Signigicant Steps towards Medium Temperature/Low RH PEMFC;

Results from the EU IPHE-GENIE project

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ECN

Energy research Centre of the Netherlands

Significant Steps towards Medium Temperature / Low RH PEMFC; Results from the EU IPHE-GENIE project

R. K. Mallant, N. P. Lebedeva, Y. M. Zhang, L. Li, J. K. Tang, V. I. Bukhtiyarov, A. V. Romanenko, I. Voropaev, B. Bauer, W. Zhang, D. J. Jones, J. Rozière, H. R. Gao

Introducing the project

The EU FP6 project

- **IPHE-GENIE**
  (**I**nternational **P**artnership for a **H**ydrogen **E**conomy for **GE**neration of **N**ew **I**onomer membranes)

Was initiated as a project affiliated to:

- **AUTOBRANE**
  (**AUTO**motive high temperature fuel cell mem**BRANE**s)

With the intention to enhance co-operation between EU and INCO / IPHE countries

Both projects aimed at developing PEMFC membranes and electrodes for operation from sub-zero up to ~120 ºC

R&D topics for both projects

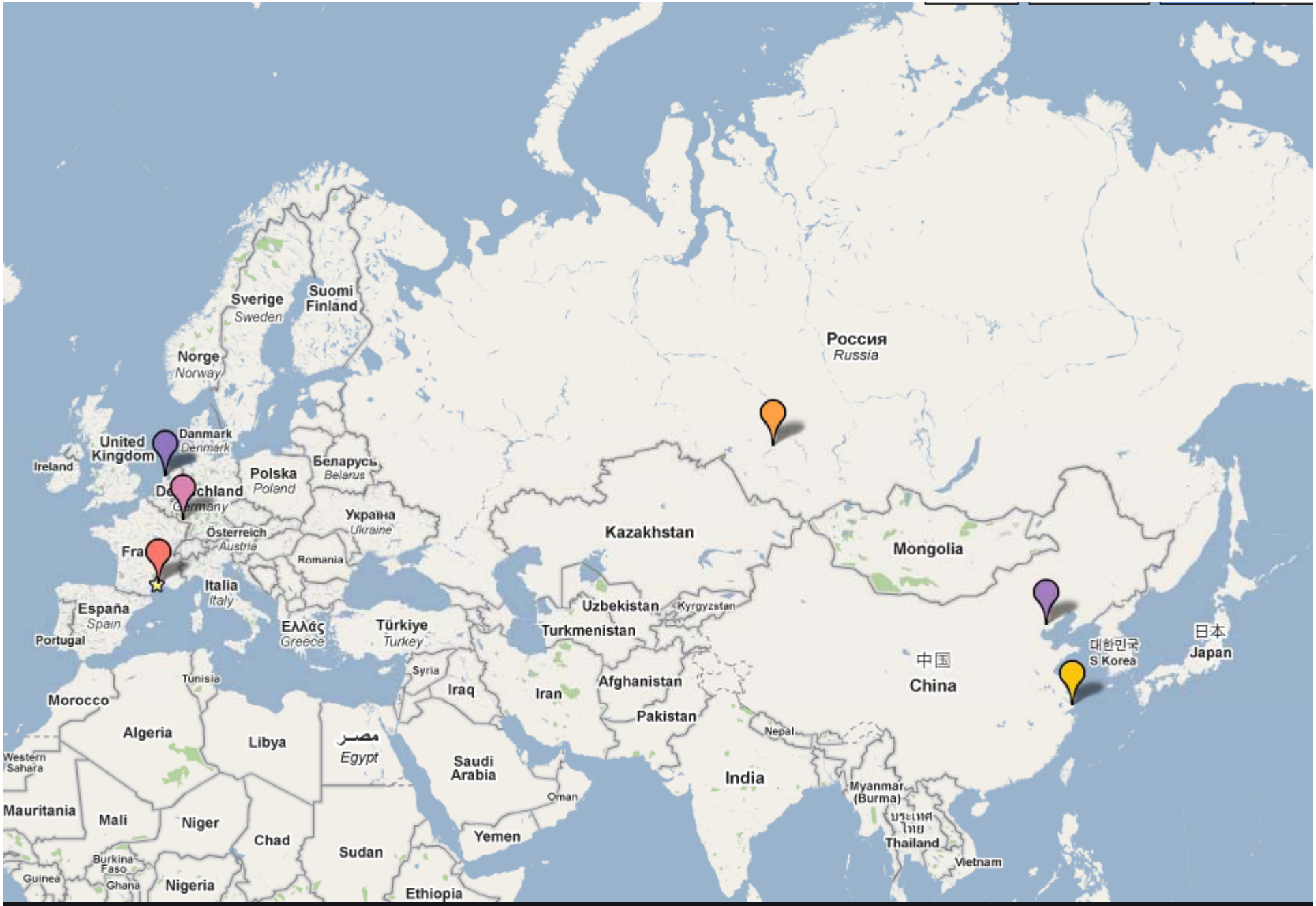
	AUTOBRANE	IPHE-GENIE
Polymers & membranes		
PFSA type	X	X
PBI type	X	
Alternative (anhydrous)	X	
Catalysts & supports	X	X
GDL	X	
Electrode & MEA	X	X
Deliverable	stack	MEA

IPHE-GENIE and AUTOBRANE; some key figures

	AUTOBRANE	IPHE-GENIE
Start date	Nov. 2005	Dec. 2006
Duration	48 months	30 months
Project cost	€ 14,379,624	€ 1,235,037
EU Funding	€ 8,299,693	€ 700,000
# Partners	31	6

IPHE-GENIE, the partners

Participant	Country
Shanghai Jiao Tong University • Polymer development	PRC
Dongyue Shenzhou New Materials Company • Polymer development / production	PRC
FuMA-Tech GmbH • Membrane casting / Membrane modification	D
CNRS Montpellier • Membrane modification / characterisation	F
Boreskov Institute of Catalysis • Catalyst development	RU
Energy research Centre of the Netherlands • Electrode / MEA development • Co-ordination	NL


Sverige
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Finland
Norge
Norway
Россия
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United
Kingdom
Danmark
Denmark
Ireland
Беларусь
Belarus
Polska
Poland
Deutschland
Germany
Україна
Ukraine
Österreich
Austria
Kazakhstan
Mongolia
Fra
Romania
Italia
Italy
España
Spain
Portugal
Ελλάς
Greece
Türkiye
Turkey
Uzbekistan
Kyrgyzstan
Turkmenistan
Syria
Iraq
Iran
Afghanistan
Pakistan
中国
China
대한민국
S Korea
日本
Japan
Tunisia
Morocco
Algeria
Libya
مصر
Egypt
Saudi
Arabia
Nepal
India
Western
Sahara
Mauritania
Mali
Niger
Chad
Sudan
Oman
Yemen
Myanmar
(Burma)
ประเทศ
ไทย
Thailand
Vietnam
Burkina
Faso
Guinea
Ghana
Nigeria
Ethiopia

The targets

Item	Value
Performance	~0.8 A/cm^2 @ 0.65V
Pt loading, sum of both electrodes	≤ 0.4 mg/cm^2
Temperature	Subzero to ~120°C
Partial water vapour pressure	max. 500 mbar
Pressure	≤ 1.5 bar(a)
Stoichiometry	H_2 <1.5, Air <2

The approach, the various steps in achieving our goal

Proton conductivity at low RH / elevated T

- Low equivalent weight PFSA to enhance proton conductivity,
- Combined with cross linking (several approaches were explored) and hybridization to preserve integrity and mechanical properties

High performance at low Pt loading

- Thin electrodes
- Optimised pore structure of Pt support
- Efficient catalyst
- All combined in single MEA

High performance MEA at reduced RH / elevated T

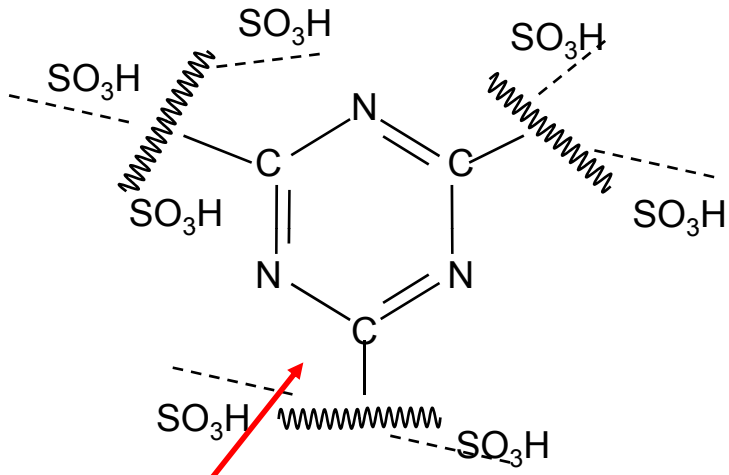
- Combine new polymer and new electrode

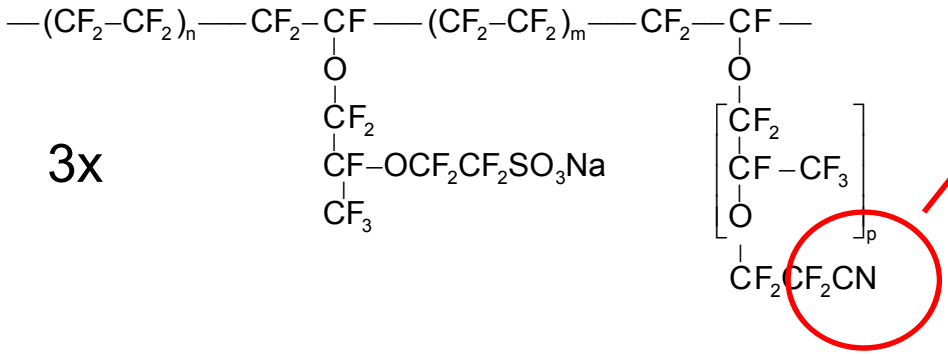
Method 1: Nitrile group cross-linking

Findings:

- Difficulties in identifying good conditions for the cross-linking reaction
- Glass transition temperature is lowered
- Non-cross-linked C≡N groups have low stability to oxidation
- Water uptake of resulting membranes is independent of temperature.

Triazine cross linking





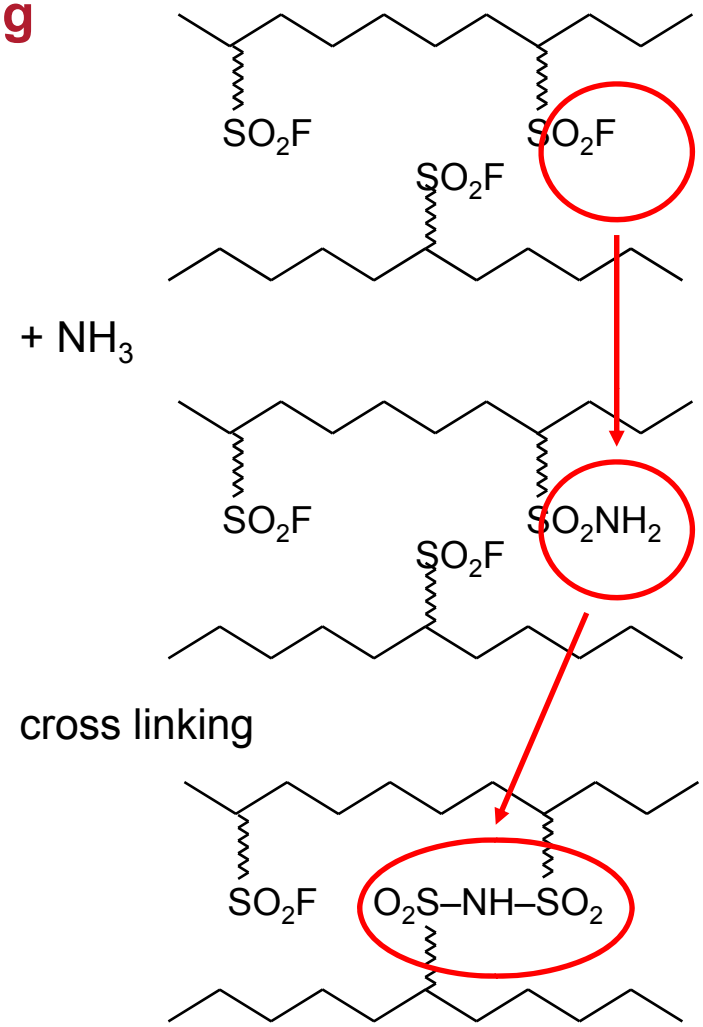
alkyl tin

Method 2: Sulfonimide cross-linking

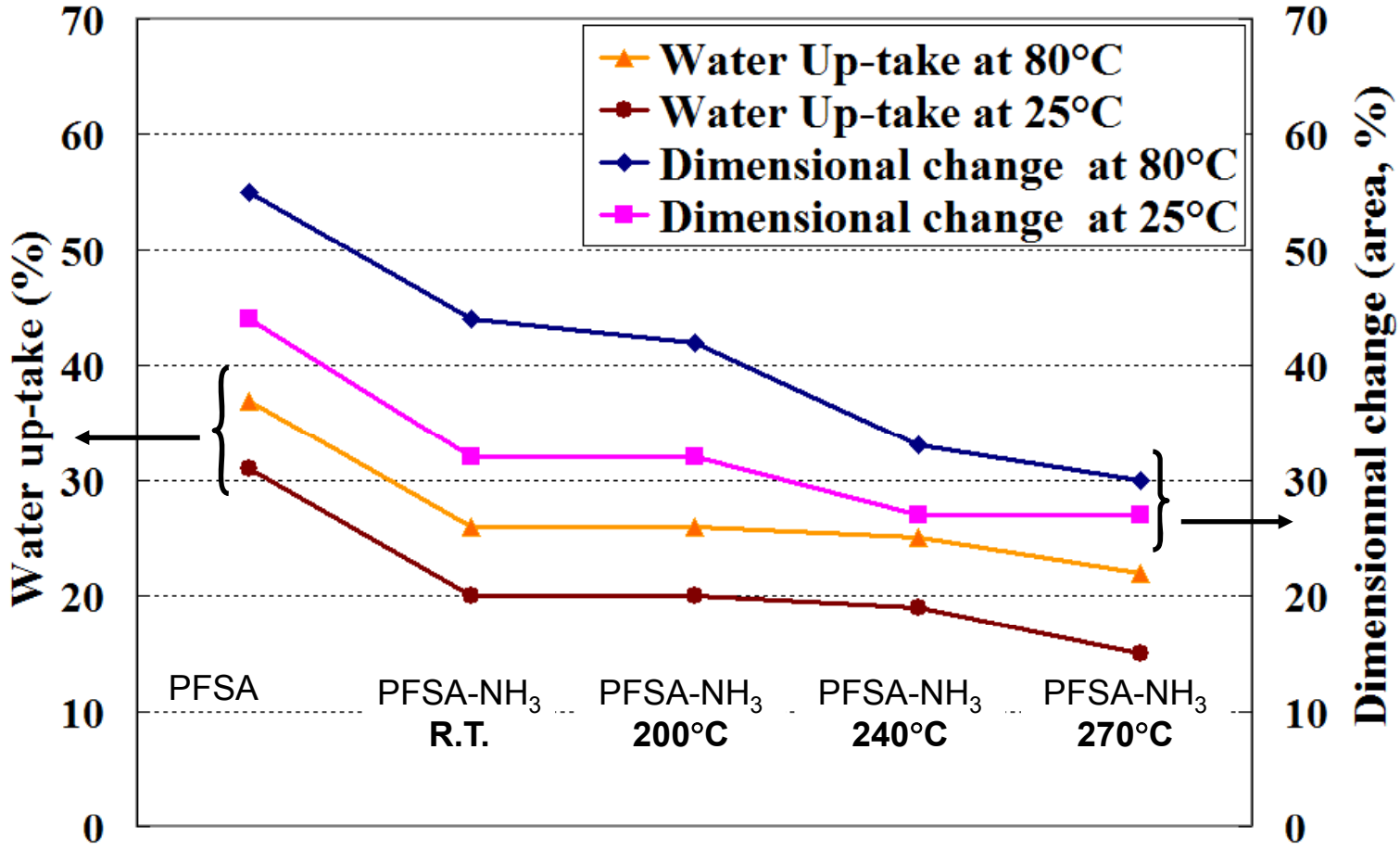
Ammonia, Hydrazine and Urea were used

Findings

- Cross-linking was confirmed by XPS
- H^+/Na exchange followed by SEM-EDAX revealed that cross linking was stronger near membrane surfaces
- Degree of cross-linking is difficult to control

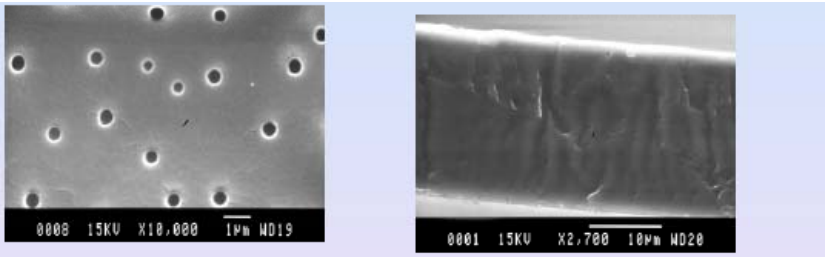


Cross-linking is effective in limiting swelling

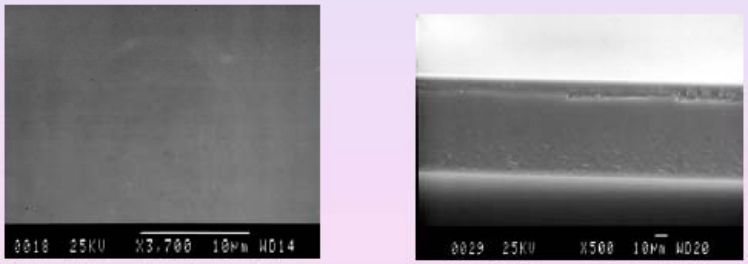


And the winner is: Perfluoroalkyl cross-linked PFSA

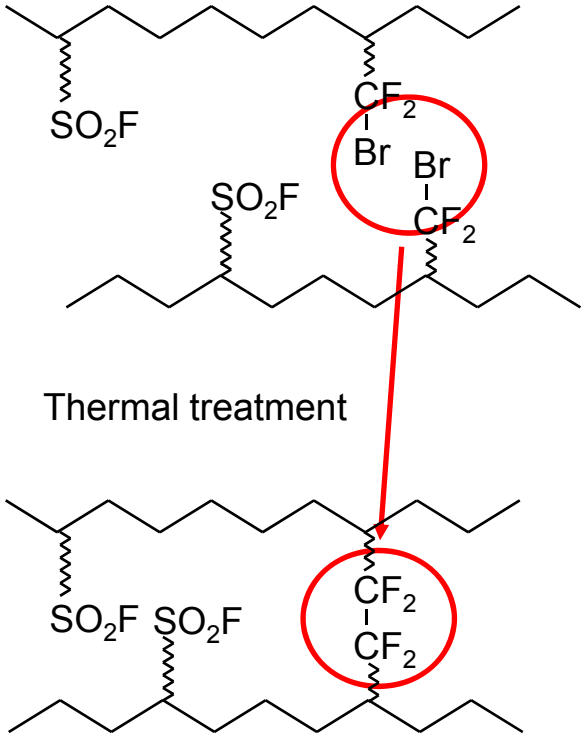
- Membrane is made by solution casting
- Next, cross linking is by thermal treatment only
- Degree of cross linking is controlled by number of Br sites



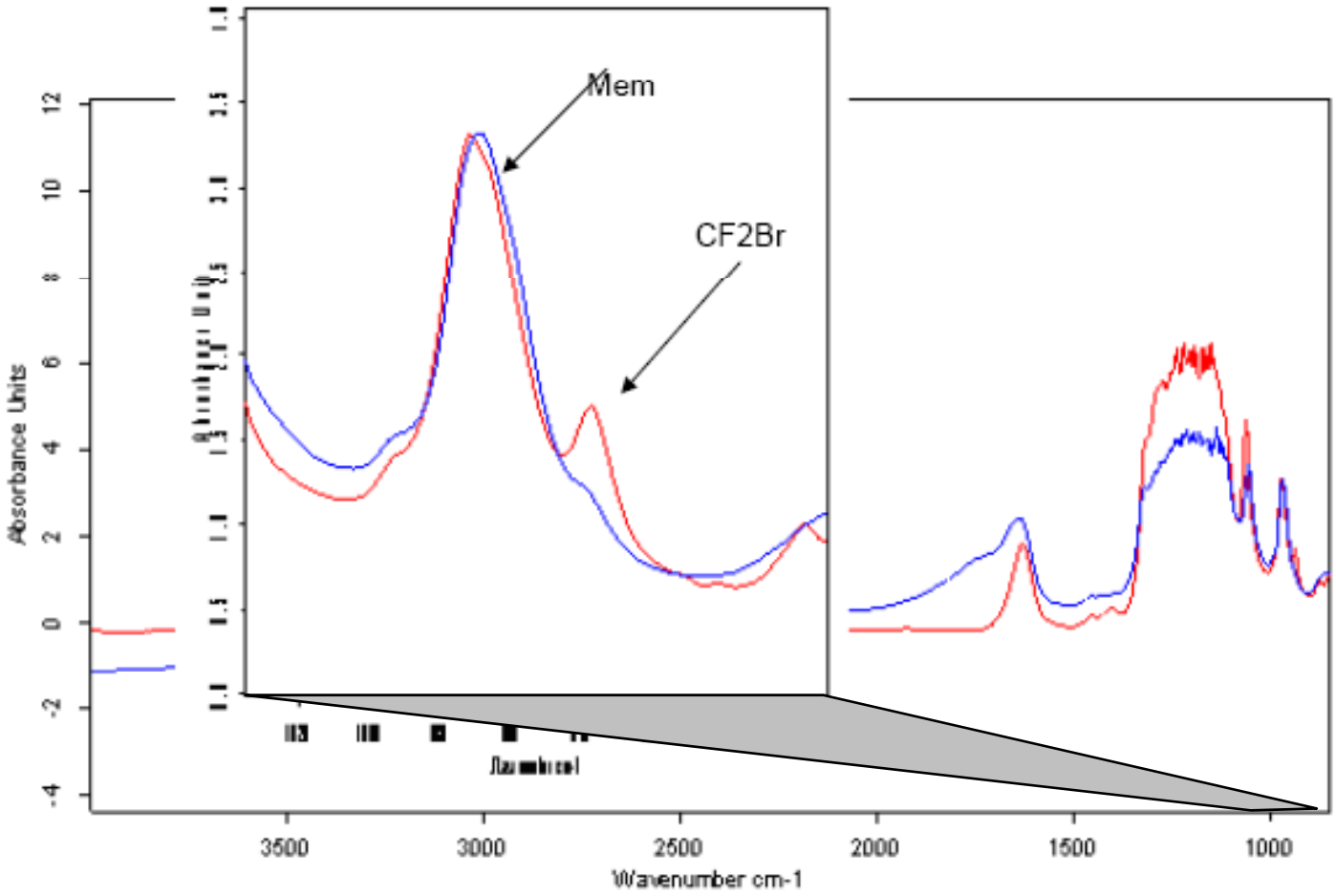
SEM of the membrane by rapid heating process



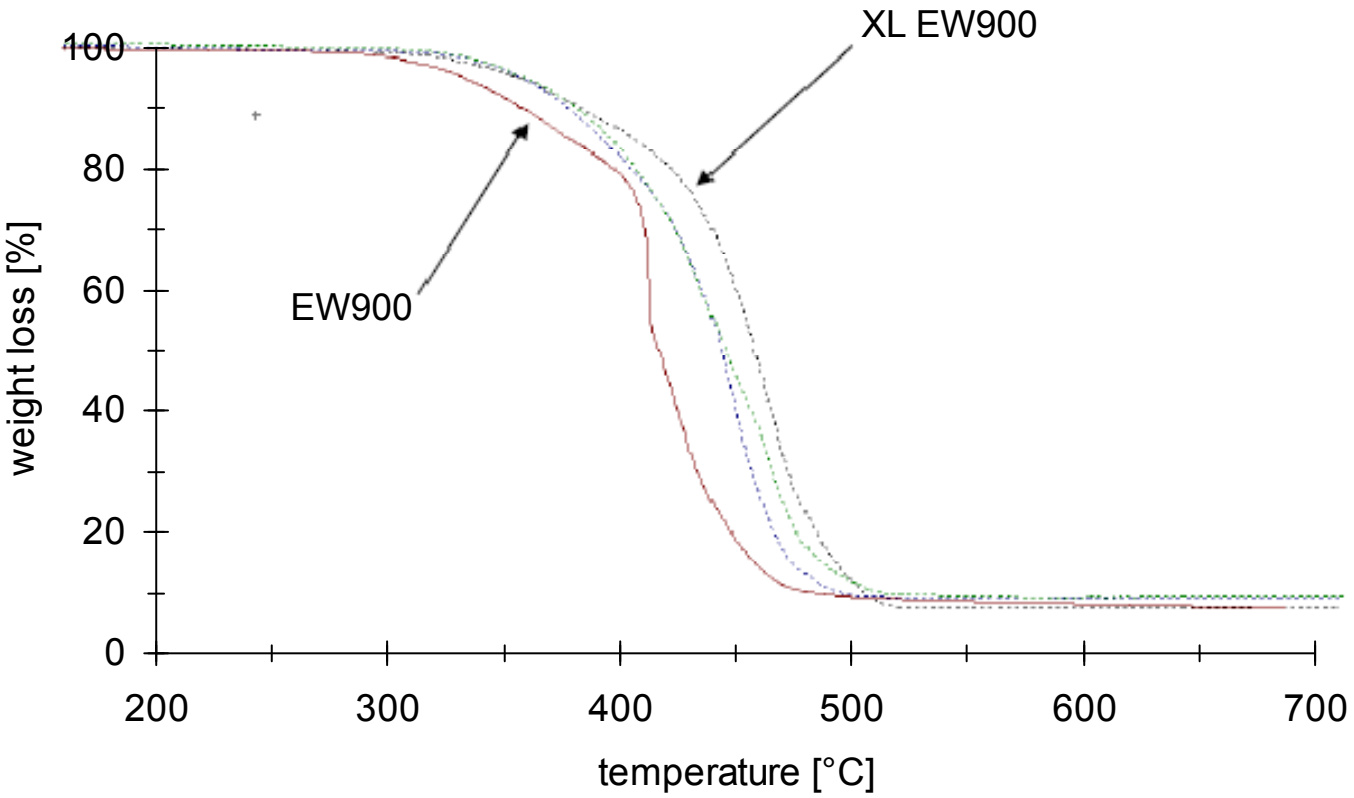
SEM of the membrane by improved heating process



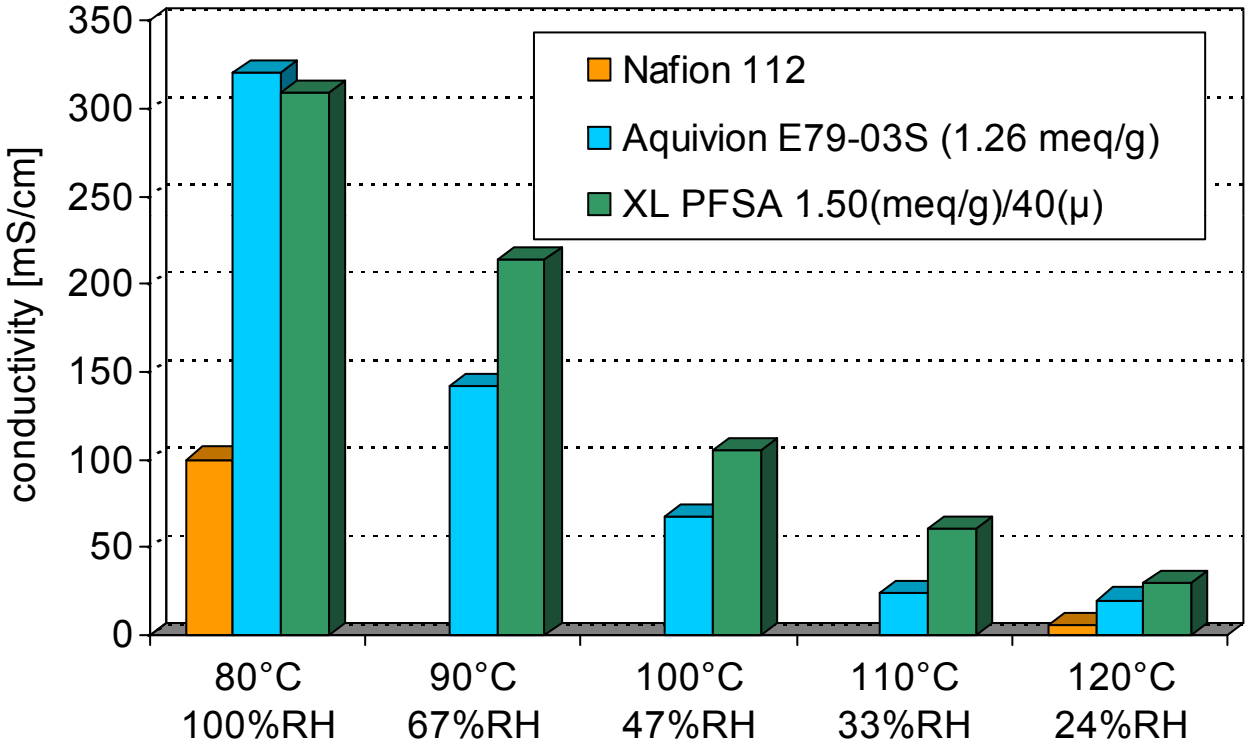
Identification of cross-linking by FT-IR



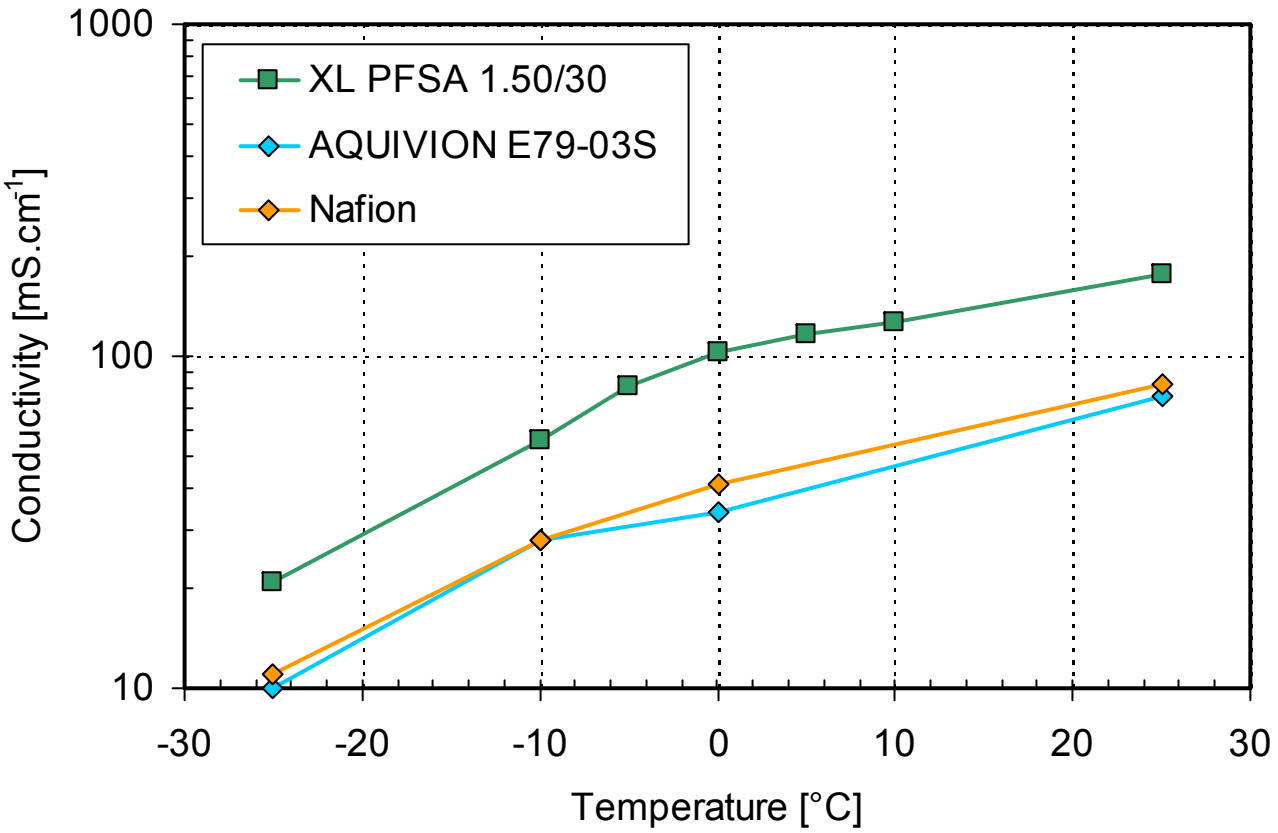
Thermal stability of cross-linked membranes



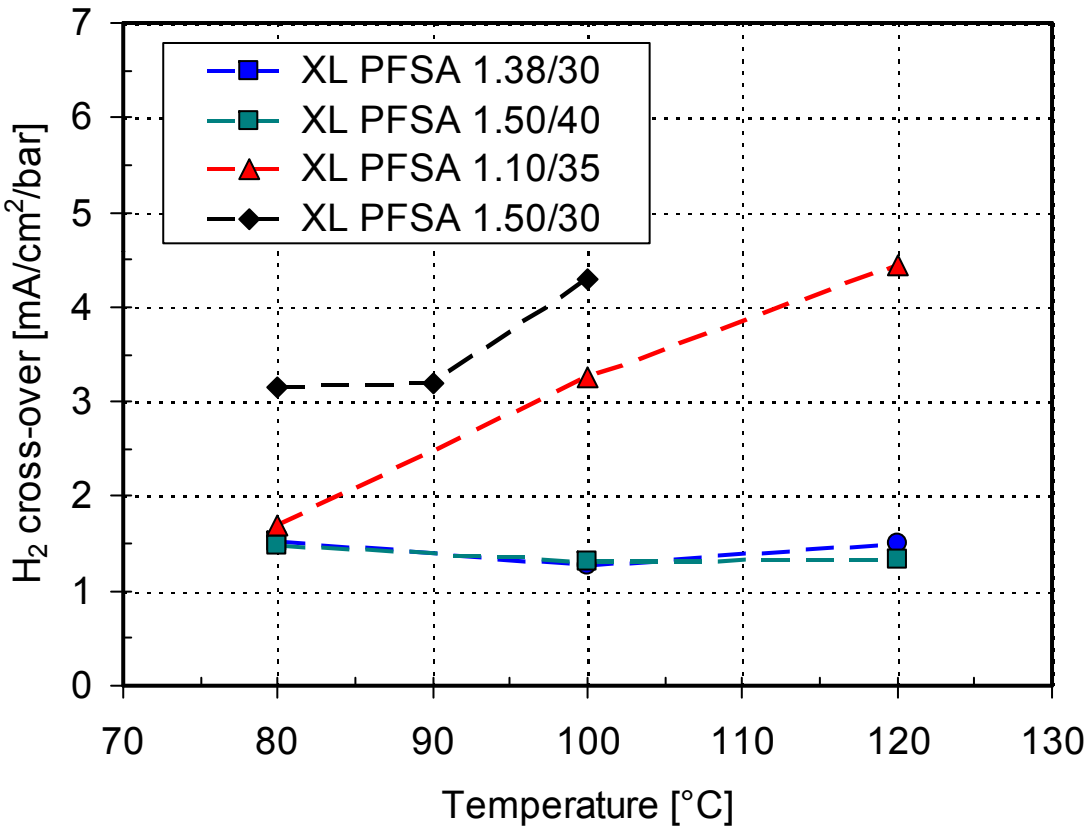
Ex-situ H^+ conductivity as function of temperature, RH



Low temperature conductivity



MEA characterisation – H_2 cross-over



- Some membranes leak profoundly
- The best membranes are gas-tight up to 120°C.

The approach

Proton conductivity at low RH / elevated T

- Low equivalent weight PFSA to enhance proton conductivity,
- Combined with cross linking (several approaches were explored) and hybridization to preserve integrity and mechanical properties

High performance at low Pt loading

- Thin electrodes
- Optimised pore structure of Pt support
- Efficient catalyst
- All combined in single MEA

High performance MEA at reduced RH / elevated T

- Combine new polymer and new electrode

Thinner electrodes for lower Pt loadings

Thin catalytic layer – aimed at reducing transport losses

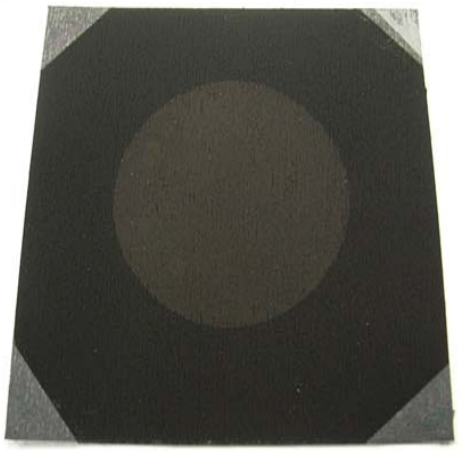
Application method:

- screen-printing on GDL

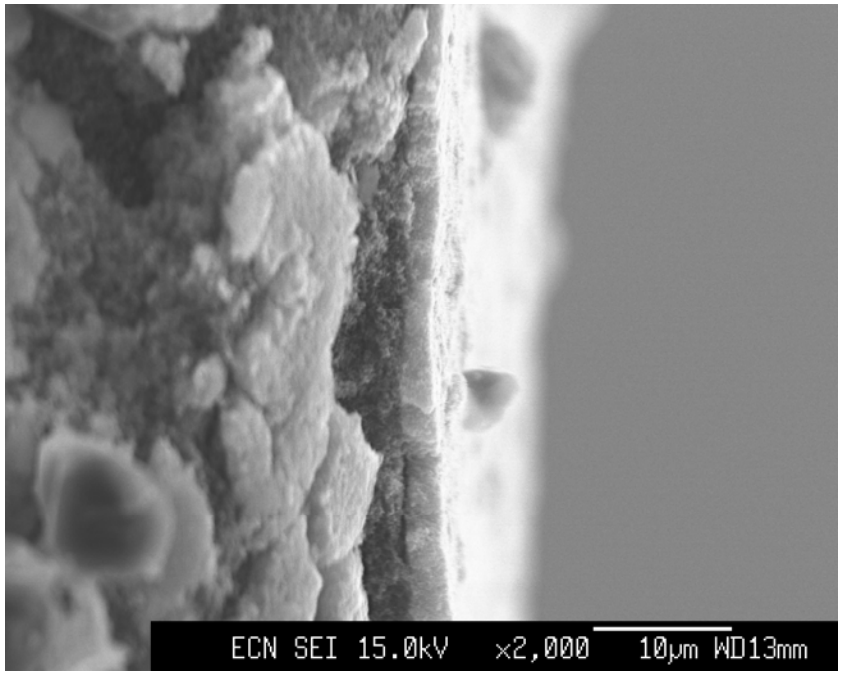
Ink composition:

- Pt/Carbon
- 1,2-propanediol
- Stabiliser
- Nafion (N:C ratio varied)

Patented:
US2004086773
WO0171840
US7186665
EP1285475



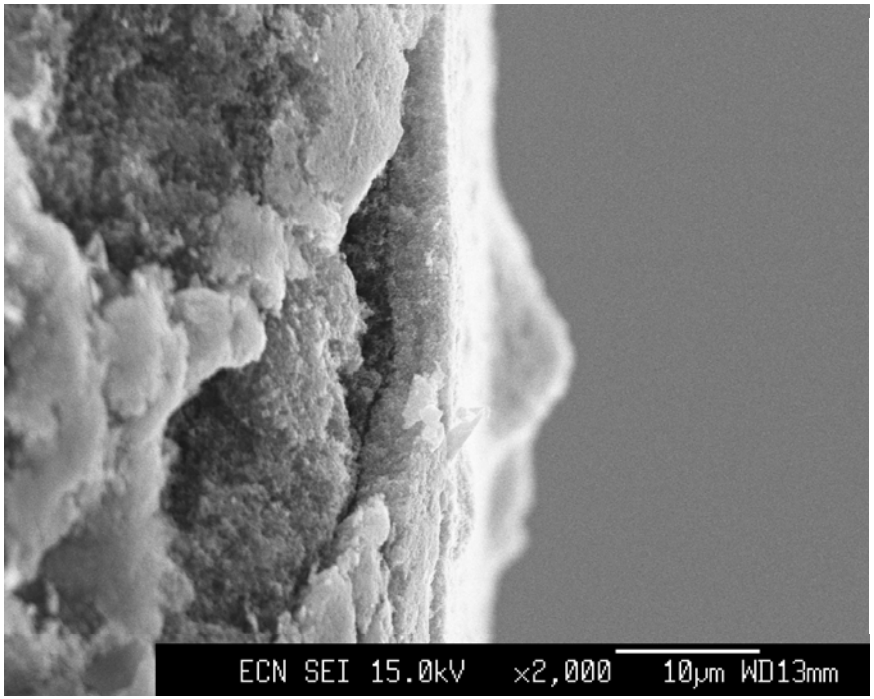
Catalytic layer - thickness



Catalytic layer thickness
2.2 ± 0.7 µm

Statistics: average ± standard deviation
- 3 production runs;
- 5 electrodes of each thickness per run;
- 15 positions on each electrode.

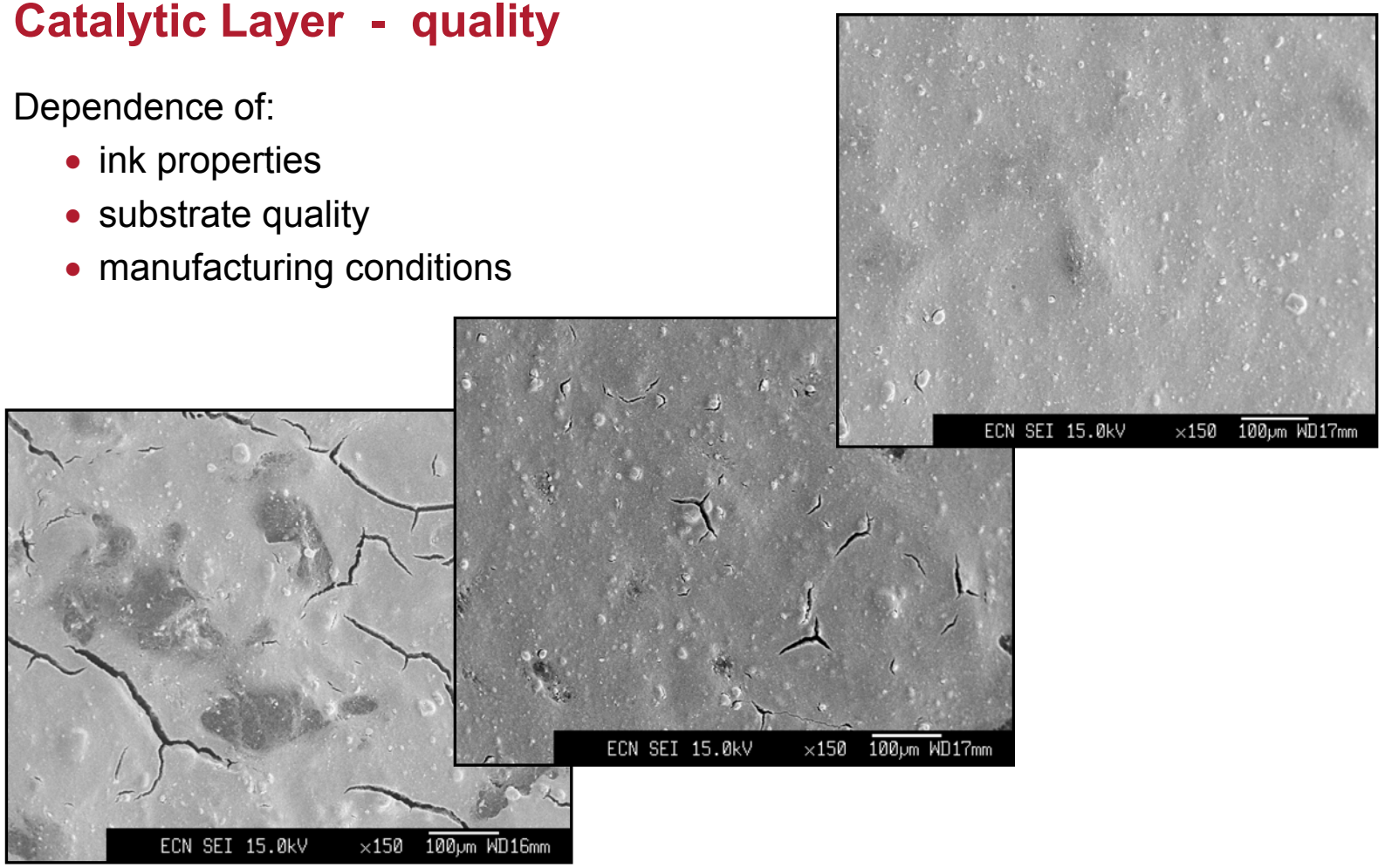
Catalytic layer thickness
3.6 ± 1.3 µm



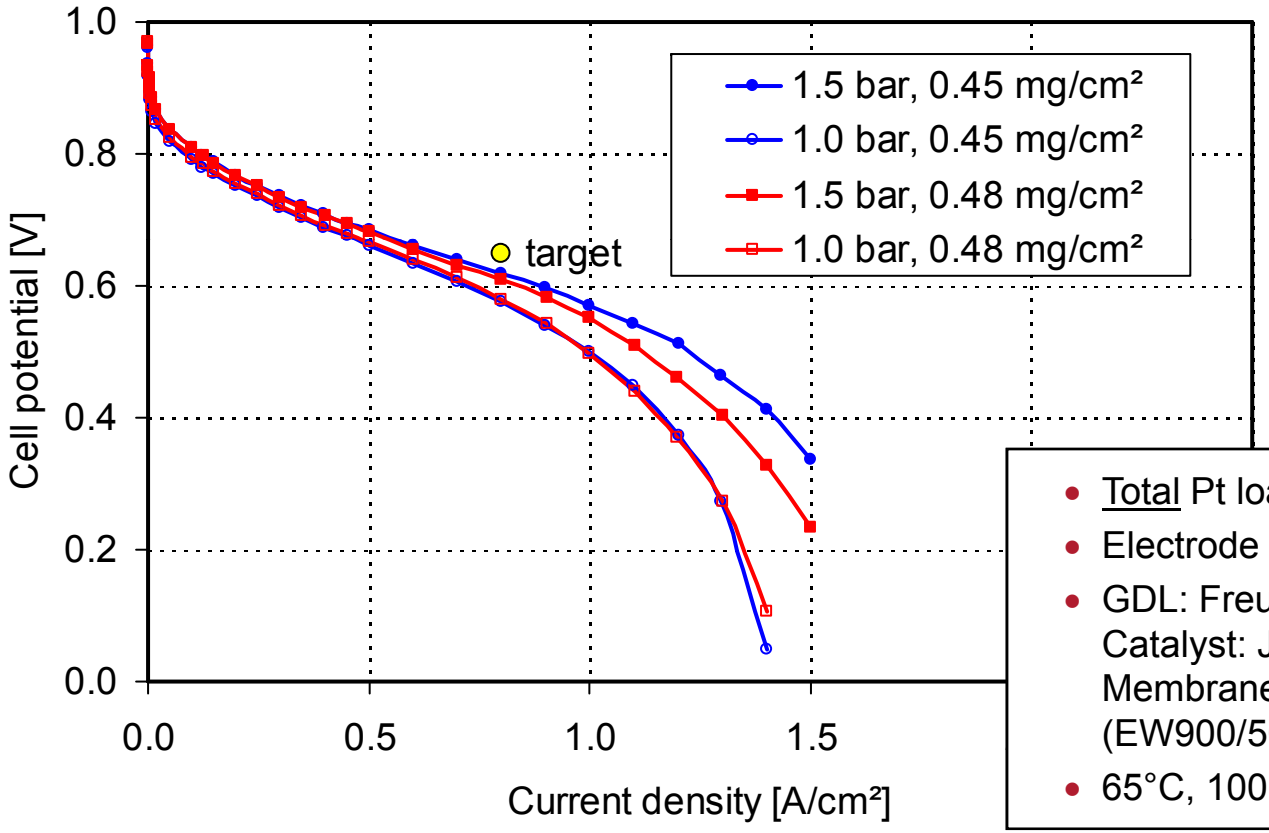
Catalytic Layer - quality

Dependence of:

- ink properties
- substrate quality
- manufacturing conditions



Catalytic layer - performance



- Total Pt loading numbers given
- Electrode thickness: 3.6 µm
- GDL: Freudenberg H2315 C2, Catalyst: JM Hispec 13100, Membrane: FuMAPEM 950, (EW900/50µm)
- 65°C, 100% RH, λ_{H2}=1.5, λ_{air}=2.0

The approach

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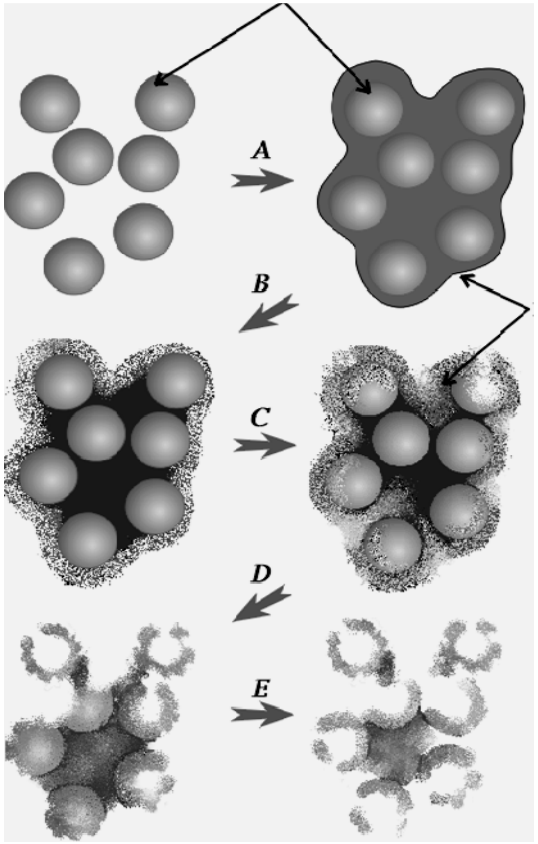
Catalyst support

Catalyst porous structure

- Sibunit carbon
- Developed at Boreskov Institute of Catalysis (BIC) in Novosibirsk, produced by IHP, Omsk, Russia

Synthesis and formation of Sibunit texture

Carbon black particles



Pyrocarbon

A – condensation (deposition of pyrocarbon onto carbon black particles)

B,C,D,E – activation (oxidative gasification of the PC/CB composite)

Likholobov V.A., et.al. React. Kinet. Catal. Lett. 54, 381 (1995)

Sibunit characteristics

Pore size distribution and specific surface area can be tailored in a wide range

- S_{BET} = 5 – 550 m^2/g, V_{pores} = 0.1 – 1.0 cm^3/g, D_{pores}= 5 – 80 nm

High Purity

- Ash content < 0.2%

High crystallinity

- *La* ~*Lc* = 3 – 4 nm, d_{002} = 0.345 – 0.350 nm

High Mechanical strength

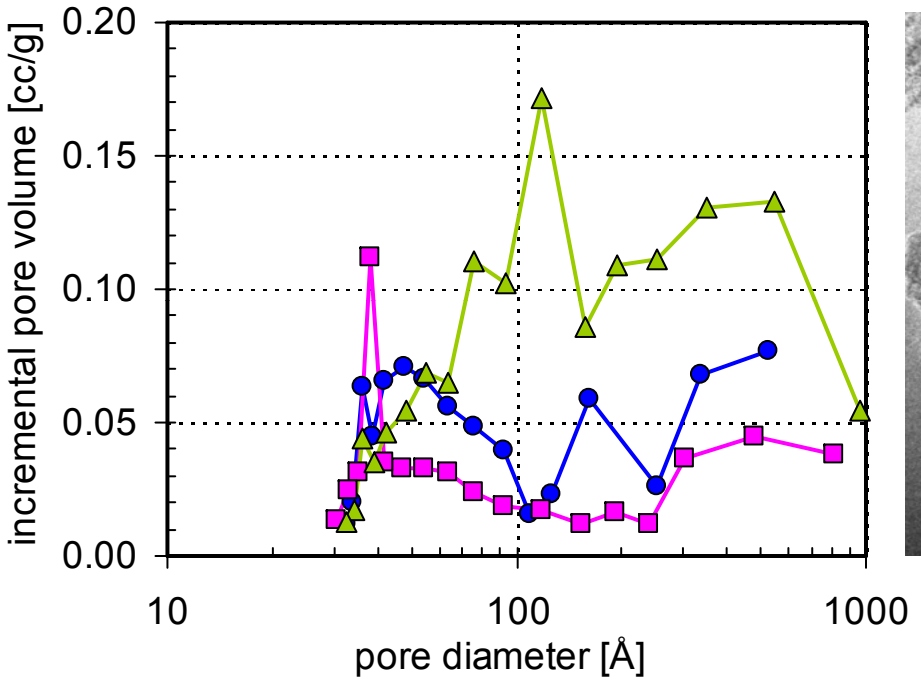
- up to 300 kg/cm^2

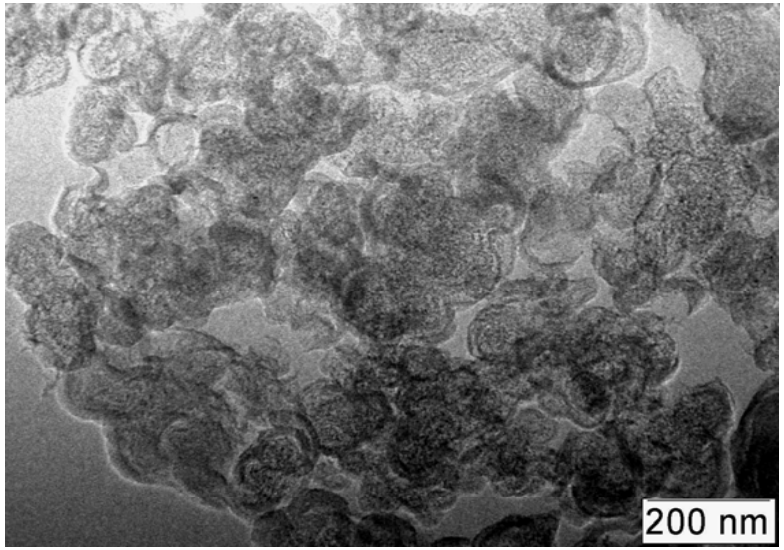
High electronic conductivity

- 0.0012 Ohm×m

High chemical and thermal stability.

Sibunit support materials used in IPHE-GENIE



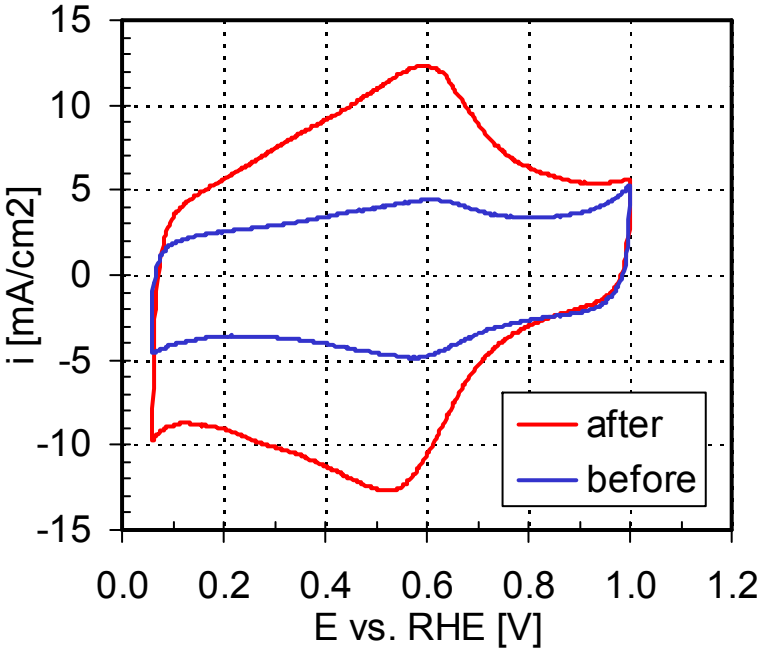


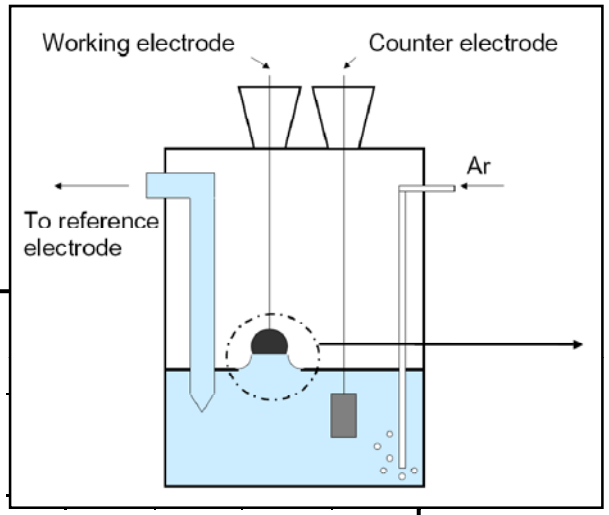
- BET surface area - 450 -500 m^2/g, total pore volume - 0.6 – 1.4 cm^3/g
- Pore size distributions calculated from the desorption branch of the nitrogen adsorption isotherm in accordance with the *BJH* model.

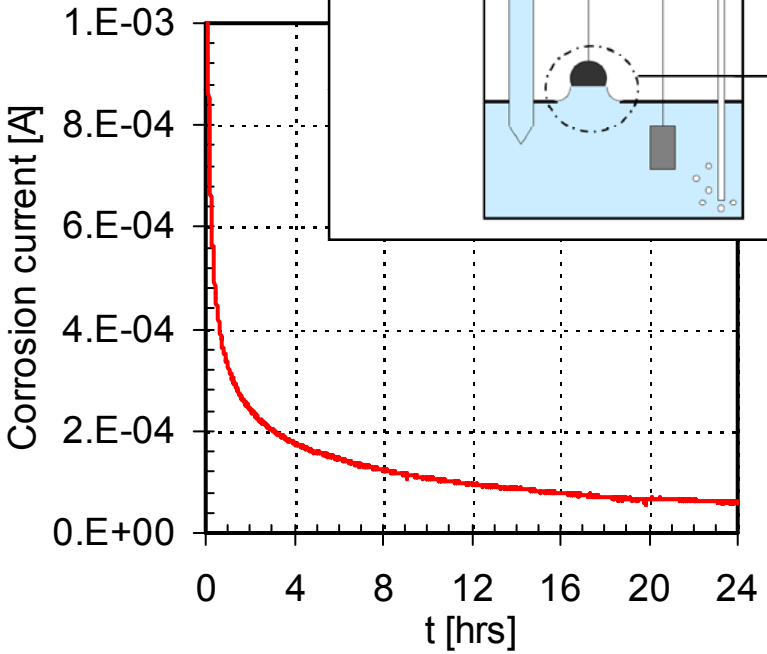
Corrosion stability of Sibunit carbons

Voltage hold at 1.2 V vs. RHE, 80°C in 1M H_2SO_4 for 24 hrs*

- $C + H_2O \rightarrow CO_2 + 4H^+ + 4e^-$
- $C + H_2O \rightarrow$ surface groups

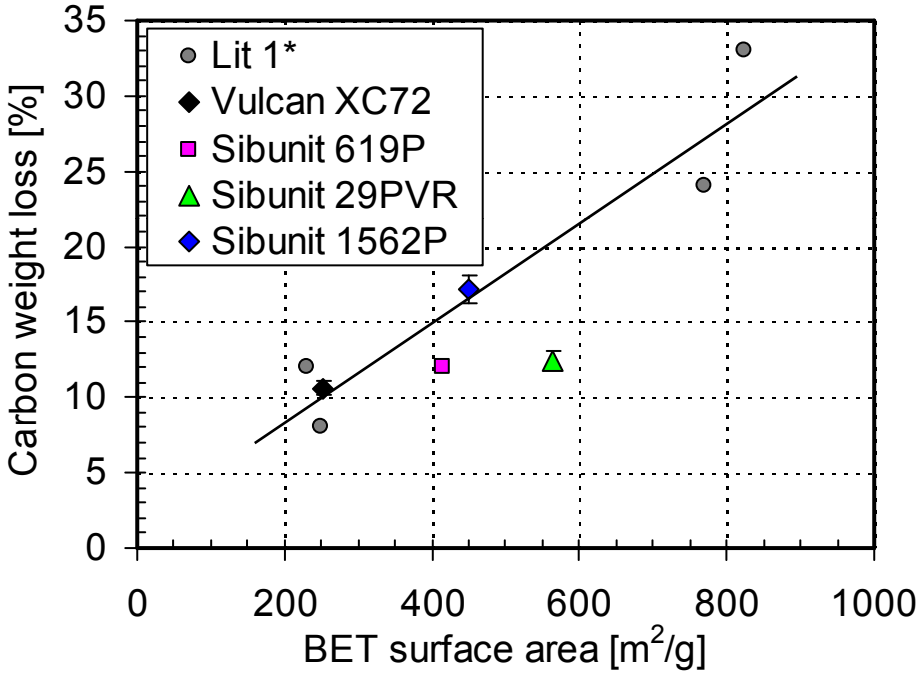




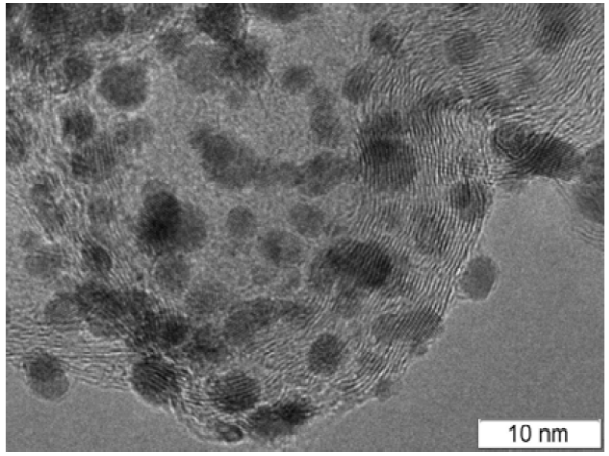


*Method: *S.C. Ball, S.L. Hudson, D. Thompsett, B. Theobald, Journal of Power Sources 171 (2007) 18-25*

Corrosion stability of Sibunit carbons

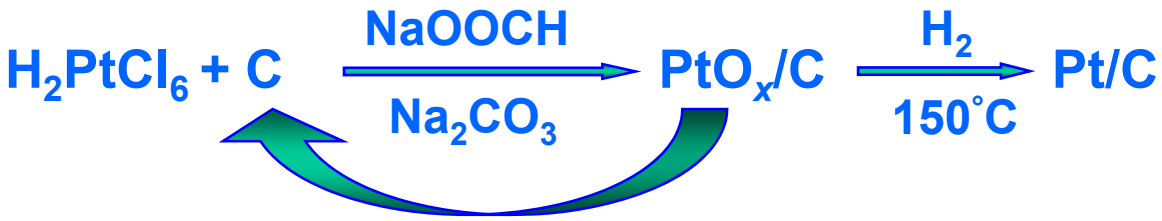


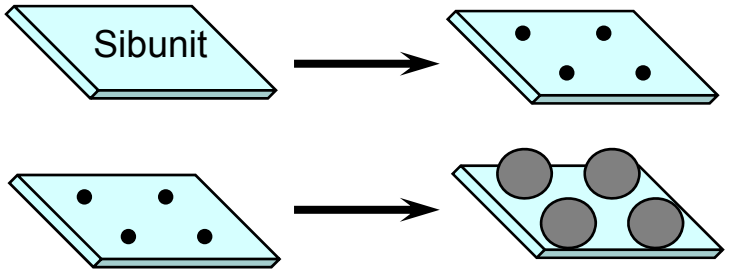
- Sibunit carbons are more corrosion resistant due to a higher degree of graphitization of the surface



*Lit 1: *S.C. Ball, S.L. Hudson, D. Thompsett, B. Theobald, Journal of Power Sources 171 (2007) 18-25*

Pt/C catalyst preparation



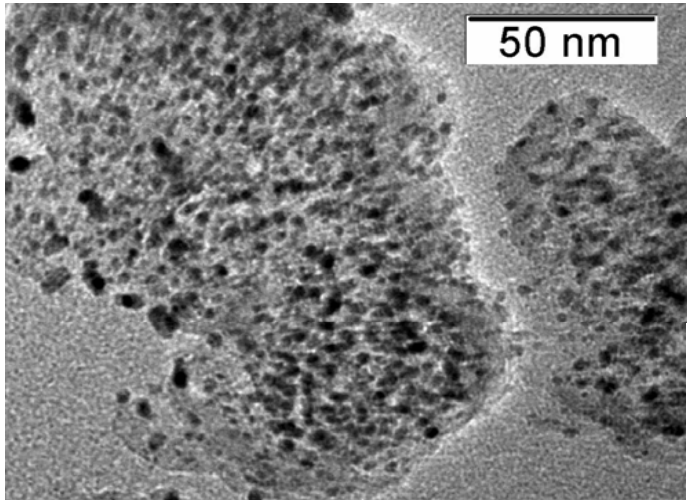


- Nuclei formation of highly dispersed metal or metal oxide particles
- Deposition of platinum onto the nuclei via chemical plating

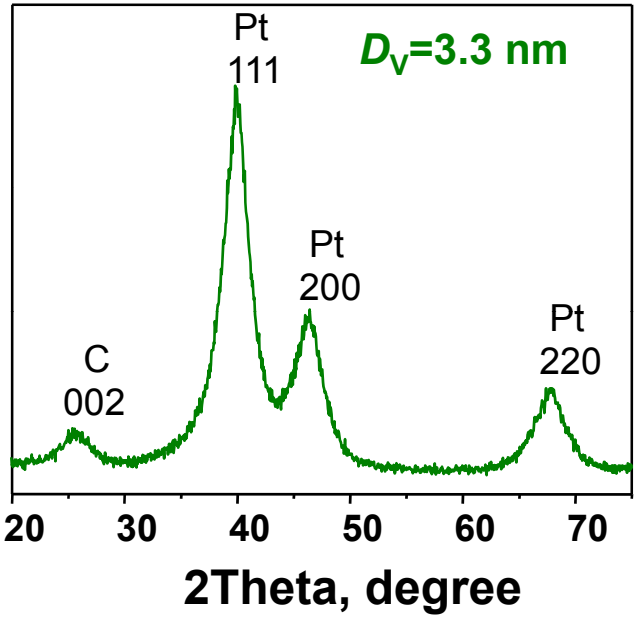
Advantages

- High platinum dispersion and narrow platinum size distribution at high metal loading.
- Easy control of platinum dispersion by variation in the number of the nuclei and weight of the deposited metal.

40wt% Pt/Sibunit 1562P catalyst

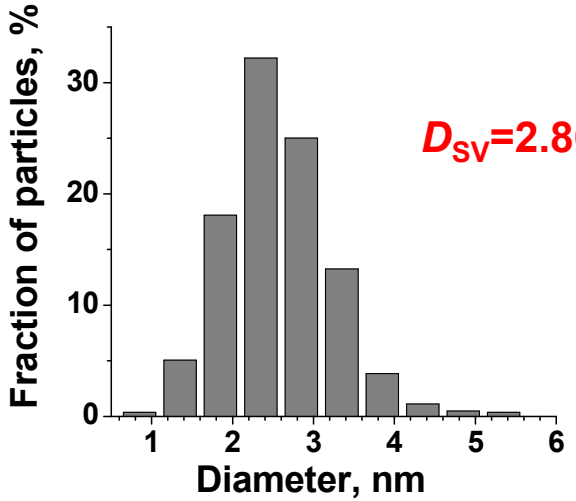


TEM



D_V=3.3 nm

XRD

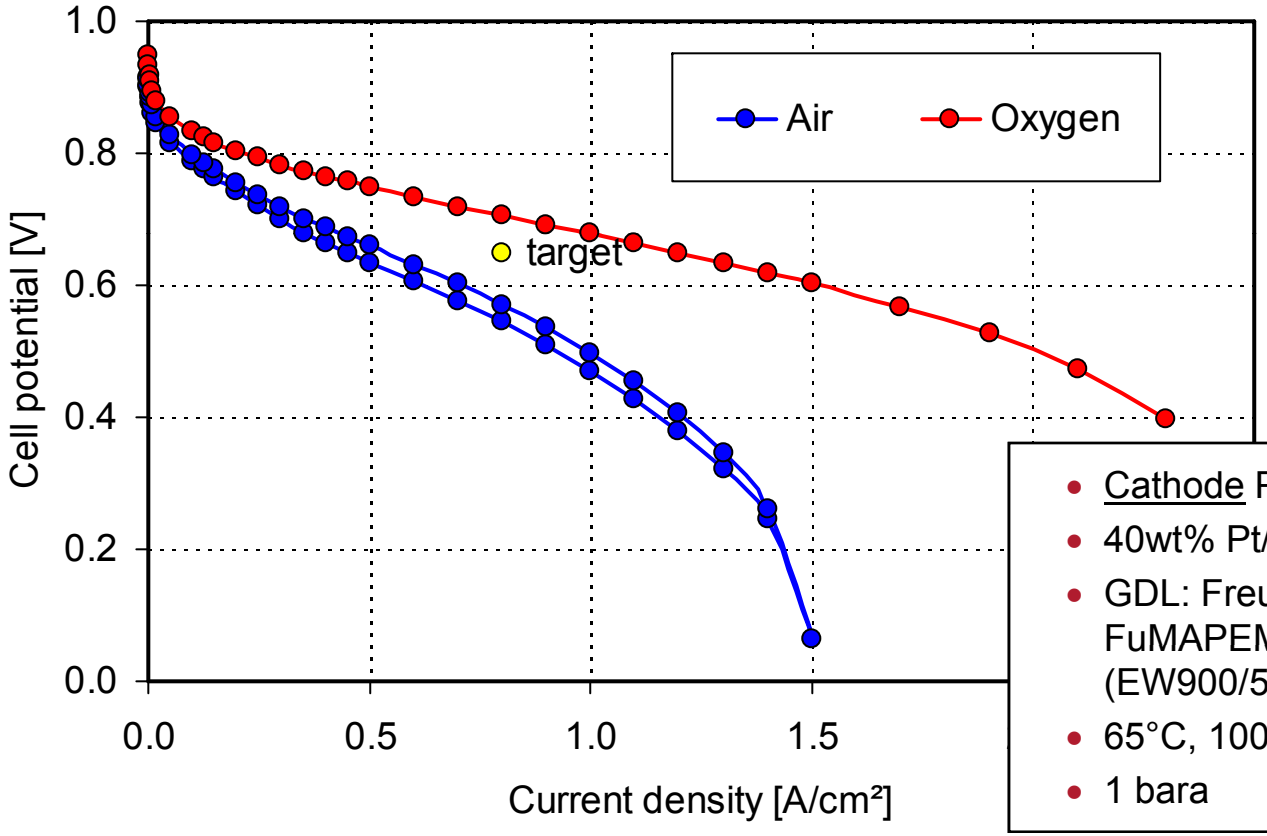


D_{SV}=2.86 nm

CO chemisorption:

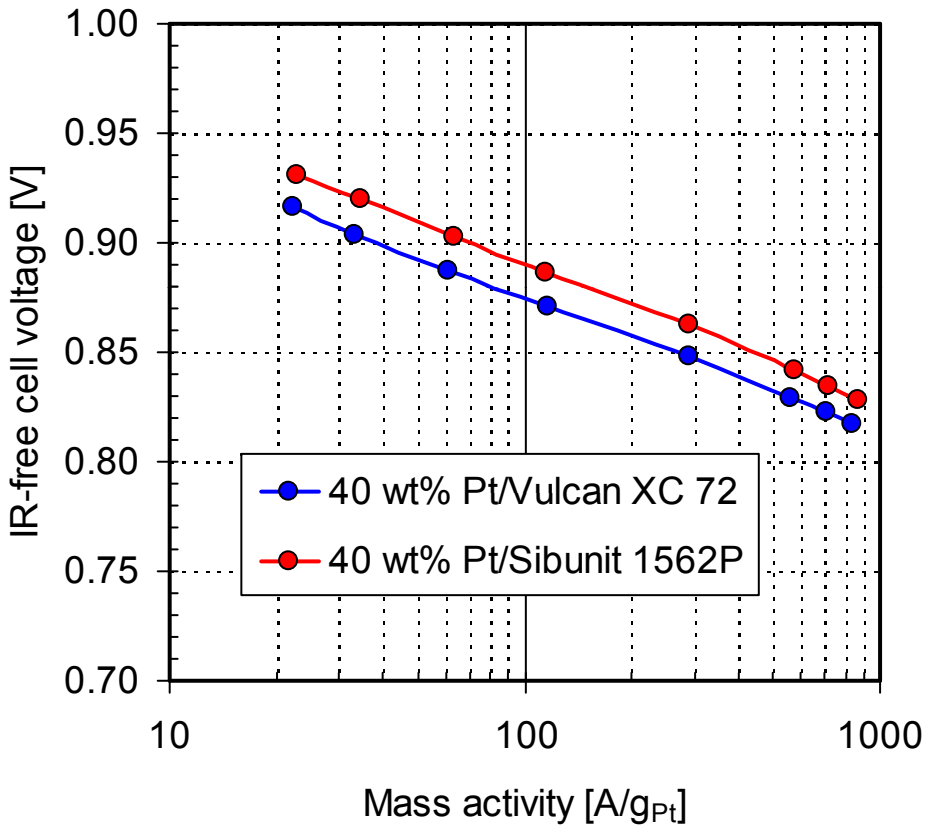
D_S=3.37 nm

Polarisation measurements Sibunit 1562P



- Cathode Pt loading 0.26 mg/cm^2
- 40wt% Pt/Sibunit 1562P
- GDL: Freudenberg H2315 C2, FuMAPEM 950 membrane (EW900/50µm)
- 65°C, 100% RH, λ_{H2}=1.5, λ_{ox}=2.0
- 1 bara

Kinetic activity ORR @ 0.9 V



Mass activity (A/g):

- 40wt%Pt/Sibunit 1562P 63 ± 5
- 40wt% Pt/Vulcan XC72R 30 ± 8

Specific activity (μA/cm^2):

- 40wt%Pt/Sibunit 1562P 104 ± 10
- 40wt% Pt/Vulcan XC72R 114 ± 10

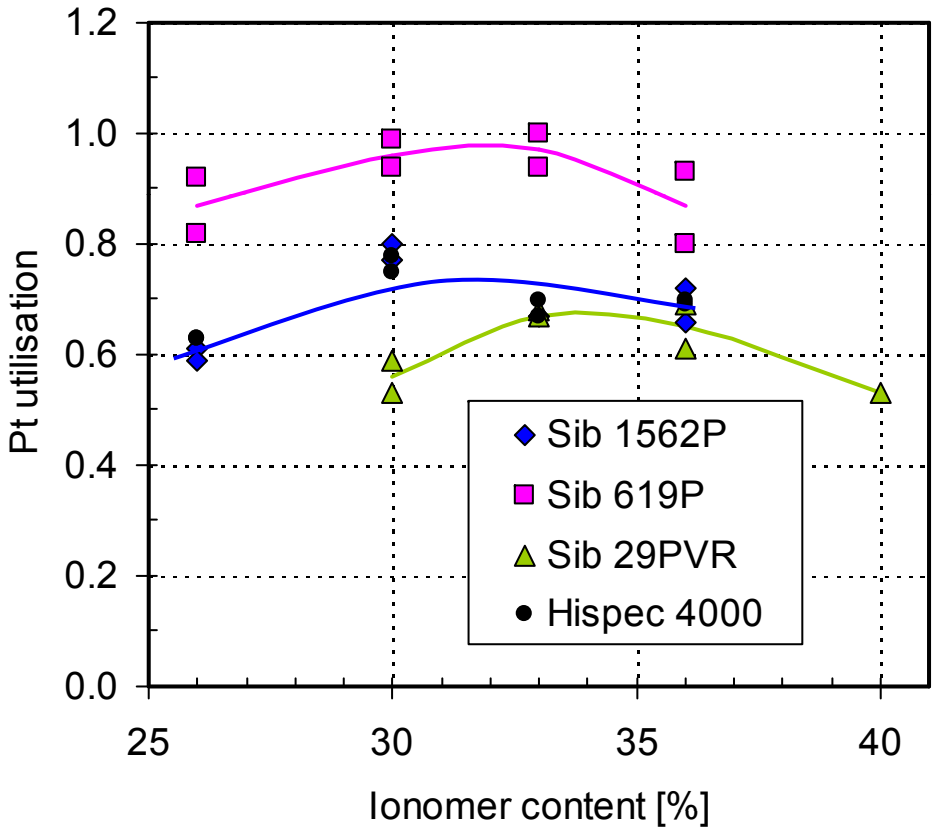
Pt utilization:

- 40wt% Pt/Sibunit 1562P 60-80%
- 40wt% Pt/Vulcan XC72R 60-80%

Note: Pt/Vulcan XC72R:
JM Hispec 4000, lot# 128106003

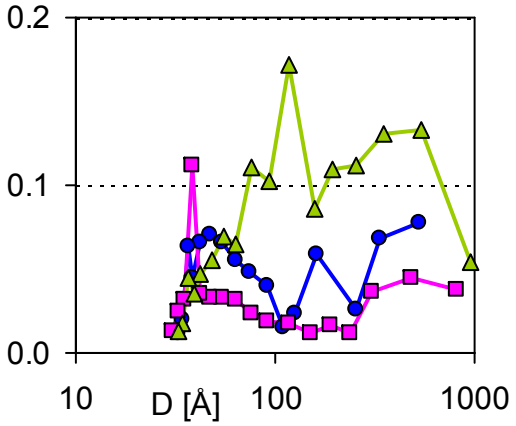
N.P. Lebedeva, et al., Fuel Cells, 9 (2009) 439-452.

Pore structure effect – Pt utilization



Pt utilisation = ECSA / SA

- ECSA: from in situ CV measurements
- SA: gas-phase CO chemisorption



Pore structure effect – Pt utilization

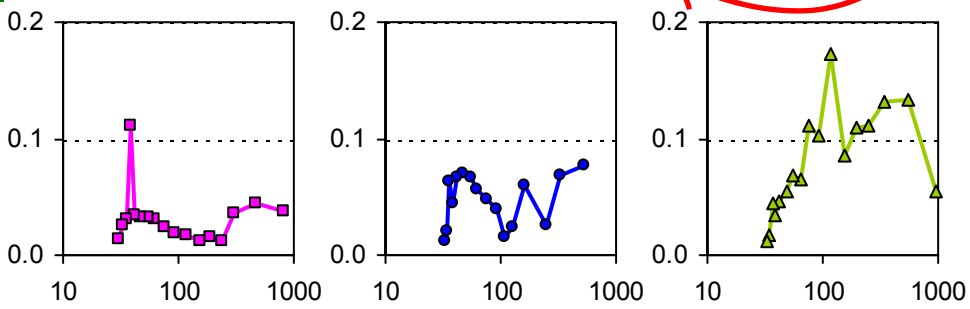
Support(s) having small mesopores show highest Pt utilisation.

However:

- 3-4 nm pores are inaccessible for the ionomer
- They tend to flood, water acts as a proton conductor
  - (J.McBreen, J.Electrochem.Soc. 1985, 132, 1112
  - Q.Wang et al, J.Electroanal.Chem. 2004, 573, 61
  - U.A. Paulus et al, J.Electroanal.Chem. 2003, 541, 77)
- Pores with d > ca. 10 nm are well accessible for the ionomer, Pt utilisation less dependent on presence of water

Transport properties

	40wt% Pt/Sibunit 619P	40wt% Pt/Sibunit 1562P	40wt% Pt/Sibunit 29PVR	40wt% Pt/Vulcan XC72R
Proton resistance in the cathode catalytic layer [Ohm cm^2]	< 0.13	< 0.12	< 0.12	< 0.12
Oxygen gain @ 1 A/cm^2, [V]	0.22-0.31	0.18-0.25	0.15-0.17	0.18-0.25



N.P. Lebedeva, A.S. Booij, I.N. Voropaev, P.A. Simonov, A.V. Romanenko, V.I. Bukhtiyarov, ECS Transactions 25 (2009) 1909-1913.

The approach

Proton conductivity at low RH / elevated T

- Low equivalent weight PFSA to enhance proton conductivity,
- Combined with cross linking (several approaches were explored) and hybridization to preserve integrity and mechanical properties

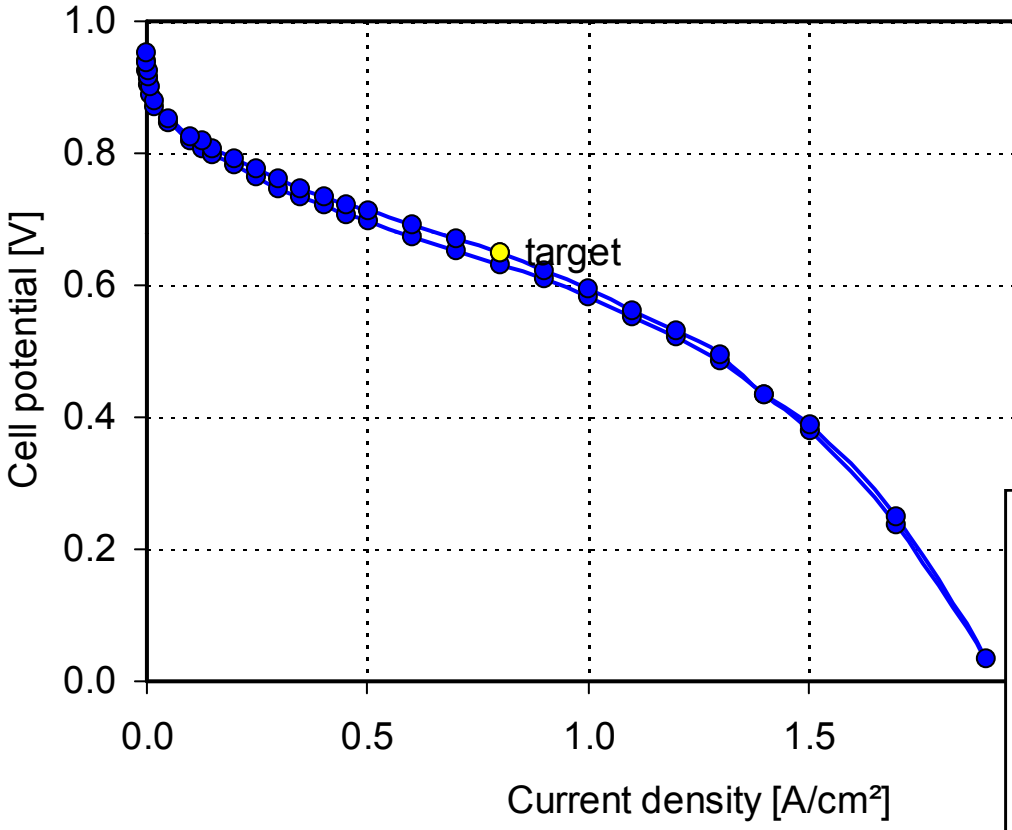
High performance at low Pt loading

- Thin electrodes
- Optimised pore structure of Pt support
- Efficient catalyst
- All combined in single MEA

High performance MEA at reduced RH / elevated T

- Combine new polymer and new electrode

Thin catalytic layer + Pt/Sibunit catalyst



- 65°C, 100% RH, λ_{H2}=1.5, λ_{ox}=2.0
- 1.5 bar
- Cathode: 40wt%Pt/Sibunit, 0.26 mgPt/cm²
- Anode: Hispec 9100, 0.14 mgPt/cm²

The approach

Proton conductivity at low RH / elevated T

- Low equivalent weight PFSA to enhance proton conductivity,
- Combined with cross linking (several approaches were explored) and hybridization to preserve integrity and mechanical properties

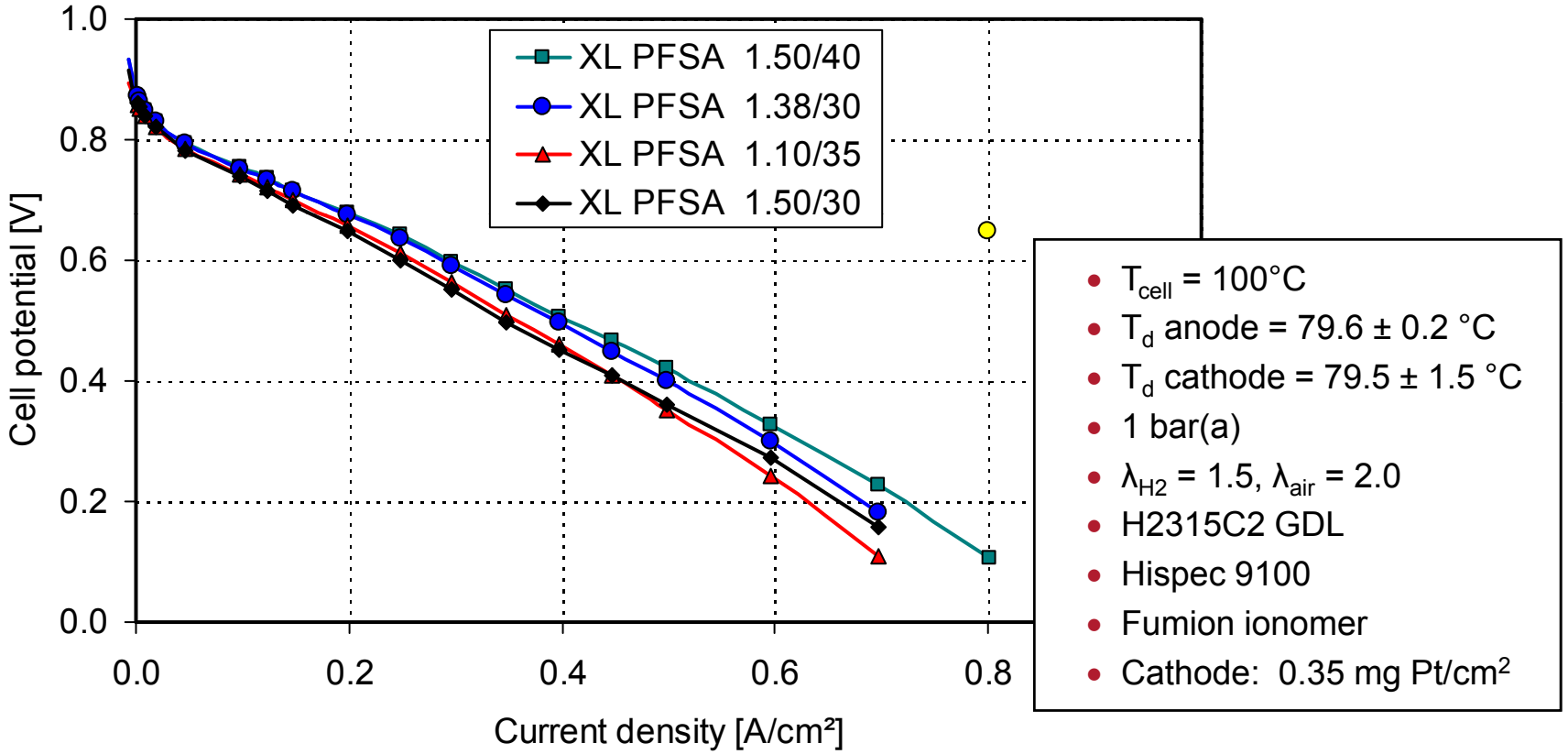
High performance at low Pt loading

- Thin electrodes
- Optimised pore structure of Pt support
- Efficient catalyst
- All combined in single MEA

High performance MEA at reduced RH / elevated T

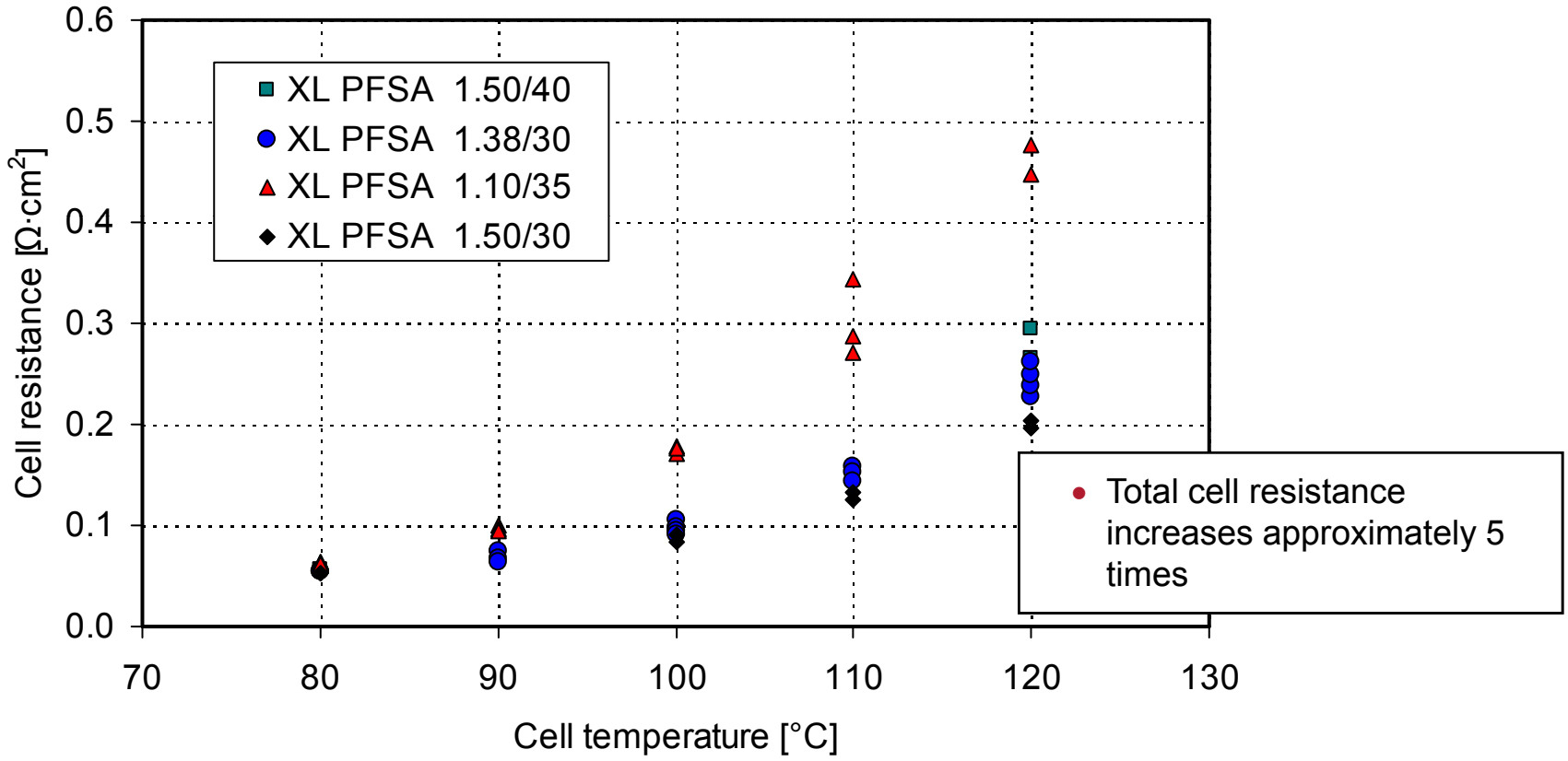
- Combine new polymer and new electrode
  - Thin electrode + XL polymer
  - Sibunit catalyst was not used yet

HT MEA test, XL PFSA membranes @ 100 ºC , 47% RH

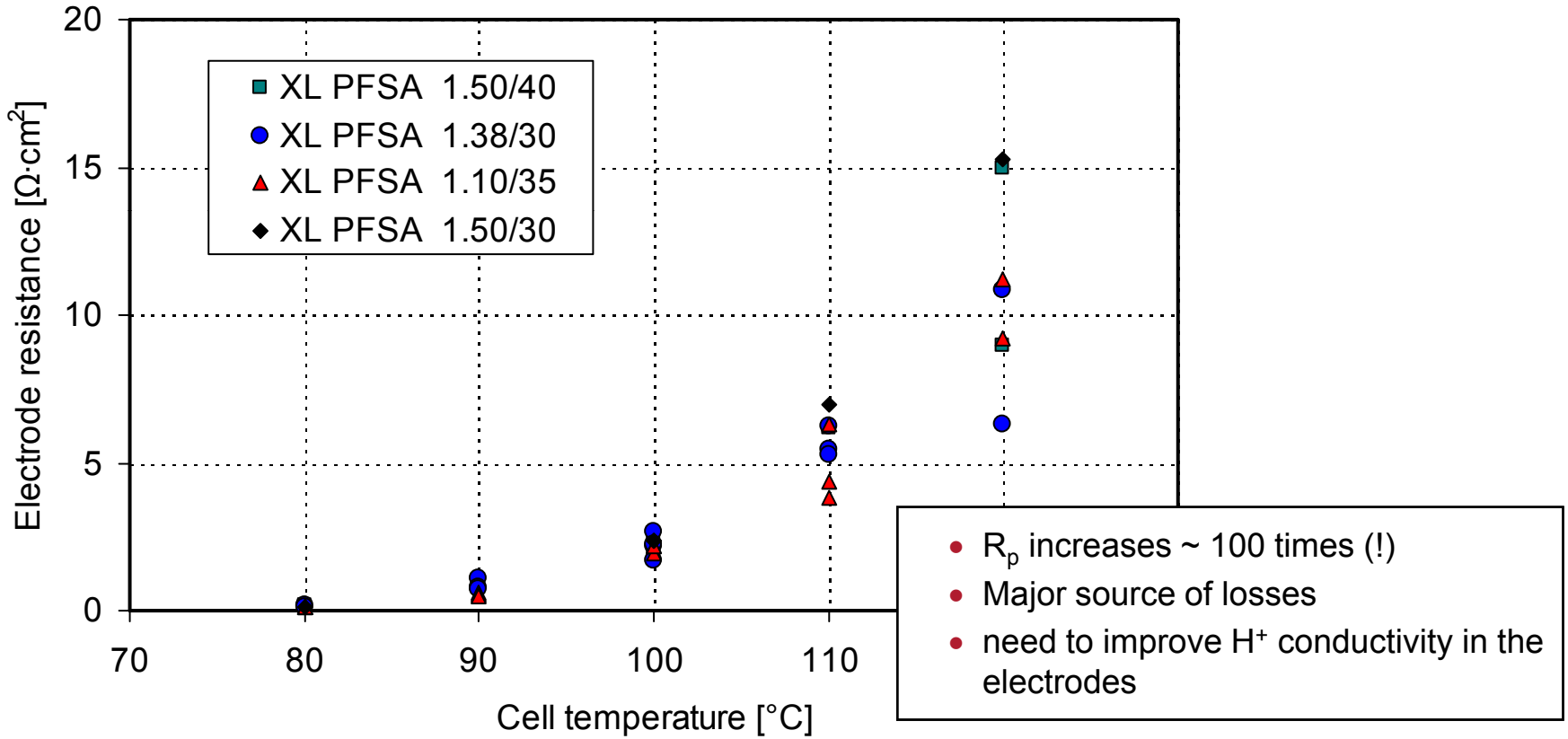


- T_{cell} = 100°C
- T_d anode = 79.6 ± 0.2 °C
- T_d cathode = 79.5 ± 1.5 °C
- 1 bar(a)
- λ_{H2} = 1.5, λ_{air} = 2.0
- H2315C2 GDL
- Hispec 9100
- Fumion ionomer
- Cathode: 0.35 mg Pt/cm^2

MEA characterisation – Total cell resistance



Proton resistance (R_p) in the catalytic layer(s)



- R_p increases ~ 100 times (!)
- Major source of losses
- need to improve H^+ conductivity in the electrodes

HT PEMFC, future work

Membrane:

- Further optimisation may be possible
- Durability studies

Electrode:

- improvement of the H^+ conductivity

Possible approaches:

- cross-linkable low EW ionomer
- optimised (thinner) electrodes
- Sibunit catalyst

Conclusions

Scientific Achievements

- Synthesis of cross-linkable monomers
- Development of cross-linked membranes
- Identification of degree of cross-linking
- Significantly improved conductivity at 120 °C / 25 % RH
- Novel Sibunit-based catalysts
- Thin layer electrode, by screen printing
- Total Pt loading of 0.4 mgPt/cm^2

More work needs to be done in order to produce an MEA that fully exploits the potential of the membrane and the catalyst!

Acknowledgements

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- EU for financial support (contract 039016)
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