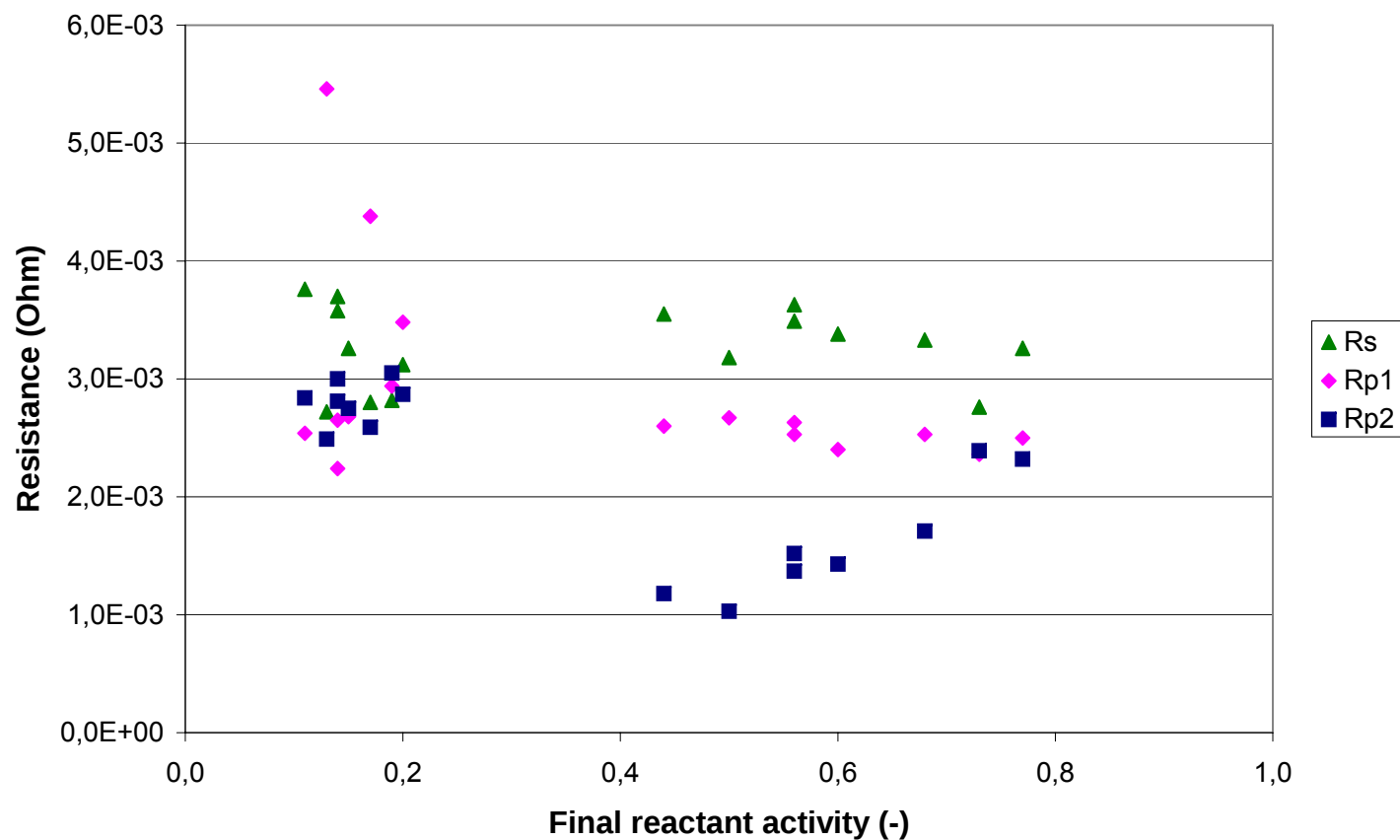
2/ Rp1 related to electrode properties not depending on fuel composition and utilisation

3/ Rp2 not materials related and depending on fuel composition/utilisation

Resistances related to reactant activity

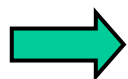
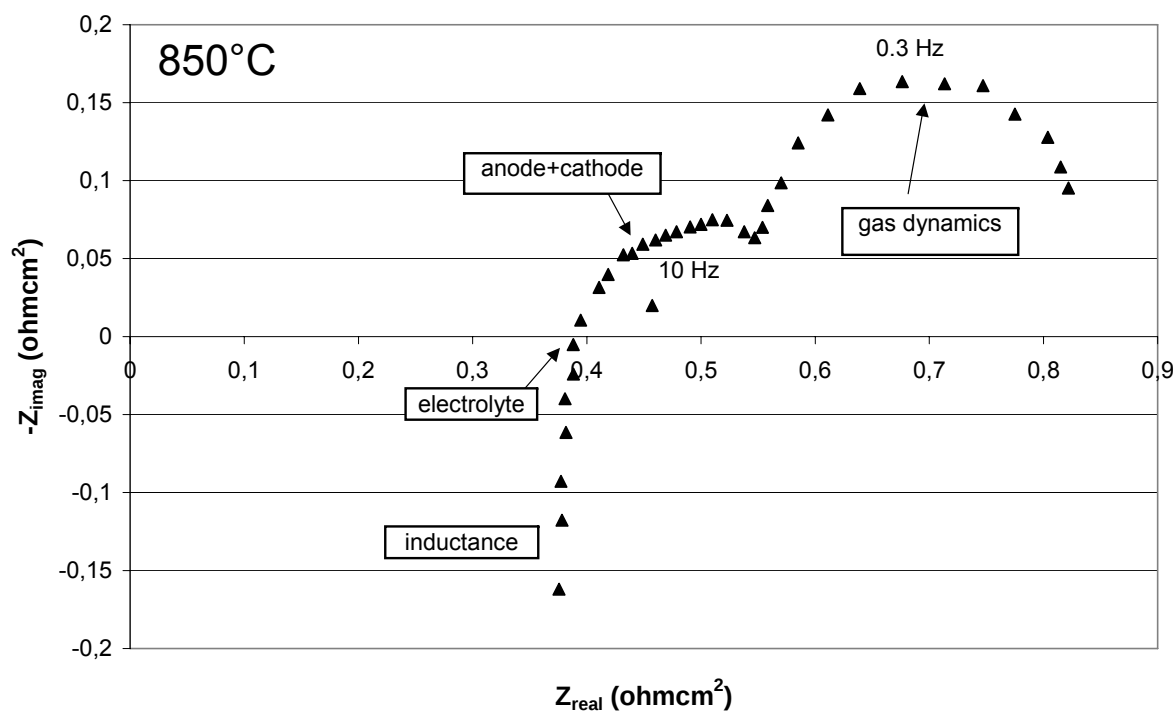


Resistances related to reactant activity



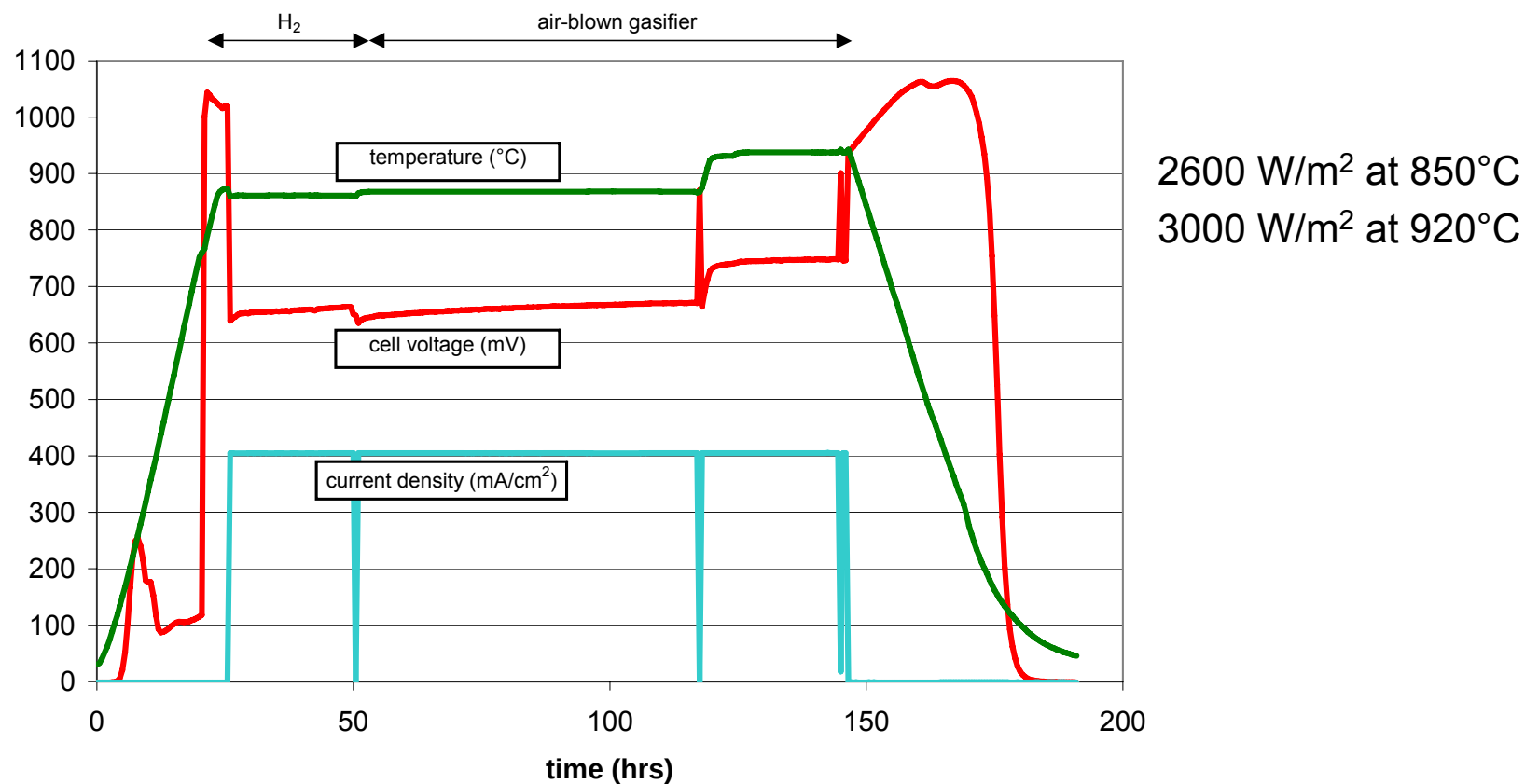
Final reactant activity seems to give best fit for Rp2

Revealing the impedance spectra



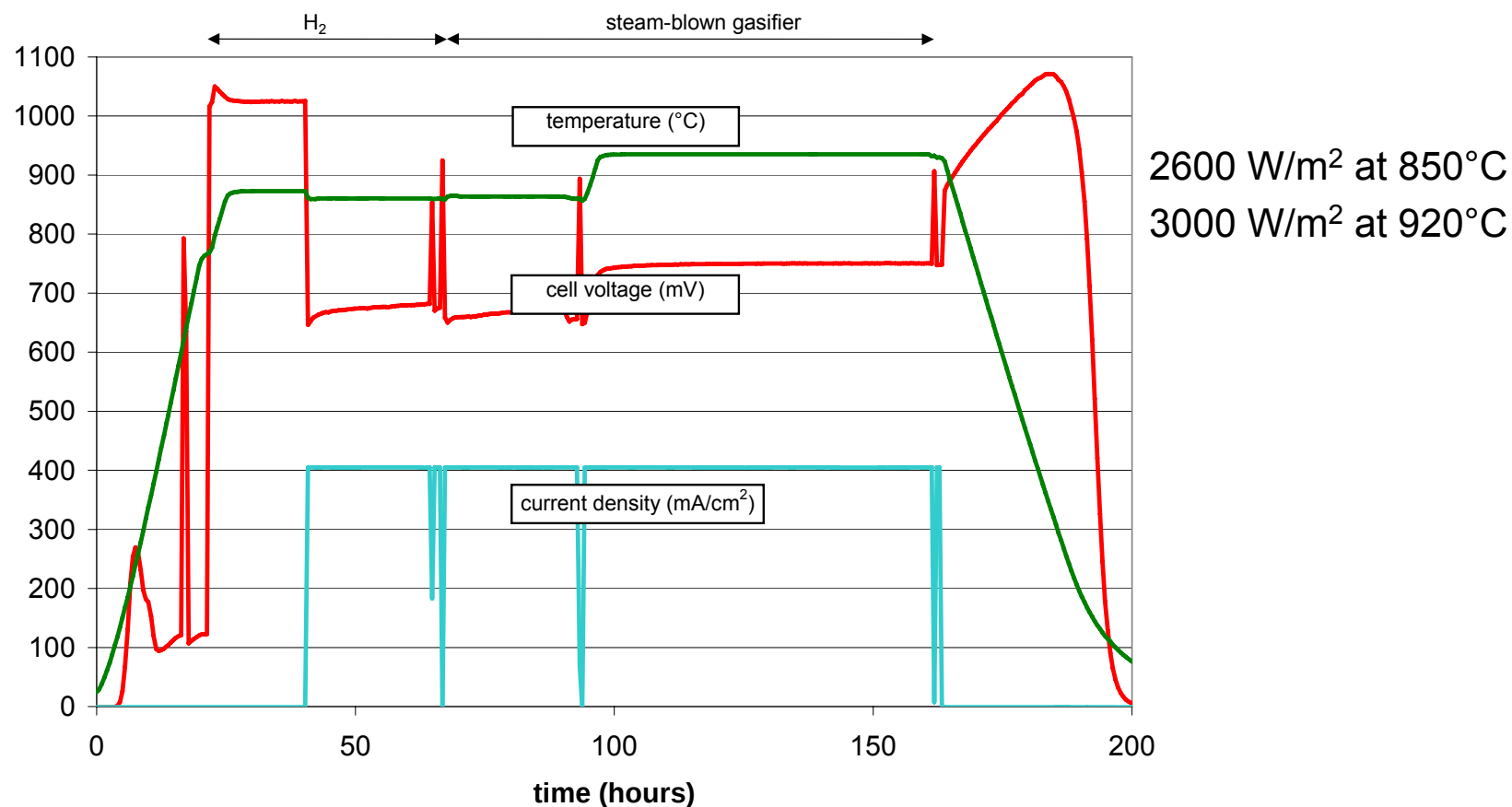
- 1/ Anode and cathode contributions cannot be distinguished
- 2/ Cell impedance: $0.6 \text{ } \Omega\text{cm}^2$ at 850°C and $0.3 \text{ } \Omega\text{cm}^2$ at 920°C

Performance with clean biosyngas from air-blown gasifier



Mixing station: H₂ 134 + CO 134 + CH₄ 20 + CO₂ 67 + N₂ 315 + H₂O 193 mln/min

Performance with clean biosyngas from steam-blown gasifier



Mixing station: H₂ 200 + CO 160 + CO₂ 40 + H₂O 166 ml/min

Conclusions

- Ni/GDC anode is active for conversion of all main components in biosyngas
- Total conversion of H₂, CO and CH₄ at 80% utilisation and 400 mA/cm²
- Identical power output under syngas from air-blown and steam-blown gasifier:
 - 2600 W/m² at 850°C
 - 3000 W/m² at 920°C
- Sulfur has impact on the electrochemical performance:
 - Methane reforming inhibited at 2 ppm H₂S
 - Hydrogen oxidation tolerates at least 9 ppm H₂S
- Impedance spectroscopy important characterization tool:
 - Low frequency arc caused by gas dynamics impedance
 - Cell impedance 0.6 Ωcm² at 850°C and 0.3 Ωcm² at 920°C
 - Anode and cathode contributions cannot be distinguished