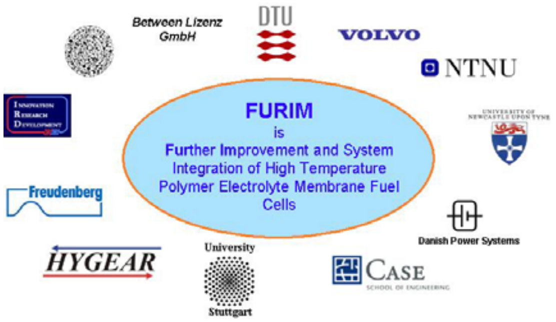
Project no. **SES6-CT-2004-502782**

FURIM

Further Improvement and System Integration of High Temperature Polymer Electrolyte Membrane Fuel Cells



Publishable Final Activity Report

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1 Summary

The new development in the field of proton exchange membrane fuel cell (PEMFC) is high temperature PEMFC for operation above 100°C. Fundamental materials, technological units and an integrated high temperature PEMFC-based power system operated on low sulphur diesel are the focus the project.

As the key materials, polybenzimidazoles and partially fluorinated sulphonated arylene main-chain polymers have been synthesized with optimized procedures, based on which cross-linked ternary blend membranes have been prepared. After acid doping the membranes exhibit promising properties in an operating temperature range from 120 to 200°C. Systematic characterizations of the membranes were carried out, showing very much improved properties e.g. proton conductivity of up to 0.10 S/cm, extended chemical stability and good mechanical strength and flexibility.

Catalysts and gas diffusion layer materials are prepared and characterized. Different techniques have been developed and optimized for fabricating gas diffusion electrodes. The influence of a range of structural parameters on the behaviour of gas diffusion electrodes was investigated. High temperature gas diffusion layers (HT-GDL) were specified and manufactured with excellent chemical, mechanical, electrical, fluid properties. Based on the materials and techniques developed, gas diffusion electrodes and membrane-electrode-assemblies (MEAs) have been fabricated. Single cell performance has been achieved of 0.58 A cm^{-2} at a cell voltage of 0.6 V with reformate and air under 4/4 bar pressure, with the best performance of 0.68 $mAcm^{-2}$ at 0.6 V at 5/5 bars of hydrogen and air. For the long term durability, a degradation rate of 5 μVh^{-1} was achieved under continuous operation with hydrogen and air at 150-160^{o}C. By defining a failure as 10 % performance loss, this degradation rate corresponds to a lifetime of 12,000 hours.

A 2 kW_{el} final stack was designed and built with internal manifolds and integrated internal cooling circuit. The stack was operational with both dry hydrogen and reformate fuel containing up to 1% CO. A fuel processing system was developed for converting diesel into a hydrogen rich gas suitable for usage in the high temperature PEM fuel cell stack. The system consisted of a pre-reformer, a desulphurisation unit, a reformer and a medium temperature water gas shift reactor.

Based on HT-PEMFC modelling, system simulation as well as system safety study, efforts were made finally to integrate the fuel processors and the stack as well as control units. The project successfully ended up with an integrated proof-of-principle high temperature PEMFC system, showing the feasibility of a diesel-fuelled, APU like fuel cell power system.

Additional efforts were made to train young researcher in the field. The efforts include university teaching and experimental courses, symposia, workshops, summer (spring) schools, and project meetings.

2 Project objectives

2.1 Introduction to HT-PEMFC

Development of new improved membrane materials was among the key motivations for the project. The entire concept of PEMFC at elevated temperature depends to a large extent on the membrane. The reason why conventional PEMFC's cannot easily be operated above 80-90ºC is that the proton conduction mechanism depends on a high water content in the perfluorosulphonic acid membrane normally applied. At higher temperatures the membrane dries out even though water is produced continuously during service. If higher working temperatures are desired to increase the tolerance to carbon monoxide the proton conduction mechanism in the membrane must not depend on water. Two main ways to replace water have been suggested. Either the sulphonic a acid side chains must be replaced with something more flexible or water (the proton shuttle) must be replaced with something with a lower vapour pressure. To date the latter approach has been most successful, in particular exemplified with the PBI/phosphoric acid system. PBI is polybenzimidazole which is doped with a significant amount of phosphoric acid in order to obtain proton conductivity. The acid plays a role similar to water in transporting the protons, and phosphoric acid is chosen because of its thermal stability and ultra low vapour pressure even at 200ºC. The cell can be seen as a hybrid between a PEM fuel cells and a phosphoric acid fuel cell, but for practical applications it is a PEM fuel cell because the electrolyte is indeed a stand alone material with the properties of a polymer.

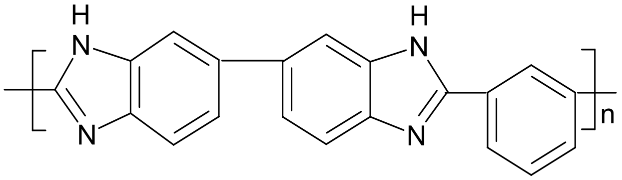


Figure 1. The structure of polybenzimidazole (PBI), one of the most successful membrane materials for HT-PEMFC when doped with phosphoric acid.

2.2 Project idea and background

The project succeeded the EU projects ASPEC (Contract JOR3-CT97-0045) and AMFC (the 5th FP, ENK5-CT-2000-00323) in which high temperature proton exchange membrane fuel cells (HT-PEMFC) were developed to some extent by a number of the partners. ASPEC was the first EU project on HT-PEMFC and AMFC addressed the integration with a methanol reformer. FURIM was meant for a further improvement (as indicated in the title), and this time the fuel developed for was diesel.

The rationale behind a diesel powered fuel cell system was the fact that heavy vehicles like trucks often have a high demand for electrical energy which can only be provided by the diesel engine and the generator. For that reason, when a truck stops overnight, it has to keep the engine idling in order to provide electricity. In this mode the engine is extremely inefficient and the pollution is severe. A fuel cell based auxiliary power unit (APU) can solve the problem, and if it is powered by the same fuel as the truck no separate fuel system or store is required.

The main project line was therefore to develop and construct a diesel/fuel cell APU of ca. 2kW electric. The reason for applying the relative new high temperature fuel cell system was the high tolerance toward carbon monoxide (CO), which is a result of the increased working temperature of 120-200ºC. At 150ºC the cell tolerates 1% (10 000 ppm) of CO in the hydrogen while conventional low temperature PEMFC’s are seriously affected by CO levels as low as 50 ppm.

FURIM, being an Integrated Project under the 6th Framework, was integrated on several levels:

1. The work included both modelling/simulation and experimental work. Moreover, training of young students and researchers was a central activity.

2. It comprised research and development on both fundamental and applied level. An overall line of activities proceeded through the project leading from modelling and simulations over materials development and manufacturing of components to the assembly of the final setup with a fuel cell stack and a complete reformer system.

3. The materials development was generally driven by two simultaneous objectives: basic materials development (long term) and to develop components for the final system (near term).

2.3 Overall project objectives

The overall objectives of FURIM were:

1. development of new or modified proton conducting polymers and membranes operational temperatures from 150-200°C with high proton conductivity (up to 0.10 S/cm) extended chemical stability and good mechanical strength and flexibility.
2. development of catalysts, gas diffusion layers, electrodes and cells for both anode and cathode in the HT-PEMFC
3. development of sealing and stack components capable of withstanding the high temperature in combination with the phosphoric acid that is stored in the membrane.

4. development of and construct a 2 kW stack using exclusively components developed and manufactured in the project
5. development and manufacture of a reformer system including a diesel evaporator, a reformer, a shift reactor and a burner
6. integration of the fuel cell stack in the reformer system and running it as one unit.
7. assist the development work by modelling and simulations
8. devotion of a significant effort to training of young students and scientists in the field of fuel cells and related technologies.

Detailed technical objectives are listed in Table 4 on page 26.

2.4 Project structure

The project was arranges in 3 levels as shown in Table 1. Work Block 0 (WB 0) covered all work on fundamental material development, from polymers, membranes, catalysts, gas diffusion layer, electrodes and Membrane Electrode Assemblies (MEA's). Work Block 1 and Work Block 2 are primarily on the level of unit development including that fuel cell stack, reformer and burner. Finally an integrated system was constructed based on the developed units as well as results from controlling, modelling and simulation.

Table 1. Overview of Work Blocks, Work Packages and Tasks. See **Table 2** for Work Block leaders identified in brackets.

WB 0. Membranes and cells (Responsible: DTU)	WP 1. Polymer	Task 1. Polymer
		Task 2. Modificat.
		Task 3. Cross-link
		Task 4. Acid-base
	WP 2. Electrodes	Task 5. GDL
		Task 6. Cathode
		Task 7. Anode
		Task 8. MEAs
WB 1. Stack (Responsible: IRD)	WP 3. Stack construction	Task 9. Sealing
		Task 10. Cooling
		Task 11. Stack
	WP 4. Stack test	Task 12. Empty
		Task 13. Stack test
WB 2. Reforming and integration (Responsible: HYG)	WP 5. Hydrocarbon	Task 14. Catalysts
		Task 15. Reformer
		Task 16. Integration
	WP 6. Burner	Task 17. Catalysts
		Task 18. Burner
	WP 7. Integration	Task 19. Analysis
		Task 20. Integration
		Task 21. Testing
WB 3. Modelling, simulation (Responsible: VOL)	WP 8. Models	Task 22. HTPEM
	WP 9. Simulation	Task 23. Mobile
	WP 10. Control	Task 24. Control
		Task 25. Test
WB 4 Training (Responsible: UNEW)	WP 11. Training	Task 26. Empty
		Task 27. Workshop
		Task 28. Symposia
		Task 29. Group
WB 5. Coordination (Responsible: DTU)	WP 12. Management	Task 30. Commun..
		Task 31. Reporting
		Task 32. Dissemin.
		Task 33. Outreach

3 Contractors involved

The project partners and their main obligations are listed in Table 2 below.

Table 2. FURIM project partners.

Participant	Short	Main roles	Country
Technical University of Denmark	DTU	Coordination, membranes, electrodes, MEA’s	Denmark
Volvo Technology Corp.	VOL	Model, simulation, test, assessment	Sweden
Norwegian University of Science and Technology	NTNU	Fuel cell catalyst, electrodes	Norway
University of Newcastle upon Tyne	UNEW	Cells, electrodes, coord. of training	United Kingdom
Elsam A/S (finished after year 2)	ELS	System considerations	Denmark
Danish Power Systems ApS	DPS	Electrodes, MEA’s production	Denmark
Case West Reserve University	CWRU	Consultancy	USA
University of Stuttgart	USTUTT	Membranes	Germany
HyGear B.V.	HYG	Reformer system and its components	Netherlands
Freudenberg FCCT	FFCCT	Electrode support (GDL), stack sealing	Germany
IRD Fuel Cell A/S	IRD	Stacking	Denmark
Foundation of Research and Technology	FORTH	Catalysts for reformer system, spectroscopy	Greece
Between Lizenz GmbH	BTW	Membranes and cells	Germany

4 Results of the project

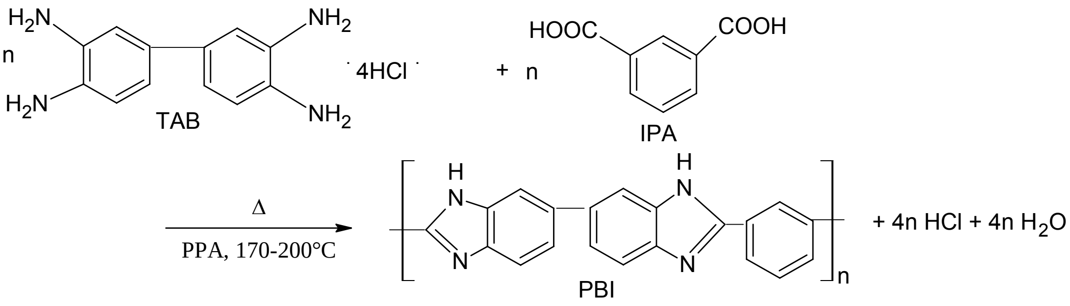
The main outcome of the project is reviewed below starting at the polymer level and then working its way up through cells, stack, reformer and system.

4.1 Polymer membranes

The project was started with synthesis of temperature resistant polymers, i.e. polybenzimidazoles (PBI) and sulphonated partially fluorinated arylene polyethers (1b). Binary blend membranes were prepared by solution casting and further doped with phosphoric acid. This ternary membrane material was extensively characterized and used in the final stack.

4.1.1 PBI synthesis

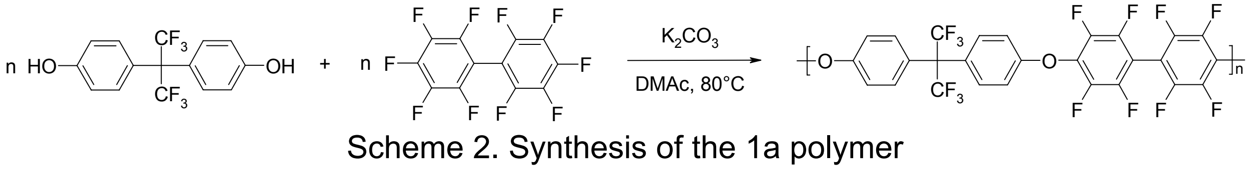
A homogeneous method was used with polyphosphoric acid (PPA) as the condensation agent and solvent and stable Tetraaminobiphenyl (TAB) as the monomer, as shown in Scheme 1. PBI with a weight averaged molecular weight of more than 30,000 g/mol has been synthesized with good reproducibility, solubility and processability.



Scheme 1. The PPA process for PBI synthesis

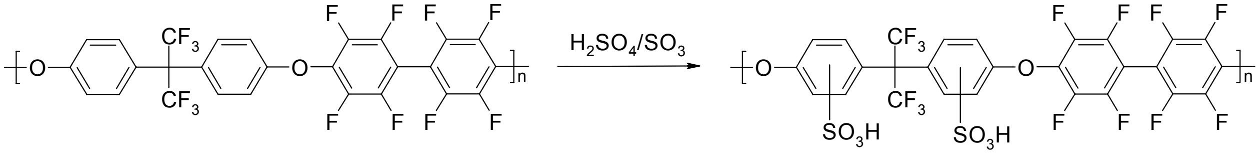
4.1.2 Synthesis of sulphonated partially fluorinated arylene polyethers

A number of acidic polymers have been synthesized and evaluated through the project. Finally partially fluorinated arylene polyether (see Scheme 2) was selected, which was first synthesized from the polycondensation reaction between 6F-diphenol and decafluorobiphenyl:



Scheme 2. Synthesis of the 1a polymer

The polymer was further sulphonated according to the following reaction:



Scheme 3. Synthesis of the sulphonated polymer (1b)

Ionomers with molecular masses of up to 140,000 Dalton (nonsulphonated) and 178,000 Dalton (sulphonated) with high sulphonation degrees of up to 2.06 SO_3H groups per repeat unit have been produced. For the sulphonation of the polymers H_2SO_4/SO_3 mixtures with SO_3 concentration of 40% and more are required to obtain sulphonated ionomers with a sulphonation degree of up to 2 SO_3H groups per repeat unit.

4.1.3 Blend membrane casting and acid doping

This polymer (1b) showed excellent stability in concentrated phosphoric acid at temperatures of up to 200°C. The polymer was blended with PBI, yielding base-acid blends with PBI in excess. The preparation was started from 5w% solutions of the polymers in DMAc. A certain amount of 5% PBI solution in DMAc was then added according to the desired composition of PBI-1b blend membranes. Membranes were cast from the mixture solution. Due to the cross-linking effect of the PBI-1b blend membranes, the acid doping was more difficult, similar to the covalently cross-linked membranes as reported recently [1, 2]. In 85% phosphoric acid at room temperature, the PBI-1b blend membranes absorb only very small amounts of acid. After more than 60 hours, the acid doping level of the blend membranes was found to be only 0.3 mol H_3PO_4 pr. mol repeat unit of PBI. As a comparison, pure PBI membranes would reach an acid doping level of around 10 under the same conditions. The blend membranes needed to be doped at higher temperatures. In 85% phosphoric acid at 80°C, an acid doping level of 11 mol H_3PO_4 was achieved after about 10 hours. At 130°C, the doping level was as high as 12.

4.1.4 Characterizations of blend membranes

Systematic characterizations of the membranes were made through the project, including water uptake and swelling, acid doping and swelling, oxidative stability, mechanical strength, proton conductivity as well as fuel cell tests. Significant improvement in chemical stability was observed for the blend membranes, as revealed by the Fenton tests (see Figure 2).

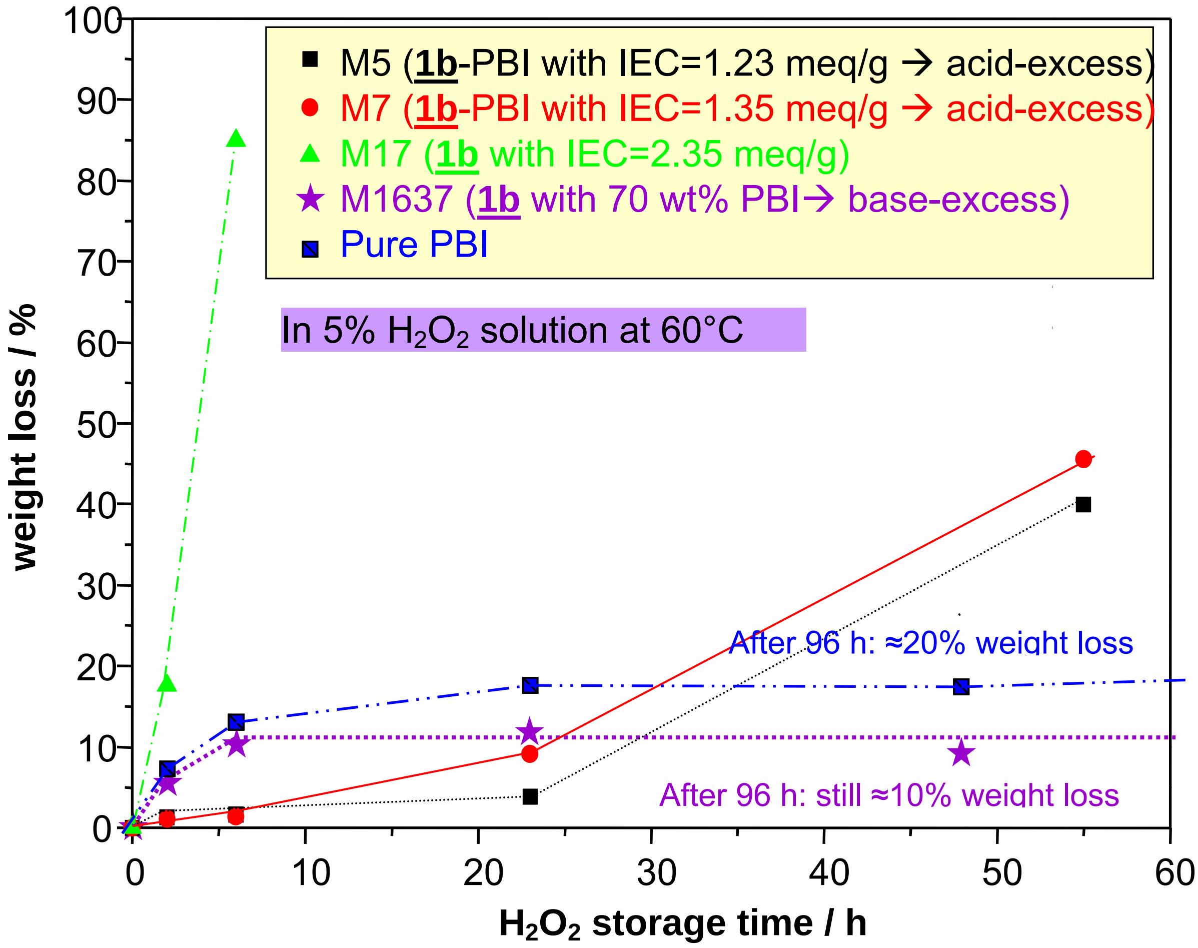


Figure 2. Weight loss of pure 1b, pure PBI, 1b-PBI blend membranes having an IEC of 1.23 meq/g and of 1.35 meq/g (acid-excess blend membranes), and of base-excess PBI-1b blend membranes with a PBI content of 70 wt% after different immersion times in a 5% H_2O_2 solution at 60°C.

The blend membranes showed also much better mechanical strength, especially at high acid doping levels, which means that with the blend membranes the acid doping level can be extended to an acid doping range of as high as 10-12, while the mechanical strength remains in a similar level as that of the pure PBI membranes doped by 5-6 mol phosphoric acid, as shown in .

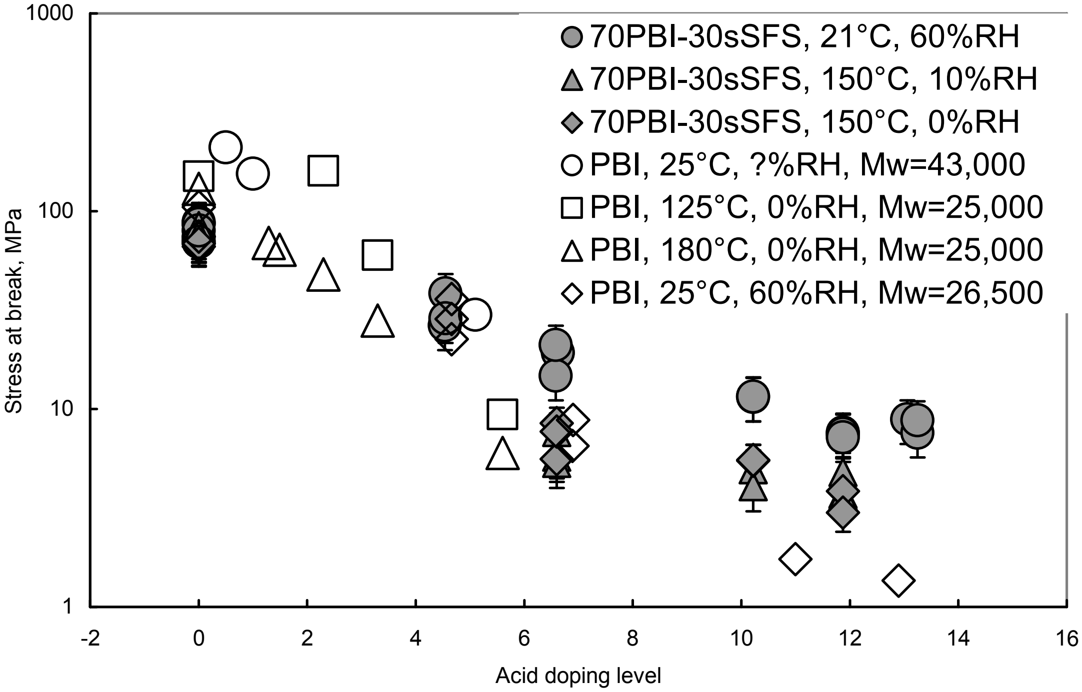


Figure 3. Tensile strength at break of PBI and PBI blend membranes as a function of acid doping level. Note the logarithmic scale on the secondary axis.

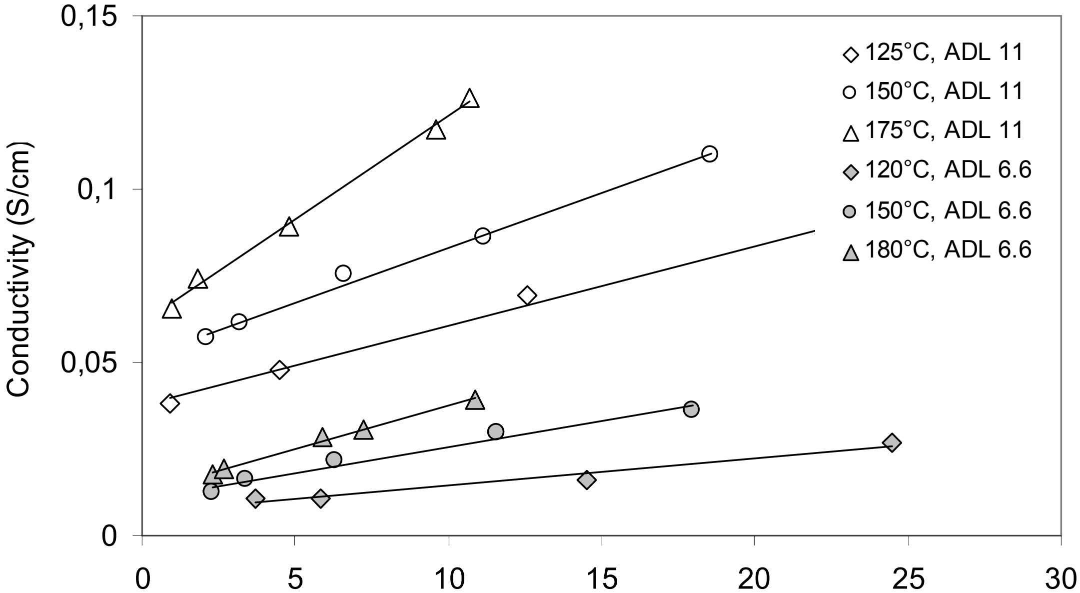


Figure 4. Proton conductivity of the blend membrane as a function of relative humidity (gray markers for acid doping level 6.6, white for 11).

The higher acid doping levels lead to higher proton conductivities. Figure 4 shows the measured conductivity of acid doped blend membranes as a function of the relative humidity at different temperatures. At higher acid doping levels, the conductivity was significantly enhanced. At an acid doping level of 11, conductivity of as high as 0.12 S/cm was observed at 175°C and 10%RH.

4.2 Catalysts, gas diffusion layers, electrodes and MEA tests

In FURIM, gas diffusion layer materials, catalysts, electrodes and techniques for preparing MEAs have been developed.

4.2.1 High Temperature GDL

Required properties of the high temperature were specified, based on which GDL materials were developed for both single cell test and the final stack. Evaluations of the materials were made with good durability, mechanical durability and chemical resistance.

4.2.2 Catalysts

Various types of electrocatalysts have been prepared such as Pt/C, PtNi/C, PtCo/C, PtRu/C, PtFe/C (metals or alloys on carbon) with different carbon supporting materials. Electrochemical techniques were used for evaluation of catalytic activities. Of the catalysts, PtNi/C and PtRu/C showed high performances in phosphoric acid solution at 150°C. Parameters for MEA fabrication and operation were investigated including Pt loading, acid loading, PTFE loading, oxidant flow rate, use of reformate and the fuel humidification. Methanol oxidation electro-catalysts and HT-DMFC based on PBI were developed. As an example, using the prepared platinum catalysts supported on carbon nanofibre, Figure 5 shows a set of polarization curves for a hydrogen/air fuel cell with low catalyst loading (0.2 mg Pt cm^{-2} on both sides) at 170°C and different pressures. With reformate gases as fuel, the best performance was achieved for hydrogen and air under 5 bar(a) at 170°C, giving a current density of 0.68 A/cm^2 at the cell voltage of 0.6 V.

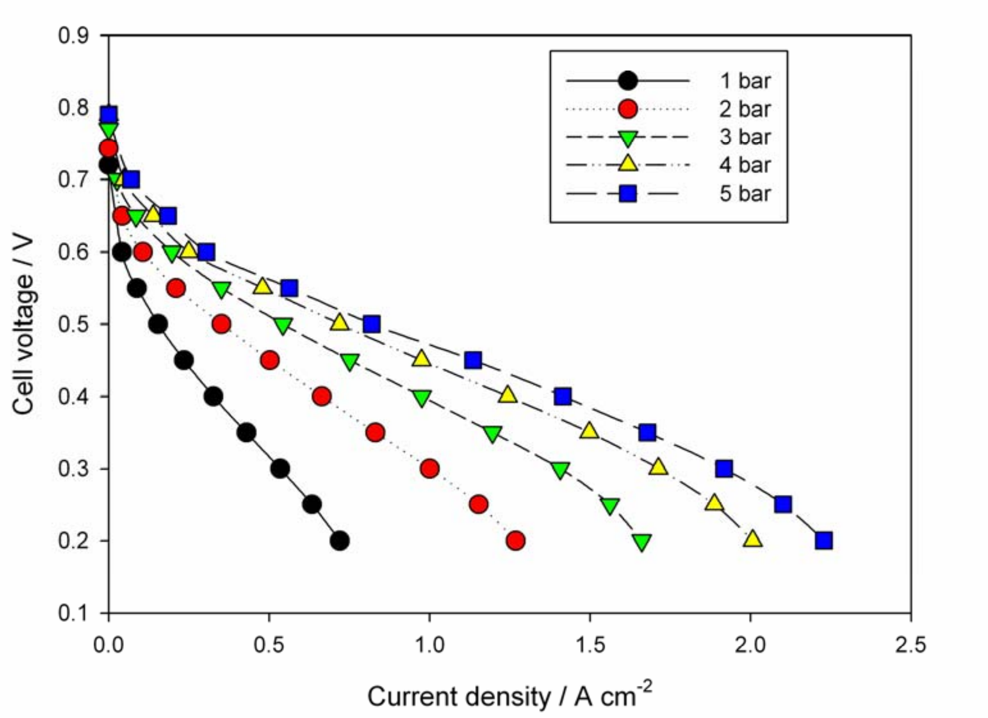


Figure 5. Polarization curves for a hydrogen/air fuel cell with low catalyst loading (0.2 mg Pt cm^{-2} on both sides) at 170°C and different pressures. The catalyst was 20% Pt on carbon nanofibers prepared within the project.

4.2.3 Electrodes

For fabrication of gas diffusion electrodes, two techniques have been developed in the project: tape-casting and spraying [3,4]. For both methods, PBI and its blends were used as the ionomer with either DMAc or acid mixtures as solvent. The loading of the ionomer in the catalyst layer was optimized by taking into account both ionic conductivity and the catalytic activity. MEAs for the final stack were prepared by the spraying method using an ink of catalyst particles dispersed in a PBI solution. Test electrodes were initially made in different small sizes, but the full size electrodes were 16x16 cm^2.

4.2.4 Durability tests

The long-term durability tests were performed in two parts, continuous operation and thermal/loading cycling. Under continuous operation with H_2/O_2 at temperatures around 150°C a lifetime of 5000 hours has been achieved at a constant cell voltage of 0.5 V. At above 180°C, the lifetime was limited, and polymer oxidative degradation is likely the reason of the failure. As the attack by H_2O_2 and •OH and / or •OOH radicals is believed to be the principal degradation mechanism of polymer membranes, the Fenton test showed significant degradation of PBI membranes. With the blend PBI membranes, significant improvement has been observed. The oxidation by air seems much less than by pure oxygen. By using air, a much longer lifetime has been demonstrated with a performance degradation rate of about 5-6 μV h^{-1}.

A thermal cycling test on a hydrogen-air cell with a daily shutdown and restart was performed (se Figure 6). Over the first 60 daily cycles, a performance loss rate of 0.7 $mWcm^{-2}$ per cycle was observed. This performance loss is significant compared with that for continuous operation, most likely due to the increased acid loss and reduction of the cathodic catalyst area. In the following period of test over a period of more than 3 years, up to 850 cycles have been carried out showing a more or less stabilized performance, however, with a sudden death at the end. The sudden death was apparently due to the breakdown of the polymer membrane, as an abnormal increase in the gas permeability occurred. A performance loss rate of 0.07 mW cm^{-2} per cycle, corresponding approximately to a voltage drop rate of 0.3 mV per cycle or 40 µV per operating hour was observed over the whole test period.

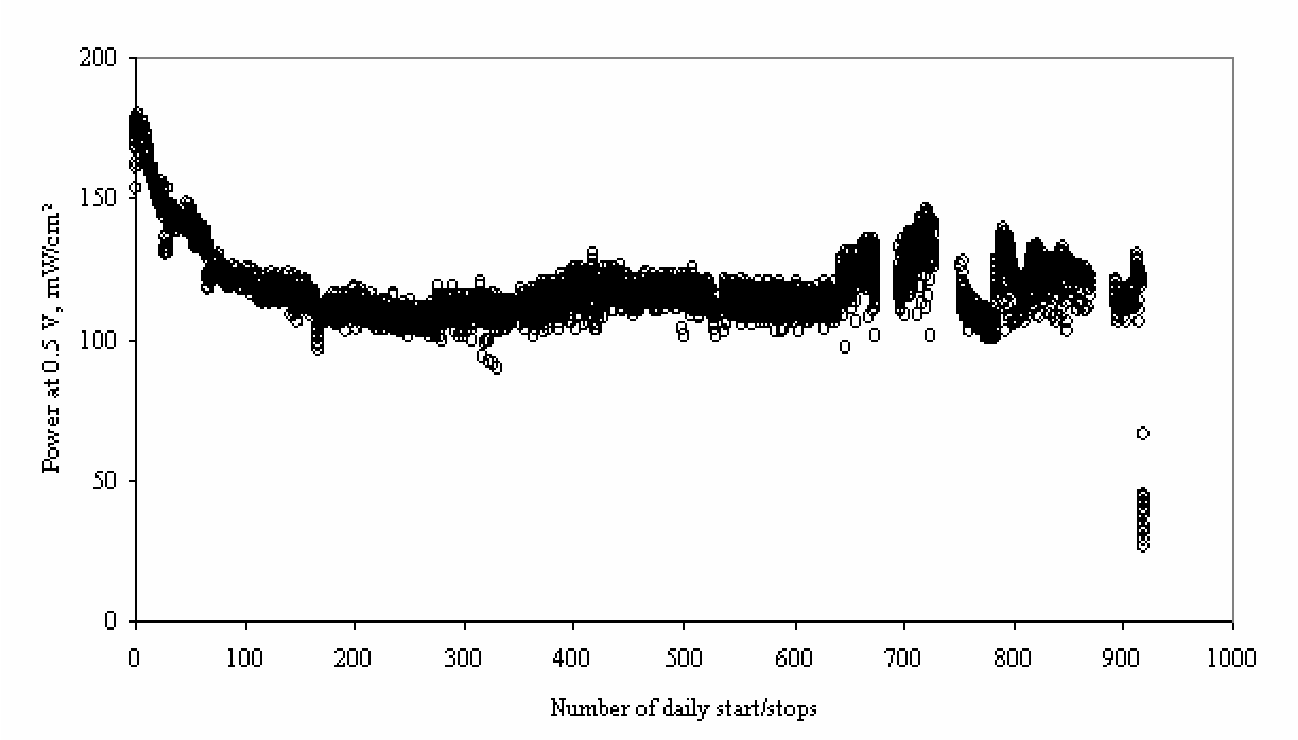


Figure 6. A daily startup-shutdown cycling test of a PBI cell operating with hydrogen and air at 150°C and ambient pressure. The calendar time was more than 3 years. The membrane was doped with 5.6 mol H_3PO_4. Catalyst loading for both electrodes was 0.61 mg Pt cm^{-2}. The cell was witched on ca. 7 hours every working day through the period of time.

4.3 Direct methanol fuel cell

A sub-project of Furim was to study direct methanol fuel cells based on the high temperature membrane.

4.4 Construction of stack

New sealing materials were developed and optimized with respect to the high temperature compatibility, resistance, durability as well as tool concept. An internal liquid cooling circuit was integrated into each cell in the stack, allowing for simple construction and easy integration into the final system. The final stack was designed in modules with 23 cells (active area of 225 cm^2 each) and constructed with bipolar plates, current collectors, end caps, in addition to MEAs. The I-V curves of the stack operating with hydrogen and air at different stoichiometries and pressures are represented in Figure 8. The initial power target of 2 kW was reached.

A short stack was build to test the stacking design and the sealing. Later the full stack was assembled. Both stacks are shown in Figure 7.

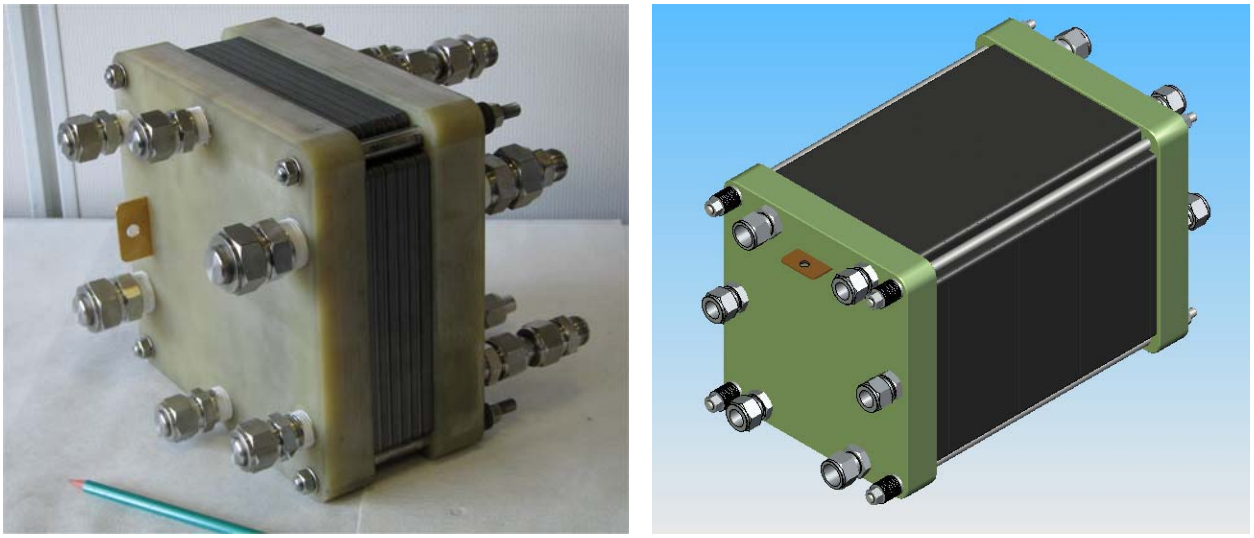


Figure 7. A short test stack (left) and the final stack (right).

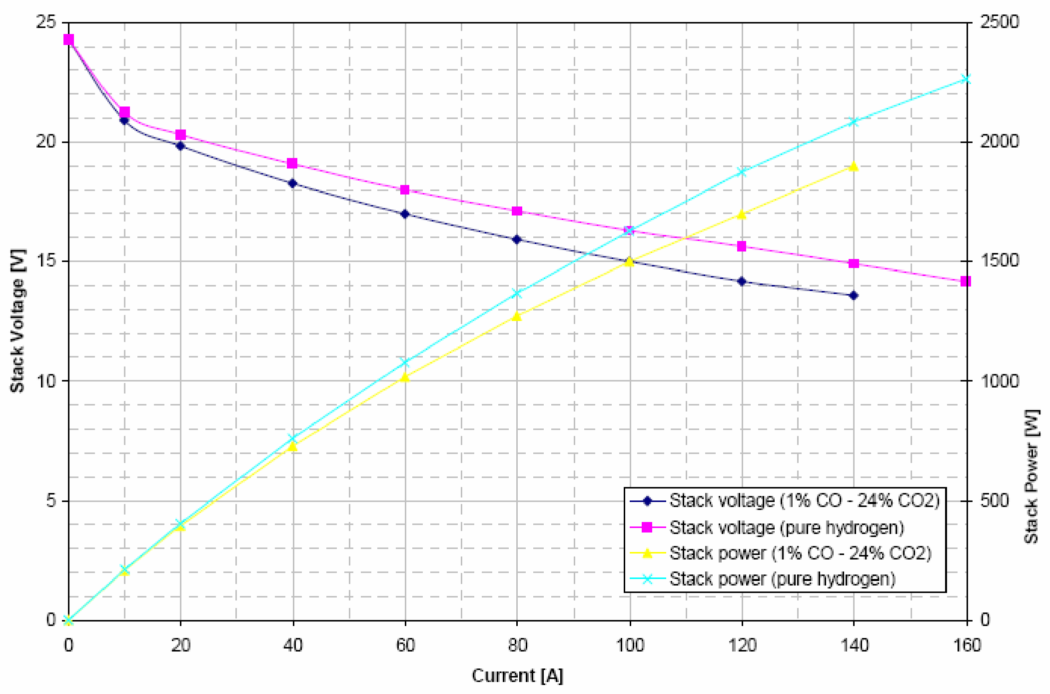


Figure 8. The performance of the final 30 cell stack with pure hydrogen and synthetic reformate. Electrodes: 225 cm^2, Temperature: 175°C, pressure: 1 bar(g). No CO clean-up was applied in the reformate case.

4.5 Reformer system

4.5.1 Catalyst characterizations

Commercial steam reforming catalysts and high temperature water gas shift (HT-WGS) catalysts have been collected and evaluated. Both reforming and WGS catalytic burning catalysts have also been prepared with modified carrier materials and characterized with respect to their composition, BET surface areas, porosity, and catalytic activities.

Ten lab-made catalysts and 6 commercially available ones were tested for steam reforming of completely desulphurized diesel and of diesel containing 10 ppm S. It was found that the decrease of the hydrogen production rate in the presence of sulphur does not exceed 20% at the worst case whereas it is lower than 10%. Lab-made nickel catalysts supported on alumina modified by barium, lanthanum and barium, or cerium oxides proved to be quite promising for steam reforming of the desulphurized diesel (10 ppm S) exhibiting comparable activities with several commercial catalysts.

4.5.2 Reformer

Upon the catalyst screening results, a fuel processing system was designed and constructed for the conversion of diesel into a hydrogen rich gas suitable for operation of the high temperature PEM fuel cell stack. The fuel processor consisted of a pre-reformer and a reformer. The pre-reformer was made of (a) a diesel evaporator, (b) a pre-reformer reactor, (c) a desulphurisation unit, and (d) a control unit. The reformer was made of (a) a reformer reactor, (b) a medium temperature water gas shift reactor and a control unit.

A set of typical test results are listed in Table 5. The steam-to-carbon ratio is a combination of the s/c ratio before the pre-reformer and the remaining steam-to-carbon ratio. The hydrogen production of the test amounts to more than 4 Nm^3/h. The CO concentration in the reformate after the reformer was in the range of 8% maximum, indicating that the reformer operates near thermodynamical equilibrium. The shift reactor was able to decrease the carbon monoxide concentration further down to levels below 1%. This means that the produced reformate gas is suitable to operate FURIM's high temperature PEM fuel cell.

Table 3. Typical results of fuel processor test.

time	**CH_4 [%]**	**CO_2 [%]**	**CO [%]**	**reformate [Nm^3/h]**	**diesel [l/h]**	**water in [l/h]**	**s/c total**	**s/c pre-reformer**
14	0,02	22,34	0,87	5,06	0,94	7,20	7,01	5,80
14,5	0,01	22,68	0,48	4,73	0,94	9,00	8,76	6,19
15	0,01	22,73	0,46	5,10	0,94	9,06	8,82	5,83
15,5	0,01	22,77	0,46	5,27	0,94	8,94	8,70	5,93
16	0,02	22,78	0,46	5,71	0,94	8,76	8,53	6,03
16,5	0,01	22,82	0,38	4,73	0,94	9,18	8,94	6,02

4.6 Modelling, simulation and system integration

The objectives of the last 12 months of the FURIM project for this work package were the integration of a pre-reformer, a desulphurisation unit, a reformer, a medium temperature water gas shift reactor, a high temperature PEM fuel cell stack and the control unit. This was done resulting in an integrated proof-of-principle high temperature PEM fuel cell system. The final system was then tested in the laboratory of HyGear. This work package and therefore also FURIM was finished with an operable fuel cell system producing 1,5 kW electrical power. The system showed the feasibility of diesel converted into hydrogen operating an APU like fuel cell system.

4.6.1 Modelling

A two dimensional mathematical model of a PMEFC equipped with a PBI membrane was developed using Comsol Multiphysics software. The model enables prediction of phenomena in the entire fuel cell including the gas channels. A 3-D model can be built on this 2-D model but Comsol Multiphysics software requires excessive run times unless several simplifications are applied to the model formulation. In addition, a model for HT-DMFC has also been developed. Figure 9 shows the validation results for the cell performance at three temperatures of operation; 125, 150 and 175ºC.

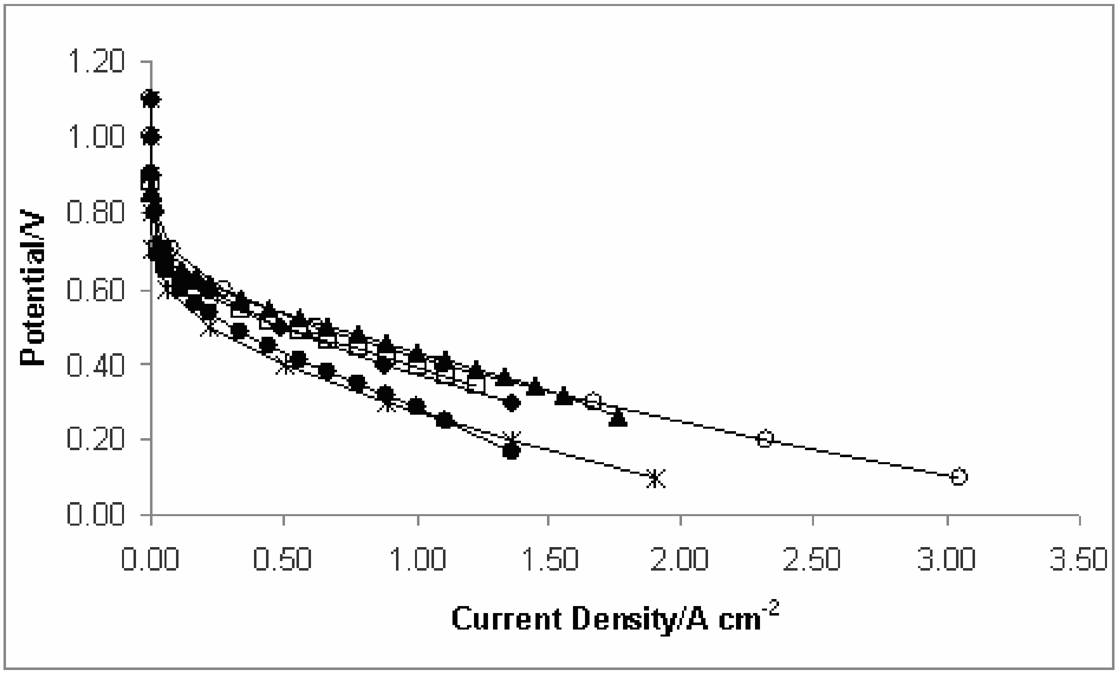


Figure 9. Comparison of model and experimental fuel cell polarisation curves. Pt Loading 0.5 mg cm-2, Pt/C ratio 50%, width 20 µm, pressure 1 bar oxygen (atmospheric pressure). Temperature: A) ●125ºC, B) □ 150ºC, C) ▲ 175ºC. Model Results at Temperature: D) 125ºC, E) ♦ 150ºC, F) ○175ºC

4.6.2 System simulation

Integration of the fuel cell with the reformer and the burner is the core system technology. Based on the system analysis and modelling, the system integration concept and control strategy were first developed. The integration concept was developed by considering start-up, normal operation and shut down. Issues of water balance and safety control were also taken into account. The system scheme was proposed including the pre-reforming unit, the desulphurization unit and the shift unit from the reformer side, and air supply, fuel supply from the fuel cell side, as well as heat exchangers, fuel off-gas recovery, and water balance, as show n in Figure 10.

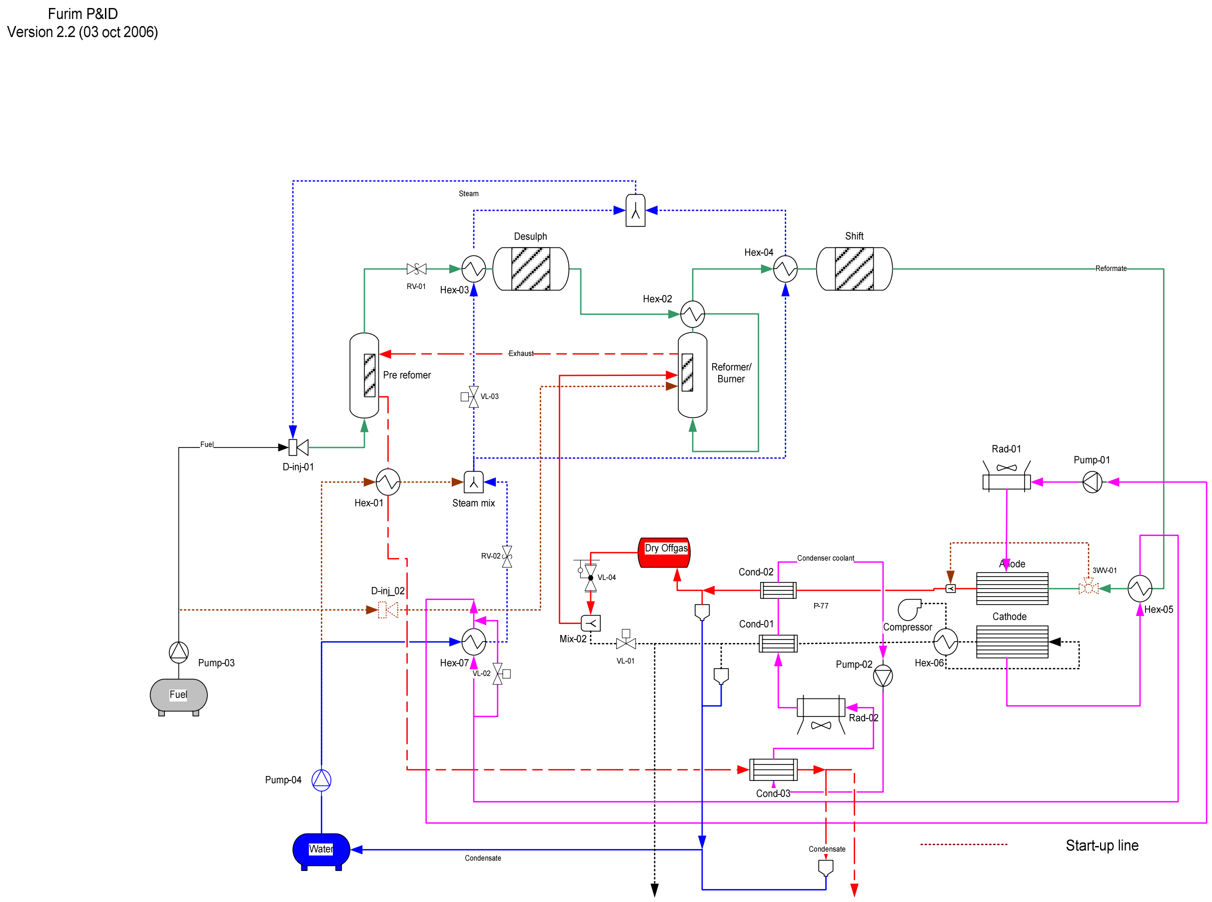


Figure 10. The full High Temperature PEMFC-APU system.

4.6.3 Safety, control and integration

Different subsystems models were developed for control of air, fuel and water supply, and combined into the overall control system model. The fuel cell stack, fuel processor, and other components were integrated into a diesel auxiliary power unit. Figure 11 shows the test rig with the integrated fuel cell system and the control units (a), the control of the fuel cell stack and the electronic load (b), the overall integrated system (c) and the fuel cell stack with the heating/cooling circuit (d).

Figure 11a Fuel cell system test rig

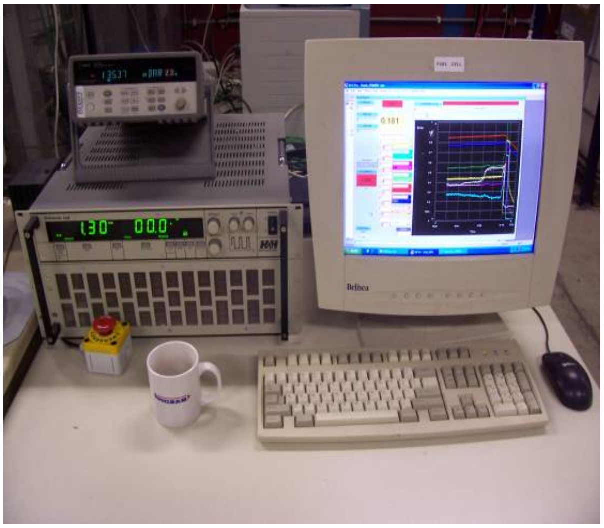


Figure 11b. Fuel cell control and electronic load

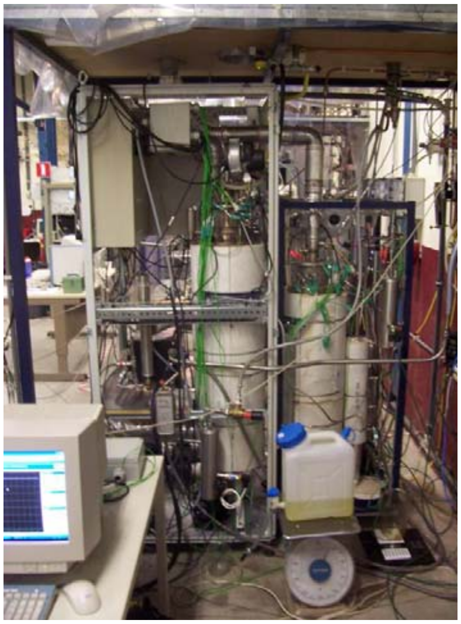


Figure 11c. Fuel cell system

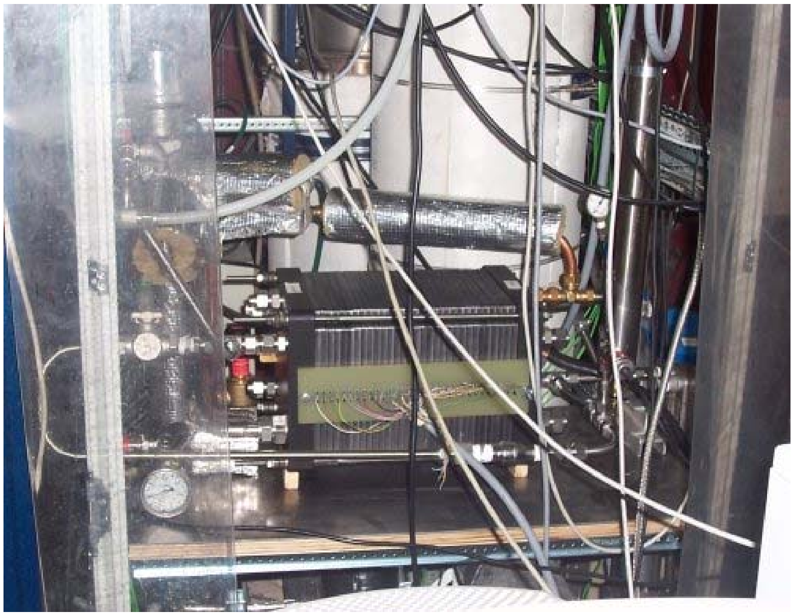


Figure 11d. Stack heating system and fuel cell stack

The fuel cell system was finally tested to fulfil the obligations of the FURIM project. It was demonstrated that a diesel fuelled fuel cell system producing electrical power with a high temperature PEM fuel cell stack. Such an auxiliary power unit for trucks consisted of components developed within the FURIM project. The reforming part of the system was able to convert diesel into a reformate gas operating a fuel cell stack. The fuel cell stack developed is capable to run at temperatures above 170 °C and to tolerate a carbon monoxide concentration of at least 0.8%. The fuel cell system was operated with a stable performance, as shown in Figure 12. The system followed the demand on electrical power immediately. A maximum fuel cell stack power of 1,8 kW was reached with reformate gas containing up to 0.9% carbon monoxide.

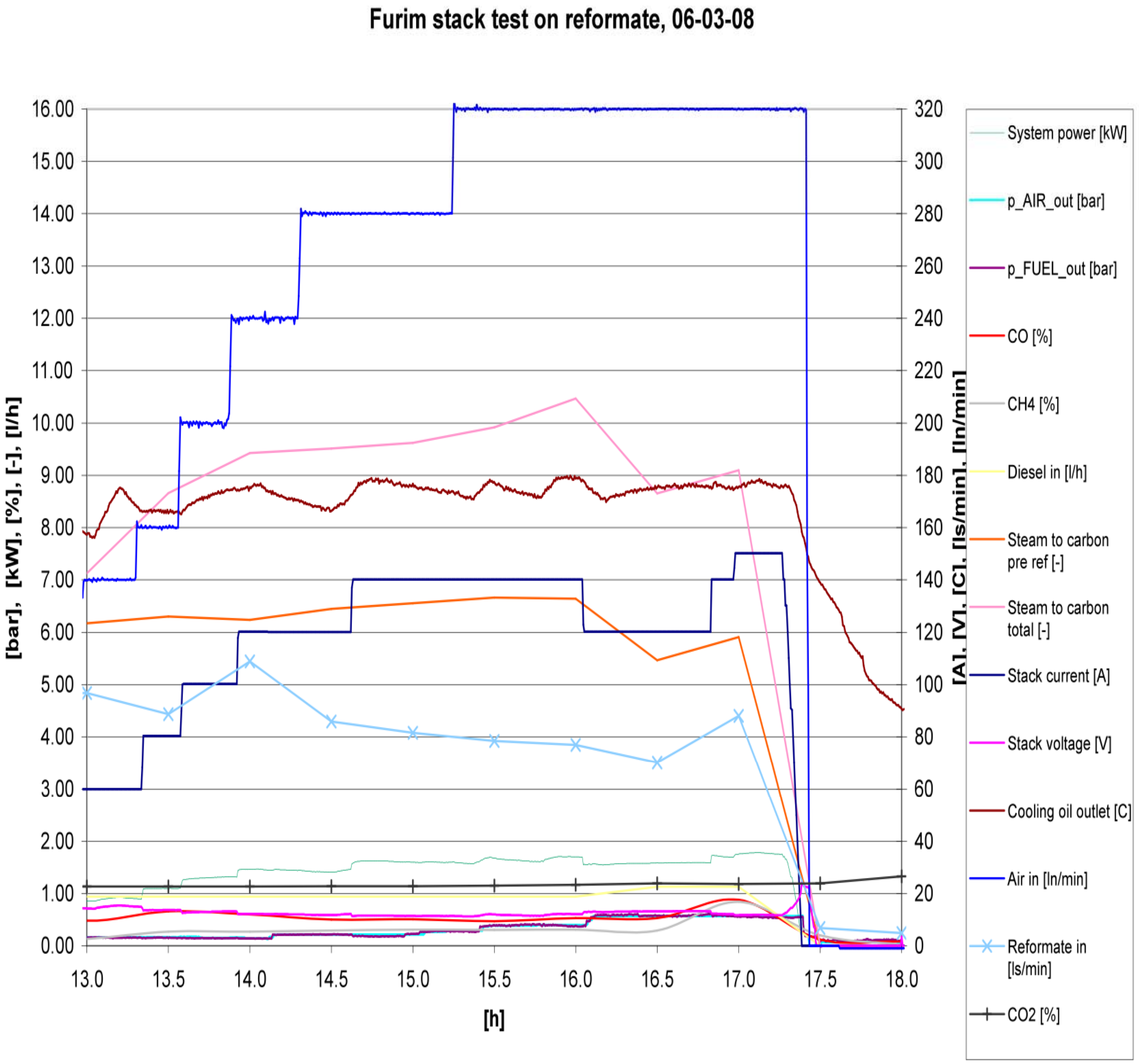


Figure 12. Performance of the HT-PEMFC and diesel reformer system.

4.7 Training

The training activities during this project are in main forms of (1) university level courses on the subject of hydrogen and fuel cell; (2) organizing international events of workshops and summer schools; (3) education of ph.d students and postdocs through project research, and (4) active participation in international summer schools and other events.

4.7.1 University courses

DTU. Course 26130 "Hydrogen Energy and Fuel Cells"
Lecture course, annually spring, 5 ECTS points. Students are ordinary DTU students, ph.d. students and many international students. Teaching manpower 100 % from Furim.

The course covers fundamentals of fuel cells, electrochemical principles, thermodynamics, ion conductors, catalysts, types of fuel cells (PEMFC, AFC, PAFC, MCFC, and SOFC), hydrogen storage, metal hydrides, fuel processing, hydrogen production, reforming, electrolysis, system integration, balance of plant, applications. Acknowledgement to FP 6 at the course.

2004: 28 students.
2005: 38 students
2006: 47 students
2007: 40 students
2008: 43 students

The course has become part of DTU's system and will continue after Furim.

DTU Course 26120 “Hydrogen and Fuel Cell Chemistry”
Experimental course, annually January, 5 ECTS points
The course covers basic chemical techniques, preparation and tests of fuel cell components, methanol reforming, water electrolysis and metal hydrides. FURIM has contributed major part of the man power (Qingfeng Li and Jens Oluf Jensen) and DTU contributed materials costs and others to the course.

2007: 10 students
2008: 12 students

The course is part of DTU's system and will continue after Furim.

DTU: Apart from the formal courses above a large number of individual students have been involved and supervised by Furim staff.

NTNU Course TMT 4285 Hydrogen Technology, Fuel Cells and Solar Cells
Lecture course and laboratory work, annually spring, 7.5 ECTS points. Students are ordinary NTNU undergraduate students (2nd year). Teaching manpower from Furim.

The course covers many areas: electrical energy from solar cells, production of hydrogen, storage of hydrogen, electrical energy from fuel cells, thermodynamic and kinetic calculations for the energy conversion processes and hydrogen safety.

2008: 60 students

NTNU Course: TMT4310 Electro Catalysis and Energy Technology
Lecture course, annually spring, 7.5 ECTS points. Students are ordinary NTNU master students (4th year). Teaching manpower from Furim.

The course covers electrochemical principles, thermodynamics, ion conductors, electrode kinetics and electrocatalysts, charge transfer, mechanisms, fundamentals of fuel cells and electrochemical characterization methods; transient methods and impedance spectroscopy.

2008: 12 students

NTNU Course: TMT4505 Materials Science and Engineering, specialist subject
Lecture course, module based, annually fall, 3.75 ECTS points pr. module. Students are ordinary NTNU masters students (5th, final year). Teaching manpower from Furim.

Specialist subject within 3 different core areas with strong interaction to ongoing research, where one is Electrochemical Energy Technology. Subjects are typically electrochemical kinetics, electrode reactions (e.g. oxygen, hydrogen and methanol), fuel cells

NTNU Course: MT8106 Electrochemical Energy Technology
PhD course, every second year (1-year course), 10 ECTS points. Students are ordinary NTNU PhD students from several faculties and international students. Teaching manpower from Furim.

This course gives a general overview of the connection between different forms of energy. Storage and conversion of chemical energy to electrical energy. Batteries, Fuel cells (PEM, AFC, PAFC, MCFC, SOFC), materials, electro catalysis, electrode reactions and kinetics, area of application, thermodynamic, mixed conductors and solar energy.

USTUTT: At USTUTT, the group has offered lectures in membrane technology, particularly in fuel cell membrane systems. The topics of the lectures include the basics of fuel cells, membranes, constructive aspects of fuel cells, low and high temperature reforming (liquid fuels), hydrogen purification, oxygenation with pressure swing adsorption. The lectures are arranged and given together with other organizations such as German Aerospace Center (DLR).

4.7.2 Symposia and educative events

Workshop in Newcastle 2004

A workshop on polymer electrolyte membranes for high temperature fuel
Place: University of Newcastle upon Tyne.
Time: 18th October
Participants: 24
Presentations: 3

Symposium in Patras 2005

Place: ICE/HT auditorium, Rio-Patras, Greece
Time: 13-15 September 2005
Symposium Statistics
    Presentations/Speakers: 20 (11 from Universities, 9 from Industries/Research Organizations)
    Total Participants: 68 (14 Females, 54 Males)
Categorized by Profession
    PhD students: 30
    Post-doctoral Fellows: 5
    Researchers-Faculty members: 33
Categorized by relation to FURIM
    FURIM Members: 28
    Outside FURIM project: 40
(http://furim_symposium.iceht.forth.gr/program.htm)

Spring school in Newcastle 2008

A training event with the subject "Low to Medium Temperature Polymer Electrolyte Fuel Cells", aiming at training EU young researchers in the flied of polymer electrolyte fuel cells and methanol fuel cells.

Place: University of Newcastle upon Tyne
Time: 17-20 March 2008
Lectures: 16
Demonstrations: 2
Participants: 41 from 10 countries (not including the lecturers)

Results compared to objectives

The outcome of the project in relation to the objectives is listed and commented in Table 4.

Table 4. Project objectives and specific target as outlined in the Description of Work. Note the list of objectives is adjusted as compare to the DoW to respect confidentiality or relevance.

Objectives/Targets	Results and comments
(1). Development of temperature-resistant membranes of polymers and their blends/composites	
Operational temperatures from 120 to 200°C with the best performance at 150-200°C	Achieved. A large number of polymers and membranes were manufactures and tested. The most significant result was a blend PBI membrane with improved mechanical stability and thus tolerance for a higher doping rate and thus higher conductivity [5, 6]
Protonic conductivity of 0.01 - 0.10 S/cm	Achieved. Conductivities from 0.05 to over 0.1 S/cm were measured with the doped blend membrane at 150ºC. At higher temperature the conductivity was higher. [5, 6]
Good chemical (oxidative) stability	Chemical stability was primarily assessed through the durability measurements (see below). Whether oxidative stability measured by the peroxide test (Fenton test) is relevant is debated. However, strongly improved performance in the peroxide test was observed for cross linked membranes (comparable to Nafion) [1, 2].
Good mechanical strength and flexibility	Achieved. Mechanical stability especially in the doped state was increased significantly with the blend membrane as compared to unblended PBI [6].
Processable thickness 40-200 micrometers	Achieved. Membranes were typically cast and handled in un-doped thicknesses

	around 50 micrometers.
Processable size over 600 cm^2	Achieved. With the batch wise solution casting technique used this size was standard. Larger sizes are also possible if larger dies are provided.
Long durability over 5,000 hours	Achieved. A durability of over 5000 hours at 150ºC at constant voltage was demonstrated. Later a cell was operated in a daily start stop mode for over 3.5 years. The cell completed 860 start stop cycles with cooling from ºC 150 to room temperature. The total operating time was over 6000 hours. [7, 8]
Cost less than 100 euro/m^2	Not achieved. Cost was not estimated for the final membrane assuming large scale production. With present lab scale manufacturing the cost is significantly higher.
(2). Optimising and fabrication of catalysts and gas diffusion electrodes with aims of	
Development of low cost gas diffusion layer materials as roll goods	Achieved. Gas diffusion layer were developed as roll goods
High performance cathode with a more open structure for air operation - Noble metal loading (≤ 0.3 mg/cm^2) - Overpotential (500 mV at current density of 600 A/cm^2) - Long durability, performance loss ≤ 5 mV/1000 h during 5000 h at 200^{o}C.	The cathode performance was improved with the developed spraying technique. The noble metal loading was not reduced from the initial ~0.5 mg Pt/cm^2. without loss in performance, so, the initial amount was maintained in order to optimize performance. Decay rate was not associated with a single electrode. See under (1)
High performance anode operational with reformate gases - Noble metal loading (≤ 0.3 mg/cm^2) - Tolerance of 30,000 – 100,000 ppm CO - Tolerance of 1,000 ppm CH_3OH, other alcohols or other hydrocarbons - Long durability, performance loss <	The catalyst loading is less critical on the anode side, and therefore the largest potential for noble metal reduction is here. The CO tolerance of Pt catalysts is known to be high at temperatures of 150ºC and higher. This was measured before FURIM [9]. Tolerance to CH_3OH and other organics was not studied specifically apart from experiments with vapour fed DMFC. There

5 mV/1000 h during 5000 h at 200°C	seem to be no serious effect apart from the well known cross over effect of DMFC. Decay rate was not associated with a single electrode. See under (1)
Catalysts and anode for direct oxidation of methanol	Vapour fed DMFC cells were built and tested. Results were not yet published by end of Furim.
(3). Technique and preparation of membrane-electrode assemblies (MEAs)	
Assemblies with 16x16 cm^2 electrodes. with a single cell performance target of 0.7 A/cm² at a cell voltage around 0.6 V	16x16 cm^2 electrodes and MEAs thereof were manufactured The stacks were based on this size. However, the target performance was not achieved without pressurization. The best performance was achieved for hydrogen and air under 5 bar(a) at 170°C, giving a current density of 0.68 A/cm² at the cell voltage of 0.6 V.
Pressurizable up to 5 bars. operational temperatures 150-200°C with 120°C as a low temperature checking point	Achieved for single cells.
Durability of more than 5,000 hours in the temperature range from 150-200°C	Achieved for 150ºC. At 200 ºC it is well known today that lifetime is shorter.
A lab scale DMFC with a power density of 400 mW/cm² for O_2 (200 mW/cm² for air) at 150°C	Not achieved.
(4). Fuel cell models	
Models for high temperature DMFC and mixed fuel-air cell	Achieved by UNEW
(5). Stack materials and construction	
Optimised elastomeric sealing materials thermal stability up to 200°C optimised sealing concept and profile good compensation of stack tolerance prototype production and low material and production cost	Achieved. Sealing materials were developed by FFCCT.
Internal manifold design	Achieved.
Developing cooling concepts and design a cooling circuit	Achieved.

Stack test of 2 kW size - Specific weight less than 1.0 kg/kW_{el} - Specific volume less than 1.0 l/kW_{el}	The weight and volume targets were not met.
(8). Hydrocarbon reforming and a test reformer	
One step (high temperature) water-gas shift catalysts	Achieved. Build and integrated.
A diesel oil reformer suitable for combination with a 2 kWe fuel cell stack assuming electrochemical stack efficiency of 50% and a fuel stoichiometry of 1.2. - CO content less than 3 %	Achieved. Build and integrated. CO most of the time below 1%.
(9). Catalytic burner, heat recovery and integration technology	
A testing burner, suitable to create enough process heat for the reformer specified in point (8)	Achieved with a flame burner. Build and integrated. Certification issues did not allow for a catalytic burner
(10). A theoretical framework for a prototype fleet management system for integration with small DG units.	
Report	Achieved. A public report by ELS (later Dong Energy)
(11). Evaluation test of materials	
(12). Evaluation test of component units	
A fuel cell stack of 2 kW_{el}	Achieved. Build and integrated
A diesel oil reformer suitable for the 2 kW_{el} fuel cell stack	Achieved. Build and integrated
A burner capable to create enough process heat for the diesel oil reformer	Achieved. Build and integrated
(13). System simulation tools	
Vehicle simulation with the HT-PEMFC as APU and part of power train	Achieved. Simulations by VOL showed that the concept is viable.

(14). System integration	
Integration of a $2kW_{el}$ HT-PEMFC stack with the diesel reformer and afterburner	Achieved. Build and operated satisfactory [10, 11]
(15). A database of HT-PEMFC literature collection	
• HT-PEMFC papers on international journals • International conference proceedings • HT-PEMFC patents • When possible, abstracts of the above publications	The database was constructed but later given up because of problems with copyrights of the papers.
(16). Training and furthering the mobility of young European researchers in the area of novel energy and environment technologies	
Training	Achieved. • 1 symposium, • 2 workshops/summer schools • University teaching (e.g. new course fully attributed to FURIM)
(17-18). Dissemination of the obtained knowledge and solidifying the leading position of the consortium partners and thus enhancing Europe's role in this area.	
	• The consortium was represented by oral presentations at annual HFP events. • Representation in the Steering Committee of the Coordination Action on membranes, CARISMA. • A large number of peer reviewed papers. • A large number of international conference contributions.

5 Additional information

Project homepage: www.furim.com

Table 5. Key responsible persons:

Responsibility	Name	Affiliation	Contact
Coordinator:	Niels J. Bjerrum	DTU	njb@kemi.dtu.dk
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WB0 overall Scientific (membranes and cells)	Qingfeng Li	DTU	lqf@kemi.dtu.dk
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WB1 Stacking	Steen Yde Andersen	IRD	sya@ird.dk
Sealing and GDL	Klaus-Dieter Wagner	FFCCT	Klaus.Wagner@Freudenberg.de
WB2 Reformer system	Michael Walter	HYG	michael.walter@hygear.nl
Reformer catalysts	Christos Contonianis	FORTH	cgk@terpsi.iceht.forth.gr
WB3 Modelling, simulation	Azra Selimovich	VOL	azra.selimovic@volvo.com
WB4 Training	Keith Scott	UNEW	k.scott@ncl.ac.uk

6 References

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[1] Q. Li, C. Pan, J. O. Jensen, P. Noyé and N. J. Bjerrum Cross-Linked Polybenzimidazole Membranes for Fuel Cells. Chem. Mater. 19 350-352 (2007)

[2] P. Noyé, Q. Li, C. Pan, N. J. Bjerrum. Cross-linked polybenzimidazole membranes for high temperature proton exchange membrane fuel cells with dichloromethyl phosphinic acid as a cross-linker. Polym. Adv. Technol. 2008; 19: 1270–1275

[3] Seland F, Berning T, Børresen B, Tunold R. Improving the performance of high-temperature PEM fuel cells based on PBI electrolyte, J Power Sources. 2006; 160: 27-36.

[4] Pan C, Li Q, Jensen JO, He R, Cleemann LN, Nillson M, Bjerrum NJ, and Zeng Q. Preparation and operation of gas diffusion electrodes for high-temperature proton exchange membrane fuel cells, J Power Sources 2007; 172: 278-286.

[5] 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).

[6] 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 Aarylene 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).

[7] Q. Li, J. O. Jensen. CARISMA Workshop: Degradation Issues for MEAS and their components 5th-6th July 2007 Grenoble

[8] Q. Li, J. O. Jensen and N. J. Bjerrum. High Temperature PEMFC Based on Acid Doped Polybenzimidazole Membranes. Durability Issues and Recent Progress. Fuel Cells Durability & Performance 2008, Las Vegas, NV USA 11-12th December (2008).

[9] Q. Li, R. He, J. Gao, J. O. Jensen and N. J. Bjerrum. The CO poisoning effect in polymer electrolyte membrane fuel cells operational at temperatures up to 200°C. J. Electrochem. Soc. 150 (12), A1599-A1605 (2003).

[10] J. O. Jensen et al. A high temperature PEMFC integrated with a diesel reforming system. 29th Risø International Symposium on Materials Science: Energy Materials - Advances in Characterization, Modelling and Application. Risø National Laboratory for Sustainable Energy, Roskilde, Denmark. 1-5 September (2008).

[11] J. O. Jensen , Q. Li, C. Pan, N. J. Bjerrum, A. Selimowic, A. Bodén, L. Johansen, F. Seland, M. Tsypkin, O. E. Kongstein R. Tunold, M. Mamlouk, K. Scott, M. Nilsson, T. Steenberg, F. Schonberger, M. Hein, J. Kerres, M. Walter, M. van Driel, A. Scholten, J. Smolenaars, K-D. Wagner, J. Wolf, S. Yde-Andersen, T. De Rycke, C. Kontoyannis, I. Zacharaki, G. Papatheodoru, T. Häring, and J. Nähring. A 2 kW Diesel Powered Auxiliary Power Unit with a High Temperature PEMFC Stack: The

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EU FURIM Project. Progress in MEA components for Medium and High Temperature Polymer Electrolyte Fuel Cells", La Grande Motte, Montpellier, France, 21st -24th September (2008)