Danish Power Systems ®

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Performance and degradation of high Performance MEAs For High Temperature PBI Fuel Cells

Thomas Steenberg, Hans Aage Hjuler, Carina Terkelsen, Thorsten Holst and Hector R. Garcia

Outline

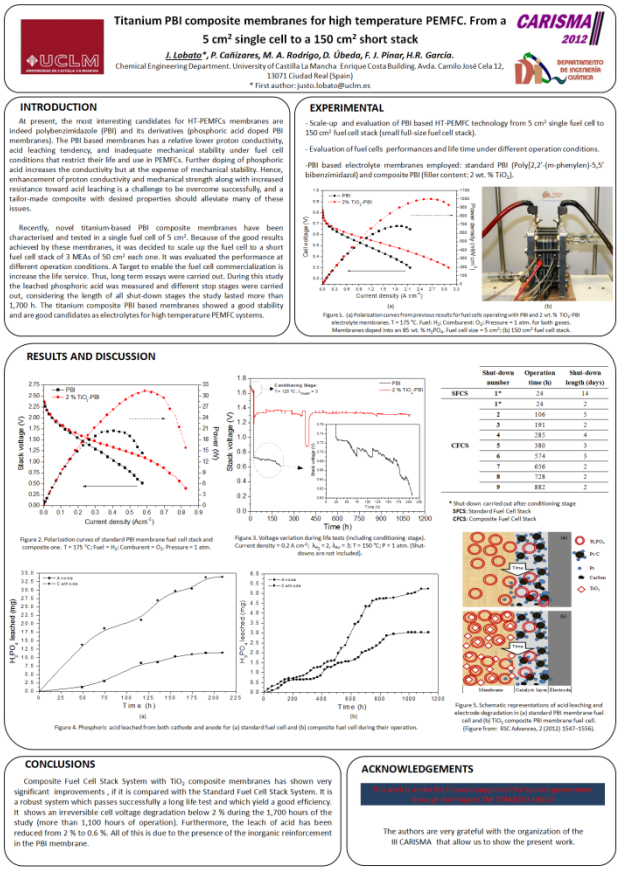
- Introduction
- Performance and quality control
- Durability
- Challenges!

Who is Danish Power Systems (DPS)?

- Strategy: To develop State of the Art MEAs and establish a manufacturing facility
- Strong relations with Danish and international companies, universities and organizations
- Key player and member of the Danish Partnership for Hydrogen and Fuel Cells

DPS contributions – posters:

Hector R. Garcia



Titanium PBI composite membranes for high temperature PEMFC. From a 5 cm² single cell to a 150 cm² short stack

CARISMA 2012

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INTRODUCTION

At present, the most interesting candidates for HT-PEMFCs membranes are indeed polybenzimidazole (PBI) and its derivatives (phosphoric acid doped PBI membranes). The PBI based membranes has a relative lower proton conductivity, acid leaching tendency, and inadequate mechanical stability under fuel cell conditions that restrict their life and use in PEMFCs. Further doping of phosphoric acid increases the conductivity but at the expense of mechanical stability. Hence, enhancement of proton conductivity and mechanical strength along with increased resistance toward acid leaching is a challenge to be overcome successfully, and a tailor-made composite with desired properties should alleviate many of these issues.

Recently, novel titanium-based PBI composite membranes have been characterised and tested in a single fuel cell of 5 cm². Because of the good results achieved by these membranes, it was decided to scale up the fuel cell to a short fuel cell stack of 3 MEAs of 50 cm² each one. It was evaluated the performance at different operation conditions. A Target to enable the fuel cell commercialization is increase the life service. Thus, long term essays were carried out. During this study the leached phosphoric acid was measured and different stop stages were carried out, considering the length of all shut-down stages the study lasted more than 1,700 h. The titanium composite PBI based membranes showed a good stability and are good candidates as electrolytes for high temperature PEMFC systems.

EXPERIMENTAL

- Scale-up and evaluation of PBI based HT-PEMFC technology from 5 cm² single fuel cell to 150 cm² fuel cell stack (small full-size fuel cell stack).

- Evaluation of fuel cells performances and life time under different operation conditions.

-PBI based electrolyte membranes employed: standard PBI (Poly(2,2'-(m-phenylen)-5,5' bibenzimidazol) and composite PBI (filler content: 2 wt. % TiO_2).

Figure 1. (a) Polarization curves from previous results for fuel cells operating with PBI and 2 wt. % TiO_2-PBI electrolyte membranes. T = 175 °C. Fuel: H_2 Comburent: O_2. Pressure = 1 atm. for both gases. Membranes doped into an 85 wt. % H_3PO_4. Fuel cell size = 5 cm²; (b) 150 cm² fuel cell stack.

RESULTS AND DISCUSSION

Figure 2. Polarization curves of standard PBI membrane fuel cell stack and composite one. T = 175 °C; Fuel = H_2; Comburent = O_2. Pressure = 1 atm.

Figure 3. Voltage variation during life tests (including conditioning stage). Current density = 0.2 A cm⁻²; λ_{H_2} = 2, λ_{air} = 3; T = 150 °C; P = 1 atm. (Shut-downs are not included).

	Shut-down number	Operation time (h)	Shut-down length (days)
SFCS	1*	24	14
	1*	24	2
CFCS	2	106	5
	3	191	2
	4	285	4
	5	380	3
	6	574	3
	7	656	2
	8	728	2
	9	882	2

* Shut-down carried-out after conditioning stage
SFCS: Standard Fuel Cell Stack
CFCS: Composite Fuel Cell Stack

Figure 4. Phosphoric acid leached from both cathode and anode for (a) standard fuel cell and (b) composite fuel cell during their operation.

Figure 5. Schematic representations of acid leaching and electrode degradation in (a) standard PBI membrane fuel cell and (b) TiO_2 composite PBI membrane fuel cell. (Figure from: RSC Advances, 2 (2012) 1547–1556).

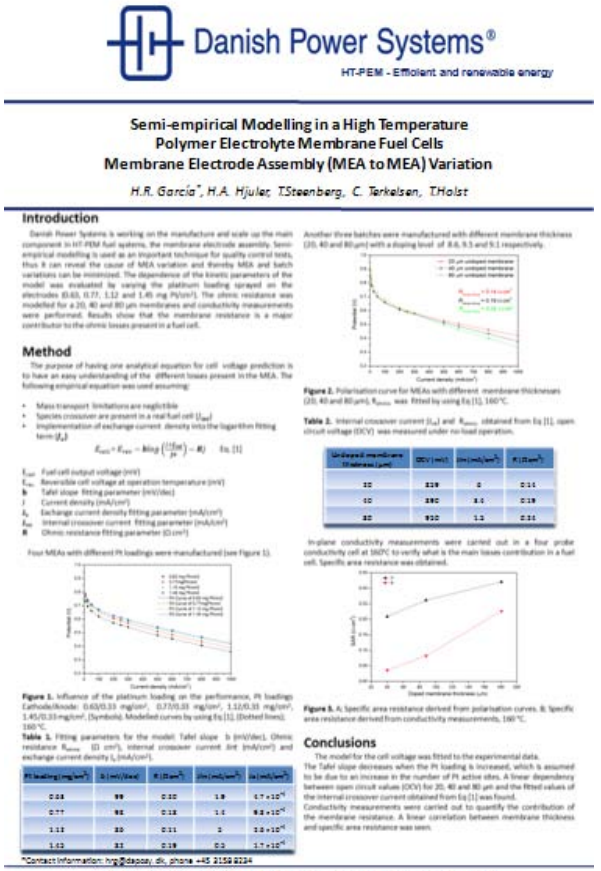
CONCLUSIONS

Composite Fuel Cell Stack System with TiO_2 composite membranes has shown very significant improvements , if it is compared with the Standard Fuel Cell Stack System. It is a robust system which passes successfully a long life test and which yield a good efficiency. It shows an irreversible cell voltage degradation below 2 % during the 1,700 hours of the study (more than 1,100 hours of operation). Furthermore, the leach of acid has been reduced from 2 % to 0.6 %. All of this is due to the presence of the inorganic reinforcement in the PBI membrane.

ACKNOWLEDGEMENTS

This work is under the financial support of the Spanish government through the Project ENE CSD2010-00015.

The authors are very grateful with the organization of the III CARISMA that allow us to show the present work.



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HT-PEM - Efficient and renewable energy

Semi-empirical Modelling in a High Temperature Polymer Electrolyte Membrane Fuel Cells Membrane Electrode Assembly (MEA to MEA) Variation

H.R. García*, H.A. Hjuler, T.Steenberg, C. Terkelsen, T.Holst

Introduction

Danish Power Systems is working on the manufacture and scale up the main component in HT-PEM fuel systems, the membrane electrode assembly. Semi-empirical modelling is used as an important technique for quality control tests, thus it can reveal the cause of MEA variation and thereby MEA and batch variations can be minimized. The dependence of the kinetic parameters of the model was evaluated by varying the platinum loading sprayed on the electrodes (0.63, 0.77, 1.12 and 1.45 mg Pt/cm²). The ohmic resistance was modelled for a 20, 40 and 80 µm membranes and conductivity measurements were performed. Results show that the membrane resistance is a major contributor to the ohmic losses present in a fuel cell.

Method

The purpose of having one analytical equation for cell voltage prediction is to have an easy understanding of the different losses present in the MEA. The following empirical equation was used assuming:

- Mass transport limitations are negligible
- Species crossover are present in a real fuel cell (I_{loss})
- Implementation of exchange current density into the logarithm fitting term (I_0)

$$E_{cell} = E_{rev} - b\log\left(\frac{i+i_{loss}}{i_0}\right) - Ri \quad \text{Eq. [1]}$$

E_{cell}: Fuel cell output voltage (mV)
E_{rev}: Reversible cell voltage at operation temperature (mV)
b: Tafel slope fitting parameter (mV/dec)
i: Current density (mA/cm²)
i_0: Exchange current density fitting parameter (mA/cm²)
i_{loss}: Internal crossover current fitting parameter (mA/cm²)
R: Ohmic resistance fitting parameter (Ω cm²)

Four MEAs with different Pt loadings were manufactured (see Figure 1).

Figure 1. Influence of the platinum loading on the performance. Pt loadings Cathode/Anode: 0.63/0.33 mg/cm², 0.77/0.33 mg/cm², 1.12/0.33 mg/cm², 1.45/0.33 mg/cm², (Symbols). Modelled curves by using Eq.[1]. (Dotted lines). 160 °C.

Table 1. Fitting parameters for the model: Tafel slope b (mV/dec), Ohmic resistance R_{ohmic} (Ω cm²), internal crossover current i_{int} (mA/cm²) and exchange current density i_0 (mA/cm²).

Pt loading (mg/cm²)	b (mV/dec)	R (Ω cm²)	i_{int} (mA/cm²)	i_0 (mA/cm²)
0.63	99	0.10	1.9	6.7×10^{-6}
0.77	95	0.12	1.1	9.2×10^{-6}
1.12	80	0.11	2	2.0×10^{-5}
1.45	81	0.10	0.3	1.7×10^{-5}

Figure 2. Polarization curve for MEAs with different membrane thicknesses (20, 40 and 80 µm), R_{ohmic} was fitted by using Eq.[1], 160 °C.

Table 2. Internal crossover current (I_{int}) and R_{ohmic} obtained from Eq.[1], open circuit voltage (OCV) was measured under no-load operation.

Membrane thickness (µm)	OCV (mV)	i_{int} (mA/cm²)	R (Ω cm²)
20	939	2	0.11
40	980	1.1	0.19
80	930	1.2	0.34

In-plane conductivity measurements were carried out in a four probe conductivity cell at 160°C to verify what is the main losses contribution in a fuel cell. Specific area resistance was obtained.

Figure 3. A) Specific area resistance derived from polarisation curves. B) Specific area resistance derived from conductivity measurements, 160 °C.

Conclusions

The model for the cell voltage was fitted to the experimental data.
The Tafel slope decreases when the Pt loading is increased, which is assumed to be due to an increase in the number of Pt active sites. A linear dependency between open circuit values (OCV) for 20, 40 and 80 µm and the fitted values of the internal crossover current obtained from Eq.[1] was found.
Conductivity measurements were carried out to quantify the contribution of the membrane resistance. A linear correlation between membrane thickness and specific area resistance was seen.

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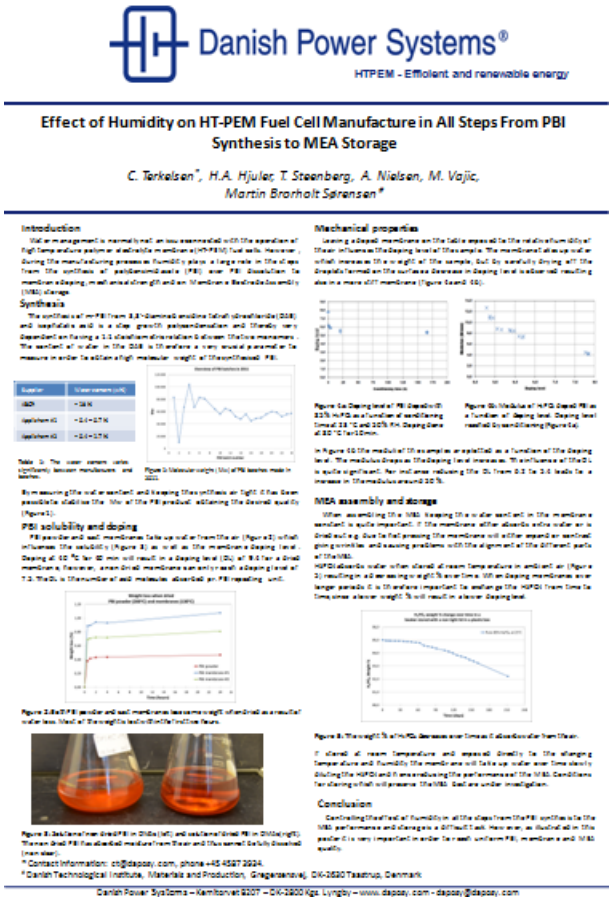

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Effect of Humidity on HT-PEM Fuel Cell Manufacture in All Steps From PBI Synthesis to MEA Storage

C. Terkelsen, H.A. Hjuler, T. Steenberg, A. Nielsen, M. Vajic, Martin Brorholt Sørensen**

Introduction

Synthesis

PBI solubility and doping

Mechanical properties

MEA assembly and storage

Conclusion

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Contributions – posters:

Thorsten Holst

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Low Energy X-ray Imaging Used to Quantify the Large-Area Thickness Variation of the Catalyst Loading on Carbon Cloth Based Electrodes for Fuel Cells.

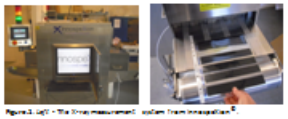
T. Holst, H.A. Hjuler, T. Steenberg, C. Terkelsen, H.R. García.*

Introduction

Fuel cells based on polymer electrolyte membranes often have microporous carbon cloth electrodes. The necessary catalytic activity is established by coating the carbon cloth surface with a suitable catalyst material, typically nano-sized platinum particles imbedded onto a high-surface area carbon structure. From a production point-of-view, it is highly desirable to be able to investigate if the catalyst layer is distributed evenly over the whole electrode area of the fuel cell.

Method

In this study, we introduce an X-ray imaging technique, which can be used to characterize the thickness variation of the Pt-loaded catalyst over a large area of, say, 20 x 20 cm². Low energy X-ray (< 25 kV) imaging is characterized by a high level of grey-scale contrast. The image contrast is mainly provided by the heavy element attenuation of the X-rays. In this case Pt being the heavy element. This makes this technique particularly suited for revealing even minute changes in the electrode's Pt-loading. A spatial image resolution in the sub-millimeter range is easily achieved, which also helps mapping out some coating artifacts.



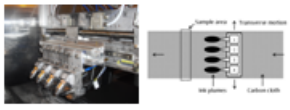
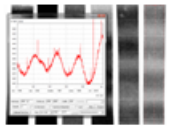
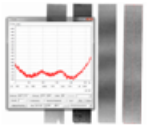


Figure 2. Left - A spray coated cloth. Four ultrasonic nozzles are used to spray a Pt/C-based radial coil in bands 300 mm long, 30 mm wide, including overlaps left out. The coil is surrounded by a semi-circular Pt/C radial coil. Right - Schematic picture of the spraying arrangement.

Results

Image software (Leaf from BAM) was used to analyze the Pt distribution, see Fig. 3 and 4. An unsprayed piece of carbon cloth was used to established a reference level of the X-ray signal. This zero loading reference level is set as the top horizontal axis of Fig. 3 and 4. The average Pt loading was established by weighting the carbon cloth before and after the spraying. The loading levels were then compared to the average change of the X-ray signal. The results are plotted in Fig. 3.





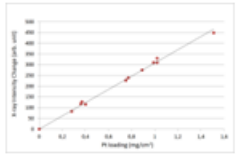


Figure 3. Linear relationship between the average Pt loadings and the average grey scale level of the digital X-ray images is demonstrated.

Conclusion

X-ray imaging of the electrode's catalyst loading gives clear pictures with good resolution. This technique was used to characterize and subsequently optimize the nozzle position. With transverse nozzle movement during spraying and proper adjustment of the nozzle position, it should be possible to obtain a thickness variation of the Pt loading < ± 5 % over the whole 300 x 20 cm² area. This will result in better electrode reproducibility and catalyst utilization in fuel cell production.

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Energy Dispersive X-ray Analysis Used to Quantify the Phosphoric Acid Doping Level in Polybenzimidazole Based Fuel Cells.

T. Holst, H.A. Hjuler, T. Steenberg, C. Terkelsen, H.R. García, J.O. Jensen#, L.N. Cleemann#, Q. Li#, N.J. Bjerrum#.*

Introduction

In high temperature polymer electrolyte membrane (HT-PEM) fuel cells, the membrane is made of polybenzimidazole (PBI). The necessary proton conductivity of the membrane is ensured by doping it with phosphoric acid (PA). The amount of PA contained in the membrane is described by the doping level (DL), which is the number of PA molecules per repeating unit of PBI. It is important for the HT-PEM fuel cell performance that the doping level is high from the beginning and that it will remain high during the lifetime of the cell. Therefore, it is desirable to have a method, which can quantify the membrane's doping level - for example as a post mortem analysis after a durability test in order to monitor a possible loss of PA over time.

Method

We have used energy dispersive X-ray spectroscopy (EDS) to establish the amount of PA in the membrane electrode assembly (MEA) structure. Elemental analysis of the membrane's content of phosphorus and oxygen from the PA relative to the carbon and nitrogen content from the PBI yields indications about the doping level. Samples were prepared by making a cross-section cut through the MEA structure. Argon ion milling was used to gently do a final polishing of the cross-sectional surface, before the sample entered the scanning electron microscope (SEM). The EDS spectra were acquired from a 10 x 10 µm² area in the center of the 30-60 µm thick membranes and analyzed with the INCA software from Oxford Instruments, see Fig. 1.

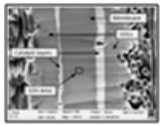

Figure 1. Cross-section SEM picture of a typical MEA structure. BDL represents Diffusion Layer. The SEM acceleration voltage was in the range 8-12 kV.

The membrane's molecular composition is assumed to have the following form:

$$P(wt\%) = \frac{DL \cdot M(PA)}{M(PBI) + DL \cdot M(PA)} \qquad O(wt\%) = \frac{DL \cdot M(O_4)}{M(PBI) + DL \cdot M(PA)}$$

$$C(wt\%) = \frac{M(C_{40})}{M(PBI) + DL \cdot M(PA)} \qquad N(wt\%) = \frac{M(N_4)}{M(PBI) + DL \cdot M(PA)}$$

where the molar masses are: $M(PA) = M(H_3PO_4) = M(PO_4) + 98.0$ g/mol, $M(PBI) = M(C_{40}N_8H_{22}) + M(C_6N_2) = 296.2$ g/mol. The hydrogen contribution is neglected, since EDS is not sensitive to this element. The difference between this model and the actual measured EDS-values is described by the following root-mean-square error function:

$$\varepsilon_{RMS} = \sqrt{\frac{\varepsilon_P^2 + \varepsilon_O^2 + \varepsilon_C^2 + \varepsilon_N^2}{4}}$$

where $\varepsilon = wt\,\%\,(model) - wt\,\%\,(EDS)$. The doping level is now defined as the value of DL, which minimizes ε_{RMS}. This is equivalent to the traditional least-squares method.

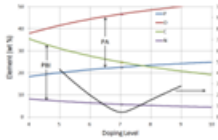

Figure 2. The measured curves show the modelled stoichiometry of the four elements as a function of the doping level. In example of the error function, ε_{RMS} is also shown. In this case, ε_{RMS} is minimum for DL = 7.0-7.1. On average, ε_{RMS} <1 %.

Results

Doping levels in the range 5-9 with an uncertainty of ± 0.5 were measured. This uncertainty is based on the observation, that the calculated doping levels depend somehow on the SEM acceleration voltage. In Fig. 3, doping level measurements are combined with durability data for three different MEAs.

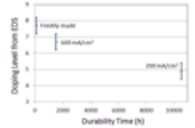

Figure 3. Doping level measurements on 60 cm² MEAs with durability data. 30 cells were operated at 160 °C and fueled with air and H2. The cell area was 45 cm². The legends state the current density used during the durability study.

Conclusion

A method, based on EDS measurements, to quantify the phosphoric acid doping level of HT-PEM fuel cell membranes is suggested. From the EDS measurements of the membrane's elementary constituents, P, O, N, and C, it can be seen that phosphoric acid is lost over time as expected. Even after + 10,000 hours of operation, the doping level is + 5, which indicates that the durability issue only in part is related to the loss of phosphoric acid in the membrane.

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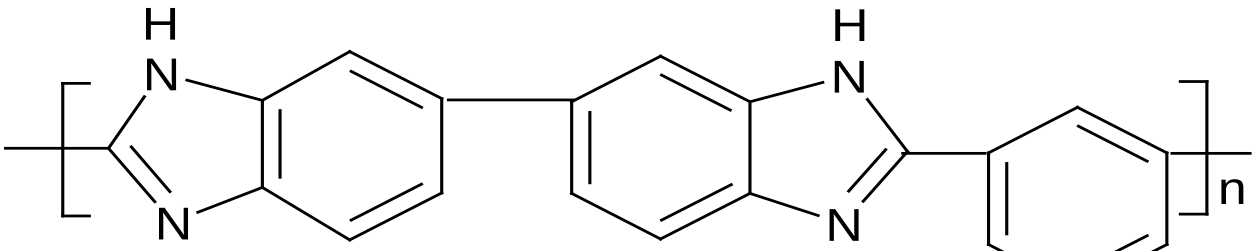
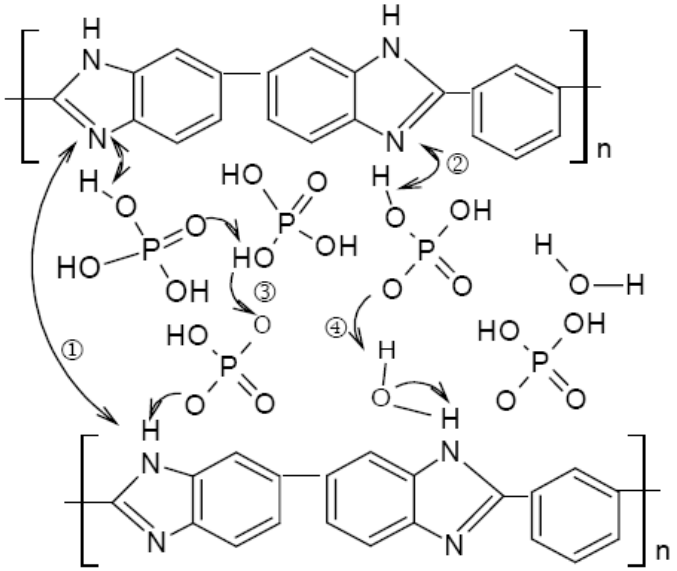
High Temperature PEM FC



Poly (2,2´-m-(phenylene)-5,5´-bibenzimidazole)

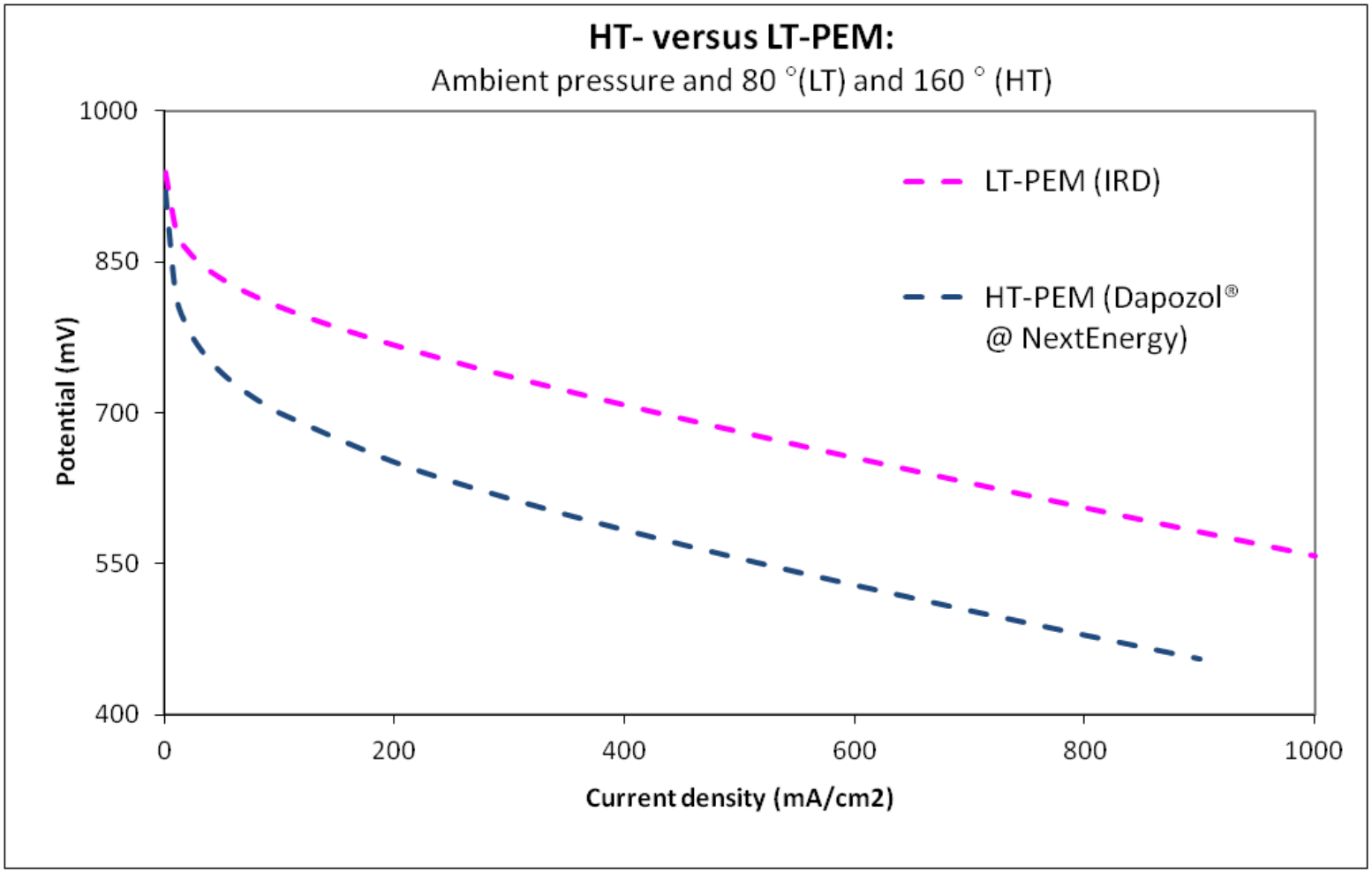
Well-known temperature resistant polymer
T_g = ~430ºC

When doped with phosphoric acid:
Proton conductor

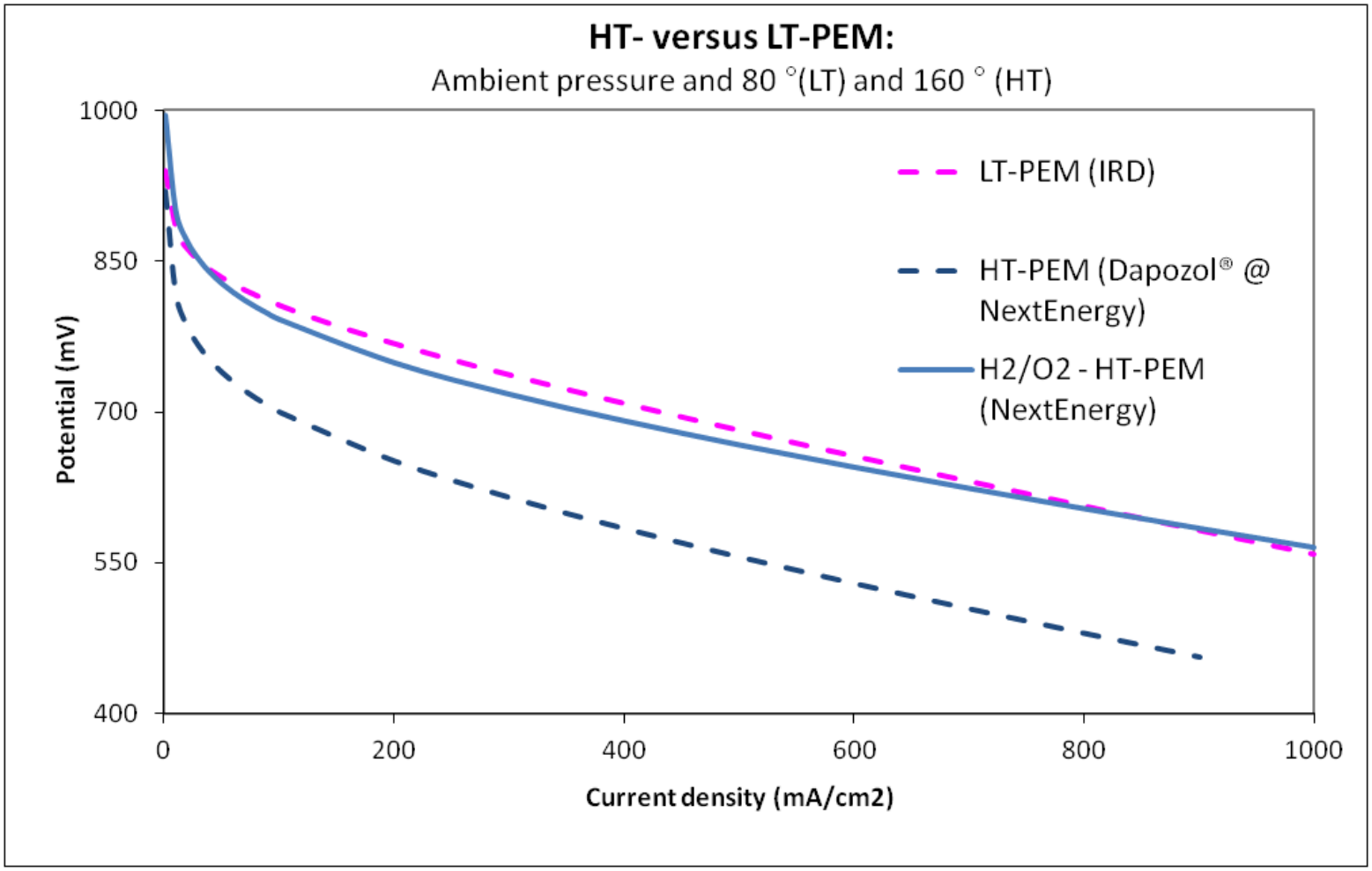


Wainright and Savinell. J. Electrochem. Soc. 142 (1995) L121

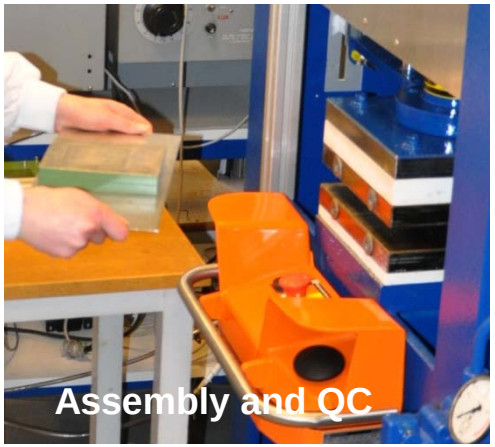
Why HT-PEM?


HT- versus LT-PEM:
Ambient pressure and 80 °(LT) and 160 ° (HT)
1000
850
700
550
400
Potential (mV)
0
200
400
600
800
1000
Current density (mA/cm2)
LT-PEM (IRD)
HT-PEM (Dapozol®
@ NextEnergy)

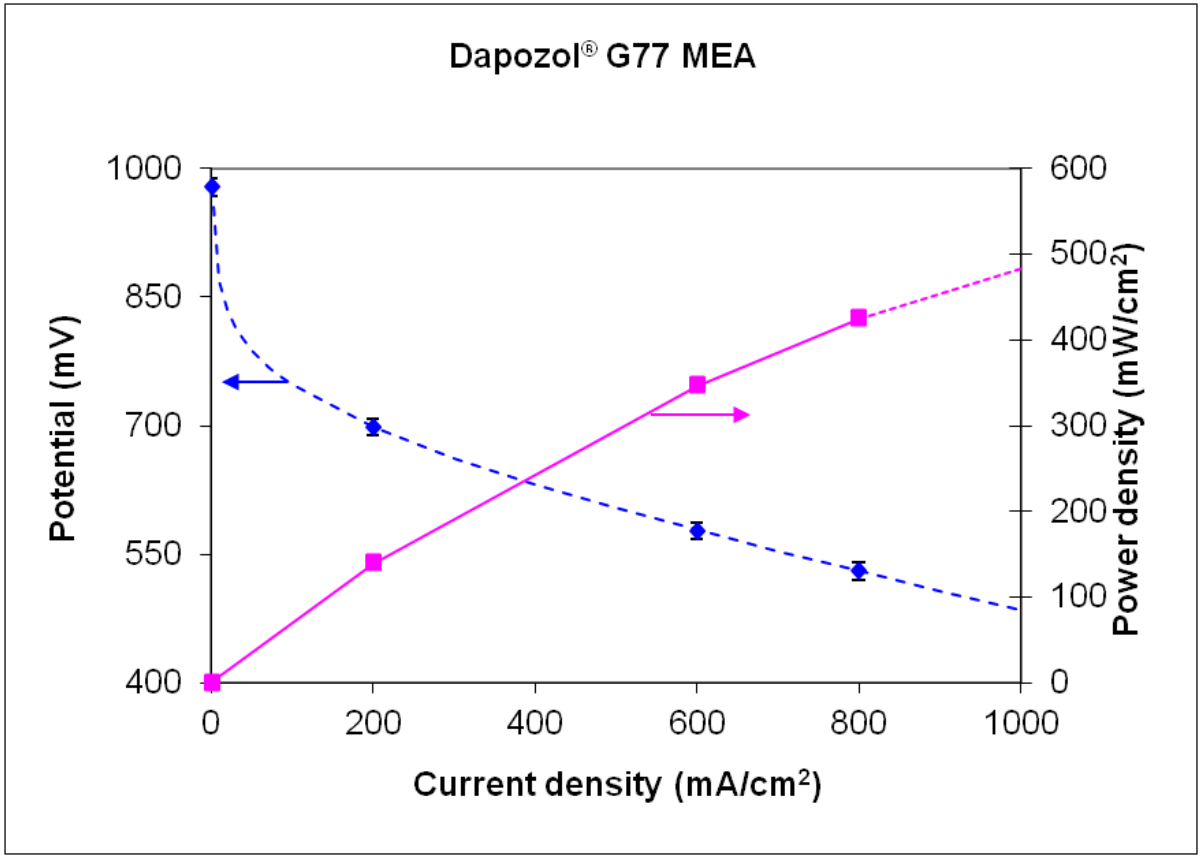
Why HT-PEM?


HT- versus LT-PEM:
Ambient pressure and 80 °(LT) and 160 ° (HT)
Potential (mV)
1000
850
700
550
400
0
200
400
600
800
1000
Current density (mA/cm2)
LT-PEM (IRD)
HT-PEM (Dapozol® @ NextEnergy)
H2/O2 - HT-PEM (NextEnergy)

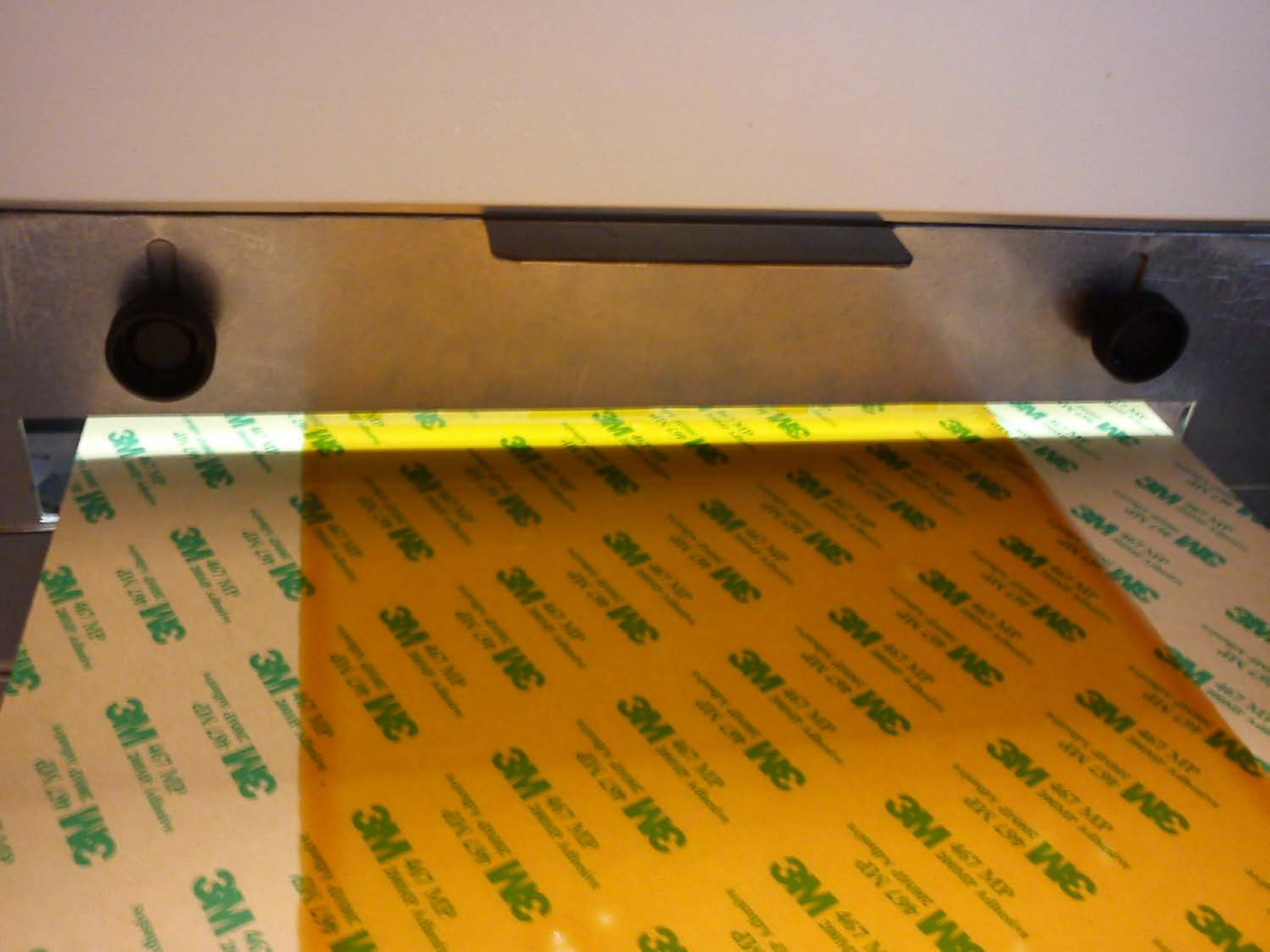
DPS' capabilities - MEA manufacturing



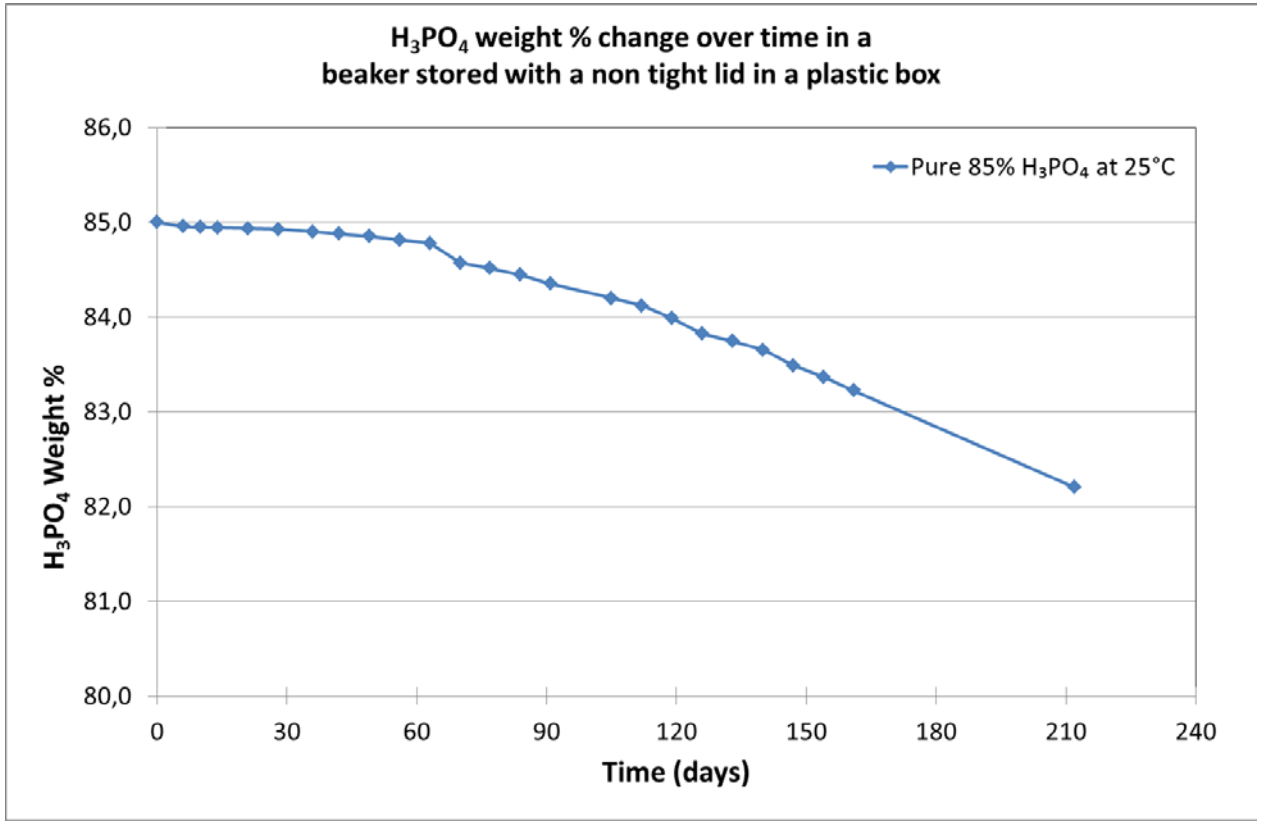
Polarization curve



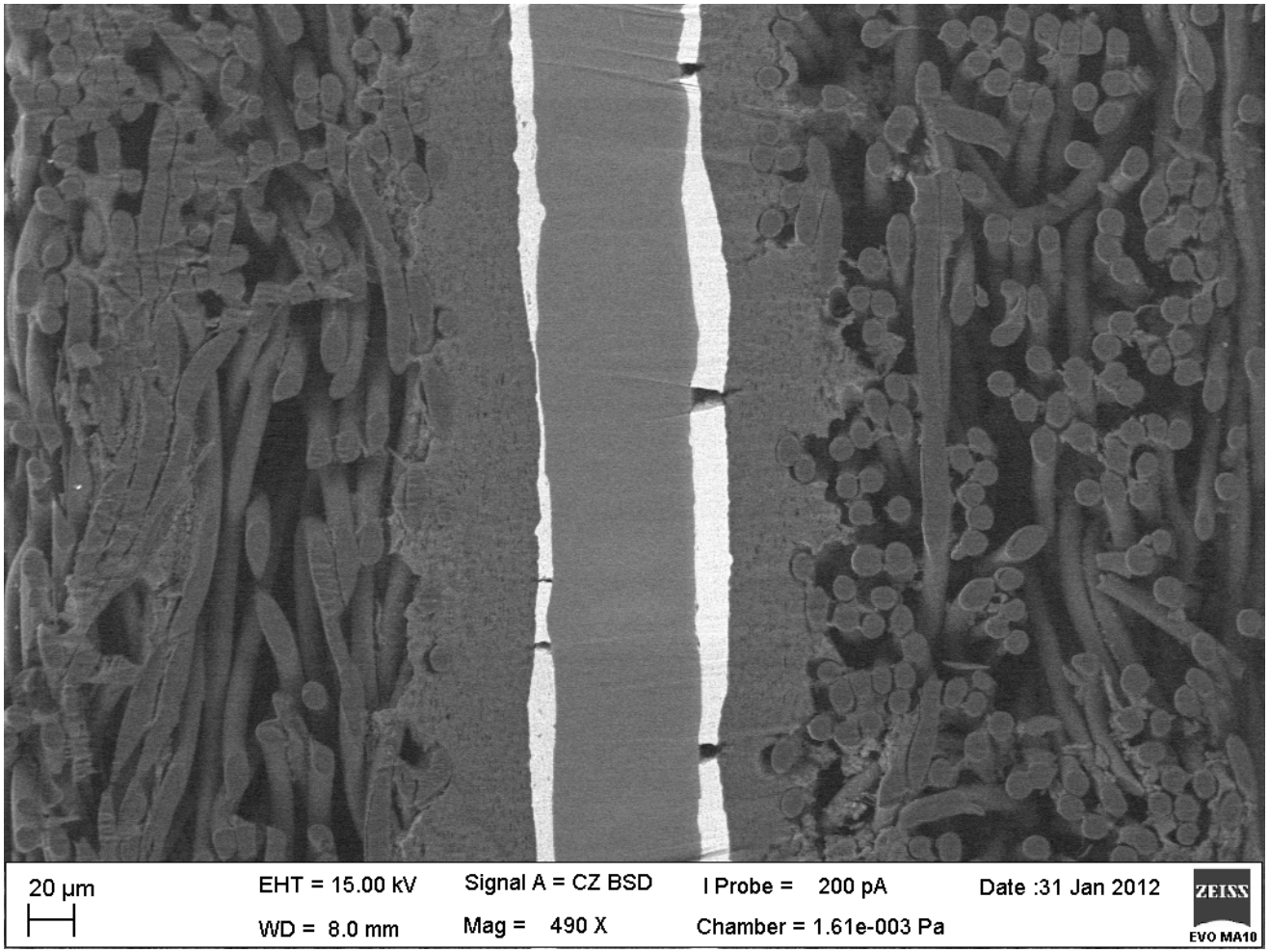
Polarization and a power curve for MEAs tested with hydrogen at 160 °C. Based on 90 identical 50 cm^2 MEAs. Error bars on the polarization curve indicates standard deviation below 2 %.


3M
467 MP

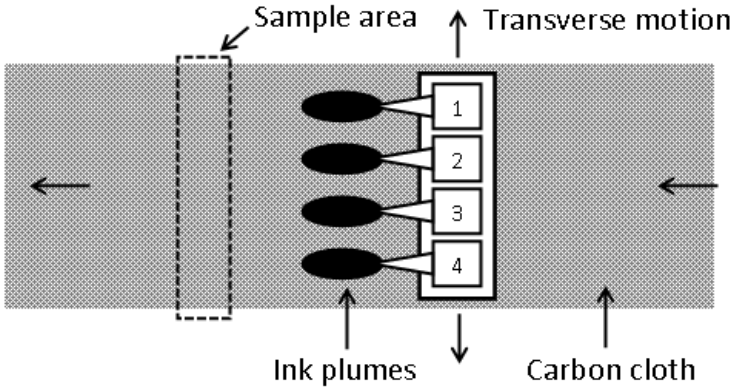
H_3PO_4 and doping:

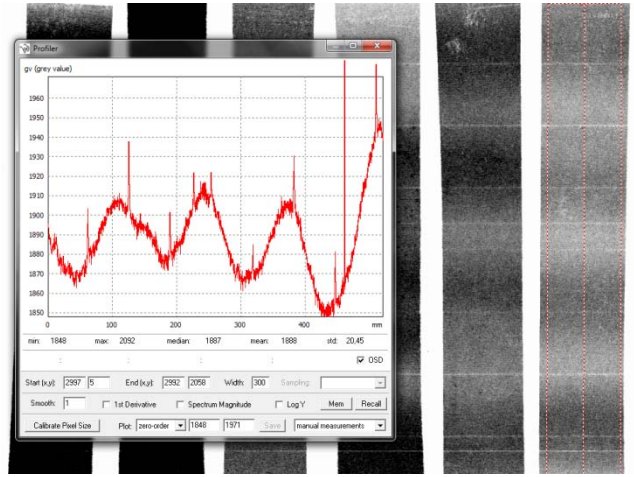


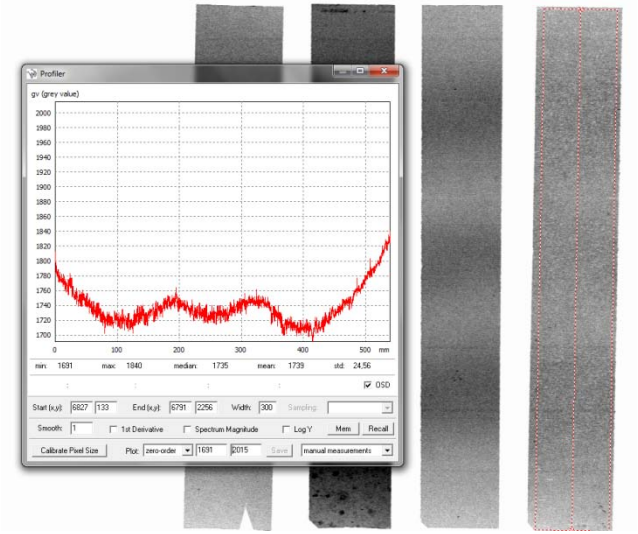
MEA cross sections – ion milled



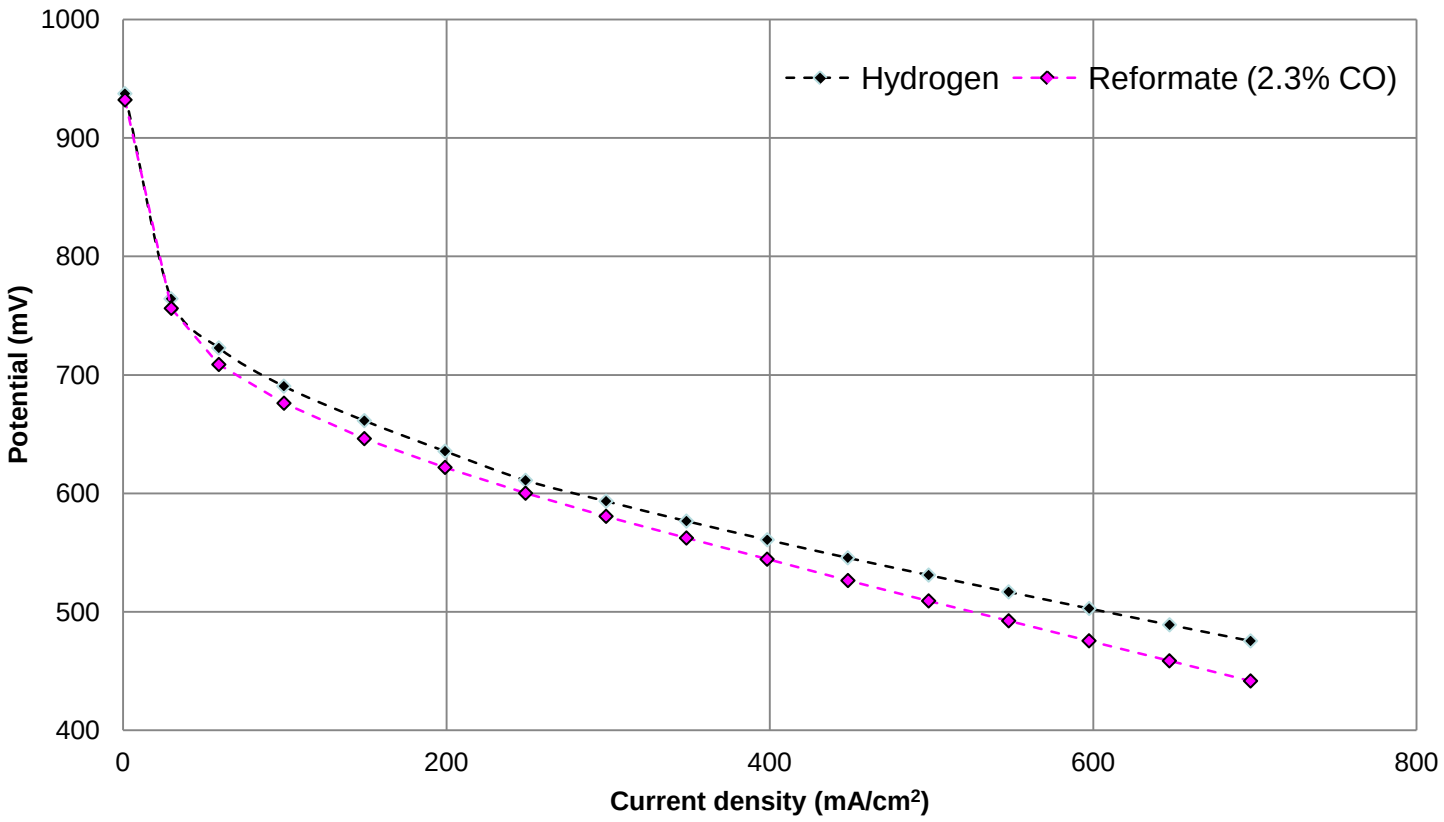
Electrodes and Pt distribution:





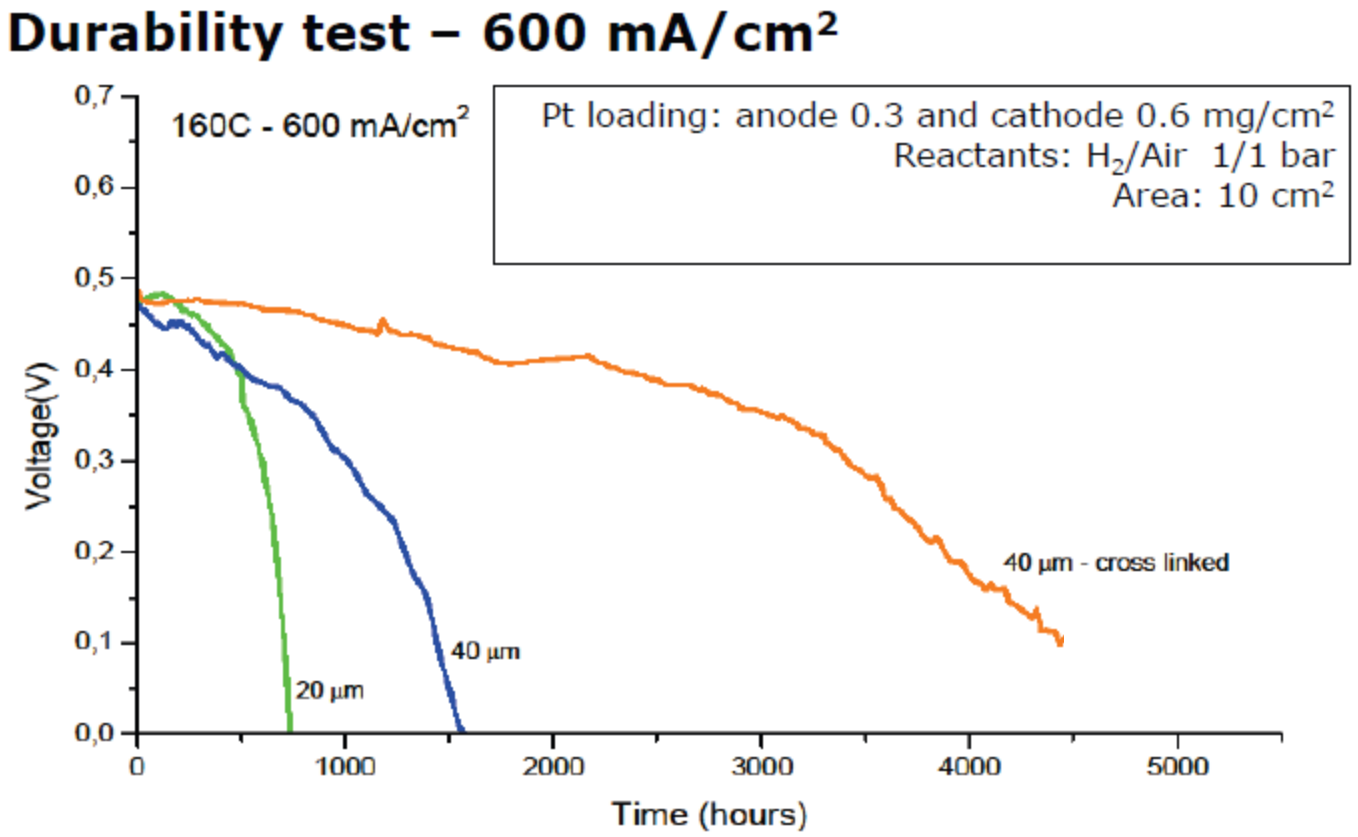


Polarization - hydrogen and reformate



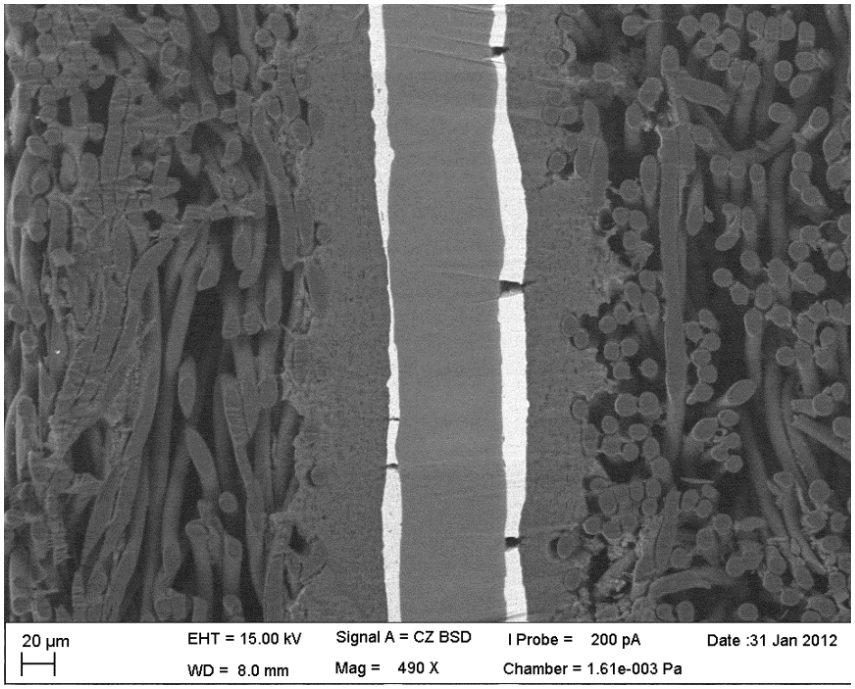
Polarization curve for MEAs tested with hydrogen and reformate at 160 °C.

Durability - 600mA/cm^2

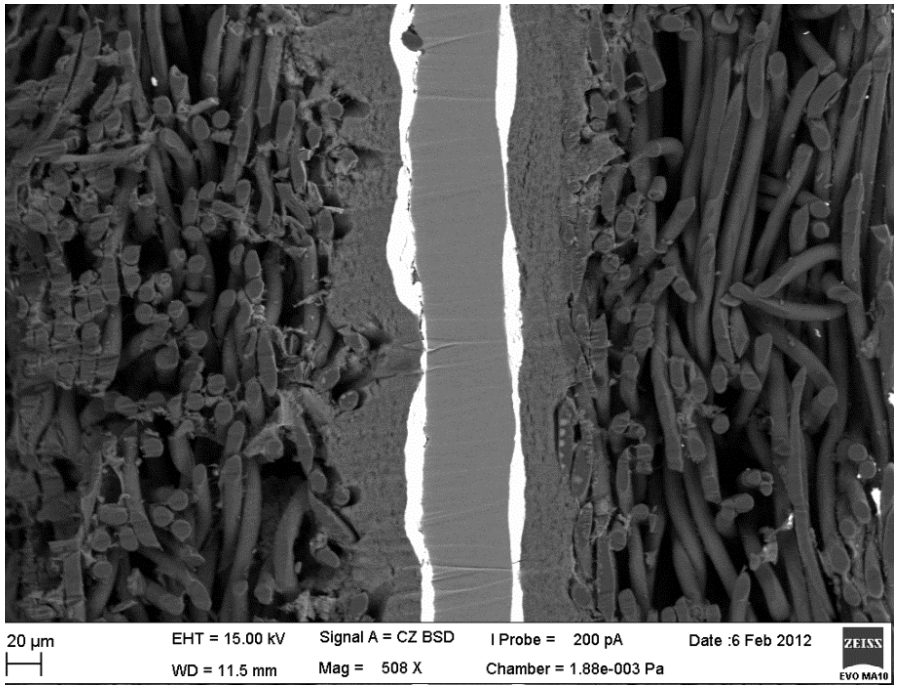


SEM investigations:

Un-used MEA:



After 4000h operation:



DPS technology status:

- PBI synthesis (uniform Mw)
- PBI membranes (standard and x-linked membranes)
- MEA’s (standard and custom sizes)
- Performance and durability

Next step:

- Pilot production in preparation
- Performance improvements
- Durability improvements
- Cost reduction

- It takes time:
  - Demonstration of lifetime
  - Market development

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Thank you!

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	Under development	Demonstration and field tests	Early markeds
MEA	IRD: membranes, electrodes, MEA's	TOFC: SOFC cell IRD A/S: PEMEC MEA's	IRD: DMFC/PEM MEA's, flow plates
Stack	IRD: DMFC/PEM/EC stacks	TOFC: SOFC stacks	IRD: DMFC/PEM stacks
Components	IRD: Humid., inverters DPS: MEA'er	TOFC: SOFC PowerCore	IRD BoP systems, CVMS Serenergy: Serenus 166 and 390
Systemer	IRD: PEMEC systems Leaneco: UpsEco G2 Green Hydrogen: Alkaline RME – 2-8 nm^3/h Dantherm Power: SOFC µCHP Dantherm Power: PEM µCHP	IRD: µ-CHP 1500W Serenergy: Ecomotion® TOFC: SOFC system Wärtsilä Dantherm Power: DBX5000 Dantherm Power: SINE project	IRD A/S: DMFC 500/800W Serenergy: HC 35 Leaneco: UpsEco G1 H2 Logic A/S: H2Drive® H2 Logic A/S: H2Station® H_2Logic A/S: Fork lifts Dantherm Power: DBX2000 Dantherm Power: 50 kW container Dantherm: UPS SINE