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High temperature membranes for DMFC (and PEFC) applications.

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High Temperature Components

CATALYSTS and MEAs

- resistance to CO up to percentage level
- ultra-low loading
- chemical and electrochemical stability
- low cost
- suitability for mass production and scale-up
- air oxidant efficient
- reciclability, CO_2 production analysis
- development and assembling of electrodes & MEAs (electrode support, structure and morphology optimisation for HT application, low cost, automated production)

MEMBRANES

- low resistance
- long term chemical and mechanical stability
- suitable mechanical strength
- resistance to swelling
- pinhole free
- low cross-over
- minimal or no dependence on external humidification
- low cost
- suitability for mass production and scale-up
- reciclability,
- CO_2 life cycle.

HT Membranes

DMFC (dreamcar)

Advantages

- Enhanced methanol and oxygen reaction kinetics
- Lower CO poisoning (coverage)
- Better thermal management

Drawbacks

- High pressure requirements to maintain good hydration inside the membrane
- cross over?

PEFC (hit cell)

Advantages

- Enhanced CO and oxygen reaction kinetics
- Lower CO purification level
- Better thermal management
- Reduction of radiator size

Drawbacks

- New Polymer with no/very low humidification constrains (high risk)

Membranes

APPROACH	CRITICAL ASPECTS and working T
1. Composite membranes: ➢Functionalised polymer + inorganic igroscopic ➢ Functionalised polymer + inorganic proton conductor	•T limit 150-180°C determined by functional groups •High pressure
2. Liquid electrolyte embedded membranes: ➢Polymer matrix PBI + phosphoric acid ➢Polymer matrix PEO + sulfuric or TFMSA	•T limit 150-200°C determined by boiling point of free acid • Dilution of acid during operation •Corrosion
3. Composite membranes 2: ➢ Non functionalised thermal stable polymer matrix + inorganic proton conductive material	High risk •percolation paths, humidity content T limit ~300°C determined by polymer matrix
4. Ceramic •inorganic ceramic proton conductive electrolytes •inorganic ceramic proton conductive electrolytes embedded in polymeric inorganic matrix	High risk percolation paths (2nd case) T limit 350-800°C determined by transport number

Dreamcar EU project

DIRECT METHANOL FUEL CELLS SYSTEM FOR CAR APPLICATIONS

1. realisation and testing of 1.25 kW module

Total Power [W]	1250
Power Density [mW /cm2]	210
Current density [mA /cm2]	500
Single cell voltage [V]	0.42
Cathode feed	air
Anode feed	Methanol 1M/2M
Stack temperature [°C]	130

2. realisation and testing of 5 kW module

Total Power [W]	5000
Power Density [mW /cm2]	300
Current density [mA /cm2]	600
Single cell voltage [V]	0.5
Cathode feed	air
Anode feed	Methanol 1M/2M
Stack temperature [°C]	130/140

Dreamcar EU project

The ***major overall innovation*** of the project lies in the development of new materials (especially membranes and catalysts) able to work at high temperature with reduced metal loading.

partners
THALES E & C
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SOLVAY
TAU / RAMOT

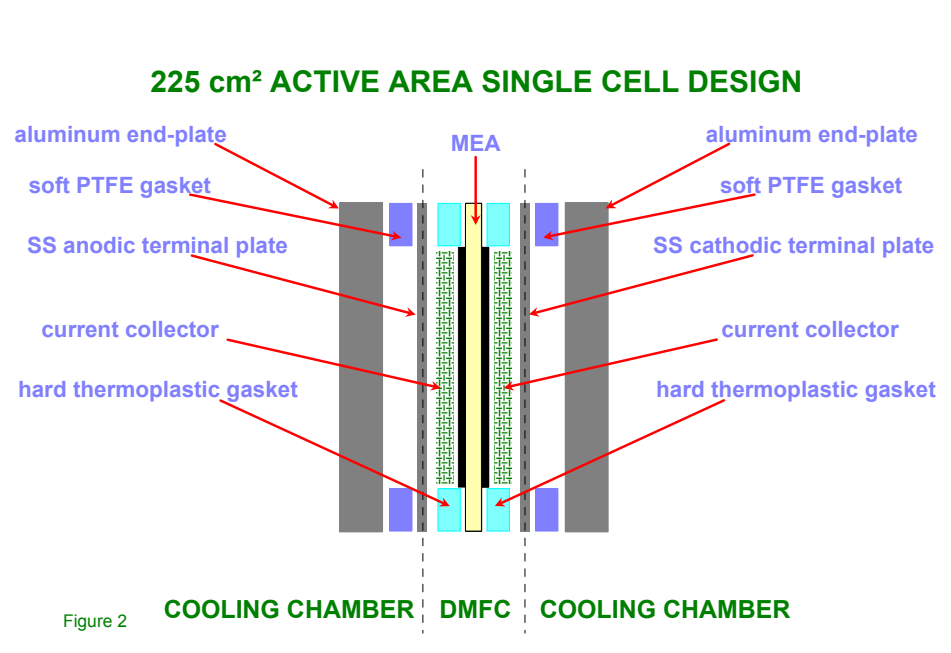


Figure 2

Membranes development approach

Two mains research routes :

- **Radiochemical grafting on fluorinated films**
- **Polymers chemical modifications**

Improvement of the membranes developed in the frame of the NEMECEL JOE3-CT-0063 Contract

Standard procedure :

- **β Irradiation of fluorinated films**
- **Grafting : Monomer + Barrier polymer + cross-linking agent**
- **Functionalisation : Sulfonation and hydrolysis.**

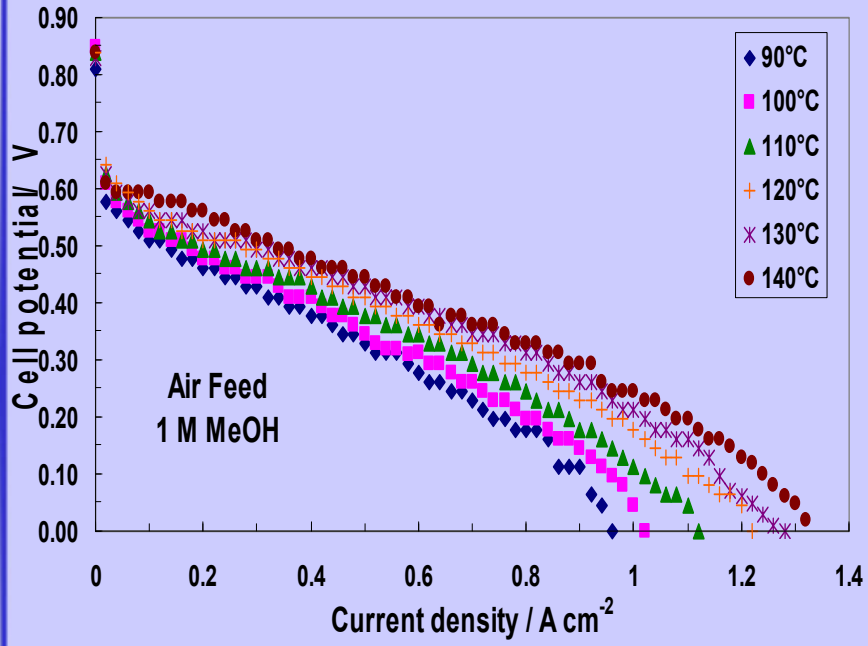
Membranes development approach

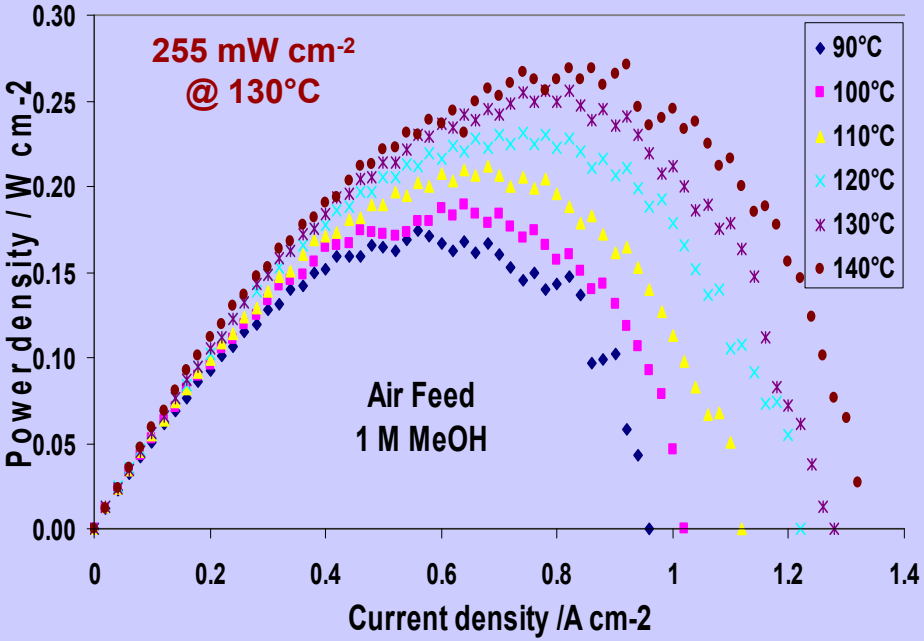
Sample reference : DREM 03 (Surface modified membrane)

- Radio-chemical grafting on fluorinated base film (ETFE)
- Thickness : 175 µm
- Exchange sites: Sulfonic acid
- Exchange capacity : 2.1 meq/g
- Area resistance: 70 to 90 mΩ.cm² (25°C; HCl 0.1 M; 1000 Hz)
- Conductivity: 190 mS/cm
- Water absorption : 60 % w

SOLVAY

Membrane Assessment



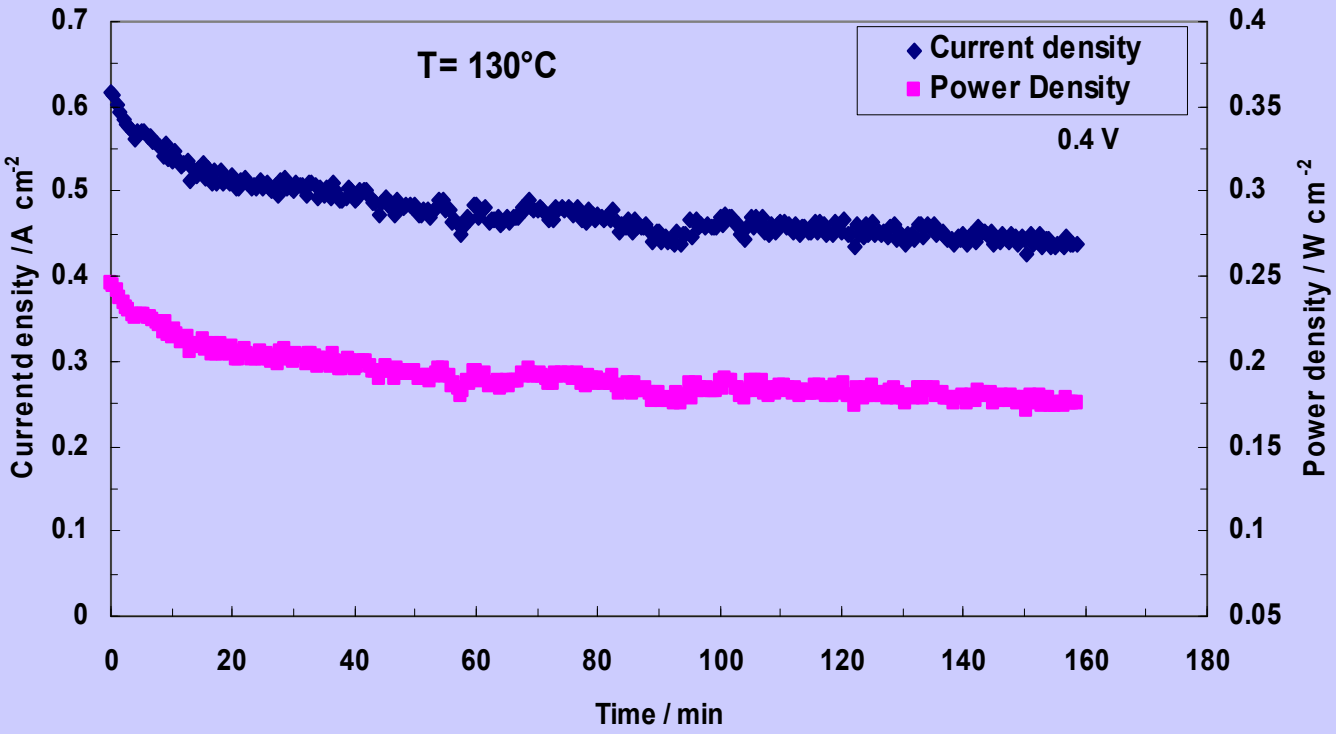


Anode Catalyst 85% PtRu/C
Cathode Catalyst 60% Pt/C
Membrane DREM 04(100microns)

Hyflon

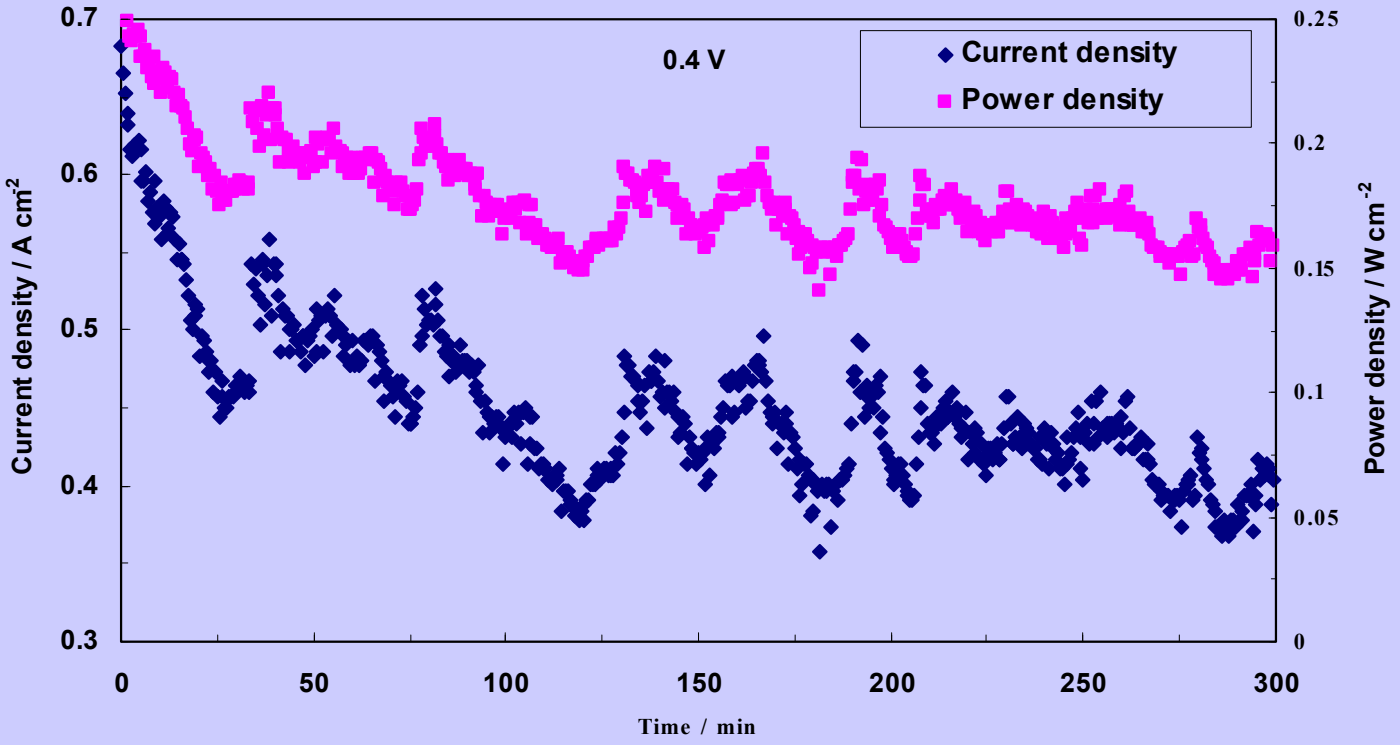
Membrane Assessment

Stability test @ 130°C



Membrane Assessment

Stability test @ 140°C

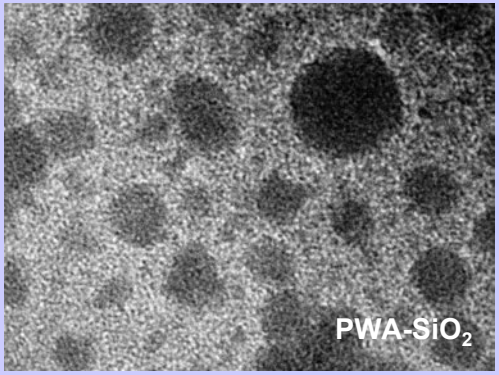


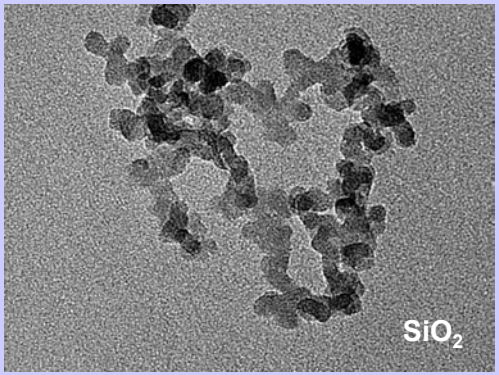
Membrane Assessment

Composite recast Nafion®-inorganic filler membranes

- Enhanced water retention properties at high temperatures
- DMFC operation up to 145 °-150 °C
- Good chemical and electrochemical stability
- Reduced methanol cross-over

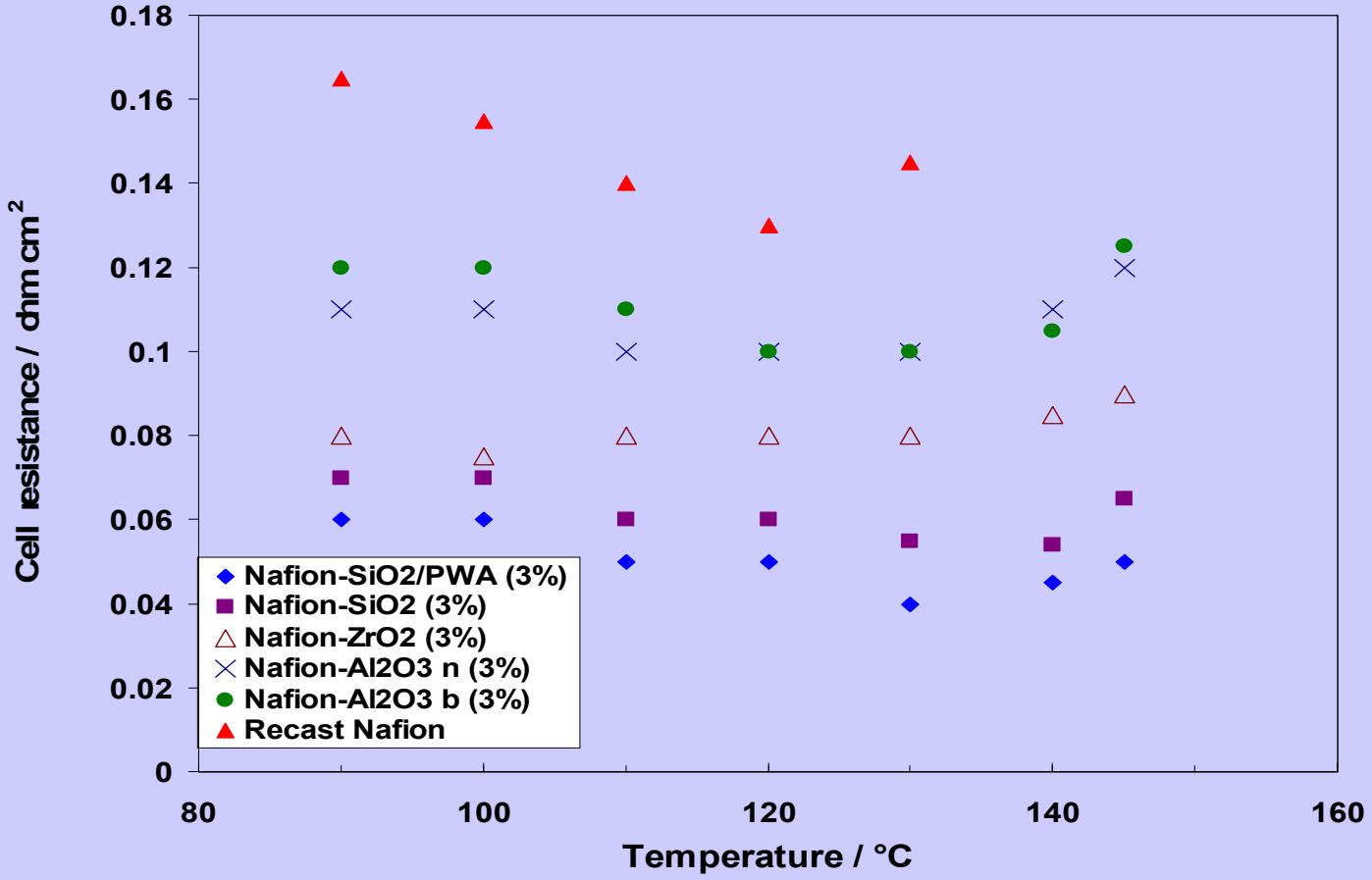
- Better understanding of the operation mechanism of these electrolytes
- Effects enhancing the proton conductivity at 150 °C
- Role of surface chemistry (filler) and morphology (filler and membrane)
- Effect of pressure



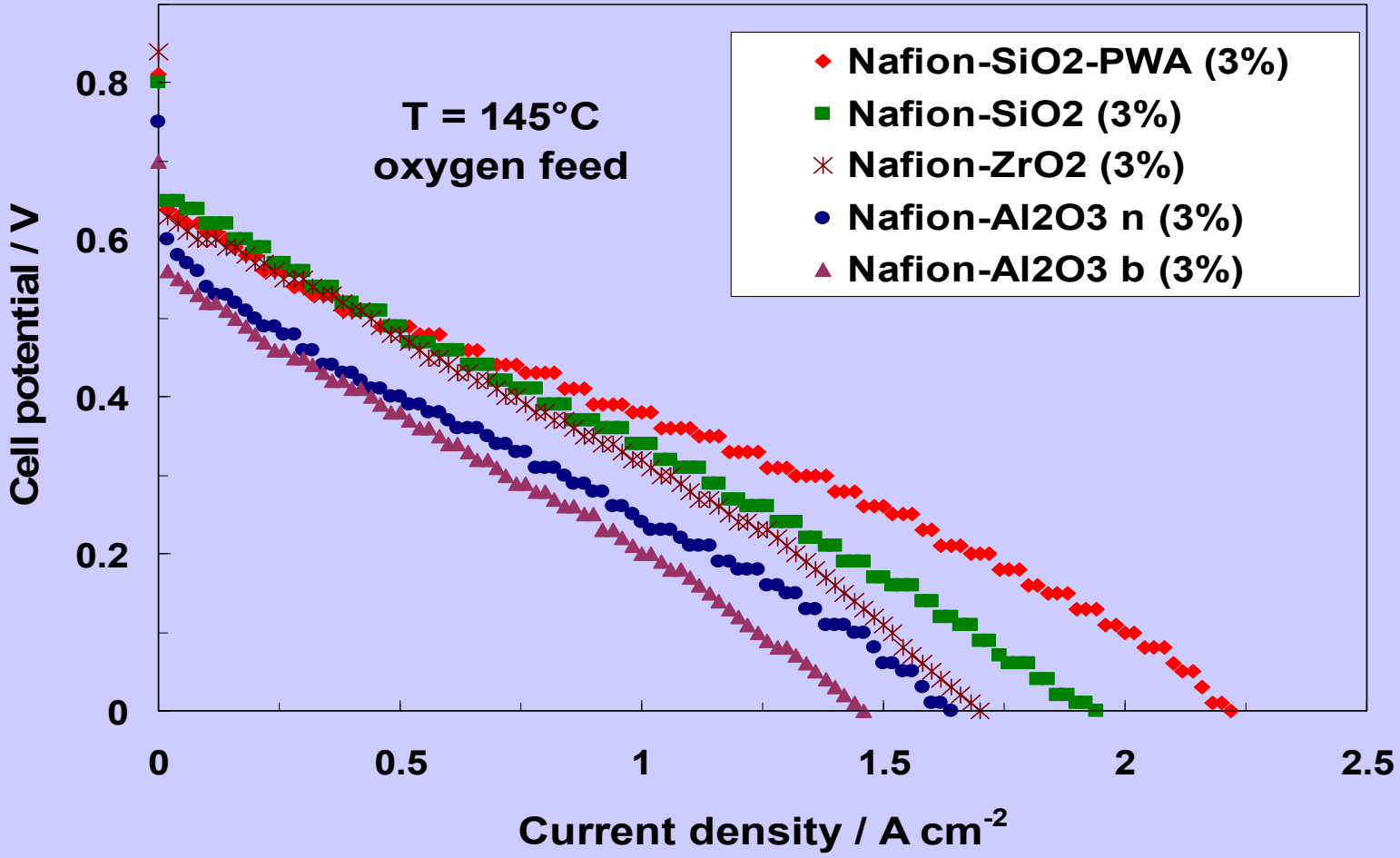


Variation of cell resistance values as a function of temperature in DMFCs

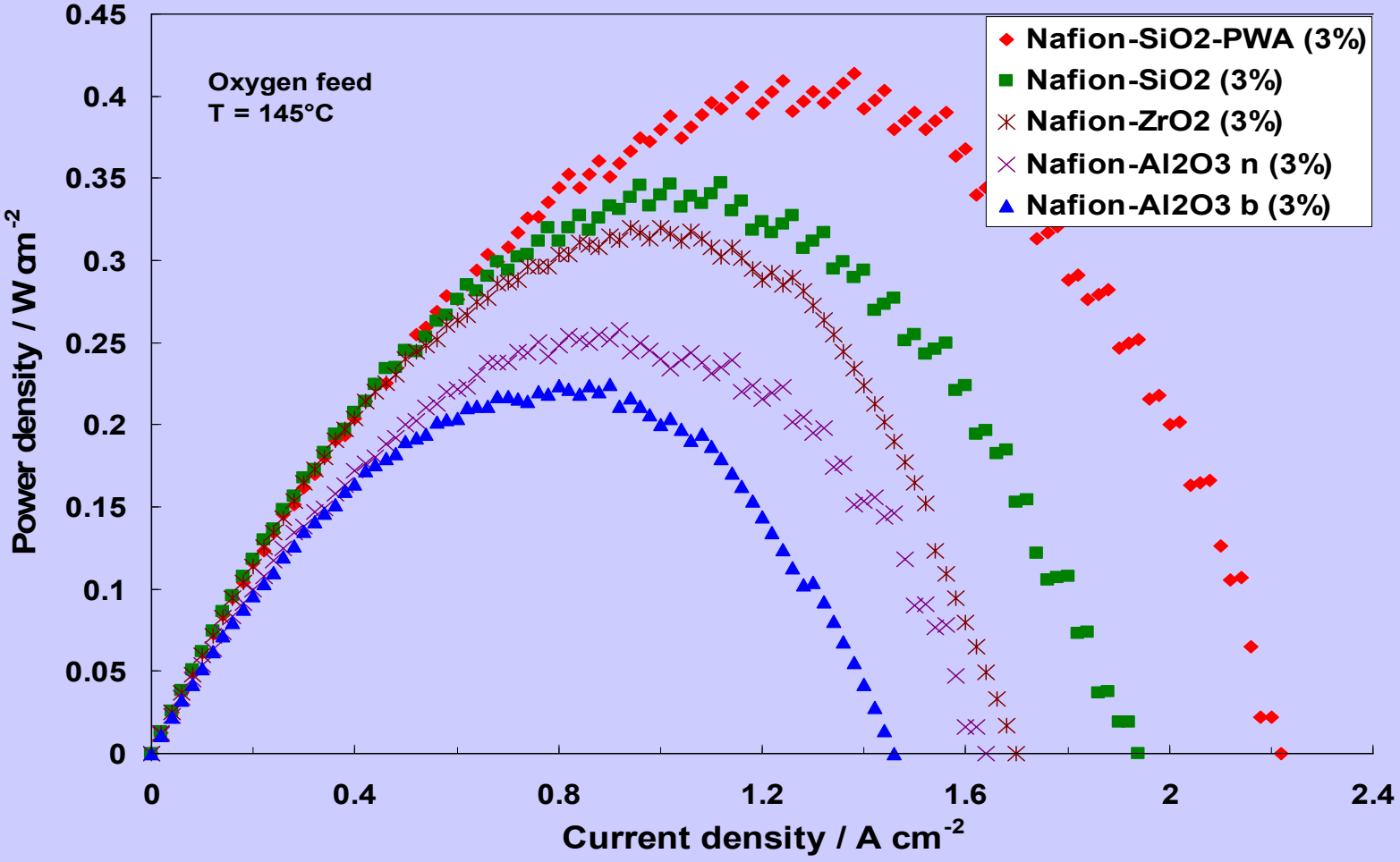
Effect of the inorganic filler



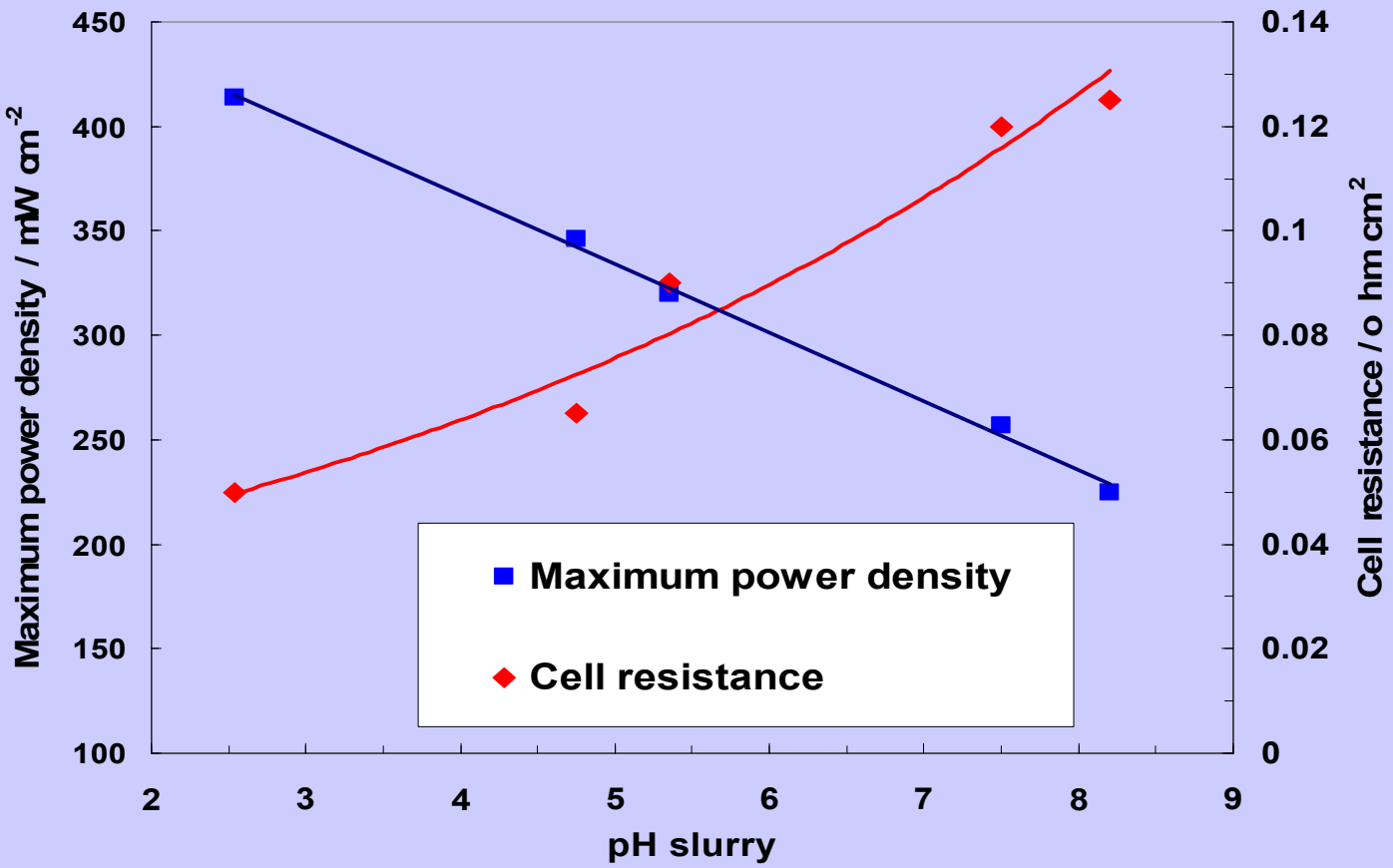
DMFC polarization curves at 145 °C



DMFC power densities curves at 145 °C



Composite recast Nafion®-inorganic filler membranes



Maximum power density and cell resistance of composite membranes-based DMFCs at 145 °C as a function of the pH of slurry of the inorganic filler.

Composite recast Nafion®-inorganic filler membranes

Acid-base properties of inorganic fillers play a key role for the water uptake and conductivity of composite membranes at 150 °C

Acidic surface OH groups facilitate water co-ordination which acts as vehicle for proton migration

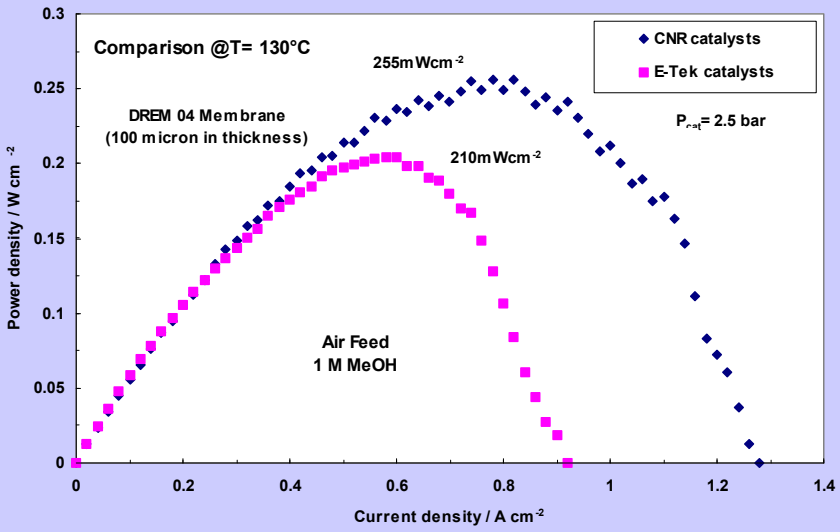
DMFC performance increases as the pH of slurry of the inorganic filler in the membrane decreases

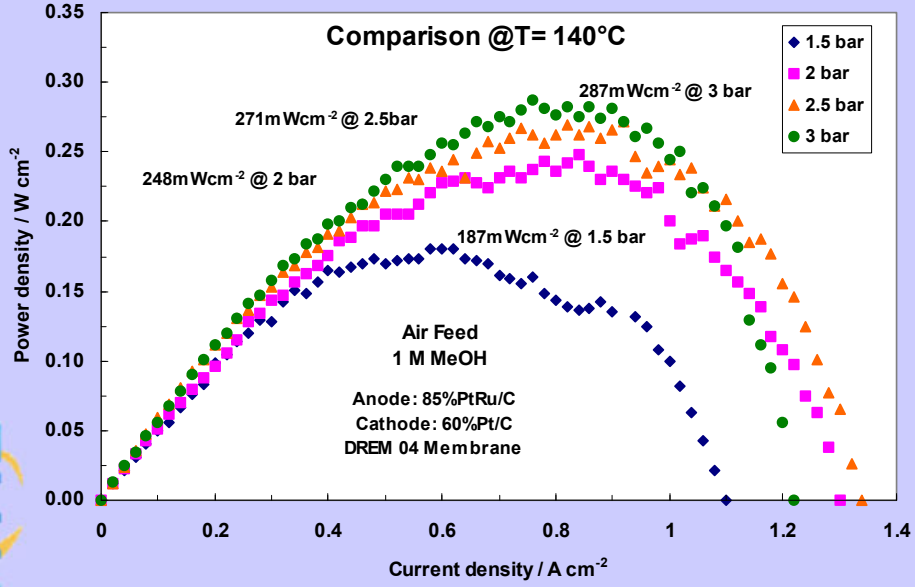
Operation at low pressure does not influence significantly hydration/conductivity characteristics of composite membranes at 150 °C

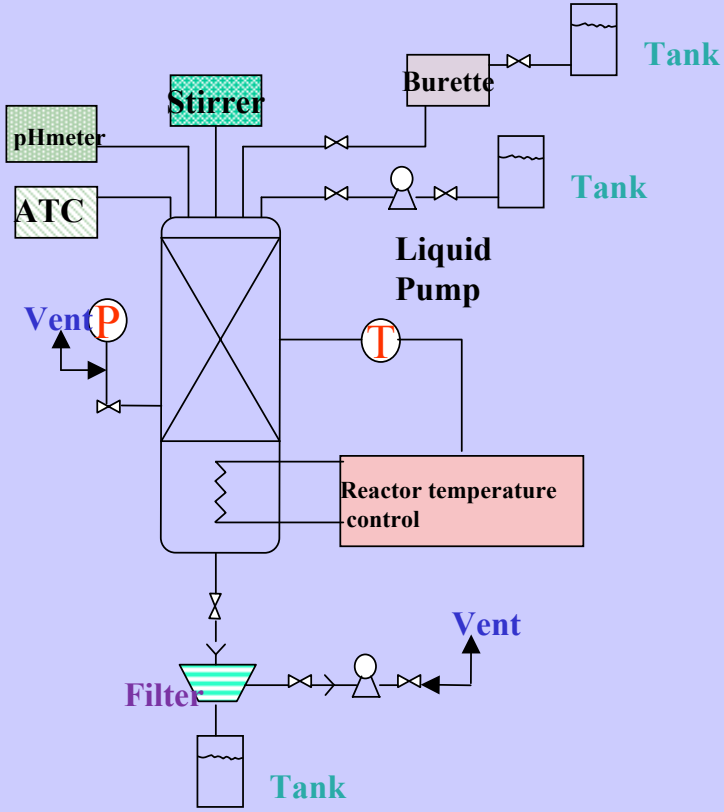
High oxygen partial pressures are needed for proper cathode operation in the presence of methanol cross-over.

The ionic conductivity of the composite membranes at high temperatures may be increased by appropriate tailoring of the surface characteristics of the added ceramic oxides

Catalysts developments







High Temperature HiT Cell (proposal)

MEMBRANES

Cooperative action :
DC, VW, Toyota E, Opel A

Time frame	S	M	L
Operation temperature	20°C - 100 °C	-10 °C - 120 °C	-30°C - 160°C
Electric properties			
Proton conductivity [S/cm] @ 20 % RH stable for 48H	0.1 S/cm @ 100°C 0.05 S/cm @ 20°C	0.1 S/cm @ 120°C 0.05 S/cm @ -10°C	0.1 S/cm @ 120°C 0.05 S/cm @ -30°C
@ 0 % RH, stable for 48H			0.1 S/cm @ 120°C
Mechanical properties			
Minimum tensile Strenght [Mpa] measured in 90 °C water in 2 directions thickness 25 µ	25	25	25
Elongation at break [%] measured at 90 °C dried during 1 hour @ 100 °C in 2 directions thickness 25 µ	> 100%	> 200%	> 200%
Max swelling in water at 95 °C	< 10 %	< 5 %	< 5 %
Tg fully soaked in water	20 ° above max operating temperature	thermal cycle stability to be defined	thermal cycle stability to be defined
Cost			
cost per m²	low	lower	20 €/m² @ 1000000 m² volumes per year