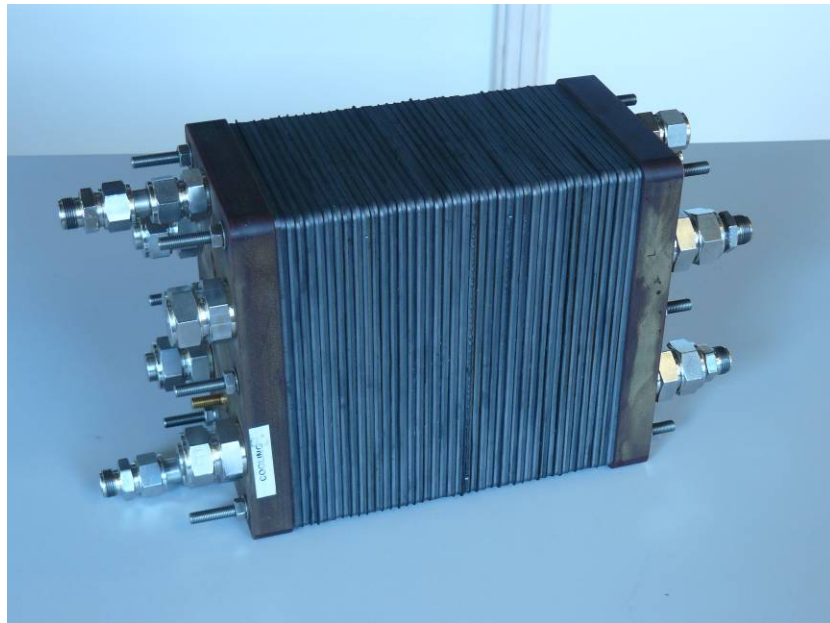


DEVELOPMENT OF HT-PEMFC COMPONENTS AND STACK FOR CHP UNIT



Project 7328
PSO R&D 2007 programme



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Summary

The aim of the project has been to further develop components for an all Danish high temperature PEM fuel cells stack for application in combined heat and power units (CHP units). The final product aimed at was a 1.5-2 kW stack for operation at 150-200°C. The project follows the previous PSO project 4760, "High Temperature PEM Fuel Cell"

The advantages of high temperature PEM fuel cells (HT-PEMFC) are plentiful. The working temperature of 120-200°C (in contrast to the usual 80°C for PEM fuel cells) makes the cells highly CO resistant and CO levels in the order of one pct. in the fuel can easily be tolerated. This means that hydrogen from a reformer need no be purified. The high temperature also makes it necessary to rely on a proton conduction mechanism that is not dependent on water and therefore water management is not needed. Finally, the excess heat produced is released at higher temperatures and represents a higher value and heat removal is much easier.

The project has addressed the HT-PEM fuel cells from a components point of view and the materials here for. The main areas were polymer and membrane development, electrode and MEA development (MEA = membrane electrode assembly, i.e. the cells.) and stack development.

The membrane development begins with the polymer. The polymerization technique was improved significantly in two ways. Better understanding of the process and the critical issues has led to more reproducible results with repeated high molecular weights. The molecular weight is decisive for the membrane strength and durability. The process was also scaled up to 100-200 g polymer pr. batch in a new polymerization facility build during the project. It is dimensioned for larger batches too, but this was not verified during the project. The polymer cannot be purchased in the right quality for fuel cell membranes and it is important that its manufacture is not a limiting factor at the present state. Experiments with other membrane casting techniques were also made.

The traditional PBI doped with phosphoric acid is still the state of art membrane for the HT-PEM fuel cells, but progress was also made with modified membranes. Different variants of PBI were synthesized and tested. The results point forwards and will lead to further research after the project period.

Electrodes have been manufactured by a spray technique in contrast to the previously applied tape casting. The hand held spray gun previously led to an improvement of the electrodes, but the reproducibility was limited. Subsequently the construction of a semi automated spray machine was started and results like of the best hand sprayed electrodes were obtained.

A viable way of MEA rim enforcement was initiated in the project. The reason for this was to create a better surface to seal against and to prevent membrane rupture during service. A special MEA pressing tool was developed for easy alignment and control of the compression.

Fuel cells stacks of the developed MEA's were constructed and tested. The aim was to construct a liquid cooled stack based on IRD's experiences. Liquid cooling is in principle similar in high temperature and low temperature PEMFC stacks, but the effect of even tiny leaks is lethal in the high temperature stacks since the coolant is not water, but another coolant that will fill the pores of it is allowed into the electrode compartments even in trace amounts.

A 40 cell liquid cooled stack was made by IRD at the end of the project. The cell area was 7x17 cm. A perfluoropolyether was chosen as coolant due to its low viscosity at all relevant temperatures combined with a low volatility. Besides an air cooled stack was built at DTU with a different materials approach which is confidential. A part of the detailed results regarding stacking was reported in a confidential annex to the main report.

According to the project partners, the project has paid an important contribution to the long term objective of developing Danish technology for high temperature PEM fuel cells.

The project duration was 2 year from beginning of June 2007 to end of May 2009. The partners were:

- Department of Chemistry, Technical University of Denmark
- Danish Power Systems ApS
- IRD Fuel Cells A/S

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CONFIDENTIAL ANNEX: ADDITIONAL STACKING DETAILS

1 Introduction

The need for development of new energy systems worldwide is tremendous. The end of cheap oil, the greenhouse effect and the Middle East are some of the keywords in that connection. The future energy solutions will most likely be a mixture of various technologies and hydrogen is predicted to play a central role as a bridge between energy production and demand. However, to date hydrogen energy solutions are not easily implemented for several reasons. Many applications are dependent on a hydrogen infrastructure that is very costly and technically challenging to establish. This does not mean that it will not be established, but only that it will not be available on a short term. The other key issue is the cost of the fuel cells and their systems. Most if not all components are still after significant cost reductions more expensive than the conventional counterparts. The depletion of some energy sources that we depend on today and the development of the energy prices will force the development toward the new technologies, but still cost reductions are mandatory.

On the short term applications that are able to function with the existing infrastructure are given the highest chance of success. For this reason CHP units are seen as one of the more obvious early markets for fuel cells, and the Danish national strategy for PEMFC development is strongly aiming at development CHP fuelled by natural gas via a reformer. Natural gas is today available to a large group of customers

When it comes to high temperature PEMFC (HT-PEMFC) the potential is for CHP is overwhelming and some of the arguments for that are:

(1) The reforming process is much simpler due to the high CO tolerance of the HT-PEMFC. With conventional PEMFC the hydrogen from the reformer must be essentially free of CO to avoid poisoning of the fuel cell catalyst. CO is always present in pristine reformat and should be removed to ppm levels by an advanced clean-up unit. The experience to date is that this is the main difficulty in the reforming technology and consequently it affects the system cost strongly. With the high working temperature of HT-PEMFC CO levels over a thousand ppm is easily tolerated and no clean-up is necessary.

(2) The temperature of the heat produced is higher, which lead to easier heat management and better utilization in with smaller heat exchangers and less critical control. Moreover, in the reforming process steam is needed, and as the temperature is high enough steam can be produced by the heat of the fuel cell. All together this allows for significant cost reductions as compared with conventional PEMFC.

The present situation in Denmark is rather promising as there are companies or research institutions involved in all links of the chain from materials development

over fuel cell construction to system integration and marketing. This way Denmark has a strong position with up to date expertise (in some cases leading positions) in all aspects from high temperature membrane development over fuel cell construction to turn key CHP units. This is a superior background not only for bringing the units to market but also to keep up the development in the future. See the figure below which shows in a simplified manner how Danish stakeholders complement each other and cover the whole development chain for CHP units based on HT-PEMFC. The project partners are in grey, and it can be seen that the whole component chain is matched by industrial partners.

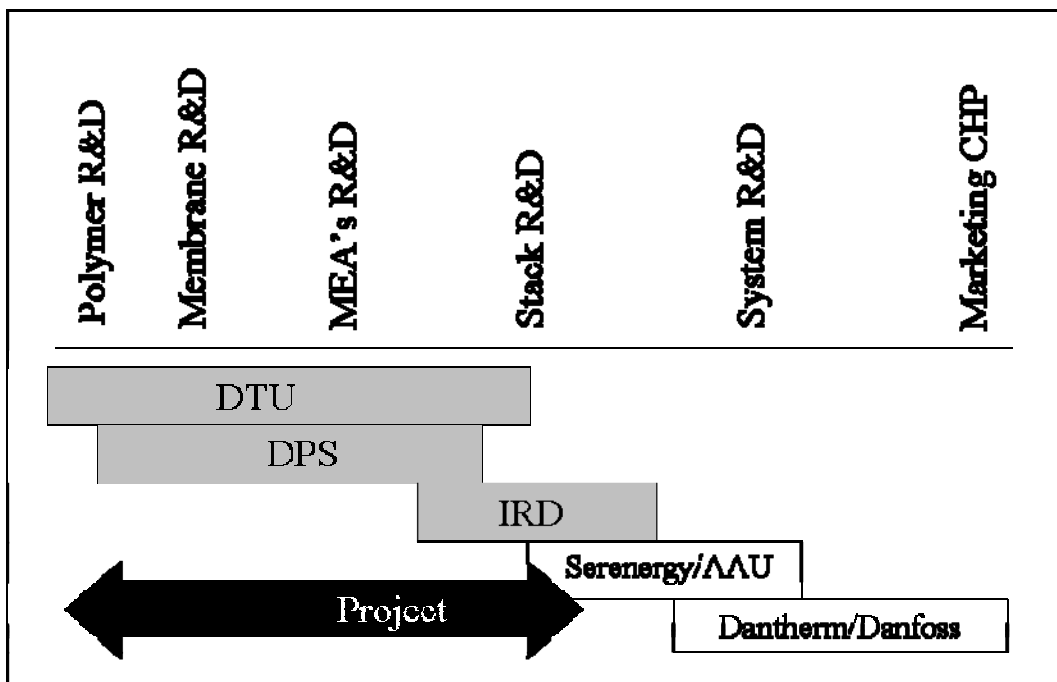


Figure 1. The value chain of HT-PEMFC in Denmark. Gray bars represent partners of the project.

The aim of the project has been to further develop components for an all Danish high temperature PEMFC stack for application in combined heat and power units (CHP units). The final product aimed at was a 1.5-2 kW stack for operation at 150-200°C. The project follows the previous PSO project 4760, “High Temperature PEM Fuel Cell”

In accordance with Figure 1, the project consortium comprises the know how for manufacturing all components from the initial polymer over electrodes and stacking plates to the final stack. This is a strong position for the establishment of a business. The project has maturing of the components as well as the final stack as the focus. There are two main objectives: 1) Improvement of and ensuring satisfactory performance of the components not only when tested individually but also in situ. The technology shall be

compatible at all levels with foreign product. 2) Improvement of the manufacturing processes to ease production and to minimize cost.

2 Membrane development and manufacture

The work on the membrane had two overall purposes, namely (1) further development and improvement of properties, and (2) the establishment of manufacturing techniques suitable for later up-scaling. These two aims are strongly interrelated since properties depend largely on the manufacturing process.

Early in the project the weak points of the MEA, or points where improvement was to be expected, were identified. Some of these points were referring back to polymer and membrane properties.

1) The membrane strength. Durability experiments carried out in other projects often ended with a “sudden death” due to rupture of the membrane rim, i.e. the area between the edge of the electrodes and the sealing gasket. The membrane strength depends on temperature and acid doping level, and a stronger membrane will allow for a higher doping level (or a thinner membrane) and thus a higher proton conductivity. However, this is not the main concern, since the conductivity is already high. Main concern is membrane failure during long term testing. Strength can be improved by higher molecular weight, cross-linking, or acid base blending. The rim can be strengthened by protective layers.

2) The unbound phosphoric acid. There are two issues with the free phosphoric acid in the membrane. It may eventually leach out, and it blocks the electrode catalyst. Leaching seems not to be as big a problem as could be expected, but it should not be neglected. The catalyst blocking is believed to be the main reason for the relative high overvoltage on the cathode (oxygen electrode). A membrane with high protonic conductivity in the addressed temperature window without any free shuttles is highly desired, but no one has really been successful yet.

3) As with any fuel cell today, the lifetime is still not satisfactory although it is approaching the desired targets.

4) For application as a direct methanol fuel cell the methanol permeability is too high. Also when powered by hydrogen the hydrogen permeability gives rise to a slightly reduced open voltage. However this is not a serious problem since the effect is minor when the cell is loaded.

5) Cost is an issue that is relevant to all components including the membrane. However, the long term cost driver in the MEA is the platinum catalyst. A reduced loading would lower the production cost. Such a reduction goes hand in hand with optimization of the electrode structure (electrode morphology).

2.1 Polymerization

The PBI polymerization process has been investigated with respect to:

- critical parameters for the polymerization process
- characterisation methods
- equipment

These investigations have resulted in up-scaling of the production capacity, higher molecular weight of the synthesised PBI and reliable characterisation methods.

2.1.1 Critical parameters

The synthesis of PBI has previously i.e. prior to this project proven highly unstable. The maximum batch size was 20 g and the percentage of PBI batches with a suitable molecular weight $>20,000$ g/mole was $\leq 50\%$.

Investigations of the various parameters have identified the purity of the monomers as the single most important factor influencing the molecular weight of the obtained PBI. Purification of the monomers has been carried out, and monomers with and without stabilizers have been used for the synthesis. Synthesis based on stabilized monomers seems in general to be more robust. By controlling the monomer degree of purity rigorously it has been possible to achieve molecular weights consistently above 20,000 g/mole and scale the batch size to 100 – 200 g. Several additional synthesis parameters were found to influence the final molecular weight of the polymer.

2.1.2 Characterisation methods

2.1.2.1 Visual inspection

PBI is isolated from the reaction mixture by slowly pouring the hot mixture into water. If the PBI precipitates as unbroken tobacco-like threads, and no free-flowing fragments are formed, it is a good indication of membrane-quality material.

2.1.2.2 Viscosity

The standard method of determining the average molecular weight of polymers is to dissolve a sample and measure the viscosity of the resulting solution. The average molecular weight can then be calculated from the Mark-Houwink equation. For PBI this is usually done in concentrated sulphuric acid. This technique gives a reliable value of the average molecular weight, and allows for comparison with literature results. It is, however, slow (proper dissolution of the samples in sulphuric acid takes ca. two days) and cumbersome (2-3 hrs work/sample). The measuring process can be automated.

2.1.2.3 Size exclusion chromatography

Size exclusion chromatography (SEC) is a chromatographic technique often used in the analysis of polymers. It is similar to HPLC and other chromatographic techniques, but based on molecular size instead of polarity. SEC has not been used much in the characterisation of PBI, because it is extremely difficult to obtain PBI samples of sufficiently narrow molecular weight distribution for calibration of the instrument. SEC, however, have the advantage of being a much faster technique than viscosity measurement. This opens a potential possibility for monitoring the reaction in progress, an integral part of reaction optimization.

Since both inherent viscosity and SEC is dependent on molecular size it is possible to establish an SEC calibration curve for PBI based on the values obtained from viscosimetry, see Figure 2, for at least a rough estimate of molecular weight.

It has been established that it is possible to monitor the reaction through the removal and hydrolyzation of samples, although the concept have not been proven yet.

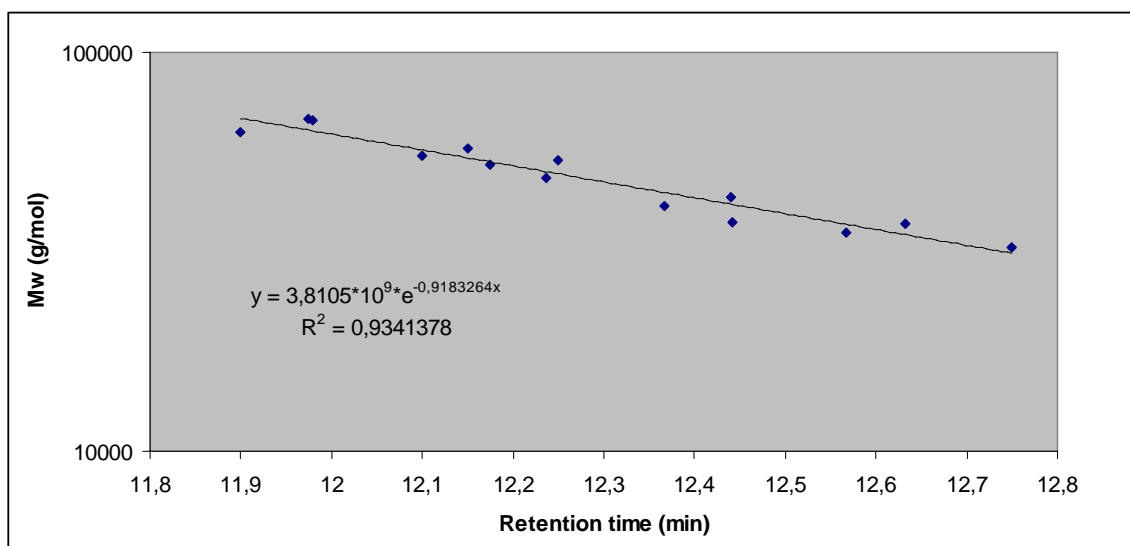


Figure 2. Molecular weights of PBI (average values from viscosimetry) plotted vs. their SEC retention times.

2.1.3 Up-scaling

Up-scaling was started at DTU and a setup with a 20 litre polymerization flask was constructed. It included temperature control, stirring and a forklift like mechanism for pouring out the hot solution. 100 g batches were synthesized successfully. 200 g batches

should also be possible with the setup. After that, DPS continued the development of the Multigram-scale production facilities.

The polymer production setup was then revised significantly. Among other things it was built into its own fume hood. See Figure 3. This equipment can handle the amounts of chemicals required for large batches of up to 500 g.

The key characteristics of the last ten batches produced during the project are shown in Table 1. They were all successful with average molecular weights above 30000 g/mol. This is sufficient polymer molecular size to preserve sufficient membrane strength after acid doping and heating to the working temperature. Scaling up from 200g to 400g does not imply any changes of the system, but this was not the priority for the time being since focus has been on quality control.

Several methods for quality control and process optimization have been identified. These methods will be investigated before further attempts to scale-up to kg-scale production (not during the project). The idea is to tune the process towards better products along each run.



Figure 3. Picture of the new setup for PBI synthesis. The reactor is surrounded by a fume hood.

Table 1. The last 10 batches of PBI produced at DPS. Inherent viscosity values were measured in conc. sulphuric acid at a concentration of 0,5 g/100 mL. Molecular weights are rounded to nearest 500. In one case (3) compound was lost upon drying, while in another (7) some phosphoric acid was retained leading to a higher yield than theoretically possible. Average molecular weights are calculated either from the inherent viscosity with standard Mark-Houwink constants or in one case (10) estimated from size exclusion chromatography.

Post	Reaction startdate	Yield (g)/ Yield (%)	Inherent visc. at 0,5 g/100 ml (dL/G)	Molecular Weight (g/mol)
1	20/1 2009	75/62	0,8	37 500
2	22/1 2009	122/94	0,7	32 500
3	29/1 2009	60/59	0,8	37 000
4	10/2 2009	95/94	1,25	65 500
5	2/3 2009	92/94	1,05	52 000
6	23/3 2009	187/87	0,93	44 500
7	20/4 2009	219/106	1,09	55 000
8	27/4 2009	196/92	1,07	54 000
9	4/5 2009	197/92	1,29	68 000
10	15/6 2009	202/96	-	53 500

2.2 Membrane casting

PBI is synthesized in homogeneous solutions with polyphosphoric acid (PPA) as solvents. Taking advantages of a moderate temperature (200-230°C) and adding the DAB monomer as the more stable tetrahydrochloride, this method is an excellent route for preparing laboratory or small scale polymer of linear, high molecular weight polymer, though a relatively large amount of acid solvent and multiple-step isolation procedures are involved.

After synthesis, PBI and acid doped PBI membranes are prepared in different ways, as schematically represented in Figure 4. Typically the polymer is first collected by isolating from the synthesis solvent. After drying the polymer is dissolved in highly polar and aprotic organic solvents such as DMAc, dimethyl sulphoxide (DMSO), *N,N*-dimethylformamide (DMF) or *N*-methylpyrrolidone (NMP). Membranes at DTU/DPS are mostly fabricated by solution casting, following by acid doping (*route 1* in Figure 4). An alternative way is to dissolve PBI in a mixture of acids or bases. Typical acids are trifluoroacetic acid (TFA) and phosphoric acid, shown as *route 2* in Figure 1. Membranes cast from the acid solution already contains phosphoric acid and its content can be precisely controlled during the preparation of the solution. Thus the obtained membranes

are in general more rubbery and softer mechanically and higher in conductivity than the *route 1 membranes*, however, high molecular weight (M_w) polymers are needed. The new method we have attempted during this project is directing casting from the polyphosphoric acid solution, specified as *route 3* in Figure 4, as described below.

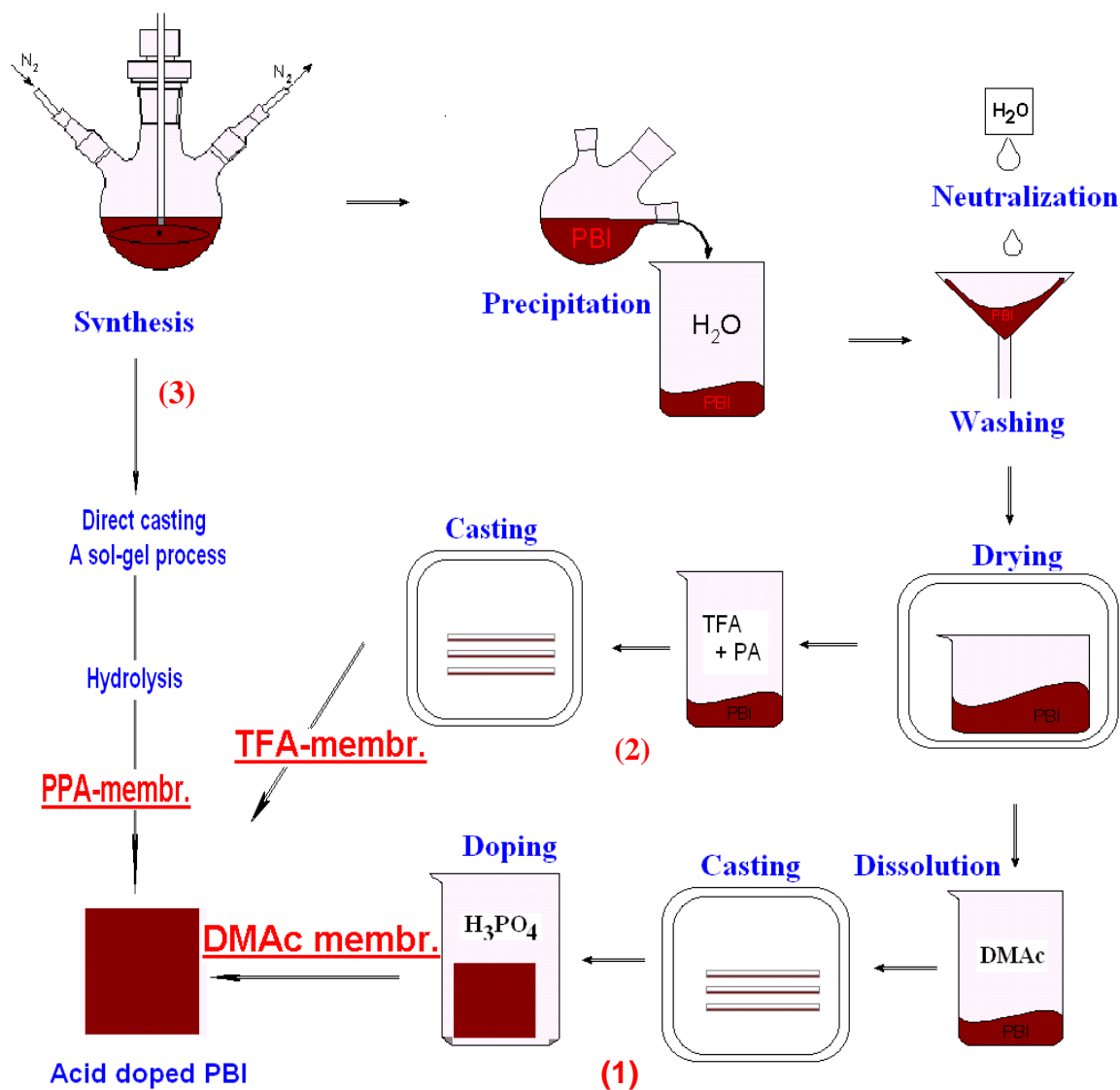


Figure 4. Schematic representation of preparation routes for acid doped PBI membranes. The number 1-3 indicate different casting routes. (1) solution casting, (2) solution casting with integrated phosphoric acid and (3) direct casting.

2.2.1 Solution casting

The PBI membranes used in the PEM fuel cells were cast by the solution casting process via slow evaporation of DMAc solutions in glass dishes (about 27x32 cm). The resulting membranes were rather wrinkled and uneven, possibly due to the formation during evaporation of a surface layer of PBI encapsulating the remaining solvent and leading to an uneven distribution of PBI material (Ref. Wadhwa et al. US Patent No. 5017681, (1991)). The phosphoric acid-doped membranes therefore had to be hot-pressed before they were cut out and used in MEAs. Furthermore the solution-casting process is slow and difficult to scale-up.

Preliminary experiments with doctor blade casting have demonstrated that more homogenous membranes can be obtained through this method. This will be further investigated in the later HotMEA project. The possibility of casting membranes by spraying onto a substrate was also investigated and could prove an important alternative.

Preliminary casting experiments shows that by controlling the temperature and PBI/DMAc ratio homogenous membranes can be obtained. This too will be further investigated in the HotMEA project.

2.2.2 Direct casting of PBI membranes

As mentioned above, polyphosphoric acid (PPA) is used as an efficient condensation reagent and solvent for the PBI synthesis. PBI-H₃PO₄ membranes can be fabricated by direct casting from the PBI solution in PPA without isolation or re-dissolution of the polymer after synthesis. In this way, membranes containing very high acid contents can be obtained, of course provided that the synthesized polymer has high molecular weight, as DPS has achieved during the present project. Figure 5 shows a picture of the direct cast membrane with a molar ratio of acid to PBI as high as 39/1. In other words, the membrane consists of 93 wt% phosphoric acid and 7 wt% polymer, which, in fact, is the polymer-networked phosphoric acid with enough mechanical strength to handle.



Figure 5. Sample of direct cast PBI membranes containing 93 wt% phosphoric acid.

2.2.3 Cross linking

Efforts have been made to introduce cross-linkers during the casting, which is expected to further strengthen the membrane both mechanically and chemically. The cross-linked membranes need however further characterization.

Further work on cross linking has been carried out. Cross linking by acid base blending (primarily carried out in other projects) showed that the mechanical strength could be increased. It was possible to increase the acid doping level from 6 to 13 acid molecules pr. repeat unit of PBI. Covalent cross linking experiments have been performed with a new linker, divinylsulphone and the membranes were studied in terms of mechanical properties, vibrational spectroscopy and solubility.

2.2.4 Proton conductivity

Figure 6 summarizes the conductivities of different types of PBI membranes doped at different acid levels. The conductivity of the TFA-cast membranes (route 2) was measured under a constant relative humidity (varied water-to-air ratio), while that of the DMAc-cast membranes (route 1) was obtained under a constant water-to-air ratio. They are only comparable at temperatures close to 200 °C. It can be seen that the TFA membranes exhibit slightly higher conductivity. With cross-linked membranes higher acid doping levels of 10-12 can be used, giving conductivities around 0.1 S/cm, as achieved in previous projects.

The membrane processing and morphology have significant effects on the proton transport and conductivity. At an acid doping level of 39, corresponding to 93 wt% phosphoric acid and 7 wt% PBI, the direct cast membranes exhibit a conductivity as high as 0.26 S/cm at 200°C under dry conditions, as seen in Figure 6.

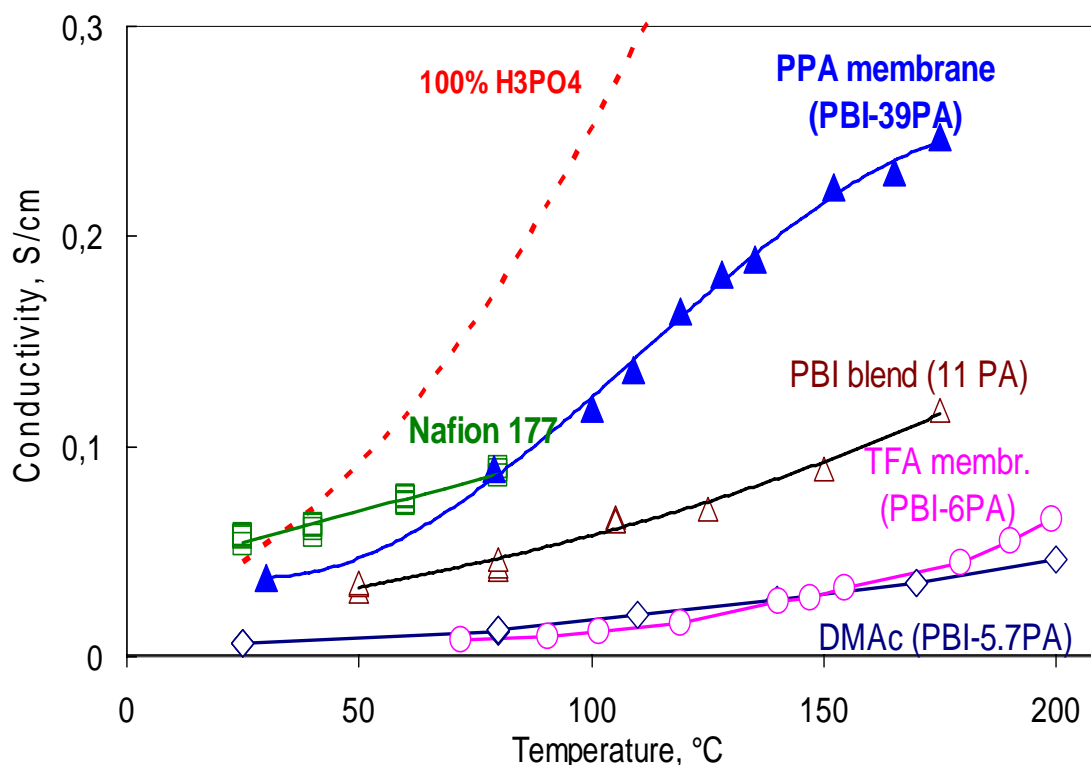


Figure 6. Proton conductivity of 100% phosphoric acid, Nafion 117 and different types of acid doped PBI membranes. The direct cast membrane was with an acid doping level of 39. Other membranes with lower acid doping levels and therefore lower conductivity were prepared in previous projects.

2.3 PBI with modified structures

The term PBI covers a whole family of polymer structures which all have in common the combined five and six-membered rings with two nitrogen in the five-membered ring - the benzimidazole ring, hence the name.. The far most common PBI is Poly 2,2'-*m*-(phenylene)-5,5'-bibenzimidazole (Figure 7). This is also the type of PBI applied by most groups including that at BASF and it is the one referred to in this context unless stated otherwise specifically. However, it is well known that even limited modifications in the

polymer repeat unit structure can result in significantly changed polymer properties. Therefore modified structures of PBI was also studied in this as well as in other projects.

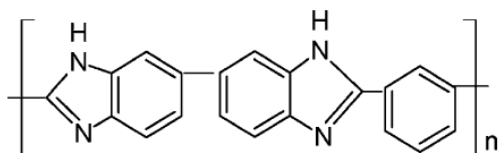


Figure 7. Poly 2,2'-m-(phenylene)-5,5'-bibenzimidazole.

2.3.1 Synthesis of modified PBI

Efforts have been made to explore the chemistry of the polymer and its applications in improving the membranes for fuel cells. One motivation of these efforts is to improve the properties such as high molecular weight and good solubility and processibility, which are of significance for mechanical stability and functionalization processing of PBI membranes. Another motivation is to tailor the basicity of the polymers for improving the acid-base membranes. These modifications are demonstrated by synthetically preparing PBI containing sulfone as well as hexafluoro groups, as shown below in Figure 8.

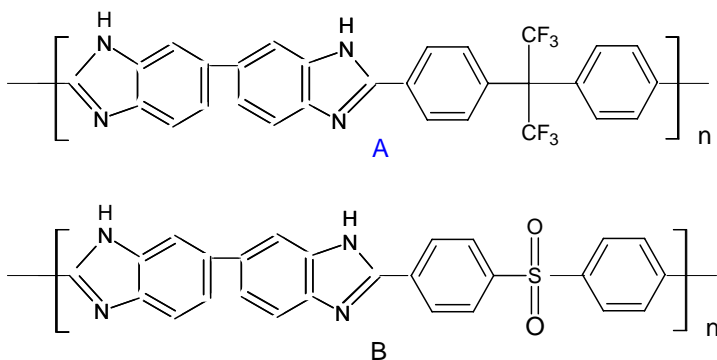


Figure 8. Structures of hexafluoro- (A) and sulfone- (B) containing PBI.

2.3.2 Chemical stability

Chemical stability of proton conducting membranes is of much concern to the lifetime of fuel cells. In situ formed H_2O_2 and $\cdot\text{OH}$ or $\cdot\text{OOH}$ radicals from its decomposition are believed to attack the hydrogen-containing bonds in polymer membranes. This is assumed to be the principal degradation mechanism of common PEMFC membranes.

Experimentally, the generation of these radicals can be achieved by $\text{Fe}^{2+}/\text{Fe}^{3+}$ catalysed H_2O_2 decomposition. Based on this method, the so-called Fenton test is used for the stability evaluation of PEMFC membranes.

By being exposed to a 3% hydrogen peroxide solution containing 4 ppm Fe^{2+} at 68°C , PBI membranes have been evaluated by the weight loss and visual observation. The PBI membrane was broken into small pieces after 30 minutes. After the first 20 hours, the PBI membrane showed a weight loss of about 15%. As a comparison, Nafion 117 membranes have only 1% weight loss during the same period of time.

It is interesting that chemically modified PBI as well as their blends showed much improved chemical stability, as seen in Figure 9. Both SO_2 - and F_6 - PBI membranes remained in a good membrane form even after 120 hours (indicated with solid lines). After the first 20 hours, about 2-5% of weight loss was observed, comparable to Nafion 117 membranes.

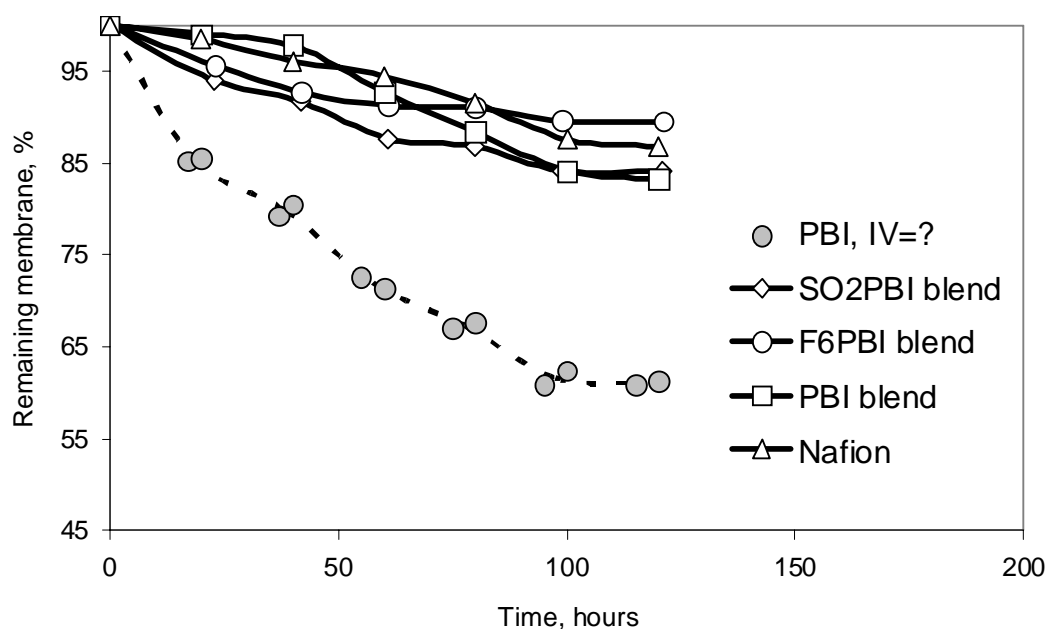


Figure 9. Degradation of PBI and modified PBI membranes as well as Nafion membranes in 3 wt.% H_2O_2 containing 4 ppm Fe^{2+} at 68°C . Solid lines indicate that the samples remained in a whole membrane form whereas dashed lines indicate that samples were broken into small pieces.

2.3.3 Mechanical properties

At room temperature, the typical tensile stress at break for PBI membranes is about 160 MPa under atmospheric humidity. At higher temperatures, 150°C for example, the stress at break is slightly lower, about 145 MPa. When the membranes were doped with phosphoric acid, the doping acid affects the tensile properties of the membrane dramatically and, fortunately can be improved by preparing blend membranes, as seen in Figure 10.

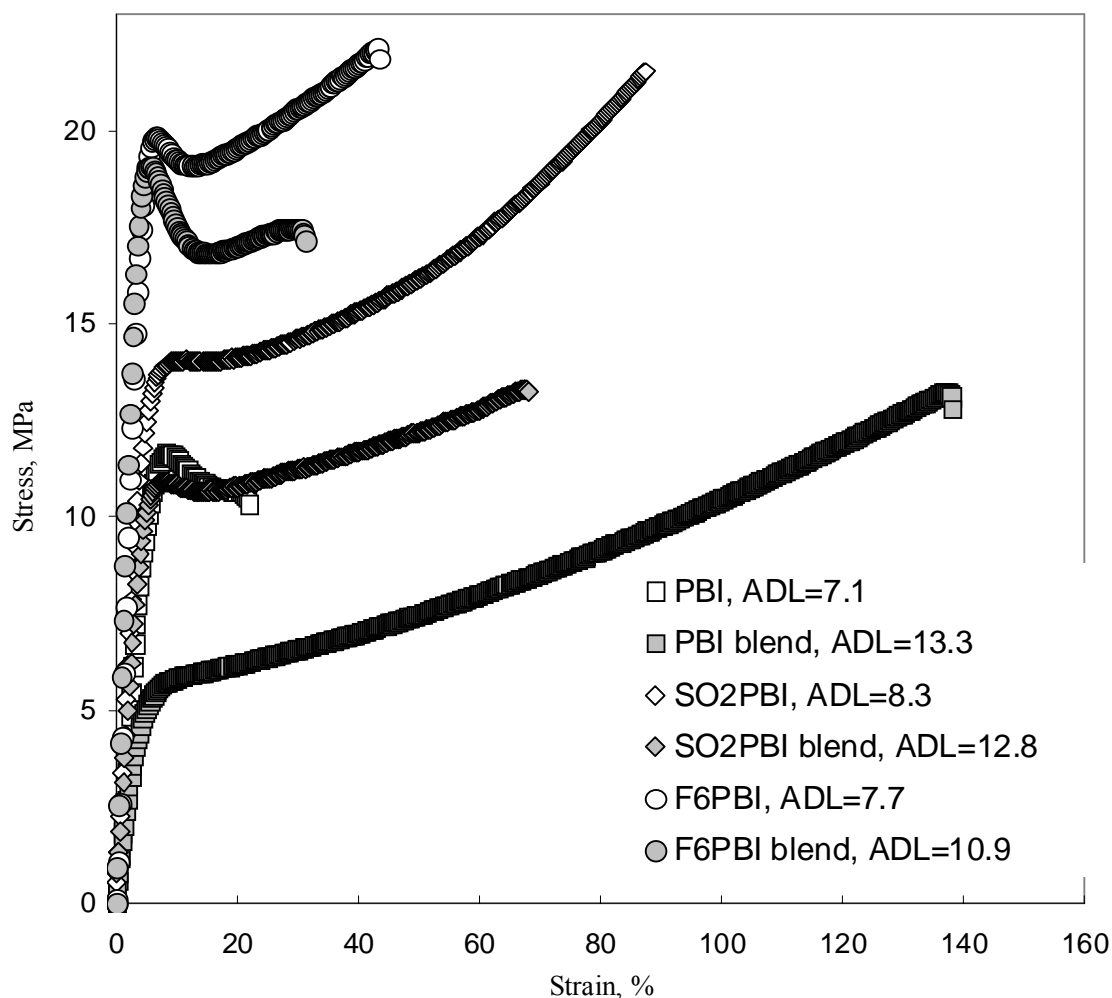


Figure 10. Tensile strength tests of PBI, SO₂PBI, F₆PBI and their blend membranes at room temperature and ambient humidity (ca. 60%). The acid doping levels (ADL) are indicated in the figure.

For SO₂PBI membranes doped with 8.3 mol phosphoric acid per repeat unit, the stress-strain curves are shown in the figure (open diamond) together with the its blend

membranes doped at a level of 12.8 (filled diamond). Significant improvement in e.g. the yield strength was observed. For pure PBI (ADL = 7.1) and its blend (ADL= 13.3) membranes, for example, the yield strength was 11.6 and 5.6 MPa. The values are 14.0 and 10.9 MPa for SO₂PBI (ADL=8.3) and its blend (ADL=12.8), respectively. Even further improvement was observed for F₆PBI (ADL=7.7, open cycle)) and its blend (ADL=10.9, filled cycle) membranes, with the yield strength of 19.8 and 19.0 MPa, respectively. Both F₆PBI and its blend membranes exhibit well defined yielding point in the stress–strain curves where a transition from the elastic deformation to plastic deformation occurs. The difference in the yield strength between the F₆PBI and its blend membranes is also small, compared to pure PBI and SO₂PBI with their blends.

3 MEA development and manufacture

3.1 Identification of improvement areas

Several routes of improvement have been identified for the MEA's. This includes edge sealing, hot pressing, assembly and catalyst. These will be discussed separately and more thoroughly in the following paragraphs.

3.1.1 Edge sealing

Tests have previously shown that the membrane has a weak point on the edge of the electrode causing it to break (Figure 11). Attempts have been made to solve this by cross linking the PBI or substituting the membrane with a blend membrane of different compositions giving rise to other problems with the MEA preparation.

Different ways of treating or reinforcing the rim has been made, and a solution is being finally evaluated. Previously rim strengthening was done by applying thin foils, but lately, cast reinforcement was made by DPS. In this project the problem has been engaged from another angle enforcing the edge with another polymeric film similar in structure to the PBI membrane. The similar structure of the two polymeric materials lets them connect well during the hot pressing process even with the presence of the phosphoric acid in the membrane. Since the implementation of this edge sealing, holes in the membranes along the electrode edge have no longer been observed during the MEA tests (Figure 11).

A sample MEA was delivered to IRD for testing with bipolar plates and sealing. MEA's for the short stack were made by the new method of reinforcing the membrane rim. The improvement was significant, but still some remaining roughness was detected. With softer gaskets the cells were tight.



Figure 11. Left: a MEA (from before the project) without edge sealing showing the characteristic holes along the electrode edge. Right: a MEA with applied edge sealing and hot pressed using the new tool.

3.1.2 Hot pressing

The hot pressing step in the MEA fabrication has previously proven to have a large influence on the MEA performance. Investigations have proven that it is important to control the compression of the electrodes and the pressure applied on the edges. Therefore a hot pressing tool has been made to improve the uniformity of the process. The tool ensures a fixed compression on both the edges and the active part of the MEA. Implementing the use of this hot pressing tool has given a more uniform product, but has also helped in making a more smooth edge.

Preliminary results have shown that the temperature, applied pressure and hot pressing time also influence the MEA performance. With a more uniform process it will be easier to identify the role of each of these parameters and they will be investigated and optimized in the HotMEA project.

3.1.3 Assembly

The MEA assembly has always been a time consuming process requiring a large amount of precision. It consists of two parts, cutting the components in the right dimensions and the actual assembly. To ensure the exact same shape and size of the different components, tools have been made for stamping them out instead of cutting them by hand. For this purpose a clicker press (ATOM SE20, Figure 12) has been purchased by DTU in order to ease cutting membranes, gaskets and electrode support etc. accurately. The cutting moulds are inexpensive and can be manufactured within about a week when new dimensions are needed. Tools for cutting the various components for the MEA's

have been designed and purchased. This has caused a significant reduction in time required for manufacturing the MEA's.

Positioning the electrodes and polymeric materials precisely on top of each other is the time consuming step of the actual assembly. The process has been done by hand giving rise to the variations of a handmade process. The hot pressing tool has been designed so that it also helps the positioning of the components during the assembly process, lowering the time consumption and heightening the uniformity of the MEA. The process is thus still handmade and gives rise to some (though smaller) variations.

A new concept of assembly offering a larger degree of precision and substantially lower time consumption throughout the whole MEA preparation process will be investigated in the HotMEA project. The new concept should also make it possible at some point to switch to an automatic assembly process.



Figure 12. ATOM clicker press for stamping out membranes, electrodes and seals.

3.2 Electrodes

In the previous PSO project electrode preparation by spraying showed promising results and improved performance. During this project the shift from tape casting to spraying the electrode was completed. Moreover, the first steps to automating the process were taken.

3.2.1 New spray system

DPS has built a new automatic spray system and the results of it are compared with previous hand spray in Figure 13. The new spray system has a special nozzle controlling the fan and thereby minimizing over spraying. The applied amount of ink can be adjusted and specified and by adding heating zones and subsequent nozzles it should be possible to control the spraying system more closely, giving rise to more uniform and reproducible electrodes and a quicker process with fewer steps.

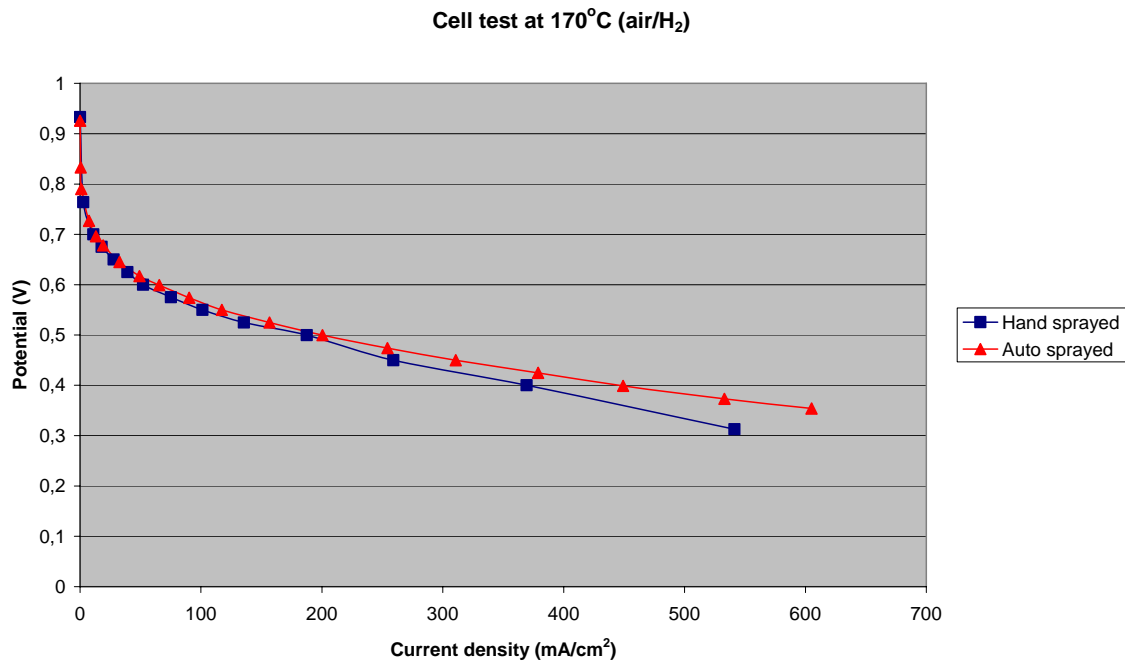


Figure 13: Preliminary cell tests of MEA's made with the same catalyst (DTU 40% Pt/C) by hand spray / auto spray showing similar performance. The auto sprayed MEA actually shows slightly higher current densities at lower potentials than the hand sprayed one even though the auto spraying has not been fully optimized.

3.3 MEA

3.3.1 Choice of catalyst

DPS has been working with different kinds of catalysts and on Figure 14 a comparison of two of the catalysts can be seen. The experiment kept the Pt loading of the electrodes and the preparation techniques fixed.

It can be seen from the figure that in this case the activation loss is slightly bigger for the DTU catalyst. However, it also has lower platinum to carbon ratio which makes it necessary to have thicker catalyst layer in order to have the same overall catalyst loading. With a thicker layer a larger fraction of the platinum has a longer ionic transport way to the membrane and consequently, the ionic transport in the catalyst layer adds to the ohmic resistance of the cell giving a larger slope of the linear part of the polarization curve. Moreover, when some catalyst particles are “separated” from the membrane to a larger extent by the in-layer ohmic resistance, they contribute less to the process and thus the other catalyst particles have to work harder. This will influence the polarization curve as if a higher current density was applied. The same membrane was been used in both MEA's. DTU and DPS are working together to make a catalyst with a 50% Pt/C loading and similar catalytic properties. This work will be carried out in the HotMEA project.

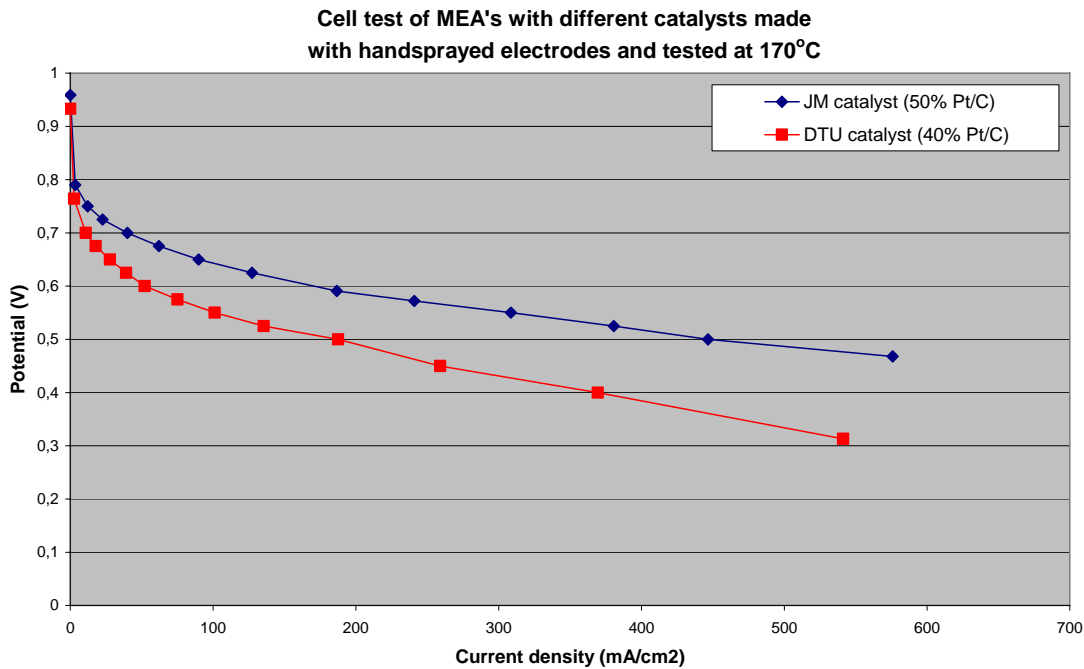


Figure 14: Both MEA's were made with approx. 0,7mg Pt/cm² on both the anode and the cathode side.

3.3.2 MEA's for the final stack

The materials for the stacks in this project was decided when the short stack was made. The membrane should be a pure PBI membrane doped with 85% phosphoric acid, the edges should be strengthened by the identified polymeric sealant and the catalyst should be the 40% Pt/C made by DTU. To be able to compare the two stacks made in this project this was kept fixed even though experiments showed that a higher performance could be obtained by using the 50% Pt/C catalyst form JM (See chapter 3.3.1).

A total of 40 MEA's with an active area of approximately 117cm^2 were supplied to IRD fuel cells for the final stack of this project.

The first 10 were sprayed by hand, but the last 30 were all sprayed by automatic spraying of electrodes. All 40 MEA's were assembled and hot pressed with the new tools described in earlier chapters. Before the last 30 MEA's were shipped they were all checked to ensure an acceptable performance. The polarisation curves can be seen on Figure 15, all MEA's show a similar performance with a current density of around $300\text{mA}/\text{cm}^2$ at $0,5\text{V}$. Due to the way the test setup is designed the curves level off after $400\text{mA}/\text{cm}^2$. This is a feature of the test setup not a sign of mass transport problems in the MEA.

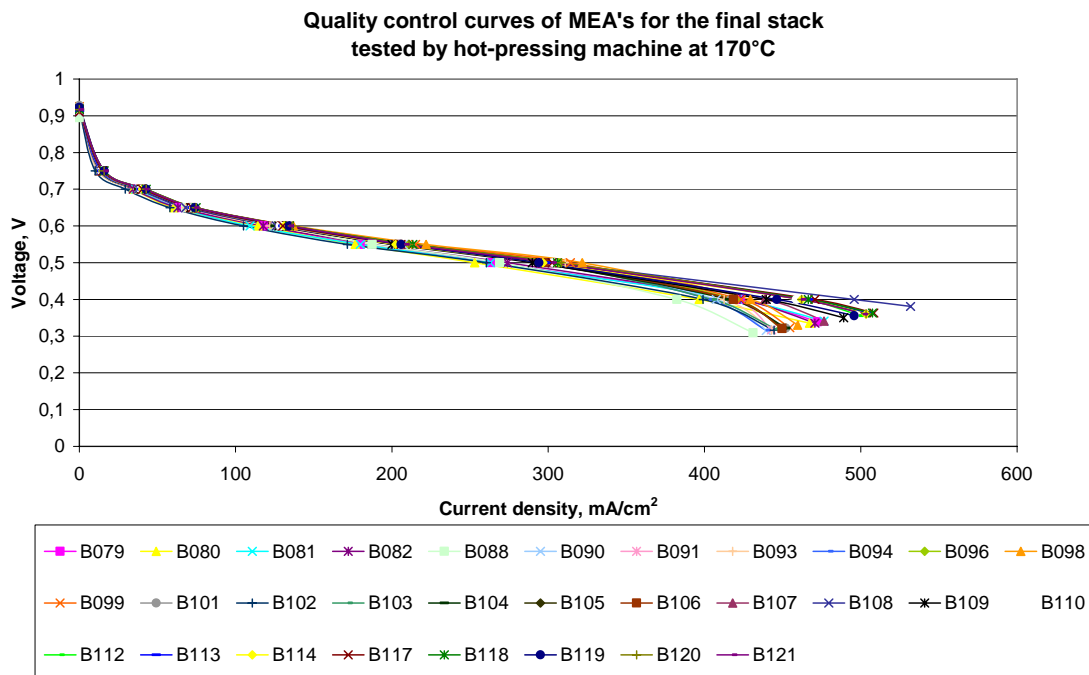


Figure 15. Polarisation curves for the last 30 MEA's supplied to the final stack. It shows that the performance is fairly reproducible and that all the MEA's are working. The MEA's for the final stack has been made with a 40%Pt/C catalyst made by DTU.

4 Stacking

IRD has been revising the fuel cell stack design for a 1.5-2 kW CHP unit. This design includes major modifications in comparison to the previous stack produced in the PSO project 4760. A reduction of pressure loss on the cathode side was one of the targets of this redesign. This would allow the efficient use of an air blower for the air supply in the CHP unit. Reduction of stack size and implementation of a new sealing design were also studied.

IRD's stack design is based on graphite composite bipolar plates with internal manifolds. The stack components apart from the MEAs were developed and constructed from the following materials:

- Bipolar plates: graphite composite blank plates
- Current collector: Au-plated copper
- End caps: glass fiber reinforced polymer composite
- Seals: Viton type gaskets

4.1 Bipolar plates

Blank plates were compression moulded at IRD (26 x 27 x 0.45 cm) from outsourced raw material. The final bipolar plates were machined on the CNC station at IRD. The construction of a mould for direct pressing of the bipolar plates is too expensive considering the low number of plates produced.

Each cell is separated with a cooling flow field, situated at the backside of the anode plate.

The blank side of the cathode plate is chemically bonded to the cooling flow field on the anode side, thus creating a bipolar plate. The cooling and cathode flow fields are based on a serpentine channel design, while the anode flow field is designed with straight parallel channels.

4.2 Sealing

Sealing of the cooling circuit is made by chemical bonding of the plates. A flat gasket combined with o-ring (both Viton types) is sealing the MEA side of the plates. Sealing of the manifold between endplate and bipolar plate is made with the same Viton o-ring.

4.3 Endplates

End plates are made of polyimide composite material and were also machined at IRD. Current collectors are integrated in a recess of the end plate. No support steel plates are needed on the final stack, as eventual bending of the end plates are compensated over the large number of cells.

4.4 Heat transfer loop

As in the previous designs (PSO project 4760), an internal liquid cooling was selected. The cooling medium selected is a perfluoropolyether (see formula below) whose low viscosity at both ambient and elevated temperature ensures relatively low pressure drops in the system (around 300 mbar).

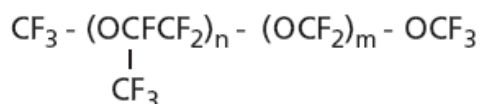


Figure 16. The perfluoropolyether selected as coolant.

However, its vapour pressure of 50 mbar at 180°C requires running the cooling system as a closed circuit. The liquid is chemically inert, so any contact with the electrode is not damaging the MEA.

The heat transfer loop is made of a circulation pump a heater element a heat exchanger and two 3-way valves. It is used for heating up the stack to operating temperature (120°C) and for temperature control at high current. A secondary circuit can be connected through the heat exchanger.

4.5 Control system

Individual cell voltage is monitored and linked to the electronic load control. Temperature of the stack is monitored through inlet and outlet temperatures of the cooling liquid.

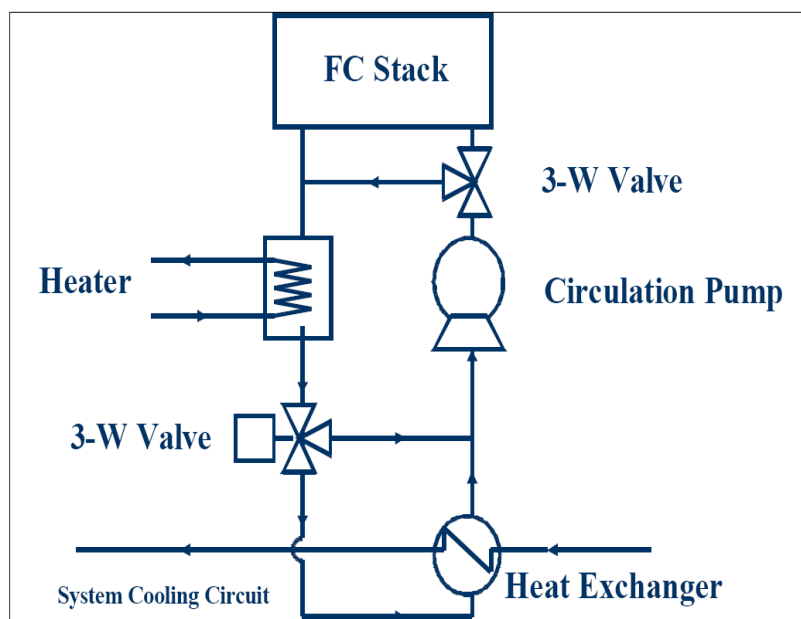


Figure 17. The heat transfer loop.

4.6 Stack construction and test

Ten MEAs from DPS were received in April and two of them were used in a short stack for test of the sealing gaskets. Those two MEAs were reused in the final stack. The final stack was built in the end of June, with 40 cells (Figure 18). Only a preliminary test of the stack has been carried out yet. The stack was heated up to 165°C and a polarization curve up to 48A (0.4 A/cm²) was done, at ambient pressure, with pure hydrogen in the anode.

The cell number 1 performance was below average and dropped sharply after 0.35 A/cm², and prevented tests at higher current (see Figure 19 and 20 below for polarization curves of the stack and individual cells).

The average cell performance is rather low and corresponds to the lower of the two cells tested in the short stack. The low open circuit cell voltage indicates a gas cross over between anode and cathode.

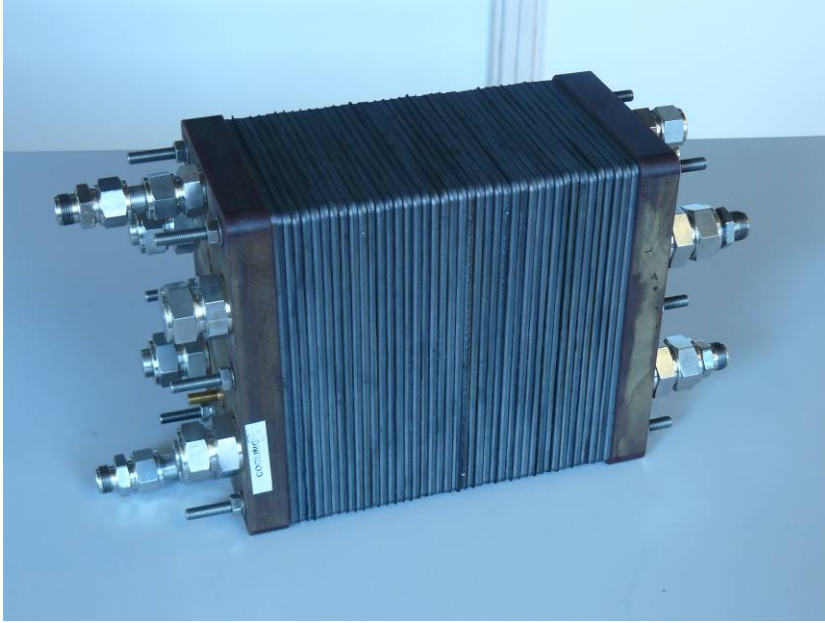


Figure 18. The 40-cell stack.

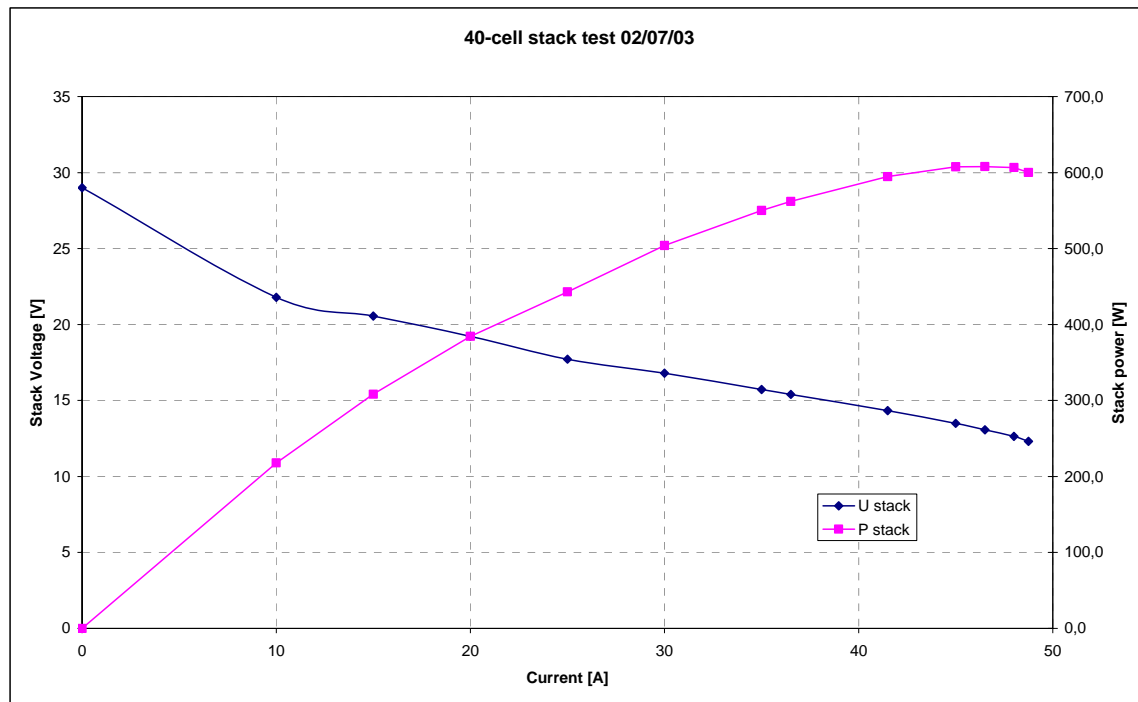


Figure 19. Performance test of the 40-cell stack, @ 165°C, ambient pressure, cathode stoichiometry 4, anode stoichiometry 1.5.

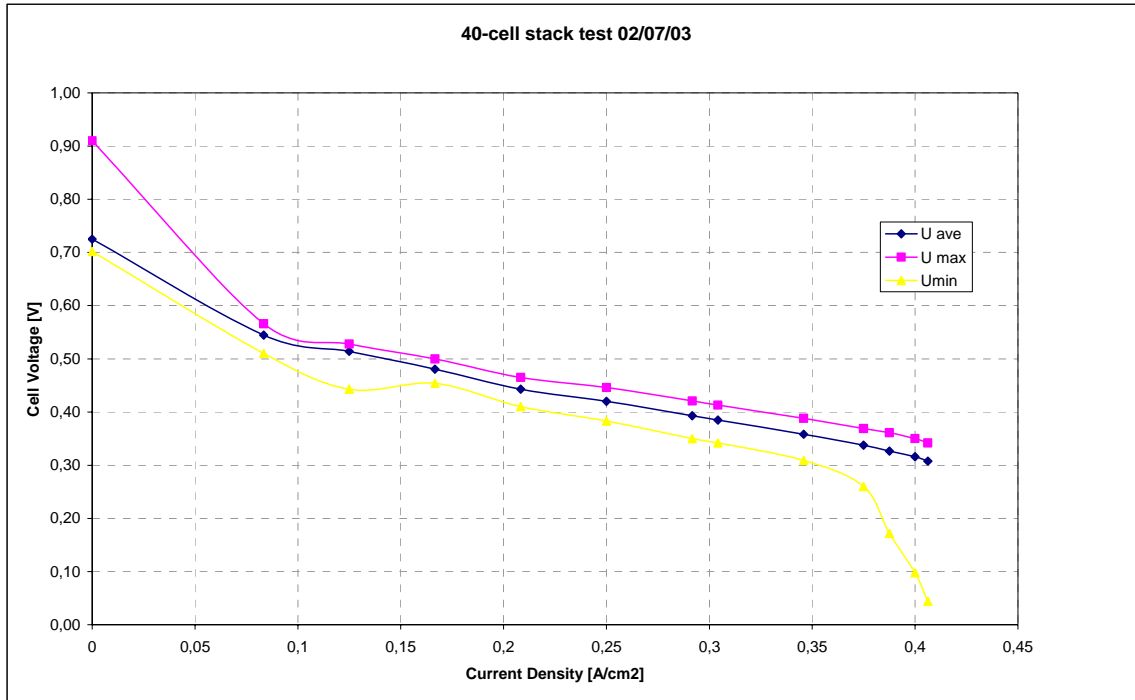


Figure 20. Performance test of the 40-cell stack, @ 165°C, ambient pressure, cathode stoichiometry 4, anode stoichiometry 1.5.

4.7 Alternative design at DTU

DTU has performed some further improvement of the stack sealing of the previous PSO stacking project 4760. Stacking was not a main task for DTU and the work has to a large extent been carried out in collaboration with students through master and bachelor projects.

The progress is described in detail in the confidential annex.

5 Outcome and conclusion on the project

5.1 Membrane

The polymer synthesis has improved decisively. It is now possible to repeatedly and with reproducibility to synthesize 100-200 g batches with high molecular weight (larger batches should be possible too). This was possible because the understanding and control of the process was improved as a result of systematic research. The upscaled synthesis was carried out in a facility built during the project.

The success with both quality and volume is a crucial achievement on the way to establishing a Danish value chain all the way from the polymer synthesis. It is now realistic to produce 0.5-1 kg of PBI a week and this is sufficient for an initial production of HT-PEM MEAs. The work with Size Exclusion Chromatography (SEC) has been brought further and now a calibration curve based on viscosity measurements has been made.

Solution casting is the state of art technique, but experiments with direct casting were also performed

PBI modified by both cross linking as well as in the primary structure was synthesized. The results are promising and will lead to further studies. However linear standard PBI is still the standard material for some time.

5.2 MEAs

The present way of MEA rim enforcement was initiated in the project. This was found to be crucial for the compatibility with the sealing of the bipolar plates of the stack. A special MEA pressing tool was developed for easy alignment and control of the compression.

Electrode spraying was replacing tape casting during the project and the first steps towards a more automated process were taken. In this area a substantial amount of work is still required in order to set up a pilot production line. This as well as the MEA hot pressing procedure will be addressed further in the next projects, especially HotMEA. For some time it has been foreseen that spraying would eventually replace tape casting. During the project this decision was finally made and this is basically a milestone.

5.3 Stacking

The stacking was addressed both at IRD and DTU with different approaches. IRD made a short test stack and finally a 40 cell stack. A suitable coolant (a perfluoropolyether) was

chosen and progress was made with bipolar plates and the sealing. The cell dimensions were modified as compared to the ones used in the EU-project Furim. One reason for this was to reduce the air pressure drop. Bipolar plates can later be compression moulding, but as the design was under development during the project the high cost of a mould could not yet be justified. However, compression moulding is a technique mastered at IRD, which eliminates the need for machining.

DTU's stack was constructed by an alternative idea which made liquid cooling difficult to implement. Therefore, and for other reasons DTU ended up focusing entirely on air cooling. The advantage of the design is that it is very compact and based on inexpensive construction materials.

5.4 Student involvement

A number of students at DTU have been involved in the development in all work packages from polymer to stacking.

5.5 Publications and presentations

The listed publications are written during the project and are all to a variable extent outcome of the project. This means that

The listed publications are written during the project and are all to a variable extent outcome of the project.

5.5.1 Scientific papers in international journals

J. Kerres, F. Schönberger, A. Chromik, T. Häring, Q. Li, J.O. Jensen, C. Pan, P. Noyé, and N. J. Bjerrum. Partially Fluorinated Arylene Polyethers and Their Ternary Blend Membranes with PBI and H₃PO₄. Part I. Synthesis and Characterisation of Polymers and Binary Blend Membranes. *Fuel Cells* **8** (3–4) 175–187 (2008).

Q. Li, J.O. Jensen, C. Pan, V. Bandur, M. S.Nilsson, F. Schönberger, A. Chromik, M. Hein, T. Häring, J. Kerres, and N. J. Bjerrum. Partially Fluorinated Arylene Polyethers and their Ternary Blends with PBI and H₃PO₄. Part II. Characterisation and Fuel Cell Tests of the Ternary Membranes. *Fuel Cells* **8** (3–4) 188–199 (2008).

Q. Li, J. O. Jensen, R. F. Savinell and N. J. Bjerrum. Acid-doped polybenzimidazole (PBI) membranes for high temperature proton exchange membrane fuel cells. *Progress in Polymer Science* **34** 449-477 (2009)

P. Pfeifer, C. Wall, J.O. Jensen, H. Hahn and M. Fichtner. Thermal coupling of a high temperature PEM fuel cell with a complex hydride tank. *Int. J. Hydrogen Energy* **34**, (8) 3457–3466 (2009)

5.5.2 Book chapters

Q. Li. and J. O. Jensen. Membranes for High Temperature PEMFC Based on Acid-Doped Polybenimidazoles. p. 61-96 Invited contribution in: *Membranes for Energy Conversion*, vol. 2. Eds.: K.-V. Peinrmann and S. Nunes. ISBN: 978-3-527-31481-2. Wiley-VCH, Weinheim, 2008.

J. O. Jensen and Q. Li. Fuel cells. P. 151-184. Invited contribution in: *Hydrogen Technology. Mobile and portable applications*. Ed.: A. Léon. Springer-Verlag. Berlin Heidelberg. ISBN 978-3-540-79027-3 (2008).

5.5.3 Conference presentations etc.

P. Pfeifer,, C. Wall, M. Fichtner, J.O. Jensen, Th. Schulenberg. Evaluation of a thermal coupling of nanocrystalline alanate with HT-PEM fuel cells. International Symposium on Metal Hydrogen Systems, MH2008” Reykjavik, Iceland, June 24-28, 2008. (abstract, oral by Pfeifer)

J. O. Jensen. Recent progress in high temperature PEM fuel cells. Electrochemical Science and Technology. Symposium of the Danish Electrochemical Society. Odense, 2-3 October 2008. (oral)

J. O. Jensen, Q. Li, C. Pan and N. J. Bjerrum. PEM fuel cells at elevated temperature. 3rd Symposium "Hydrogen & Energy" Braunwald, Switzerland, 25. - 30. January 2009. (Invited keynote talk)

J. O. Jensen, Q. Li, C. Pan and N. J. Bjerrum. High Temperature PEM Fuel Cells. From Membranes to Stacks. HySA Systems Seminar, Cape Town, South Africa, 31 March – 1 April 2009 (Invited talk)

6 Outlook and further development

The project was one in a line of so far three projects supported by ForskEl starting with “High Temperature PEM Fuel Cell” and the work will continue in the newly established consortium “HotMEA”. They all relate to the national strategy for development of HT-PEMFC as an all-Danish product. The achievements of the present project are significant and encouraged the project partners to agree on going for a larger consortium which is expected to bring the process closer towards a commercialization. Key challenges are to improve the MEA performance and to develop the spray technique for electrodes further.

The potential for performance improvement is large, because the high working temperature makes it reasonable to expect that. The fact that the partners are capable of playing with all the components in the cells and that multiple development pathways are opened (membrane modifications, catalyst development, electrode morphology in connection with manufacturing processes etc.) makes it likely that new encouraging results can and will be obtained.

The consortium HotMEA consists of the same partners as well as an end-user (Dantherm Power). An important issue before initiating the consortium is to clarify the patent situation and secure that patent issues are not later hindering a commercial production of PBI-based fuel cells, all the way from components, in Denmark. Negotiations between DPS and the patent holder, Case Western Reserve University (Ohio, US), have led to a license for producing HT-PEM based MEAs by DPS.

In general, the development of Danish HT-PEM technology has progressed significantly, but there is still plenty of room for improvements, both nationally and internationally, to exploit the performance advantage that the high working temperature makes a strong potential for.

The next steps will be to

- 1) improve membrane, especially its durability. The results with modified structures are promising. On the longer term, a phosphoric acid free membrane is highly desirable, but the route to this is not known, although some ideas with inorganic proton conductors are worth while looking into.
- 2) improve the electrode performance. The electrode morphology has not yet been studied in great detail and this will be addressed in HotMEA.
- 3) continue the development of manufacturing means, the automation of the spraying and the membrane casting etc. This is not only the way to reduced manufacturing cost, but also to reproducible products and volume.
- 4) improve the liquid cooled stack and to test it in a system.
- 5) decide whether the DTU/DPS is a viable alternative to other air cooled stacks.