PROJECT FINAL REPORT

Maestro

FINAL PUBLISHABLE SUMMARY REPORT

GRANT AGREEMENT NUMBER:	256647
PROJECT ACRONYM:	MAESTRO
PROJECT TITLE:	MembrAnEs for STationary application with RObust mechanical properties
FUNDING SCHEME:	FCH-JU-2009-1 - Application Area SP1-JTI-FCH.3: Stationary Power Generation & CHP - SP1-JTI-FCH.3.2: Materials Development for cells stacks and balance of plant

DATE OF LATEST VERSION OF ANNEX I AGAINST WHICH THE ASSESSMENT WILL BE MADE: 23-09-2013

PERIODIC REPORT: **1st** □ **2nd** □ **3rd** □ **4th** ☒

PERIOD COVERED: **from** 01-01-2011 **to** 31-03-2014

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1. EXECUTIVE SUMMARY

The primary objective of MAESTRO was to improve the mechanical properties of low equivalent weight (EW) state of the art perfluorosulfonic acid (PFSA) membranes using chemical and thermal ionomer processing and fibre network and filler reinforcement methodologies.

Benchmark MEAs prepared using benchmark state-of-the-art short-side-chain Aquivion ionomer of EW 790 g/mol decayed significantly in performance as the temperature was increased to 100 and 110 °C. Further, accelerated durability testing via an open circuit voltage (OCV) hold test showed that the benchmark membrane failed after only 100-200 hours and highlighted the need for significant improvements to the robustness of the low EW membranes.

A range of different approaches was used to prepare membranes having robust mechanical properties using an ionomer of EW lower than that of the benchmark, 700 g/mol. These approaches included ionomer cross-linking during emulsion polymerisation, which leads to non-linear ionomer molecules with high molecular weight, and cross-linking during the process of membrane casting by use of a reagent to cross-link through a small fraction of the sulfonic acid groups. Attempts were also made to associate these two approaches (during polymerisation/casting). Electrospinning was used to fabricate organic and inorganic fibres to be employed as mechanical reinforcements of low EW Aquivion. In all cases the nanofibre reinforcement led to a significant improvement of mechanical properties of the final composite membranes, and the conductivity was higher than that of the benchmark membrane. The possibility to mechanically reinforce Aquivion by ionic crosslinking induced by incorporation of inorganic nanoparticles was also investigated, and composite membranes prepared using filler types of different hydrophobicity. All the membranes showed strongly enhanced elastic modulus and yield stress in comparison with the benchmark Aquivion membrane.

First durability testing at the 18 month stage of the project exhibited significant enhancements in lifetime from the new membrane approaches.

In the second phase of the project, three configurations of the most prospective individual membrane stabilisation routes were associated, cross-linked EW 700 ionomer being used in all new membrane developments, and membrane formulation and thickness were optimised to develop improved robustness membranes.

The month 26 metric to have improved tensile properties by 50% was exceeded with several of the novel membrane materials developed in MAESTRO. Further, the approaches developed to increase mechanical stabilisation did not compromise conductivity and, in some cases, improved conductivity compared with the project start point was observed. Critical assessment of the results of in situ and ex situ characterisation led to final down-selection of three most promising candidates. Although the original project plan had been to select one membrane only for a long-term accelerated durability test, the promising results allowed the partnership to extend the ambition of the project to stack testing, using a stack comprising membrane electrode assemblies (MEAs) incorporating different membrane types. The stack testing protocol developed to simulate conditions realistic for micro-CHP type application included continuous operation and load cycling as well as aggressive accelerated ageing conditions of stop/start cycling. Under these conditions, cross-linked Aquivion membranes showed greater durability than benchmark membranes, while cross-linked Aquivion with an electrospun nanofibre reinforcement showed the most significant improvement in durability; these MEAs displaying less than 3% voltage loss after 2,000 hours of operation, including 500 hours of cycling between 12 hours operation/12 hours stop, and a further 250 hours of cycling between 4 hours operation/4 hours stop, thus comfortably achieving the final project objective.

Non-confidential results have been communicated at the most important fuel cells/electrochemistry conferences in Europe and overseas. Four papers have been published to date. The website www.maestro-fuelcells.eu lists dissemination activities carried out for the project, and the password-protected partners-only area collects all project documentation, presentations and reports.

2. SUMMARY DESCRIPTION OF PROJECT CONTEXT AND OBJECTIVES

PROJECT CONTEXT

The European Strategic Energy Technology (SET) Plan has identified fuel cells and hydrogen among the technologies needed for Europe to achieve the targets for 2020 - 20% reduction in greenhouse gas emissions, 20% share of renewable energy sources in the energy mix, and 20% reduction in primary energy use – as well as to achieve the long-term vision for 2050 towards decarbonisation. The challenge facing fuel cells and hydrogen technologies is of great complexity, and their contribution to Community policies, in particular energy, environment, transport and industrial competitiveness is very important.[1] FCH-JU1 objectives for stationary power generation and combined heat and power (CHP) were ambitious both in terms of volume (100 MW installed electric capacity) and cost (€ 4,000 – 5,000 kW for micro-CHP, €1,500 – 2,500/kW for industrial units) targets for 2015.

Uninterruptible Power Supply (UPS) and power supply to residential buildings are important fuel cell markets requiring units of ca. 5 kW and 1-2 kW respectively. Generation of electricity and heat at the site of demand can save a significant amount of primary energy compared to the central generation of electricity and the generation of heat on site: electricity is lost during transmission and distribution[2], being >6% in Europe and North America and >10% in developing countries, and the heat generated at central production is lost or wasted. A survey[3] makes known that in 2008, deliveries of fuel cells for small stationary applications rose by 79% to reach 4,000 units, the majority of the systems being sold for UPS applications but there were advances too in the use of small units for µ-CHP applications. While both solid oxide fuel cells (SOFC) and PEMFC are in development for small stationary applications, over 95 per cent of the units delivered in 2008 were based on proton exchange membrane (PEM) electrolytes. The same survey reports that during 2008 North America (USA and Canada) produced nearly two thirds of all units and Asia produced a further 25%. Europe produced the rest, which leaves enormous room for improvement in the worldwide small stationary market for European industry, which is of strategic importance given the forecast made for a significant increase in units shipped to over six million units, with a fairly even split between UPS and µ-CHP, by 2019.

An issue clearly highlighted in the FCH-JU1 Multi-Annual Implementation Plan in the stationary application area was the need to address lifetime requirements of 40,000 hours for cell and stack, and the call for new or improved materials leading to step change improvements over existing technology in terms of performance, endurance, robustness and cost. In general, failure mechanisms of PEMFC membranes are of two main types: chemical, of which the best understood at present arises from attack by peroxide radicals on susceptible polymer end groups and side chains, and mechanical, which originates from weak intermolecular interactions between polymer chains. While methods of chemically stabilising the polymer end groups have been developed, and other work has significantly advanced on incorporation of radical scavengers in the fuel cell membrane electrode assembly to avoid polymer chain scission events, including of the side-chain functional groups, failure due to inadequate membrane mechanical properties limits cell and stack lifetime. The problem is exacerbated by the trend in use of membranes of much reduced thickness (<30 µm, compared with the use of membranes of ca. 175 µm some 10 years ago) which negatively impacts membrane strength, thin membranes being required for their low area specific resistance and for their enhanced water back diffusion properties. In particular in conditions of use of stop/start (as in summer season use in residential application for example) or load cycling (as in spring/autumn seasons), the variation in relative humidity causes

[1] FCH JU Multi-Annual Implementation Plan 2008-2013

[2] *The current status of fuel cell technology for mobile and stationary applications,* F. de Bruijn, *Green Chem.* 7 (2005) 132-150.

[3] Fuel Cell Today Small Stationary Survey 2009, www.fuelcelltoday.com

membrane swelling and contraction that ultimately leads to membrane failure, in particular in areas of the fuel cell where the membrane is subject to greatest compression.

Furthermore, higher temperatures of operation are required to increase the overall efficiency and approach the FCH-JU1 targets of electrical efficiency of >80% for CHP units. Low equivalent weight ionomers are required to reach the membrane conductivity at higher temperature and lower humidity, and the MEA performance targets for stationary operation, to enable stationary PEMFC systems to achieve superior overall system yield to competitive technologies. In stationary applications, where the situation of deep MEA dehydration and frequent open circuit voltage events can be reasonably avoided, the most relevant failure mode in extended life time operation is associated with membrane mechanical failure. Such high ion exchange capacity (low equivalent weight) polymers show increased tendency to dimensional variation under wet/dry cycling and increased mechanical instability.

PROJECT OBJECTIVES

The MAESTRO project aimed to establish methods to increase the mechanical stability of state-of-the-art short-side-chain perfluorosulfonic acid (PFSA) membranes for stationary application of proton exchange membrane fuel cells (PEMFC) to increase their durability and cell lifetime. Such membranes were operated at temperatures up to 110-120 °C in stacks developed in the FP6 Autobrane "automotive fuel cell membranes" project, which involved all of the technical partners of MAESTRO. The membranes were therefore already known to represent a viable option for operation at higher temperature/lower relative humidity for PEMFC small stationary applications, whereas their long-term durability required improvement.

MAESTRO proposed to develop solutions to the above bottlenecks by developing and screening a range of approaches to improve the mechanical stability of short-side-chain PFSA type PEM fuel cell membranes. To achieve these objectives, the project partners identified five routes to develop robust membranes (i) by increasing polymer molecular weight to increase inter-chain entanglement; (ii) by increasing molecular weight and associating original polymer cross-linking approaches, carried out during polymerisation and/or during membrane casting, to avoid membrane dimensional change; (iii) by tailoring membrane thermal annealing at identified temperature/relative humidity couples; (iv) by embedding electrospun nanofibre mats providing mechanical stability into a PFSA matrix, and by associating electrospun inorganic oxide fibres in cast PFSA; (v) by ionic interaction between PFSA and a dispersed inorganic phase. The final project target for the membrane was to have increased the tensile strength (compared with the benchmark material at the project beginning) by 50%, with a milestone at the mid-term stage of improvement by 20-25% - without detriment to the membrane conductivity. MAESTRO further intended to characterise stabilised membranes for their ex situ properties and to integrate selected candidate membrane materials into MEAs and validate them by evaluating single cell performance and durability under accelerated stress testing conditions designed to enhance chemical and/or mechanical degradation. The objective of the second phase of the project was to associate the most prospective individual approaches, and then down-select most promising candidate membranes on the basis of the membrane proton conductivity and tensile properties, and MEA fuel cell performance and durability on OCV hold and in wet-dry cycling. The final aim of the project was to submit these candidate membranes, after MEA preparation, to accelerated durability testing over 1000 hour periods comprising repeated stop-start events and voltage cycling, in conditions simulating those encountered in a micro-CHP application, with a target durability indicator of achieving voltage loss below 10 percent of that at beginning of life.

3. Description of the Main Scientific and Technical Results

3.1 WP1: Specifications, Protocols and Testing

Objectives

The objectives of this work package were:

- To establish a set of characterisation and test protocols for ex situ and in situ characterisation of baseline and novel membranes and MEAs, including both performance and accelerated stress testing conditions appropriate to stationary applications of PEM fuel cells;
- To establish baseline membrane and MEA benchmarks, and characterise them using MAESTRO protocols to provide data against which progress could be assessed;
- To select candidate membranes for down-selection and transfer to WP3 for integration in MEAs.

To achieve deliverables D1.1-1.2 and Milestone MS1 in RP1

Summary of Output from WP1

In task 1.1, characterisation protocols were defined for membranes and MEAs (Deliverable Report 1.1). The properties characterised for the membranes include conductivity and stress-strain measurements under set temperature and relative humidity conditions, water uptake and thermal properties. For the MEAs, the protocols identified the conditions under which performance and durability were determined. A detailed accelerated durability test protocol with a four 'season' simulation was created, in which each season was considered to last for 250 hours, allowing simulation of "1 year" of testing within a given 1,000 hour time period. The 1,000 h protocol was designed to simulate the operating conditions for winter, spring, summer and autumn, in which the MEAs were subject to long term constant load demands, changing load demands, and thermal cycles. The changing load demands led to different humidification within the MEA.

Within task 1.2, partners defined a benchmark membrane provided by SLX to serve as reference throughout the project, and benchmark MEAs integrating this membrane were fabricated by JMFC and SLX and provided to the partners for benchmark testing.

The properties of the benchmark membrane including conductivity, hydration number and tensile properties were determined at UNIPG. These provide a set of data representing the reference for comparison with the properties of project membranes prepared in WP2.

Benchmark MEAs were prepared at JMFC and SLX using respectively assembly of the membrane with catalysed gas diffusion electrodes (GDE), and of catalyst coated membranes (CCM) with gas diffusion layers. The performance of the benchmark MEAs was determined under a range of temperatures and anode/cathode relative humidity representing current and future conditions of fuel cell operation for stationary applications at CNRS, SLX and JMFC. Similar trends in performance were seen in the testing at the different partner laboratories. Differences in absolute performance between SLX and JMFC MEAs arose from the use of different catalyst types and loadings, ionomer and gas diffusion layers, as well as MEA construction. In situ testing on the benchmark MEAs, designed to accelerate membrane chemical degradation (OCV hold) or mechanical degradation (wet/dry cycling at OCV), was carried out at CNRS, SLX and JMFC. These results indicated that the non-reinforced benchmark membrane was unlikely to achieve the lifetime requirement for the programme, and underlined the need for mechanically stronger membrane materials. Deliverable Report D1.2 describes the characterisation of the initial down-selected membranes and MEAs.

DETAILED SUMMARY OF ACHIEVEMENTS IN WP1

Membrane, MEA and stack characterisation protocols

The membrane characterisation protocols are described in deliverable report D1.1. These protocols were divided into a priority list that included the minimum required properties of membranes for further evaluation, and a second list including a wider range of characterisation protocols. The priority list contains general aspects such as solubility, swelling, handleability, membrane conductivity at two temperatures and a range of relative humidity (RH) values, and stress-strain measurements at ambient temperature and RH. Comprehensive membrane characterisation of down-selected membranes comprised investigation of tensile properties at higher temperature and RH, and of conductivity at two additional temperatures, as well as determination of glass transition temperature, thermo-oxidative stability, and stability to liquid phase Fenton testing.

The MEA characterisation protocols refer to in situ experiments conducted to determine the baseline performance and thereafter the durability of this performance when the MEAs were submitted to stresses designed to accelerate ageing of key MEA components (and in particular the membrane). A final endurance test was designed to simulate a practical stationary load demand, and performed in the second phase of the project on three final down-selected membrane materials. In designing these protocols, reference was made to the recommendations of the Fuel Cell Committee of Japan (FCCJ) for stationary applications, which were used as a guide for determining temperature and RH set points for test protocols to be used within the MAESTRO programme.

The MEA active area and break-in procedure was standardised throughout the partners. The protocols for evaluation of performance of benchmark and new materials used conditions relevant to stationary applications. In addition the protocols explored the operating range of the new materials by testing over a wide temperature (60-110 °C) and RH range (dry to 100% RH). The protocols selected for these conditions were representative of current and future market trends typical of stationary and back-up power as well as automotive fuel cell sectors.

The accelerated test protocols were chosen to accelerate membrane degradation mechanisms. They comprised accelerating chemical degradation through OCV hold testing, and accelerating mechanical degradation through wet/dry cycling. The degradation modes caused by the selected accelerated test procedures were representative of those that were expected to be encountered in the accelerated durability test protocol, so as to enable appropriate down-selection of candidate membranes.

A set of relevant conditions for µ-CHP operation were those that simulated the annual four seasons in a reduced time period. Each season has specific energy requirements in terms of space heating, hot water etc., and these were simulated by modifications in load, stop/start cycling, change in cell temperature level (reflects the different system heat management depending of different load). A detailed protocol with a four 'season' simulation was created, in which each season was considered to last for 250 hours, allowing simulation of "1 year" of testing within a given 1,000 hour time period. To increase the amount of knowledge output, long term testing in these conditions was carried out in a stack incorporating different types of MEA in series. A fully automated testing station was used with a 9 x cell 50 cm2 active area screening stack. The 1,000 h protocol was designed to simulate the operating conditions for winter, spring, summer and autumn (Table 1.1), in which the MEAs were subject to long term constant load demands, changing load demands, and thermal cycles. The changing load demands led to different humidification within the MEA. The summer cycle was judged to be particularly stressing on the membranes due to thermal cycling between 80 °C and room temperature, which was thought likely to lead to dimensional changes causing stresses within the membrane, particularly at interfaces with seals.

Table 1.1: **1,000 h test protocol for membrane/MEA performance and durability evaluation.**

Season	Winter	Spring		Summer		Autumn	
	0-250 h	251-500 h		501 – 750 h		751 – 1000 h	
J (A/cm2)	0.6	0.6	0.3	0.3	0 (stop)	0.6	0.3
Cycle	No	12 h	12 h	12 h	12 h	12 h	12 h
Gas	H2/air	H2/air	H2/air	H2/air	N2	H2/air	H2/air
Cell temp / °C	80	80	80	80	Amb	80	80

The other test conditions for all four durability cycles were 50 kPag inlet pressure and 30% inlet relative humidity (RH) at 80 °C stack temperature. Gases were supplied at 1.5 x stoich for anode and 2.0 x stoic for cathode unless otherwise stated in the description below.

As reported in WP3, two 1,000 hour short stack durability evaluations were performed towards the end of the project. For the second stack test, as one of the incumbent new membrane types was exhibiting exceptional stability, the final autumn cycle was replaced by a further 'accelerated' summer cycle in order to deliberately stress the membrane to probe the limits of its stability. This accelerated summer cycle was run under the same conditions as the regular summer cycle described above, but with the cycle timings reduced to only 4 hour periods for each "on" and "off" cycle rather than the 12 hour periods employed for the standard summer cycle. This significantly increased the temperature and humidity cycling that the membrane had to endure (3 times more on-off cycles in the overall 250 hour summer cycling test). It was shown that with these shorter cycle periods the cell still attained a steady temperature and potential profile before the end of each cycle. All other conditions such as the current densities used and the gasses present at each electrode, and the forced cooling protocol on switch off, were maintained as in the standard summer cycle.

A full definition of all baseline materials (including all MEA components) and the complete description of the characterisation protocols are given in deliverable report D1.1, which was developed in collaboration between all the partners, and delivered in M6.

- **Baseline membrane characterisation - Ex situ physicochemical characterisation of E79-03S - UNIPG**

Ex situ characterisation of extruded EW 790 Aquivion membranes (E79-03S, 30 µm thick) was performed by conductivity measurements, stress – strain mechanical tests and water uptake determinations under the environment conditions of mechanical and conductivity tests.

Conductivity measurements

The in-plane (σ_{ip}) and through-plane (σ_{tp}) conductivity of E79-03S membranes was measured at 90 and 120 °C at increasing RH in the range 25-90% (Figure 1.1).

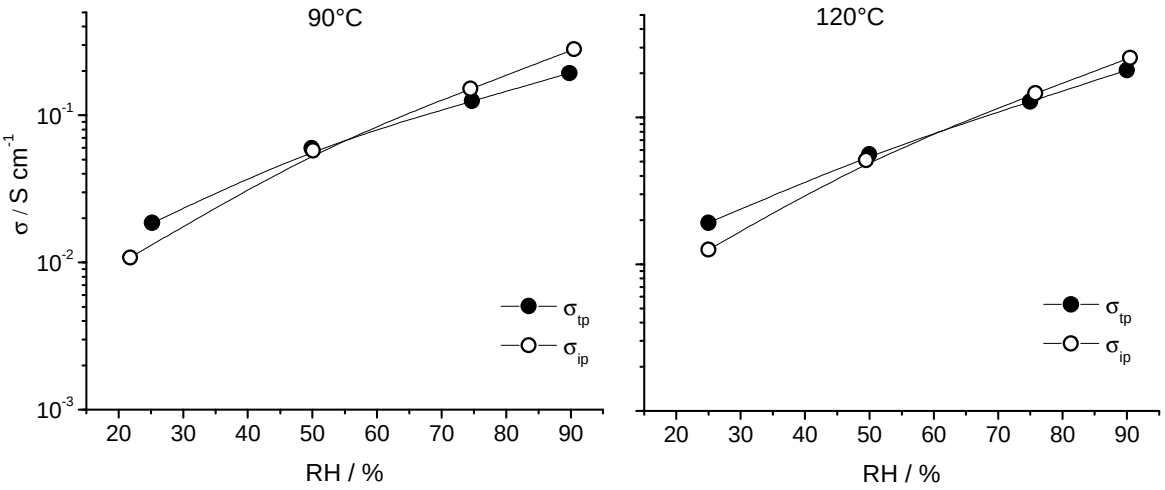


Figure 1.1: **In-plane and through-plane conductivity vs RH for E79-03S membranes at 90 and 120 °C.**

The conductivity turned out to be weakly dependent on temperature but strongly influenced by RH changes, extending from values around 0.01-0.02 S cm^{-1} at 25% RH to values of around 0.25 S cm^{-1} at 90% RH. There was a substantial agreement between σ_{ip} and σ_{tp} values at 50 and 75% RH, while $\sigma_{ip}<\sigma_{tp}$ at 25% RH and $\sigma_{ip}>\sigma_{tp}$ at 90% RH. In order to investigate the conductivity dependence on hydration, the water uptake of E79-03S samples (λ, number of water molecules per sulfonic group) was determined as a function of RH at 90 and 120°C: λ is ~4 at 25% RH and increases up to ~ 11 at 90°C and up to ~ 13 at 120°C (Figure 1.2), while σ_{ip} depends linearly on λ (Figure 1.3).

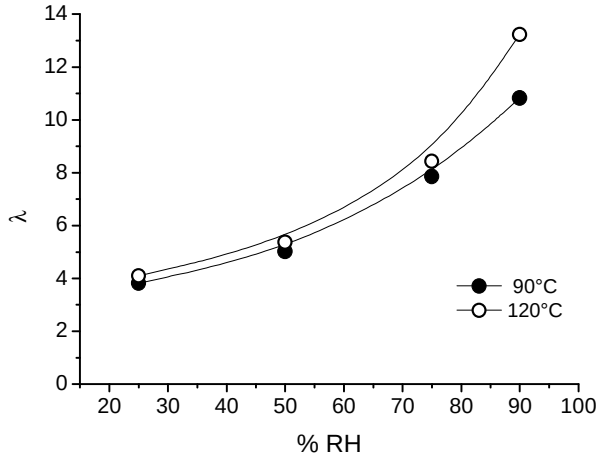


Figure 1.2: **Hydration versus RH for E79-03S membranes at 90 and 120 °C.**

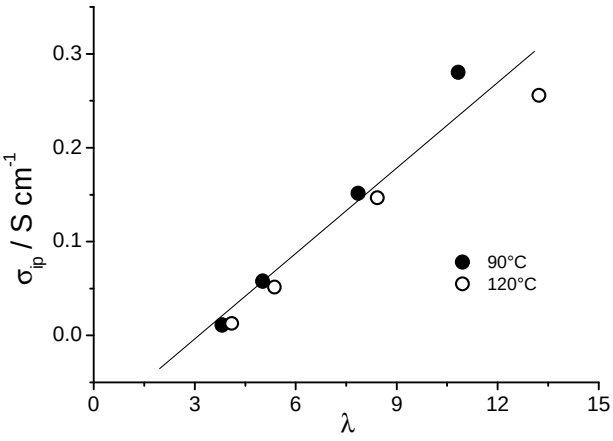


Figure 1.3: **Conductivity versus RH for E79-03S membranes at 90 and 120 °C.**

The fact that points collected at 90 and 120 °C gathered around the same straight line was surprising and could have arisen from membrane modifications associated with temperature and hydration changes during the two series of measurements. In order to highlight the conductivity dependence on temperature at constant hydration (λ=13), σ_{ip} was measured at decreasing temperature from 120 to 80 °C with RH=90%. The results are shown in Figure 1.4 as an Arrhenius plot. The activation energy for conduction (E_a), calculated on the basis of the Arrhenius equation ($\sigma T = \sigma_0 \exp(-Ea/kT)$, is 0.10 eV.

Mechanical tests

Stress-strain curves were collected at 80 °C and controlled RH (30, 50, 80%) with speed of 30 mm/min. Before measurements, samples were equilibrated at 80 °C for one day at the desired RH value. A typical stress – strain curve is shown in Figure 1.5. The elastic modulus (E), yield stress (σ_Y), stress at break (σ_b) and elongation at break (ε_b) are listed in Table 1.2. The water uptake (λ), determined at 80 °C for each RH value, is also reported.

Table 1.2: **Mechanical properties of E79-03S membranes.**

T / °C	%RH	λ	E / MPa	σ_Y / MPa	σ_b / MPa	ε_b^* / %
20	53	4.2	149 ± 29	10.8 ± 2.3	36	450
80	30	3.0	79 ± 12	8.8 ± 0.4	33	640
80	50	4.7	61 ± 3	7.7 ± 0.3	28	590
80	80	7.2	48 ± 5	5.1 ± 0.9	16	600

As a general trend, the increase in RH from 30 to 80% resulted in the increase in λ from ~3 to ~7 and in the concomitant decrease in E, σ_Y and σ_b, while ε_b was weakly affected by RH changes. The E value at 50% RH was significantly lower than that correspondingly determined at room temperature (E = 149 MPa) for a similar water content (λ=4.2).

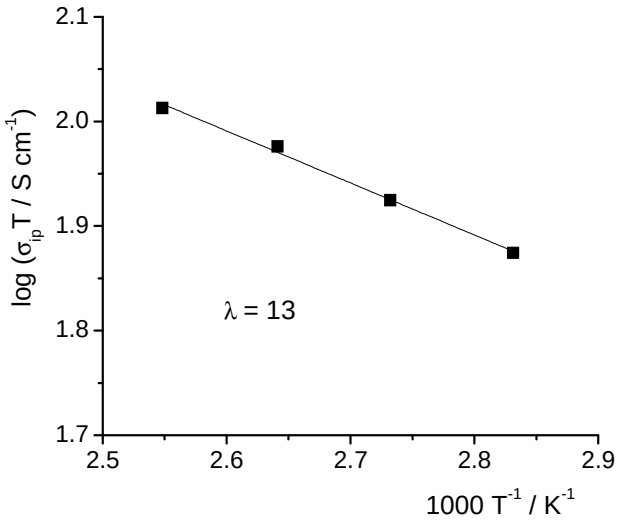


Figure 1.4: **Arrhenius plot for E79-03S.**

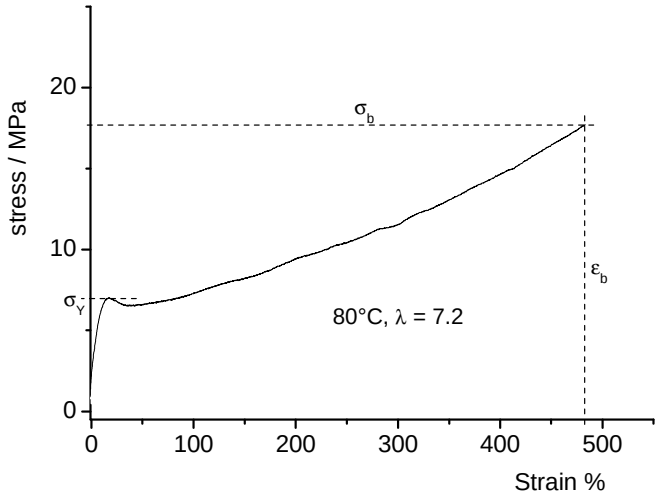


Figure 1.5: **Typical stress – strain curve for E79-03S.**

- **Baseline CCM and MEA development – SLX and JMFC**

JMFC completed definition, fabrication and supply of calibration/benchmark MEAs and reference electrodes to partners. Several batches of the benchmark 30 µm Aquivion® E79-03S membrane were provided by SLX to enable fabrication and supply of benchmark (calibration) MEAs to project partners and fabrication of MEAs for use by JMFC. MEAs were fabricated to the partner bespoke hardware requirements using process parameters defined for successful fabrication of MEAs via GDE (gas diffusion electrode) route.

Benchmark MEAs, comprising a 30 µm Aquivion C79-03S (cast)/E79-03S (extruded) membrane were fabricated by SLX using the CCM approach. The catalyst was from Tanaka (0.25 mg/cm^2, 50% Pt/C) at cathode and anode, the GDL and SGL Sigracet 10BC, and a rigid sub-gasket 32 µm per side was used.

- **Baseline CCM and MEA characterisation – JMFC, CNRS, SLX**

Testing of benchmark MEAs was performed using the baseline performance characterisation protocol described in D1.1 deliverable report. A performance comparison of the benchmark Aquivion® E79-03S membrane (benchmark MEA) with an MEA made with a JMFC internal reference membrane (30 µm, EW 930 g/mol) with identical electrodes to the benchmark MEA was completed. The MEA with Aquivion® E79-03S membrane showed improved performance and lower resistance across all operating conditions *vs*. the higher EW PFSA membrane. Baseline performance evaluation of benchmark CCMs provided by SLX were also completed.

Figure 1.6 compares the performance of the SLX benchmark CCM and the JMFC benchmark MEA. The differences in absolute performance between the benchmark MEAs were attributed to the different material sets of the part designs, including catalyst and ionomer type, loadings, GDL type and MEA construction. Under wet conditions and at low current density, the JMFC MEA showed higher performance than the SLX CCM. This result is attributed mainly to the higher metal loading of the JMFC MEA as the resistance of the two part designs was comparable under these conditions. Under drier conditions and at high current density, a performance benefit is seen for the SLX benchmark CCM; this was thought to be a consequence of improved water management and lower resistance due to incorporation of the low EW ionomer in the catalyst layers in this part design. The same trend has also been seen for a CCM made at JMFC incorporating a low EW ionomer. The overall trend in performances of the JMFC and SLX benchmark MEAs measured at JMFC and CNRS using the defined performance protocol was very similar.

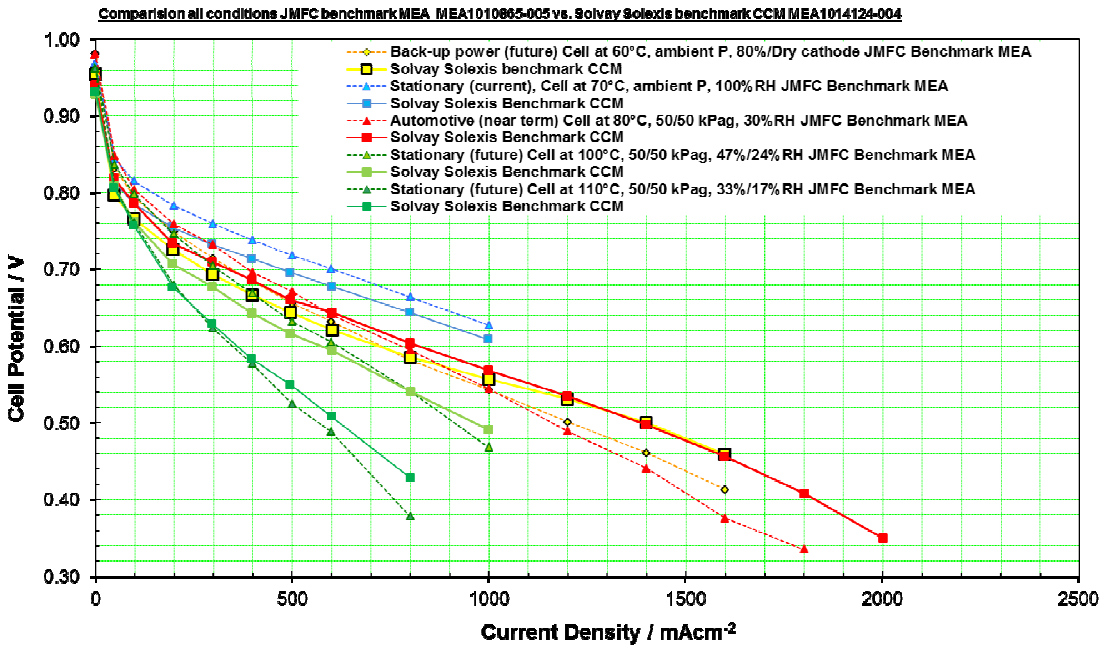


Figure 1.6: **JMFC and SLX benchmark MEA performance comparison, tested under the baseline performance characterisation protocol described in D1.1 deliverable report. Testing sequence used was 80, 60, 70, 100, 110 °C.**

OCV hold testing was performed at 85 °C and 13% RH according to MAESTRO protocols. Using the JMFC MEA, the open cell voltage steadily decreased up to ca. 30 h, and thereafter decreased more rapidly until failure at ca. 100 h. For the SLX CCM-type MEA, the OCV was much lower (880 mV) than the initial open cell voltage given by the JMFC MEA, and the test was ended at 160h due to the observed voltage loss. This data confirmed that the non-reinforced benchmark membrane was unlikely to achieve the lifetime requirement for the project.

3.2 WP2: PFSA Membrane Mechanical Stabilisation

Work package 2 aimed at developing long life mechanically stable membranes by means of different approaches including:

- Production of extruded membranes with different molecular weights and different polymer structure (Task 2.1, SLX);
- Production of ultra-high cross-linked polymers and production of cast membranes (Task 2.2, SLX);
- Thermal annealing of baseline and advanced PFSA membranes (Task 2.3, UNIPG);
- Electrospinning of ionomers and polymers into nanofibre mats and their incorporation into composite membranes; electrospinning of inorganic fibres to be used as ultrafine membrane reinforcements (Task 2.4, CNRS);
- Incorporation of zirconium phosphate (ZrP) based fillers in preformed extruded membranes and in ionomer dispersions to obtain cast membranes (Task 2.5, UNIPG).

To achieve deliverables D2.1-2.3, D2.5-2.7 in RP1 and Deliverables D2.4, 2.8-2.10 in RP2

Summary of Output from WP2

In Tasks 2.1 and 2.2, SLX developed two types of cross-linked membrane obtained either by a single cross-linking process, consisting in the formation of bridges between the sulfonic groups of EW790 and EW 700 Aquivion ionomers, or by a double cross-linking process where the sulfonamide bridges were formed in the above ionomers that had been previously cross-linked during emulsion polymerisation.

In Task 2.3 a systematic determination of the counter-elastic-force index of the ionomer matrix was undertaken by UNIPG to study the annealing behaviour of EW 870 and EW 790 Aquivion extruded membranes, using DMSO as annealing agent. While EW 790 Aquivion was insensitive to the thermal treatments, it was possible to increase the elastic modulus of EW 870 Aquivion in such a way that the room-temperature elastic modulus of a membrane annealed at 135 °C was by 250% higher than that of the as received membrane, which is by far beyond the MS3 target of increasing the membrane tensile properties by 50% compared to the benchmark membrane available at the project start.

At CNRS, activities in Task 2.4 led to development of three main types of membrane incorporating ionomer and polymer electrospun nanofibre reinforcements. Attention was focussed on one of these, due to its superior mechanical properties, and the nanofibre mat was associated with a cross-linked EW 700 ionomer developed by SLX. These membranes were scaled-up in size to make them suitable for durability testing. Composite membranes based on Aquivion loaded with electrospun zirconium phosphate nanofibres were also developed in collaboration with UNIPG.

Various membrane types were developed in Task 2.5 at UNIPG by combining different polymer matrices (including EW 830, EW 700 and EW 700X Aquivion) with fillers made of ZrP or organically modified ZrP. The membranes containing organically modified ZrP showed at the same time improved conductivity and mechanical properties together with a reduced hydration at high relative humidity.

For all of these membranes the improvement of the elastic modulus in comparison with the benchmark Aquivion E79-03S membrane was significantly beyond the MS3 target, while the conductivity was in all cases higher than that of the benchmark membrane.

WP2 very successfully concluded with down-selection of three membrane types that were scaled up and transferred to WP3 for MEA fabrication and accelerated durability stack testing. In an approach that was not originally part of the work plan, two of the final membrane types associated two of the MAESTRO preparation approaches: cross-linked low EW ionomer and nanofibre reinforcement, and inorganic-organic composites prepared using low EW cross-linked ionomer.

Summary of Achievements in WP2

Detailed descriptions of the results obtained have been described in deliverable reports D2.1-2.10, D1.2 on Phase 1 Down-Selection of Promising Down-Selected Membranes for MEA Fabrication, and in the M28 internal project marker report on Characterisation of Down-Selected Materials.

A great deal of consideration was given to selection of membranes to be transferred to WP3 for integration into an MEA for performance and durability testing. Final selection of membranes for scale-up for MEA development for accelerated durability stack testing was made on the basis of ex situ mechanical properties and conduction properties: conductivity at 80 °C, 50 and 90% RH, and elastic modulus and yield stress at 70 °C, 80 %RH, and durability in OCV hold testing (85 °C, 13% RH) and wet-dry cycling at OCV (10 minute cycles, 85 °C). Some of the characteristic properties of down-selected MAESTRO membranes are shown in Figures 2.1-2.3.

Characteristic properties of down-selected MAESTRO membranes

Elastic Modulus and Yield Strength

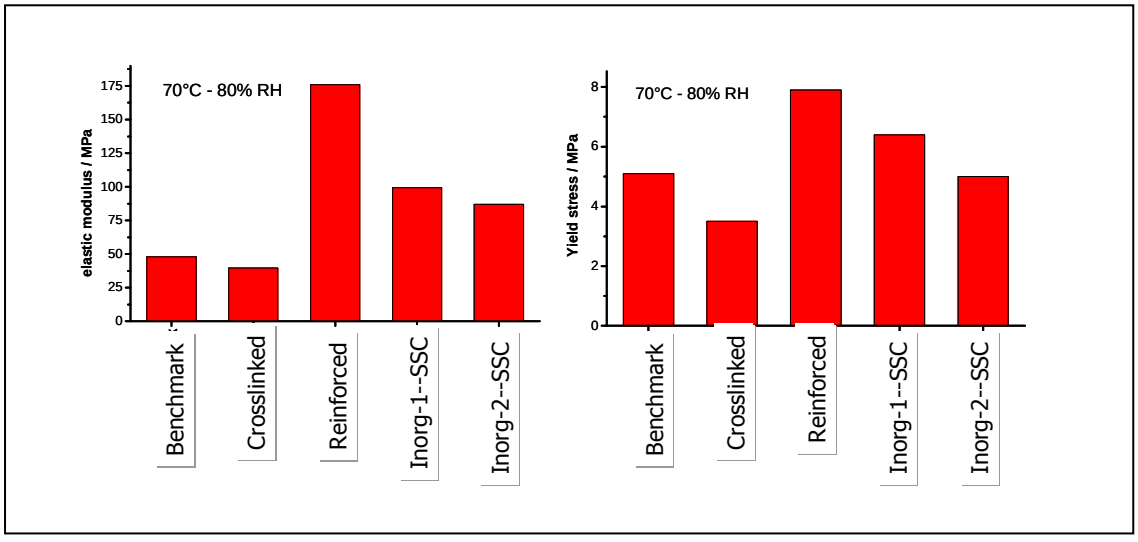


Figure 2.1: **Mechanical properties of MAESTRO down-selected membranes are significantly improved compared with the project benchmark. Elastic Modulus increased by >300%; yield stress by >50%.**

Proton Conductivity

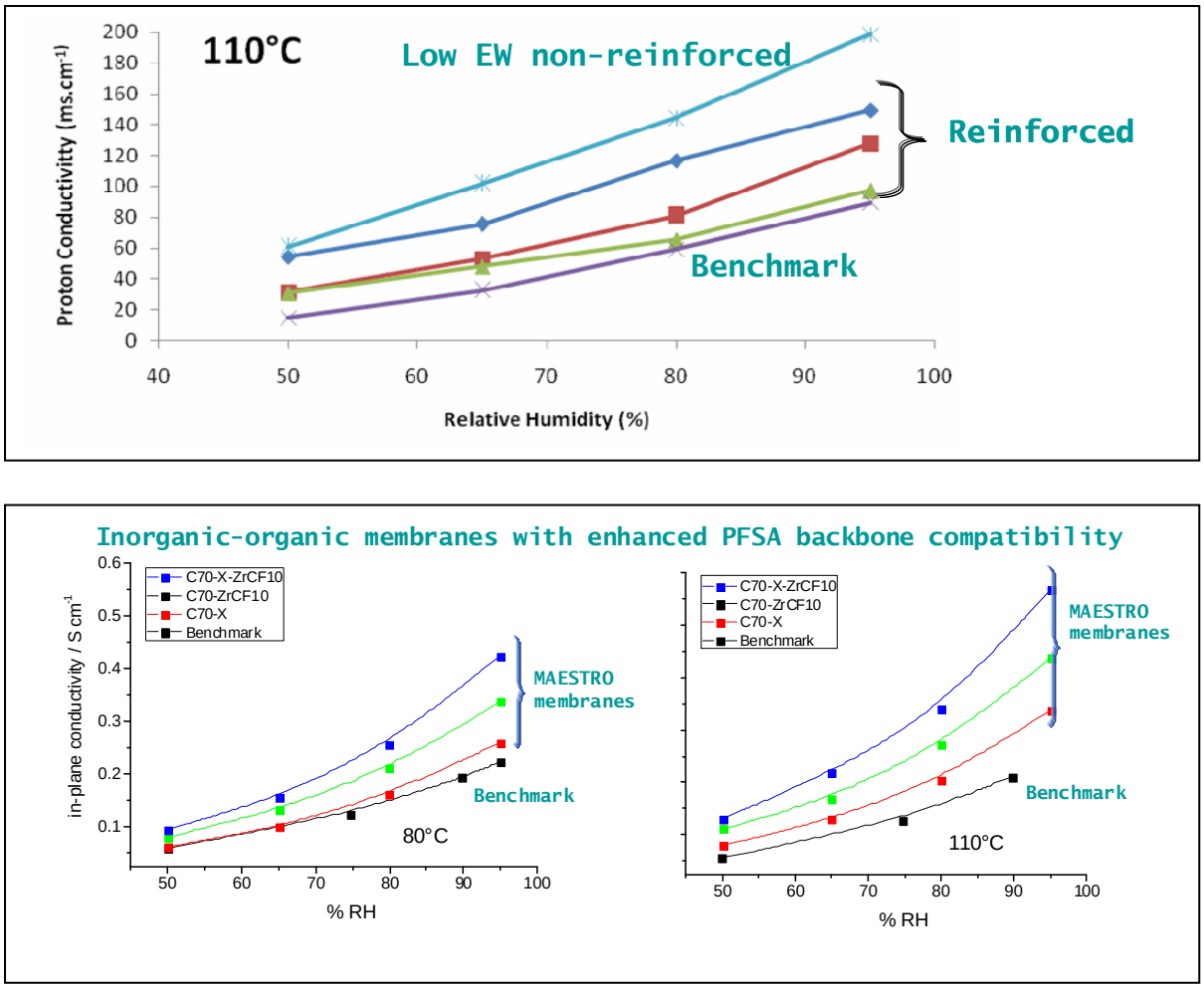


Figure 2.2: **The approaches developed to mechanical stabilisation do not compromise conductivity and, in some cases, improve the conductivity of the project start point, state-of-art SSC membrane.**

Fuel Cell Performance

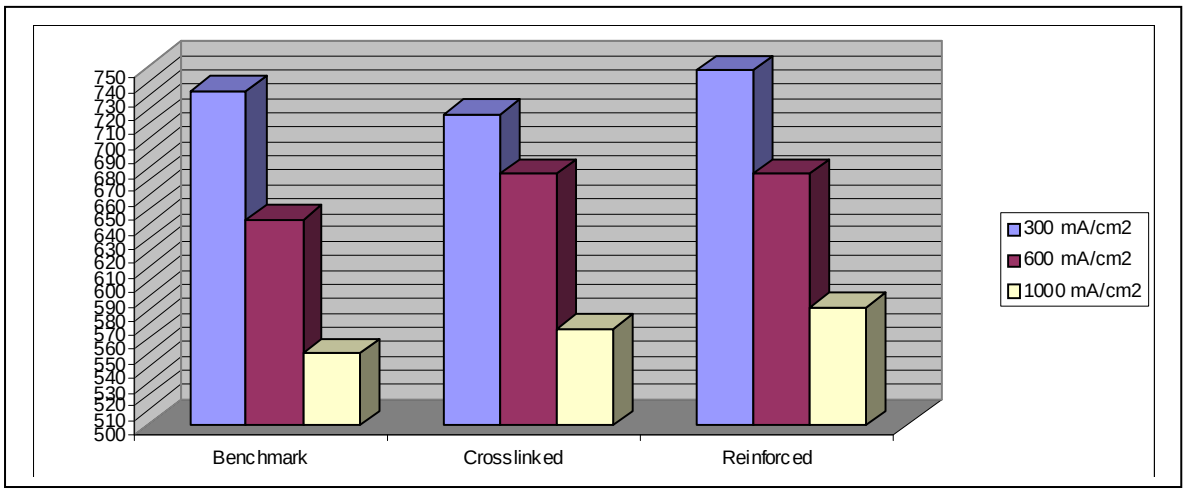


Figure 2.3: **MEAs incorporating cross-linked low EW and novel reinforced low EW SSC membranes show improved performance in *in situ* fuel cell testing at hotter, drier conditions compared to the project start point, state-of-art SSC membrane.**

Task 2.1 Extruded baseline membranes production (SLX)

The consortium defined to select Aquivion® E79-03S membrane as baseline, giving continuity to the activities of Autobrane project where this membrane was selected as the best available material for automotive application. The characterisation of this membrane and MEAs elaborated using the GDE and CCM approach was carried out in WP1, and is described in Deliverable Reports D1.2 and D3.1.

Task 2.2 Ultra-high molecular weight cross-linked PFSA and membranes (SLX)

The aim of the first project period RP1 was to inject a baseline version of Aquivion® membrane, to develop a new membrane with different EW and high MW by different process (cross-linking during emulsion polymerization) and to study its behaviour. Until M12 the given focus was the cross-linked membrane with an average EW of 750 g/mol, thus comparable to standard membrane with EW 790 in terms of mechanical properties and durability in cell. During M12-M18 lower EW and baseline cross-linked membranes were synthesized and investigated. Production and evaluation of the Solvay cast membrane material with an EW in the range of 700-790 (cross-linked) was performed as planned.

C70-03XS and C79-03XS membrane (cross-linked, 30 micron membrane) were synthesised using a cross-linking agent during the polymerization reaction together with standard monomers (TFE and SFVE) so to modify the molecular structure from linear to branched. The net effects were a substantial increase of the molecular weight and, even if at very low level, formation of 'bridges' between molecules (cross-linking). Due to the low value of melt flow index which caused impossibility to melt extrude this material, the corresponding membranes C70-03XS and C79-03XS were produced by casting.

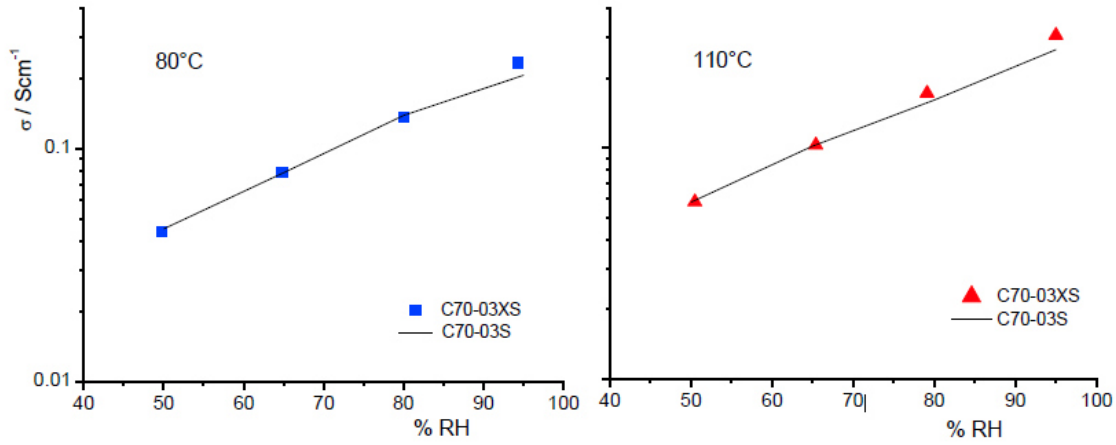


Figure 2.4: **In-plane conductivity of cast cross-linked C70-03XS and non-cross-linked C70-03S membranes.**

There was no difference in the in-plane conductivity of cast cross-linked C70-03XS and non-cross-linked C70-03S membranes at either temperature of measurement (80 and 110 °C), Figure 2.4. The proton conductivity of C70-03XS at different temperatures, as a function of relative humidity, is shown in Figure 2.5. This membrane displayed very high conductivity of 400 mS/cm at 120 °C/95% RH, and 60 mS at 120 °C/50 % RH.

In the period M19-M39, the aim of the project was the synthesis of a new membrane using two different cross-linking processes. The first of these was a cross-linking process applied after polymerisation using different concentration of an agent to cross-link through a small number of sulfonic acid groups. As in the case of EW 700 and 790 ionomers obtained by cross-linking during polymerization, such polymers could not be

extruded, and the membranes, with different degrees of cross-linking, were prepared by casting, providing membranes C70-03XXS.

The second approach was the final optimization of cast, high MW membranes obtained using a combination between the two different types of cross-linking processes, performed both during and after the emulsion polymerization. Thus an EW 700 polymer, first partially cross-linked through its polymer chains during polymerization, was further cross-linked through its sulfonic acid groups after polymerization with different concentrations of cross-linking agent, providing membranes C70-03XXXS.

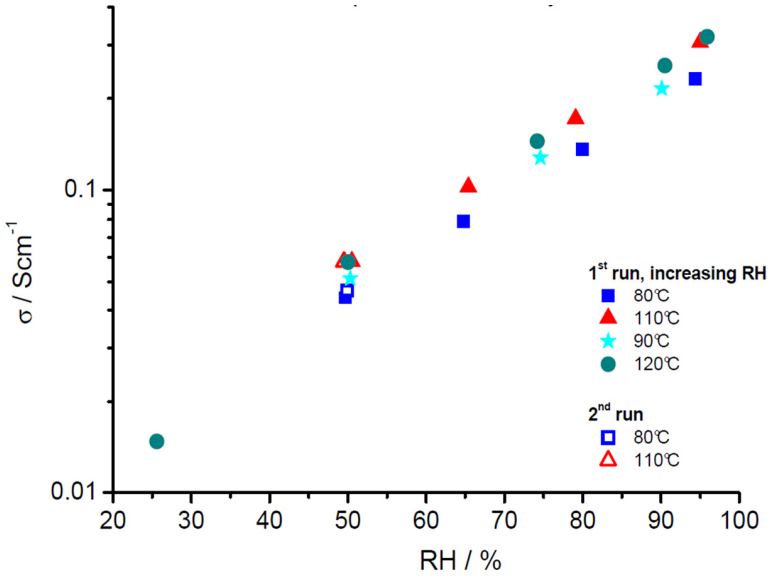


Figure 2.5: **In plane conductivity of C70-03XS cast cross-linked membrane.**

From the results of ex situ and in situ characterisation described in deliverable reports D1.2, D2.2-2.4, D2.9 and M28 internal project marker report, the decision was made to down-select the cross-linked membrane C70-03XS, branched ionomer type (cross-linking through polymer chains), for accelerated durability stack testing.

Furthermore, and in an approach that was not part of the original programme of work, the corresponding low EW ionomer 700-X was used in the membrane developments carried out at UNIPG and CNRS in tasks 2.5 and 2.4 respectively, during RP2. Final membranes from tasks 2.4 and 2.5 therefore combined two approaches to membrane stabilisation: ionomer cross-linking and membrane reinforcement with electrospun nanofibre reinforcements (task 2.4), and ionomer cross-linking and ionic cross-linking in inorganic-organic composites membranes (task 2.5).

Task 2.3 Thermal annealing, baseline and advanced PFSAs (UNIPG)

Both temperature and relative humidity can have a major influence on ionomer stability under FC conditions. The shifts of the plots nc vs T at constant RH can be utilized as a measurement of the obtained stabilization or destabilization at the used RH value. The effect of RH in the range 90-100% can be then easily predicted. Since this method requires the determination of the nc/T plot of as received membrane, which is then used as a reference plot, this plot was determined for the E79-03S membrane. Comparison of this plot with that of as received Nafion 1100 membrane showed that the plots were very similar in shape and that the plot of the Aquivion was shifted towards low temperatures by about 20°C. The thermal stability of Aquivion 790, in spite of its low EW, is therefore comparable with that of Nafion 1100.

Aquivion E-87-10S membranes were first annealed in the presence of DMSO (140 °C for 3 days). These preliminary results showed large shift of the plot nc/t, corresponding to excellent thermal ionomer stabilisation. The DSC curve of the annealed membrane, after dehydration and elimination of DMSO, showed an endothermic peak centred around 170 °C, which compared favourably with the melting temperature (Tm ~ 150 - 160°C) estimated from the nc/T plot, indicating that a semi-crystalline phase was formed during the annealing procedure.

On the basis of these results, systematic annealing tests were carried out both on this membrane and on extruded E79-03S membranes, and completely different results were obtained for the two membrane types (Figure 2.6).

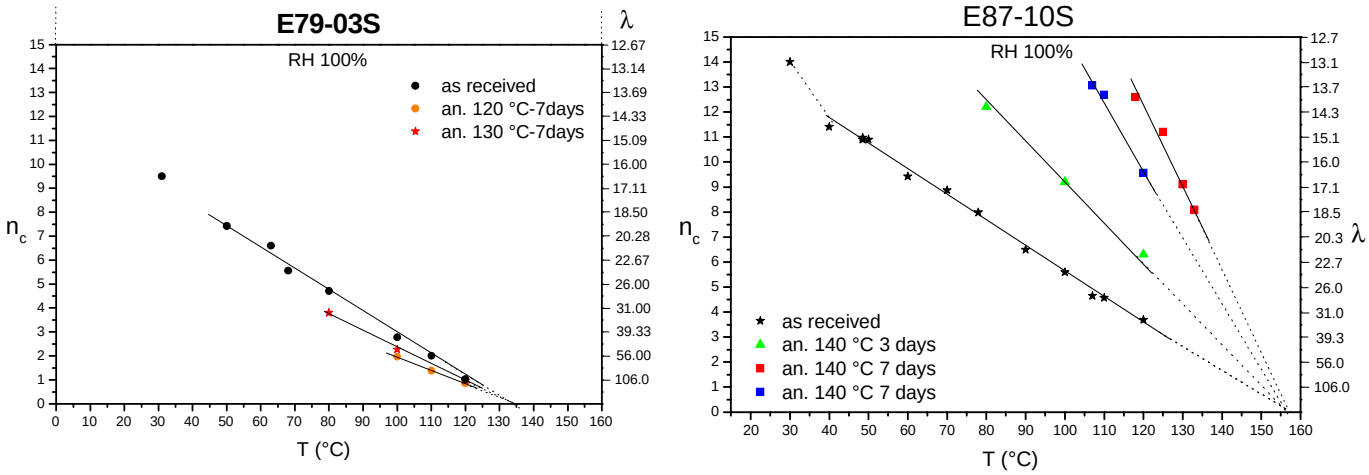


Figure 2.6: **n_c/T plots for E79-03S and E87-10S membranes.**

The annealing treatment of E79-03S at 120 and 130 °C for seven days resulted in a slight decrease in the n_c values in comparison with the as received membrane (Figure 2.6), thus indicating that the annealing process had a negative impact on the membrane mechanical properties. The different results obtained for the two types of membrane seem to indicate that the ionomer equivalent weight was a critical parameter for the annealing to be successful.

An E87-10S membrane was annealed at 140 °C for seven days and then heated in water at 135 °C for 200 hrs so that $\lambda = 19$ and $n_c = 7.5$. For the as-received membrane, measured at the same temperature, $\lambda = 53$ and $n_c = 2.14$. Since n_c is proportional to the elastic modulus, it was concluded that after annealing in DMSO at 140 °C and subsequent hydrothermal treatment at 135 °C, the elastic modulus of the annealed membrane was increased by 250% in comparison with the as-received membrane, which is by far beyond the MS3 target of a 50% increase in tensile properties. At 100 °C, the conductivity of the annealed membrane was nearly coincident with that of the as received membrane.

Since a strongly positive effect on mechanical properties after thermal annealing was only observed for a thicker Aquivion membrane of high EW, while the objective of MAESTRO concerned low EW ionomer membranes of thickness ca. 30 µm, the membranes of task 2.3 were not selected for further detailed study in the framework of the project. The approach remains of clear interest for applications requiring thicker membranes and higher EW. Their preparation and characterisation is described in Deliverable Report D2.5.

Task 2.4 Electrospun PFSAs, organic and inorganic fibres (CNRS)

The objective in this task was the development of organic polymer and ionomer and inorganic nanofibre electrospun reinforcements and elaboration of methodologies for the preparation of composite membranes prepared with low EW Aquivion, in particular in RP2 with cross-linked EW 700-X ionomer.

Polymer nanofibre reinforcements: Polymer nanofibre mats were prepared following optimisation of solvent, concentration, and solution viscosity parameters. Under the conditions used, the electrospun nanofibres showed an average size of around 200 nm with a relatively narrow fibre size distribution between 140-280 nm.

The thickness of the nanofibres were further controlled through the use of coaxial electrospinning with an external solvent sheath to confine the central polymer jet. Through the use of a solvent sheath, the evaporation and drying of the fibre during electrospinning was delayed, resulting in further stretching of the nanofibres during electrospinning and ultimately thinner fibres, with a fibre size distribution between 60-160 nm. The nanofibre mat thickness is controllable between 5 and 25 µm. On the basis of the conductivity and mechanical properties, a nanofibre mat thickness of 10 µm was targeted. Using a protocol for impregnation of 700-X Aquivion dispersion into the nanofibre reinforcements, membranes of 30 µm thickness were prepared. There was no visible separation between the polymer nanofibres and the PFSA matrix after freeze-fracture, indicating a strong interface interaction between the surface of the fibres and the PFSA.

The composite membranes had a lower elongation at break, which indicated that their structural integrity was dependent mostly on the polymer nanofibre mat, whereas the non-reinforced membranes show a very high plasticity and allowed for a significant amount of deformation prior to rupture. However, due to the strength of the polymer nanofibres, the composite membranes still showed a higher breaking strength compared to the non-reinforced cast membranes. Most notably, the composite membranes showed significantly greater elastic modulus and yield strength (Figures 2.1 and 2.9), largely exceeding the MS3 milestone, which translated to a significantly greater creep resistance, a factor important for the long-term durability of the membrane.

From the results of ex situ and in situ characterisation described in deliverable reports D1.2, D2.6, 2.10, and M28 internal project marker report, the decision was made to down-select the polymer nanofibre-reinforced cross-linked membrane RFS-C70-03XS for accelerated durability stack testing.

Both the polymer nanofibre reinforcements and the final composite membranes were scaled-up in size in RP2 to the size required for durability testing in the JMFC stack.

Inorganic proton conducting nanofibres: Zirconium phosphate (ZrP) has been well-studied as a proton conducting filler for PFSA membranes, however until now has never been prepared in a nanofibre form. A novel ‘reactive’, coaxial electrospinning approach was developed in MAESTRO where ZrP was formed in situ during fibre formation. In this approach, core and shells solutions containing the zirconium and phosphorus precursors respectively were loaded into two separate syringes and mounted on separate syringe pumps in order to obtain separate flow rates for the two solutions. The syringes were connected to the coaxial needle for electrospinning on to a rotating drum collector. The resultant mat, Figure 2.7, comprised fibres of 100-600 nm diameter that decreased in size after calcination.

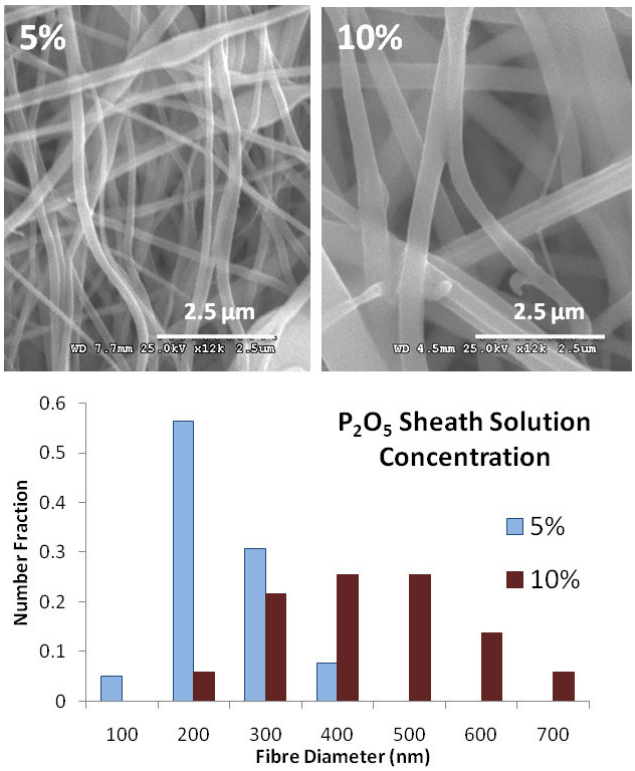


Figure 2.7: **SEM images and fibre size distribution of electrospun ZrP fibres**.

TEM cross-section of the fibres showed that the material was porous and granular, while HRTEM EDX analysis indicated that the ZrP content of the fibres was the same throughout the fibre thickness.

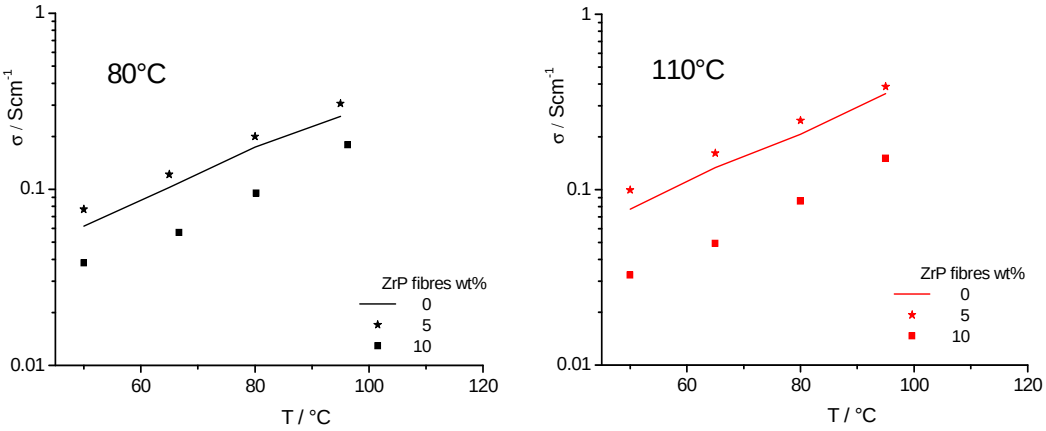


Figure 2.8: **In-plane conductivity of ZrP nanofibre-Aquivion 700-X membranes at 80 and 110 °C.**

Membranes containing 5 wt% ZrP fibres in 700-X ionomer displayed higher conductivity at 80 and 110 °C than the C70-03XS membrane, Figure 2.8, and the elastic modulus shows an improvement >180%. Despite its favourable properties set, given that the fabrication of the ZrP nanofibres involved several processing steps and that there was no clear advantage of the nanofibres over other ZrP morphologies (cf. task 2.5), this membrane type was not down-selected for scale-up and stack durability testing.

With respect to the M36 milestone for WP2, all the approaches developed in Task 2.4 led to an improvement in the mechanical properties compared to the benchmark membrane. Use of polymer nanofibre reinforcements allowed the target of +50% in E-modulus to be largely exceeded; at 70 °C/80% RH, the membrane modulus was increased by a factor ca. 350%. The E-modulus and yield point of Task 2.4 membranes are compared with those of the benchmark and cast 700-X membranes in Figure 2.9.

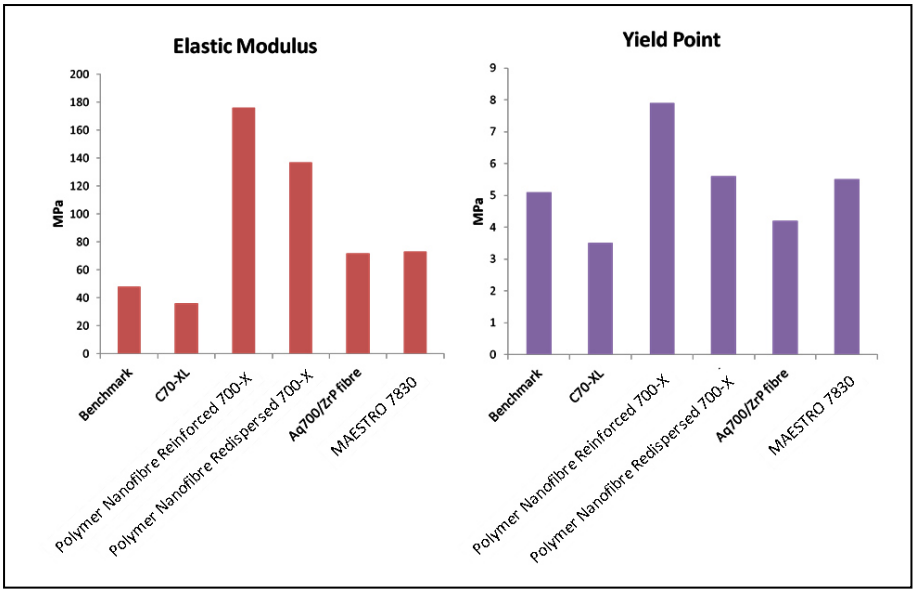


Figure 2.9: **Mechanical properties of nanofibre reinforced membranes at 70 °C, 80%RH**

Task 2.5 Ionic cross-linking by incorporation of Zr phosphates (UNIPG)

The main activity at UNIPG within this task was the synthesis and the ex situ characterisation of the following three types of composite membrane:

- membranes based on EW 830 Aquivion filled with organically modified ZrP bearing hydrogenated alkyl chains (ZrP(C12)x)
- membranes based on EW 700 Aquivion filled with ZrP and organically modified ZrP bearing 0.9 fluorinated alkyl chains per Zr atom (ZrPF) ;
- membranes based on EW 700X Aquivion (where "X" indicates that the ionomer was crosslinked during the polymerisation) filled with ZrP and ZrPF.

All membranes were prepared by casting mixtures of the ionomer dispersions with gels of the filler according to the procedures reported in the Deliverable Report D2.8.

Comparison is made in Figure 2.10 of the mechanical properties of the composite membranes prepared with ionomer 700-X at 70°C – 80% RH. This Figure shows the proportional changes in elastic modulus (%ΔE) and yield stress (%$\Delta\sigma_Y$) of the composite membranes with respect to E79.

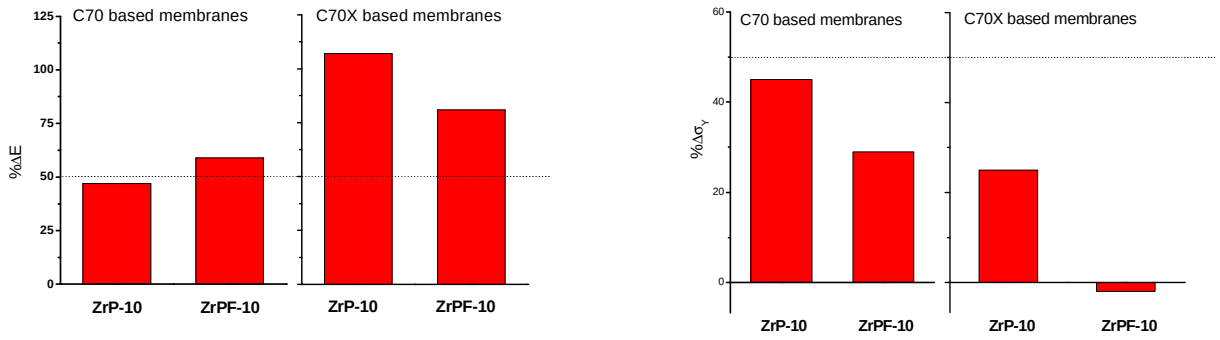


Figure 2.10: **Elastic modulus proportional changes (%ΔE) and yield stress proportional changes (%$\Delta\sigma_Y$) for the indicated membranes with respect to E79, at 70°C/80% RH.**

It was observed that:

- For all of the composite membranes the improvement in the elastic modulus ranges from slightly less than 50%, for C70/ZrP-10, to slightly more than 100%, for C70X/ZrP-10. Therefore, the MS3 target of increasing by at least 50% the mechanical properties of the composite membranes was reached for all membranes at least in terms of elastic modulus.
- The elastic modulus of the C70X based membranes was significantly higher than that of the C70 based membranes.
- The filler influence on the yield stress (σ_Y) was less strong than the influence on the elastic modulus (the maximum increase in σ_Y is about 45%). In only one case (C70X/ZrPF) the yield stress of the composite membrane was slightly lower than that of the benchmark. In general the higher σ_Y values were observed for the C70 based membranes, among which C70/ZrP-10 shows the maximum %$\Delta\sigma_Y$ value.

If the sum %ΔE+%$\Delta\sigma_Y$ is taken as an estimate of the overall improvement in the mechanical properties, then the following sequence of "overall mechanical stability" was obtained:

C70X/ZrP-10 > C70/ZrP-10 ~ C70/ZrPF-10 ~ C70X/ZrPF-10

With regard to the proton conductivity, all composite membranes were more conductive than the corresponding ionomer, except for C70X membranes filled with 5 and 10% ZrP. In comparison with the benchmark membrane (E79), a decrease in conductivity was only observed for the C70 and C70X membranes loaded with 5 and 10% ZrP, the membranes filled with ZrPF being more conductive than E79. The proportional conductivity changes, at 80 and 110 °C, referred to E79 (%$\Delta\sigma$) are shown in Figure 2.11. It can be observed that, independent of the ionomer matrix,

- for a given temperature, %$\Delta\sigma$ values at 50% RH were larger (i.e. more positive or less negative) than the corresponding values at 90% RH;
- for a given RH, %$\Delta\sigma$ values at 110°C were larger than the corresponding values at 80 °C.

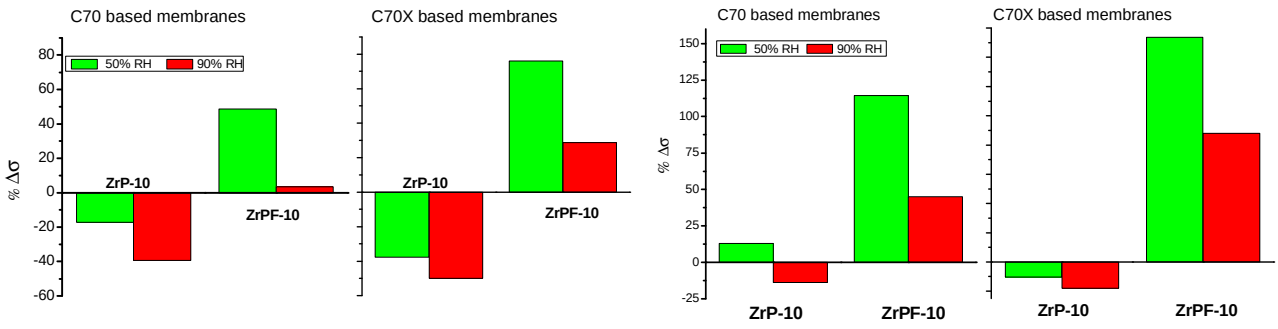


Figure 2.11: **Conductivity proportional changes (%Δσ) for ZrP-composite membranes with respect to E79, at 80 °C (left) and 110 °C (right).**

On the basis of the %Δσ values of Figure 2.11, the following sequence of conductivity was obtained for all of the four T-RH combinations:

C70X/ZrPF-10 > C70/ZrPF-10 >C70/ZrP-10 ~ C70X/ZrP10.

Taking into account the results of the ex situ characterisation it was concluded that, in comparison with the benchmark, a significant mechanical reinforcement was generally achieved with all C70(X) based membranes filled with both ZrP and ZrPF.

While C70X/ZrP membranes showed the largest mechanical stabilisation, those made of ZrPF loaded C70X were the most conductive. Since these two membrane types showed similar durability in OCV testing (cf. WP3), C70X/ZrP membranes were selected for durability stack testing in WP3 due to their easier scale-up in the time available. Results of ex situ and in situ characterisation are described in deliverable reports D1.2, D2.7, D2.8 and the M28 internal project marker report on Characterisation of Down-Selected Membranes.

CONCLUSIONS

The approaches developed in WP2 by the project mid-term were used in the second part of the project to mechanically reinforce low equivalent weight Aquivion. On the basis of the encouraging results shown by several of the membrane stabilisation routes, a "double-strand' approach was followed by simultaneously associating the most stable ionomer (Aquivion 700-X, crosslinked after polymerisation) with the membrane reinforcements comprising polymer nanofibre mats and zirconium phosphate nanoparticles and nanofibres.

As a result, the MS3 target of increasing the membrane tensile properties by over 50% was achieved, and in most cases was by far exceeded, for double cross-linked ionomers (Task 2.2), thermal annealed membranes (Task 2.3) and membranes reinforced with both fibre mats (Task 2.4) and ZrP nanoparticles (Task 2.5).

In general, the mechanical reinforcement did not compromise the ionomer conductivity and in some cases the composite membranes were even more conductive than membranes made from the un-reinforced ionomer alone. As expected, the mechanical reinforcement had the beneficial effect of limiting membrane dimensional changes during hydration/dehydration cycles. Accordingly most reinforced membranes showed better durability than the benchmark membrane in OCV hold tests, performed both at constant relative humidity and in wet-dry cycling conditions.

The newly developed cross-linked Aquivion 700-X without any additional mechanical reinforcement, the Aquivion 700-X reinforced by polymer nanofibre mats and by nanosized zirconium phosphate were selected as the membranes for final long-term durability testing in a short stack. These results are described in WP3.

3.3 WP3: MEA Fabrication of Down-Selected Membranes, Testing

Work package 3 focussed on the fabrication of MEAs and CCMs using benchmark and novel membranes provided by WP2, as well as single cell screening and short stack durability testing of final MEAs. It included:

- In RP1, fabrication of CCMs and MEAs of initial down selected membranes and first characterisation of their performance and durability under accelerated ageing conditions according to the project protocols;
- In RP2, to instigate an effective MEA screening procedure with focus of efforts on applying performance and accelerated ageing protocols to MEAs prepared with the best novel membranes from WP2 and to evaluate their durability relative to the benchmark MEA under the same conditions.
- Testing of final down selected MAESTRO membranes in a dedicated stack in the final 4 months of RP2, following the accelerated durability test procedure developed in WP1 (representative of a µ-CHP application), and comparison of their lifetime and performance with the project benchmark.

To achieve deliverables D3.1 in RP1 and Internal Project Markers on MEA Delivery at M33, and results of accelerated durability stack testing at M39

Summary of Output from WP3

Final single cell testing at JMFC and Solvay focussed on MEAs fabricated from membranes comprising the cross-linked Aquivion EW 700 XL ionomer; either as the unreinforced ionomer, and also with electrospun polymer nanofibre mechanical reinforcement and the inorganic ZrP stabiliser additions. This clearly demonstrated the benefit of the lower EW ionomer compared to the project benchmark EW790 ionomer, particularly at higher current densities under the drier operating conditions, almost certainly reflecting the improved water retention characteristics of the lower EW materials. The polymer nanofibre reinforced C70-XS membrane maintained this performance enhancement at the 80 °C, 30% RH condition. Cell testing of MEAs with the ZrP additives was less conclusive, and performances were generally slightly lower than achieved from the equivalent membrane not containing ZrP.

Accelerated durability testing via OCV hold tests and wet-dry cycling at CNRS clearly showed that a remarkable improvement in the stability of membranes prepared with the cross-linked ionomer 700-X was achieved through the incorporation of the polymer nanofibre reinforcement. The ZrP doped membranes also exhibited improved stability compared to the unreinforced equivalent and had similar degradation rates to the benchmark EW790 MEA in the wet-dry cycling test.

For the final short stack testing it was decided to evaluate MEAs incorporating the new cross-linked low EW C70-03XS membrane without any additional mechanical reinforcement, the electrospun polymer nanofibre reinforced version and also the same ionomer with ZrP nanoparticle additive. Membranes were supplied to JMFC for MEA fabrication and CCMs with the ZrP membrane were also fabricated and provided by Solvay. The 1,000 hour protocol, made up of 4 x 250 hour sub-protocols representing the four seasonal operational conditions that a µ-CHP application would encounter, was operated for 2 short stacks to enable as many of the new and also benchmark comparative MEAs to be evaluated. Several of the same polymer nanofibre reinforced EW 700 XS membrane based MEAs were operated in both stacks, thus accumulating 2,000 hours accelerated test time.

Short stack testing confirmed again that the low 700EW ionomer gave the predicted resistance benefits which allowed the incorporation of the electrospun polymer nanofibre reinforcement with no loss in performance when compared to the project benchmark MEAs fabricated from an unreinforced membrane of the higher equivalent weight 790EW ionomer. The polymer nanofibre reinforced MEAs showed a great enhancement in durability, particularly through the most stressful summer on/off cycling protocol, with no

membrane degradation being observed, markedly in contrast to the non-mechanically reinforced membranes which all failed during this protocol.

The ZrP composite membranes revealed a greatly improved resistance over all other project membranes in the stack testing, but the overall performance was compromised, as the membranes were too permeable, even at the start of testing. Further work on incorporating this kind of additive without inducing the observed permeability issues is needed.

Overall, however, the polymer nanofibre reinforcement clearly exhibited the ability to markedly enhance the durability of membranes fabricated from the new low 700EW cross-linked ionomer, and survived over 2,000 hours of testing against a range of testing protocols, including some aggressive accelerated testing, without any significant intrinsic decay. At a typical operating current density for the stationary application, of 0.3 Acm^{-2}, the decay in cell voltage after 2,000 hours accelerated testing was no more than about 3% of the original cell voltage, and can be argued as comfortably achieving the final project objective of less than 10% performance decay at a practical operating current density for the stationary application.

Thus the WP3 objectives for the period regarding the fabrication and evaluation of MEAs from down-selected membranes from WP2 in a short stack test for durability over an accelerated test protocol for a minimum of 1,000 hours (and up to 4,000 hours if time permitted), representative of a µ-CHP application, was successfully accomplished. Furthermore, the key target performance metric of less than 10% performance decay at a practical operating current density for the stationary application, was also successfully achieved for the electrospun polymer nanofibre reinforced crosslinked Aquivion EW 700-XS membrane.

Detailed Summary of Achievements in WP3

Membrane and MEA Screening in Single Cells

Table 3.1 summarises results of fuel cell performance testing at 80 °C/30 % RH, and accelerated stress testing (OCV hold testing, wet/dry cycling at OCV) performed according to the MAESTRO protocols of D1.1 on down-selected WP2 membranes.

Table 3.1: **Cell voltage at 300, 600, 1000 mA/cm^2 at 80 °C/30%RH, and durability in OCV hold testing and wet/dry cycling at OCV, provided by MEAs incorporating C70-03XS, electrospun polymer nanofibre reinforced 700-X (30 µm) and C70X-ZrP-10 (30 µm) incorporating 10 wt% of nanometric zirconium phosphate. All membranes prepared with the 700-XS ionomer. Comparison with benchmark membrane MEA of extruded EW 790 Aquivion, 30 µm.**

Membrane	Polarization test at 80°C/30%RH (mV)			Open circuit voltage (OCV) hold test at 85°C – No. days for 10% reduction in OCV		Wet/dry cycling test at OCV No. cycles for 10% reduction in OCV
	300 mA/cm^2	600 mA/cm^2	1000 mA/cm^2	50% RH	13% RH	
E79-03S - benchmark	741	667	573	2	2	180
C70-03XS cast, cross-linked	727	659	557	18	<1	48
Polymer nanofibre reinforced C70-03X cast, cross-linked	738	669	561	n/a	6	432
C70X-ZrP-10	650	550	450	10	-	256

At SLX, screening was performed between membranes of cross-linked ionomers of EW 790, 750 and 700 g/mol. Figure 3.4 shows a comparison between the new cross-linked membranes (C79-03XS, C75-03XS, C70-03XS) and the benchmark membrane C79-03S at 110 °C with anode/cathode RH of 33/16%. The MEA integrating the C70-03XS membrane showed the highest performance under these conditions. Figure 3.1 shows the low performance of C79-03XS at high temperature (not possible to reach 0.6 A/cm^2).

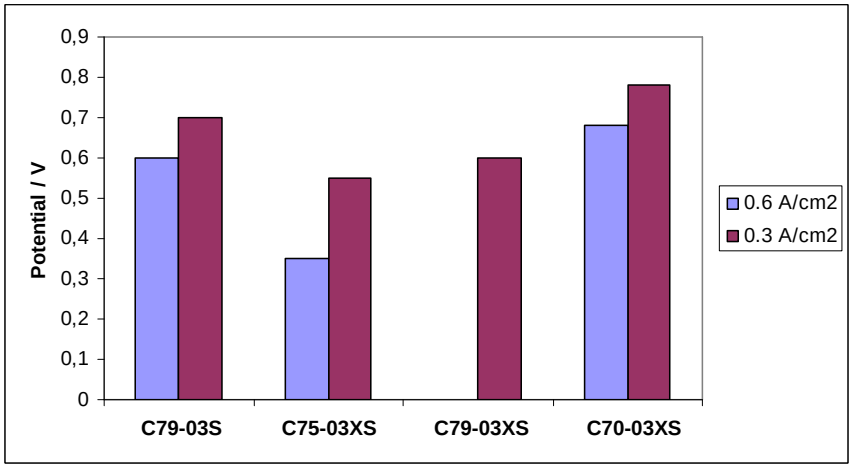


Figure 3.1. **MEA performance at 0.3 and 0.6 A/cm^2 at 110 °C with anode/cathode RH of 33/16%.**

CNRS contributed to the down-selection of membranes by applying the accelerated stress testing protocols of the deliverable D1.1 to partner membranes. In each case the membranes were assembled with benchmark gas diffusion electrodes provided by JMFC.

OCV hold testing at 85 °C/13% RH was used as a first test of chemical/mechanical durability under the accelerated ageing conditions imposed by the high voltage, high temperature and low RH. Under these conditions the OCV of the MEA comprising the benchmark membrane decreased steadily up to 80 hours, and then more sharply to around 100 hours. At this point the OCV was unacceptably low, and the high hydrogen cross-over indicated permeability/perforation of the membrane. The un-reinforced C70-03SX membrane showed high permeability under these accelerated conditions; the OCV dropping below 800 mV after ca. 20 hours (Figure 3.2).

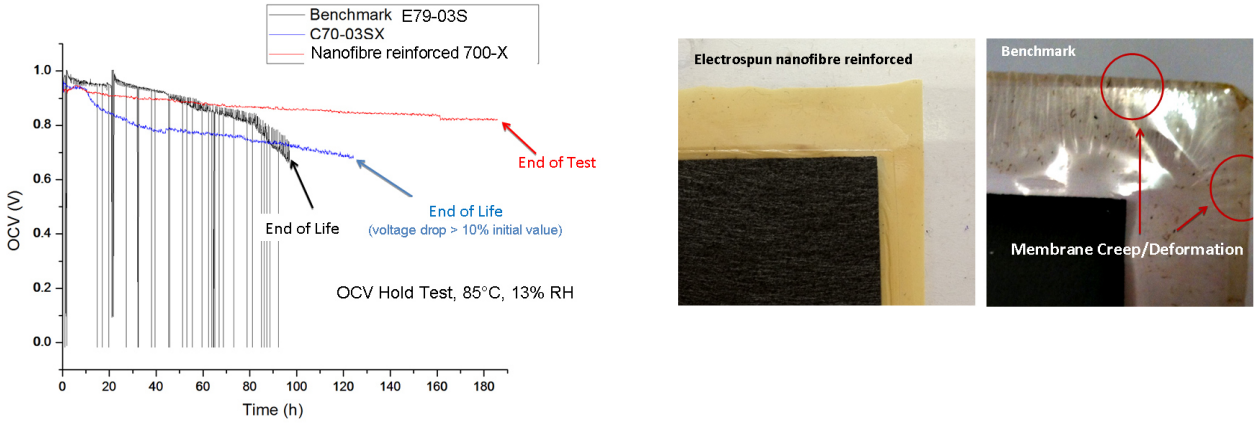


Figure 3.2: **OCV hold, 85 °C, 13% RH. Left Comparison of benchmark MEA, and MEAs comprising C70-03SX and electrospun nanofibre reinforced EW 700-X membranes 30 µm thickness. Right: MEAs after OCV hold testing with (left) electrospun nanofibre mat reinforced Aquivion EW 700 MEA and (right) benchmark membrane JMFC MEA.**

The results shown in Figure 3.3 were obtained using this protocol on the benchmark MEA, R79-03S (experimental ePTFE reinforced EW 790), C70-03SX, electrospun nanofibre reinforced 700-X and membranes prepared with 700-X filled with nano-ZrP and fluoroZrP. All membranes are of the same thickness (30 µm). The results obtained for the ZrP-containing membranes suggested that the degradation rate was similar for both MEAs and similar also to that of the benchmark MEA, although the increase in degradation rate at >150 h observed for the benchmark MEA was not seen with MEAs incorporating the zirconium phosphate particles. The nanofibre reinforcement appears to provide mechanical strength and integrity against the stresses caused by volumetric changes upon hydration and dehydration, resulting in greatly improved stability.

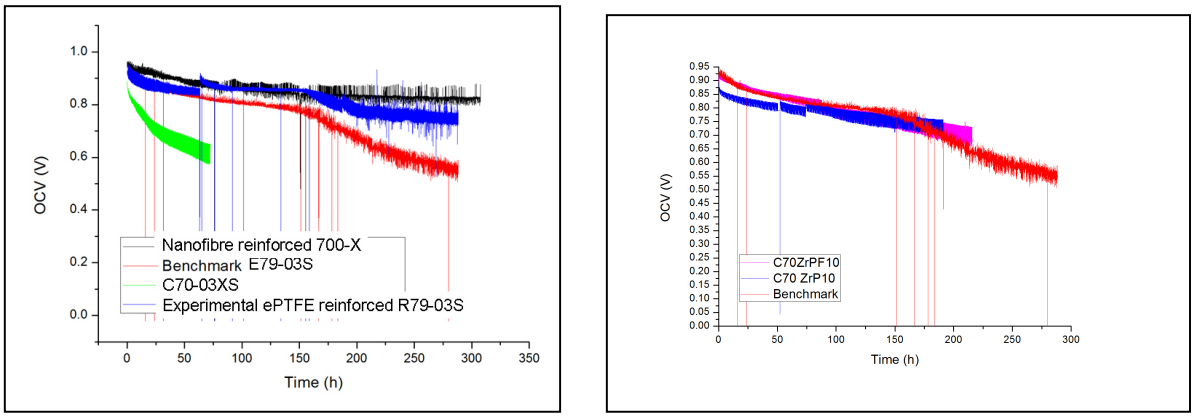


Figure 3.3: **Wet-dry cycling at OCV, 80 °C (10 mins dry gas, 10 mins 90 °C dewpoint). Left: Comparison of benchmark MEA and MEAs prepared with C70-03SX, electrospun nanofibre mat-reinforced 700-X, and an experimental ePTFE reinforced R79-03S membrane. Right: Comparison of benchmark MEA and MEAs prepared with C70ZrP10 and C70ZRPF10 membranes.**

Stack Testing

For the short stack testing at JMFC a fully automated testing station was used with a 9-cell 50 cm^2 active area screening stack. Larger active areas are typically desirable for membrane durability testing due to testing realistic stresses on the membranes, particularly at interfaces with seals/gaskets. Reduced membrane sizes can limit stresses due to reduced x-y movement from any membrane swelling and contraction. Due to the size of membranes available for evaluation, it was decided that a 50 cm^2 active area stack was appropriate.

A 1,000 hr durability protocol was developed by the project partners to simulate the practical load demands for a µ-CHP stationary system. The test protocol was designed to simulate an annual four-season cycle with protocols for winter, spring, summer and autumn (see WP1). All seasons were tested under 50 kPag inlet pressure and 30% inlet relative humidity at 80 °C stack temperature. The testing protocol subjected MEAs to long term constant load demands, changing load demands, and thermal cycles. The changing load demands led to different humidification within the MEA. The summer cycle was particularly stressing on the membranes due to thermal cycling between 80 °C and room temperature which led to dimensional changes causing stresses within the membrane particularly at interfaces with seals. A humidity cycle was also introduced during the transition from H_2/Air to N_2.

Between each 250 hour durability season a full 3-way performance polarisation was performed to obtain further information on the nature of any performance losses occurring on testing of the MEAs. These polarisations included OCV measurements, voltage as a function of operating current under H2/Air, H2/Helox (21% O2, balance helium) and H2/O2 and resistance measurements. These polarisations were performed at 80 °C stack temperature, 30% RH inlet and 50 kPag inlet.

Hydrogen takeover measurements were also taken between seasons (also known as the OCV decay test). This test involved supplying the anode with hydrogen but stopping air flow to the cathode. Hydrogen crossover reduces the MEA voltage and the rate of the voltage decay was used as an early indicator of impending membrane failure/thinning (resulting in higher hydrogen crossover).

Once MEAs were removed from the stack they were also subjected to individual crossover leak tests by imposing a differential pressure across the MEA and measuring the volume of gas crossover. The MEAs were also subjected to leak mapping where the MEAs were exposed to a differential pressure with water covering the ambient side of the MEA: the location of leaks was then visually observed.

The "4-seasons" durability protocol was scripted and tested in conjunction with the commissioning of the screening stack hardware. This extensive initial commissioning work was performed using internal JMFC MEAs for validation purposes. Excellent reproducibility across the entire stack was seen with no difference in performance observed related to MEA position in the stack. MEAs were then fabricated at JMFC to the specification defined previously in the project using the project benchmark membrane as well as the three down-selected project membranes containing the 700 EW crosslinked ionomer, an electrospun polymer reinforcement and the ZrP inorganic additive for stack durability testing.

Stack 1 testing

Due to the limitations of having a 9-cell short stack hardware and requiring to have a number of repeat MEAs with each membrane type in the stack to most reliably assess reproducibility, two 1,000 hour stack tests were performed to test the project benchmark membrane as well as the three down-selected new project membranes. The first stack test included the benchmark, un-reinforced EW 700 XL and the electrospun polymer reinforced EW700 XL membrane containing MEAs. It should be noted that the stack test showed good reproducibility between MEAs of the same type throughout the testing. The beginning of life (BOL) polarisation performance measured at the start of the protocol (Figure 3.4) showed both project membranes gave performances comparable to, or better than, the benchmark MEAs. The performance of the MEAs was consistent with that seen in the BOL single cell polarisation curves with the 700XL membranes showing the best performance due to the lower resistance obtained with the 700EW ionomer. Throughout the course of the winter hold all three MEA types showed a decrease in measured performance; all three decay rates were very similar and were therefore not thought to be related to the membrane. At the end of the winter hold the diagnostic polarisation curves clearly revealed the decrease was recoverable and it was therefore concluded that this reversible loss in performance was due to flooding of the catalyst layers and not due to any intrinsic irreversible decay issues emanating from the membranes. During the spring durability cycle, the potential was switched between 12-hour holds at 0.3 and 0.6 cm^{-2}. This was slightly more stressing to the membrane, but throughout the spring cycle no degradation of the membrane was seen, but again a constant slow decay in observed performance throughout the protocol. The diagnostics again showed most of the performance loss was recoverable and thus again likely to be due to catalyst layer effects.

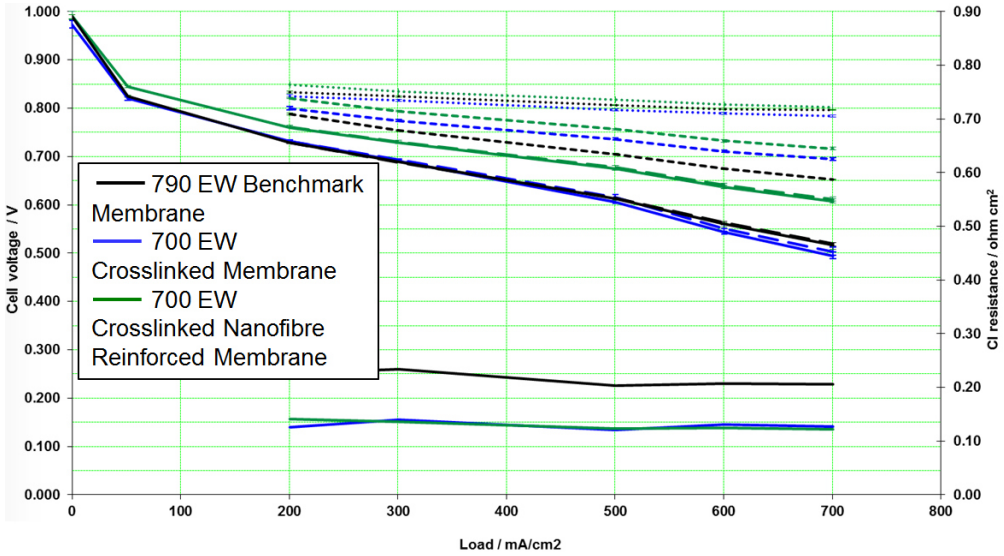


Figure 3.4: **Average Beginning of Life Polarisation Curves for Stack 1 MEAs – 50 kPa, 80 °C, 30% RH**

The summer durability cycle, which included on/off cycling inducing both temperature and humidity cycles , was expected to be the most stressing on the membranes due to the inherent swelling and contracting of the membranes under these conditions. At the start of the summer cycle the performance was the same as that recorded during the spring cycle with the performance of the 700XL membrane outperforming the benchmark and electrospun nanofibre reinforced membrane, due to low resistance and improved water management respectively, at 0.3 A cm^{-2} and the benchmark and nanofibre reinforced MEAs showing very similar air performance at 0.6 A cm^{-2}. During the summer cycle the benchmark and unreinforced 700EW membrane samples were observed to decay at a much greater rate than the nanofibre reinforced membrane. This resulted in the nanofibre reinforced membrane now being in the highest performing MEA by the end of the summer cycling, as a result of its much lower decay over this cycle.

At the end of the summer cycle the benchmark and 700EW membrane MEAs revealed that high hydrogen crossovers detected electrochemically in the diagnostic testing. At this point the stack was disassembled due to the poor performance of the two unreinforced MEA types and each MEA was transferred into a single cell where the OCV and hydrogen crossover measurements were made individually. From these tests it was clear that there was a large hydrogen crossover and consequently low OCV for all of the non-reinforced MEAs; highly illustrative of membrane failure. However, no significant hydrogen crossover was measured for the nanofibre reinforced MEAs. The OCV and hydrogen crossover rates are plotted in Figure 3.5.

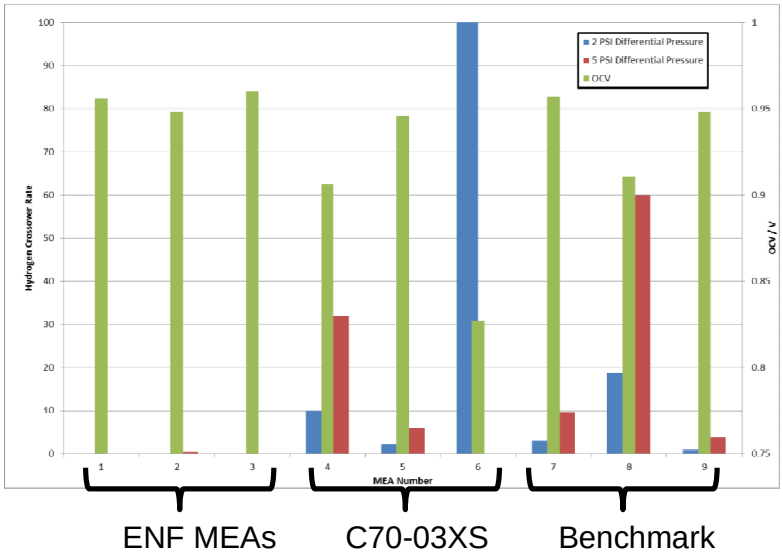


Figure 3.5: **OCV (green) and hydrogen crossover rates (blue and red at 2 and 5 PSI differential pressure respectively) after the summer durability cycle for electrospun nanofibre (ENF) reinforced 700-X, C70-03XS and benchmark membrane MEAs.**

At the end of the final autumn cycle the electrospun reinforced membrane still showed no significant sign of any intrinsic membrane degradation, with no hydrogen crossover or decay in OCV detected. It was therefore decided to include these tested nanofibre reinforced membrane MEAs in the second stack test along with some fresh nanofibre reinforced MEAs and the ZrP containing composite membrane samples to get a comparison of the ZrP membrane samples with the electrospun nanofibre reinforced membrane, as well as seeing how the nanofibre reinforced membrane performed after running through two full 1,000 hrs '4-seasons' protocols.

Stack 2 testing

After the winter hold was completed the ZrP MEAs fabricated at JMFC were removed as they had failed to perform and were replaced with ZrP CCMs from Solvay, which had performed adequately in their earlier single cell testing. The BOL performance of these MEAs was very different to the other MEAs tested, with a poor OCV and low current density performance but with the performance being more comparable at the higher current densities. The ZrP MEAs did, however, have a very low resistance and with further optimisation it was thought likely that a membrane could be made with improved performance at low current densities. Even at the BOL the ZrP membrane MEAs showed a measureable hydrogen crossover rate, strongly suggesting that the membranes were already permeable to hydrogen at the start of the testing.

By the end of the spring cycle of stack test 2, the three ZrP MEAs had failed due to membrane failure as a result of excessive hydrogen crossover. This was unexpected, as the spring cycling had previously been seen to be non-stressing on the membranes and suggested that the ZrP membranes were compromised from at the start of the testing. Further optimisation will be needed in order to produce a non-permeable ZrP composite membrane and to then properly evaluate its long-term durability.

At the end of the summer cycling the MEAs containing the electrospun nanofibre reinforced membrane remained functional in the stack, and still showed no signs of intrinsic membrane degradation. At this point it was decided that an 'accelerated' summer cycle should be run on the remaining MEAs, rather than the scheduled autumn cycle, to stress these membranes as much as possible in the final period of testing. To accomplish this, the number of startup – shutdown cycles run per day was increased from one to three. This increase in temperature and humidity cycling was expected to significantly stress the membranes of the

remaining MEAs left in the stack. This new protocol was run for approximately 350 hours and it was quite an achievement to record that there was still no significant decay in performance, including for one of the original electrospun reinforced MEAs, which by now had seen over 2,000 hours of testing. The data recorded at the BOL, after 1,000 hours of testing and after 2,000 hours of testing are plotted in Figure 3.6.

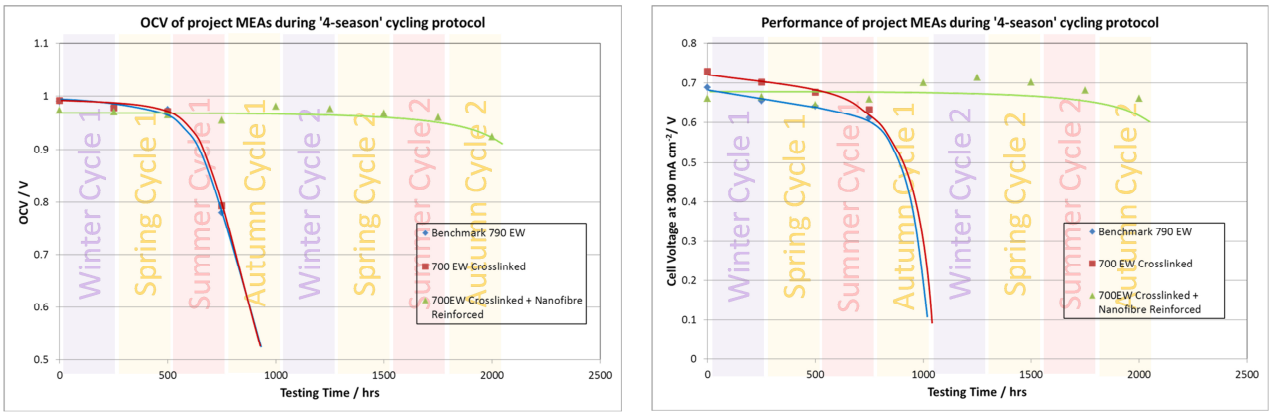


Figure 3.6: **Short stack durability test showing OCV (left) and Performance (right) throughout the project defined "4-season" durability protocol. Data for the project benchmark, 700EW cross-linked and 700EW cross-linked + nanofibre reinforcement plotted (in blue, red and green respectively). Trend lines added to guide the eye.**

It can be seen that there is barely any performance decay for the nanofibre reinforced MEAs over the lifetime of the test and this degradation was of course clearly much less than seen for the other membrane types - all of which failed much earlier. It should be noted here that the error bars marked on these polarisation curves do show greater variation in performance the longer the test went on, with some MEAs improving performance after 1,000 hours, likely due to the conditioning effects. Overall the resistance of the membranes remained unaltered throughout the 2,000 hours testing. It can also be seen that at a typical operating current density for the stationary application, of 0.3 A cm^{-2}, the decay in cell voltage after 2,000 hours was no more than about 3% of the original cell voltage, despite increasing the severity of the test protocol in the final test cycle.

CONCLUSIONS

Over the course of the short stack testing it was seen that the low 700EW ionomer gave the predicted resistance benefits allowing the incorporation of the electrospun reinforcement with no loss in performance when compared to the project benchmark MEAs fabricated from an unreinforced membrane of the higher equivalent weight 790EW ionomer. The electrospun nanofibre reinforced MEAs showed a great enhancement in durability, particularly through the most stressful summer on/off cycling protocol, with no membrane degradation observed for these MEAs in contrast to the non-mechanically reinforced membranes which all failed during this procedure.

The electrospun nanofibre reinforced MEA performance at the beginning of life could be improved with optimisation of the reinforcement, mainly by enabling a more rapid (and acceptable) conditioning process in contrast to the protocol that had to be employed, which involved extensive and prolonged cathode reduction cycles to fully hydrate the MEA.

The ZrP composite membranes showed a greatly improved resistance over all other project membranes, but the overall performance was compromised, as the membranes were too permeable, even at the start of testing. Further work on incorporating this kind of additive without inducing the observed permeability issues

is needed. Once work to enable the incorporation of the ZrP additive is complete it is possible the benefit of the very low resistance in combination with the durability benefits of the electrospun reinforcement could provide a hybrid route to an extremely high performing and durable membrane.

Throughout the stack testing, issues with catalyst layer flooding were seen. Hence, work to improve the catalyst layer structures for operation under the selected conditions is required. The inclusion of the low EW ionomer in the catalyst layer and adjustment of ionomer levels should lead to both enhanced performance and reversible performance losses not associated with membrane degradation being minimised.

However, it is quite significant that the electrospun polymer nanofibre reinforcement clearly exhibited the ability to markedly enhance the durability of membranes fabricated from the new low 700EW ionomer, and survived over 2,000 hours of testing against a range of testing protocols, including some aggressive accelerated testing, without any significant intrinsic decay, and also comfortably achieved the project objective of less than 10% performance decay at a practical operating current density for the stationary application.

4. Main Dissemination Activities, Potential Impact and Exploitation of Results

4.1 Main Dissemination Activities during the Project Lifetime

Dissemination channels have included a dedicated project website, presentations at national and international conferences, and publications in international scientific journals.

Dedicated Project Website

The dedicated project website was one of the main dissemination channels towards the public and the broad scientific community. A first version of the website *www.maestro-fuelcells.eu* was released at month 3 from the project start. The website has been fully operational since 28th April 2011.
Note that the project website also includes a link to a "*Members Area*", i.e. an area to which access is restricted to authorised users.
The public section features:

- General description of the project and its objectives
- Information about the consortium and links to partners' websites
- Public documents, such as public deliverables, publications (open-access provided), project posters
- Contact information

The web site will be kept open and updated with information on publications and other project output until a year after the project end date, when the situation will be reassessed with the MAESTRO partners.

Participation in International Conferences

The consortium has attended prominent international conferences, workshops and symposia. All presentations have followed the agreed dissemination protocol, i.e. abstracts and publications have been cleared with all partners prior to disclosure.

1. **Materials Research Society Spring Meeting, Symposium "Protons in Solids" San Francisco, April 2011**
   - *Proton conducting materials for intermediate temperature proton exchange membrane fuel cells*, D. J. Jones, J. Rozière, CNRS Montpellier, France
2. **ECS, Boston, USA, 9-14 October 2011**
   - *On Electrospinning of PFSA: A Comparison between Long and Short-Side Chain Ionomers*, S. Subianto, S.Cavaliere, D. J. Jones, J. Rozière, Institut Charles Gerhardt, Université Montpellier 2, Montpellier, France
3. **TICME 2011 - Trento, Italy, 12-14 December 2011**
   - *Aquivion/zirconium phosphate nanocomposite membranes: conductivity and mechanical properties*, M. Casciola[1], P. Cojocaru[2], A. Donnadio[1], L. Merlo[2], M. Pica[1], [1]Chemistry Department, Perugia, [2]SOLVAY SOLEXIS, Bollate, Milan, Italy
4. **E-MRS Spring Meeting, Strasbourg, France, 15-17 May 2012**
   - *Reactive Electrospinning of Zirconium Phosphate Nanofibres for Fuel Cell Membrane Applications*, S. Subianto[1], S. Cavaliere[1], A. Donnadio[2], M. Pica[2], M. Casciola[2], D. Jones[1], J. Rozière[1], [1]Equipe AIME, Institute Charles Gerhardt, Université Montpellier 2, France, [2]Dipartimento di Chimica, Universita di Perugia, Italy
5. **95th Canadian Chemistry Conference, Symposium "Polymers for Fuel Cells and Batteries" Calgary, May 2012**
   - *Tailored polymer materials for fuel cells,* D. J. Jones, CNRS Montpellier, France

6. **Solid State Proton Conductors Conference - SSPC16 conference, Grenoble, France, 10-14 September 2012**
   - *Highly proton conductive Aquivion/zirconium phosphate composite membranes with improved mechanical properties,* M. Casciola[1], P. Cojocaru[2], A. Donnadio[1,3], L. Merlo[2], M. Pica[1], [1]Perugia University, Perugia (Italy) [2] SOLVAY SOLEXIS, Bollate, MI, Italy, [3]National Research Council, Institute for Membrane Technology (ITM–CNR), Rende CS, Italy

7. **223rd ECS meeting, Toronto, Canada, 12-17 May 2013**
   - *Hybrid Proton Conducting Membranes based on Short Side Chain Perfluorosulfonic Acids and Organically modified Zirconium Phosphate, A. Donnadio[1],* M. Pica[1], S. Subianto[2], D. Jones[2], P; Cojocaru[3] and M. Casciola[1], [1]Università degli Studi di Perugia, Italy- [2] CNRS Montpellier, France - [3]Solvay Solexis Spa, Bollate, (Mi) Italy
   - *Nanofibre-Reinforced Composite Proton Exchange Membranes for Fuel Cell Applications,* S. Subianto[1], S. Cavaliere[1], D. Jones[1], Luca Merlo[2], and Jacques Rozière[1], [1] CNRS Montpellier, France - [2]Solvay Solexis Spa, Bollate, Italy
   - *Reactive Coaxial Electrospinning of ZrP/ZrO2 Nanofibres,* S. Subianto[1]*, A. Donnadio[2],* M. Pica[2]*,* S. Cavaliere[1]*,* M. Casciola[2]*,* D. Jones[1]*, and* Jacques Rozière[1], [1]CNRS Montpellier - [2]Università degli Studi di Perugia, Italy

8. **4th European EFCF and H2 Forum 2013, Lucerne, Switzerland, 2 - 5 July 2013**
   - *Improved Mechanical Properties of Low Equivalent Weight Short Side Chain PFSA,* [1]D. Jones, S. Subianto, J. Rozière, S. Cavaliere, Y. Nedellec, [2] P. Cojocaru and L. Merlo, [3]G. Hards and S. Burton, [4] M. Casciola, M. Pica and A. Donnadio, [1] CNRS Montpellier, France - [2] Solvay Speciality Polymers, Bollate, Italy - [3]Johnson Matthey Fuel Cells Ltd., Swindon, U.K. - [4]Università di Perugia, Italy
   - *Zirconium phosphate reinforced Aquivion membranes,* M. Casciola[1], P. Cojocaru[2], A. Donnadio[1], S. Giancola[1], L. Merlo[2], Y. Nedellec[3], M. Pica[1], S. Subianto[3]**,** [1] Chemistry Department, Perugia University, Perugia, Italy - [2] Solvay Speciality Polymers, Bollate, MI, Italy - [3] CNRS Montpellier, France

9. **64th International Society of Electrochemistry Annual Meeting, Querétaro, Mexico, 7-12th September 2013**
   - *Low Equivalent Weight Short Side Chain PFSA with Improved Mechanical Properties*, [1]D. Jones, S. Subianto, J. Rozière, S. Cavaliere, Y. Nedellec, [2] P. Cojocaru and L. Merlo, [3]G. Hards and S. Burton, [4] M. Casciola, M. Pica and A. Donnadio, CNRS Montpellier*, France - [2] Solvay Speciality Polymers, Bollate, Italy - [3]Johnson Matthey Fuel Cells Ltd, Swindon, U.K. - [4]Università di Perugia, Italy*

PRESENTATIONS AT FCH-JU REVIEW DAYS AND WORKSHOPS

10. **Fuel Cells & Hydrogen Joint Undertaking Review Days, Brussels, Belgium, 22-23 November 2011**
    - Oral presentation of the MAESTRO project, D. Jones, CNRS, France

11. **Materials Issues Workshop, Grenoble, France, 26-27 March 2012**
    - Oral presentation of the MAESTRO project, D. Jones, CNRS, France

12. **FCH-JU review days, Brussels, 28-29 November 2012**
    - Oral presentation of the MAESTRO project, D. Jones, CNRS, France

13. **FCH-JU review days, Brussels, 11-12 November 2013**
    - Oral presentation of the MAESTRO project, D. Jones, CNRS, France

JOURNAL PUBLICATIONS

The Consortium has published a number of individual or jointly authored publications to international scientific journals.

1. **Effect of Side Chain Length on the Electrospinning of Perfluorosulfonic Acid Ionomers**, S. Subianto, S. Cavaliere, D. J. Jones and J. Roziere, CNRS, France –*Journal of Polymer Science – Part A: Polymer Chemistry, Journal of Polymer Science Part A: Polymer Chemistry, Volume 51, Issue 1, pages 118–128, 2013* DOI: 10.1002/pola.26286
2. **Physical and chemical modification routes leading to improved mechanical properties of perfluorosulfonic acid membranes for PEM fuel cells**, S. Subianto, Monica Pica, M. Casciola, P. Cojocaru, L. Merlo, D. J. Jones, G. Hards, CNRS, Montpellier (France), University of Perugia, Perugia (Italy), Solvay Solexis, Bollate (MI, Italy), Johnson Matthey Fuel Cells, Sonning Common, Reading (UK) – *Journal of Power Sources, Volume 233, 2013, Pages 216–230* DOI: 10.1016/j.jpowsour.2012.12.121
3. **Aquivion 830 and its composite membranes with nanosized zirconium phosphate: hydration, mechanical properties and proton conductivity,** M. Pica, A. Donnadio, M. Casciola, P. Cojocaru and L. Merlo, UNIPG, Italy and Solvay Solexis - J. Mater. Chem., 2012,22, 24902-24908 - DOI: 10.1039/C2JM34958B
4. **Layered zirconium alkylphosphates: suitable materials for novel PFSA composite membranes with improved proton conductivity and mechanical stability,** A. Donnadio, M. Pica, D. Capitani, V. Bianchi and M. Casciola, University of Perugia, Perugia (Italy) – *Journal of Membrane Science*, in press – DOI: 10.1016/j.memsci.2014.03.021

EDUCATION ACTIONS & OUTREACH ACTIVITIES

Two education actions towards non-specialist scientists (general public and schools) have been undertaken by the consortium. Their purpose was to increase the understanding of the implications of peaked oil reserves and the need for alternative energy sources, the role played by use of hydrogen for energy storage and as a fuel, and the role of fuel cells for residential and other small stationary applications.

- **EDUCATION ACTIONS**

1. **Lecture notes on Solid State Chemistry – University of Perugia, Perugia, Italy –15-16-18 May 2013 – 15 students on average**

   Le celle a combustibile e la conversione dell'energia chimica in energia elettrica, M. Casciola, University of Perugia, Perugia (Italy)

2. **Masters in Energy –** (*http://www.master-energie.univ-montp2.fr*), **Montpellier, France, October-March 2011-2012-2013.**

   Lecture course on Fuel Cells and Hydrogen Generation Technologies– J. Rozière, CNRS, Montpellier (France)

- **OUTREACH ACTIVITIES**

1. **U3A - The University Of The Third Age** (*http://www.u3a.org.uk/*) - **11th June 2012 – Mid-Wales, UK**
   Fuel cells explained – Sarah Burton, JMFC, UK. Public lecture to an audience of ~150-200 people for 1 hr with a question and answer session that followed.

DISSEMINATION SUPPORT MATERIALS

Various supports were developed to ensure a visual identity for the MAESTRO project. These included a project logo, and a powerpoint presentation template, used for project presentations at conferences, workshops, progress meetings etc.

4.2 FUTURE DISSEMINATION PLANS

The consortium will be engaged in conducting further activities for promoting and disseminating the project results. The following measures are planned to follow up the project:

MAESTRO WEBSITE

The MAESTRO website will first of all be kept as an information source of the activities performed in the project. The website will also continue to receive and publish papers online related to the project. The website will be updated to reflect the current status of the project as finished. Reports and final results will be clearly communicated through relevant news items and reports.

JOURNAL PUBLICATIONS

Future academic articles and reports will be produced. This is an important component in the continuation of communicating the results from the research undertaken. The members of the project will target specifically relevant well-recognized academic journals for the future publications. The following publications are accepted for publication:

1. **Reactive Coaxial Electrospinning of ZrP/ZrO_2 Nanofibres**, S. Subianto[1], A. Donnadio[2], S. Cavaliere[1], M. Pica[2], M. Casciola[2], D. J. Jones[1], and J. Rozière[1], [1]CNRS Montpellier, France, [2]Università di Perugia, Italy *accepted for publication* J. Mater. Chem. A.
2. **Promising Short-Side-Chain Perfluorosulfonic Acid Composite Membranes based on Fluoroalkyl Zirconium Phosphate for PEMFC Application**, A. Donnadio[1], M. Pica[1], S. Subianto[2], D. J. Jones[2], P. Cojocaru[3] and M. Casciola[1], [1]Università di Perugia, Italy, [2]CNRS Montpellier, France, [3]Solvay Specialty Polymers, Italy *accepted for publication in* ChemSusChem.
3. **Zirconium phosphate reinforced short side chain perflurosulfonic acid membranes for medium temperature proton exchange membrane fuel cell application,** M. Casciola[1], P. Cojocaru[2], A. Donnadio[1], S. Giancola[1], L. Merlo[2], Y. Nedellec[3], M. Pica[1] and S. Subianto[3], [1]Università di Perugia, Italy, [2]Solvay Specialty Polymers, Italy, [3]CNRS Montpellier, France, *accepted for publication in* J. Power Sources.

CONFERENCE PRESENTATIONS

MAESTRO partners will continue to disseminate the project results at conferences, in particular once IP has been protected. The results shall continue to be conveyed through lectures and participation in relevant conferences, including:

1. **Fuel Cells 2014 Science & Technology conference, A Grove Fuel Cell Event, Amsterdam, 3-4 April 2014**
   - *Stack Testing of MEAs Incorporating Low Equivalent Weight Aquivion™ Membranes*. J. Blake[1], S. Burton[1], G. Hards[1], W. Turner[1], D. Jones[2], M. Casciola[3], P. Cojocaru[4]. Johnson Matthey Fuel Cells, United Kingdom[1], [2]Institut Charles Gerhardt, Université Montpellier 2, Montpellier, France, Università di Perugia, Italy[3], Solvay Specialty Polymers, Bollate, Italy[4].
   - *Proton conducting membranes made of a short side chain perfluorosulfonic acid mechanically reinforced with organically modified zirconium phosphate*, [1]A. Donnadio, [1]M. Pica, [2]S. Subianto, [2]D. J. Jones, [3]P. Cojocaru, [1]M. Casciola; [1]Università di Perugia, Italy, [2]Institut Charles Gerhardt, Université Montpellier 2, Montpellier, France, [3]SOLVAY Specialty Polymers, Bollate (MI), Italy
   - *Nanofibre-Reinforced Composite Proton Exchange Membranes With Enhanced Durability for Fuel Cell Applications,* S. Subianto[1], S. Cavaliere[1], D. Jones, L. Merlo[2], and J. Rozière[1], [1]Institut Charles Gerhardt, Université Montpellier 2, Montpellier, France, [2]SOLVAY Specialty Polymers, Bollate (MI), Italy

– *Reactive Coaxial Electrospinning of ZrP/ZrO2 Nanofibres,* Surya Subianto[1], Anna Donnadio[2], Monica Pica[2], S. Cavaliere[1], M. Casciola[2], and D. J. Jones[1], and J. Rozière[1] , [1]Institut Charles Gerhardt, Université Montpellier 2, Montpellier, France, [2]Università di Perugia, Italy

2. **E-MRS Spring Meeting, Lille, France, 26-30 May 2014**
   – *Increased Durability Membranes for Stationary Applications***,** S. Subianto[1], S. Cavaliere[1], D. Jones[1], J. Rozière[1], S. Burton[2], J. Blake[2], G. Hards[2], L. Merlo[3], 1. CNRS, Montpellier, France. 2. Johnson Matthey Fuel Cells Ltd., Swindon, UK 3. Solvay Speciality Polymers Italy S.p.A., Bollate, Milan, Italy.

3. **Gordon Conference on Fuel Cells, Providence, USA 3-8 August 2014**
   - Improved membrane materials for medium and high temperature PEMFC, D. J. Jones, CNRS Montpellier
   -

4.3 POTENTIAL IMPACT AND EXPLOITATION OF FOREGROUND

POTENTIAL IMPACT

Fuel cell technologies represent a tremendous opportunity for Europe for improving the quality of the air, reducing the emissions that contribute to climate change, playing a significant role in meeting the 2020 targets, and contributing to the long-term vision for 2050 towards decarbonisation. PEM fuel cell technology is versatile and has potential applications in portable power, transportation and stationary/distributed power. In particular the use of PEMFCs as stationary CHP power applications in different market sectors like community and residential use is very attractive. The presence of stationary commercial and residential power reduces energy losses through transmission lines and offers large possibility for modularity. Besides cost, a crucial problem to be solved to allow large commercialisation of CHP systems is the fuel cell lifetime, which has been specified by industry targets as five years on-load operation.

The development of new proton exchange membranes, endowed with improved mechanical properties and based on known, highly proton conducting ionomer material, is fundamentally important with regard to achieving the lifetime requirements for cell and stack. The combination of long lifetime, arising from excellent chemical stability and enhanced mechanical properties, with sufficiently high fuel cell operating temperature, and will contribute to **improve the fuel cell performance** and systems efficiency, and to **reducing costs** of the stationary power generation system thus **making Europe competitive** in this market area.

The availability of such membranes is also expected to have positive impact on sectors other than stationary power generation such as, for example, the **transportation sector**. Thin and robust membranes are required for cells for automotive fuel cell stacks, for low area resistance and to favour water transport properties even when operated at low relative humidity. MAESTRO membranes undoubtedly have potential impact in this application area.

STEPS NEEDED TO BRING ABOUT THESE IMPACTS

It has been shown that the technology developed in the MAESTRO project can be introduced into existing PEMFC stack designs.

Further steps required to bring about the expected impact therefore are therefore limited to:

1. Further scale-up of materials components.
2. Further development of catalyst coated membranes and MEAs
3. Incorporation of the novel MEAs in stacks
4. Use of these stacks in PEMFC system architectures by the producers of stationary power production units and automotive OEMs

POTENTIAL IMPACT FOR INDUSTRIAL PARTNERS OF MAESTRO

JMFC: JMFC's core business is in the development and manufacture of membrane electrode assemblies (MEAs) for PEM fuel cells, for a range of applications, and is one of the world's leading manufacturers of these key fuel cell components. JMFC works closely with developers of ionomers and membranes to secure the best possible materials for its MEA products. The application of low equivalent weight perfluorosulphonic acid (PFSA) ionomers is of vital importance to open up the practical operation of PEMFCs to hotter and drier conditions (such as are found in typical automotive and some stationary applications), as the low EW ionomers can retain and diffuse water more readily than higher EW materials. However, lower EW ionomers can also swell and distort quite dramatically in operation and therefore need to be both chemically and mechanically stabilised to provide a robust membrane with the best possible durability and thus lifetime. In MAESTRO JMFC has gained valuable experience on the fabrication and evaluation of MEAs comprising membranes based on the new low equivalent weight (EW700) Solvay Aquivion ionomers.

The membranes have included the un-reinforced pure EW700 cross-linked ionomer (thus chemically stabilised) from Solvay, a mechanically reinforced membrane variant of the same chemically-stabilised ionomer made from electrospun nanofibres at CNRS and a composite membrane made from adding ZrP nanoparticles to the ionomer from University of Perugia. Single cell testing showed the beginning-of-life (BOL) performance benefits obtained from the low EW ionomer compared to the project benchmark membrane of Aquivion EW790, especially under the hotter, drier conditions. The intrinsic performance benefits of the lower EW ionomer meant that the performances obtainable from the mechanically reinforced variants were not compromised compared to the non-reinforced benchmark membrane. Durability testing in a short stack, involving exposure of the MEA to conditions it would typically see in a one-year operation in a micro-CHP application, clearly showed an impressive durability from the reinforced EW700 membrane, with barely any degradation being observed.

The stack test clearly highlighted the need for mechanical stabilisation of the low EW ionomer (as the non-reinforced variant suffered from excessive hydrogen cross-over due to membrane leakages, following the aggressive repeated on-off cycles of the summer seasonal phase of the testing), but also showed that it could be successfully accomplished. MAESTRO has successfully provided much confidence to JMFC that long lifetimes will be possible from the low EW ionomer materials developed in the project. JMFC wishes to continue the interaction with Solvay to further optimise and scale up the 700EW Aquivion ionomer, and with the other partners to fully explore the benefits of the novel reinforcing technologies, and will be exploring the options to ensure this can be made a reality.

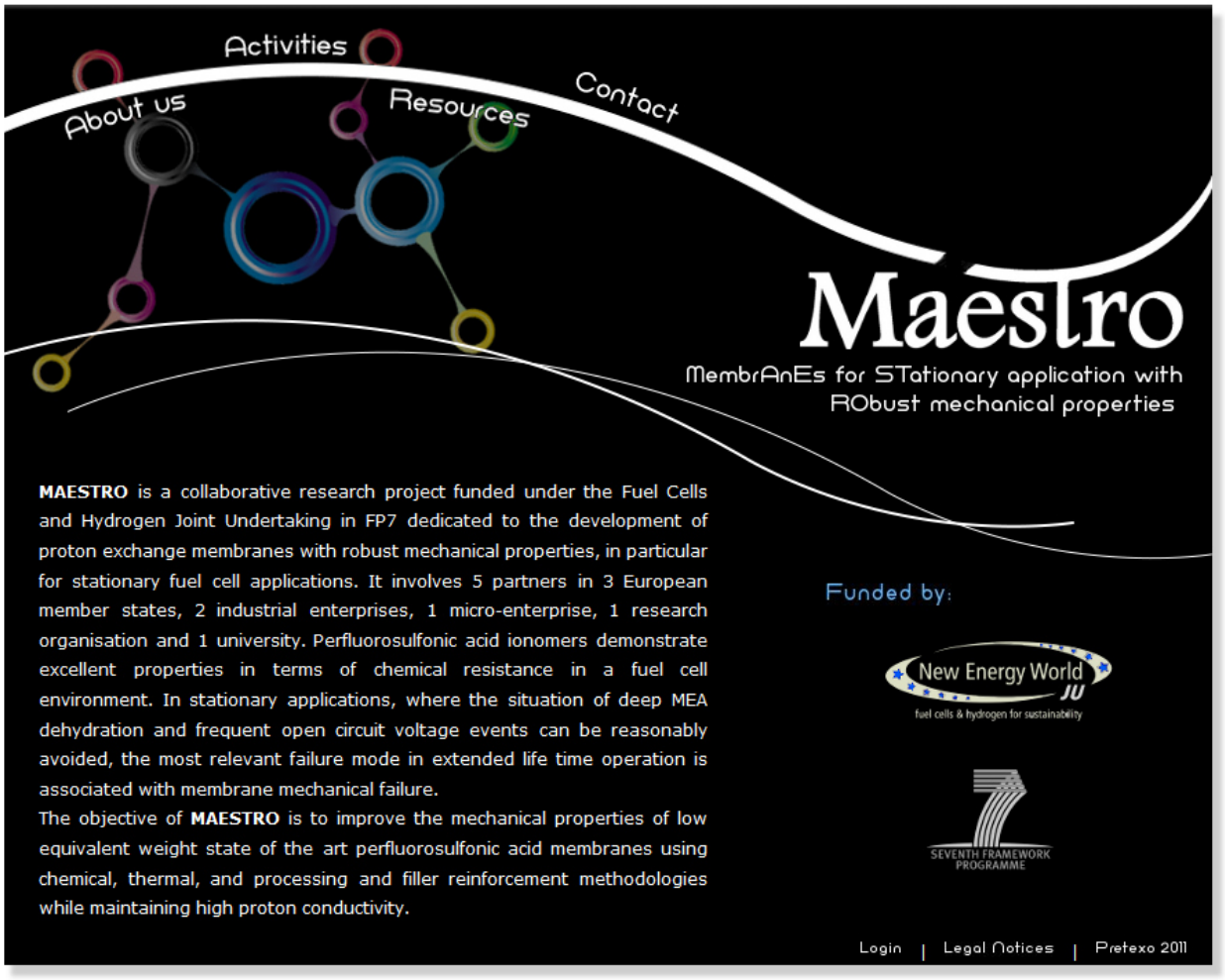
Solvay Specialty Polymers: No impediments are foreseen to the industrial scaling of the processes selected in MAESTRO. It is a fact that different selected solutions have different industrial maturity, as polymerization process and casting process of dispersions. The production of large quantities of Aquivion® ionomer and dispersion in the grade selected for MAESTRO (EW 700g/eq, branched version) is already industrial in Solvay Specialty Polymers. Today, the scaling of membrane casting process may be implemented in two different ways. The first is the possibility to adapt a pilot casting line already present in Bollate R&D Centre, and the second is to seek an appropriate toll manufacturer for ionomer dispersion casting. This second solution has the advantage of the possibility of confining this production step in a controlled/clean environment, which is very important for the membrane quality. The solvent mixture adopted for Aquivion® membrane casting comprises no toxic materials. One solvent is flammable and shall be treated according to proper precautions. The shelf life of Aquivion® dispersion is usually longer than 2 years. It is anyway clear that there are no evident showstoppers to the industrial scaling of the developed solutions and, to the best of the knowledge of the partners, no huge investment is required to run these processes and no IP barrier exists today.

EXPLOITATION OF FOREGROUND: MAESTRO has led to four exploitable foregrounds.

EXPLOITATION OF FOREGROUND IN FUTURE COLLABORATION BETWEEN PARTNERS

Discussions have been initiated on how to use best the results of this very successful project in a next stage of development dedicated principally to pilot level scale-up, materials and processing optimisation, cell and stack development, for the automotive sector.

5. Address of the Project Public Website



http://www.maestro-fuelcells.eu

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