AQUIVION™ IONOMER MEMBRANE

AQUIVION™
Low-EW PFSA Membranes
Product Description

Solvay Solexis' Aquivion™ ionomer membranes are melt-extruded products based on the unique Short Side Chain (SSC) copolymer of Tetrafluoroethylene and a Sulfonyl Fluoride Vinyl Ether (SFVE) $F_2C=CF-O-CF_2CF_2-SO_2F$ of low molecular weight produced by Solvay Solexis.
Aquivion™ ionomer membranes are available in the acid form and feature lower Equivalent Weight (EW) than most competitive proton exchange membranes. The SSC copolymer allows higher crystallinity, improved mechanical properties and better proton conductivity.

Typical applications of Aquivion™ membranes are PEM fuel cells, water electrolyzers, H_2 separators, pervaporation or gas humidification systems. Membrane grades are presently subdivided in two families E87 and E79 which exhibit different EW of 870 or 790 g/eq SO_3H. The value is controlled systematically according to an internal titration procedure. Nominal thicknesses are 30 or 50 µm - with E87 also available at 100. Others may be available upon request.
For some applications, it can be recommendable to use chemically stabilized membranes (recognizable through their S-suffix). E79 grades are exclusively available in their chemically stabilized form.

Type	EW	Thickness		Weight	
		µm	mils	g/m²	10^{-3} lb/ft²
E87-03	870 ± 20	30 ± 3	1.2 ± 0.15	62 ± 7	12.7 ± 1.3
E87-05	870 ± 20	50 ± 5	2.0 ± 0.21	103 ± 11	21.2 ± 2.2
E87-10	870 ± 20	100 ± 10	4.0 ± 0.41	206 ± 21	42.4 ± 4.3
E79-03S	790 ± 20	30 ± 3	1.2 ± 0.15	62 ± 7	12.7 ± 1.3
E79-05S	790 ± 20	50 ± 5	2.0 ± 0.21	103 ± 11	21.2 ± 2.2

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HEALTH SAFETY AND ENVIRONMENT

Aquivion™ membranes are not harmful if used and handled according to standard processing procedures (see for example the "Guide to the Safe Handling of Fluoropolymer Resins" issued by the Society of the Plastics Industry). If handled inappropriately, membranes may release harmful toxic chemicals. Please refer to the Material Safety Data Sheets for more information on handling and safety.

PACKAGING, SHIPMENT AND STORAGE

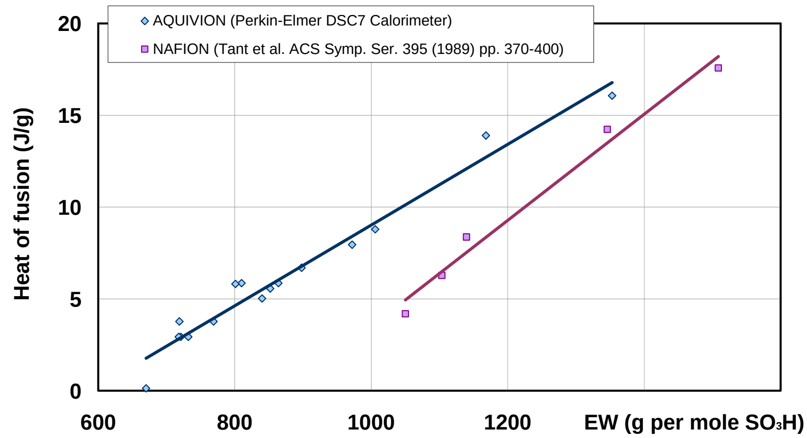
The membranes are usually available in sheets of customized formats or rolls in various lengths (dimensions are based on dry product conditioned at 23 °C and 50 % Relative Humidity). They are sealed in an inert environment with a multilayer protection film before packaging inside a shock-protected cardboard box. It is recommended to store the product in a clean, controlled humidity environment and protected from direct sun light or other sources of heat.

MOLECULAR STRUCTURE

The Aquivion™ ionomer is a copolymer produced from tetrafluoroethylene, C_2F_4, and Ethanesulfonyl fluoride,1,1,2,2-tetrafluoro-2-[(trifluoroethenyl)-oxy], C_2F_3-O-$(CF_2)_2$-SO_2F. The section between the ether bridge and the functional unit SO_2F is typically called the “side chain”. The characteristic of Aquivion™ to have a very short and light side chain incurs a number of advantageous factors for the end user as laid out in the following sections. The comonomer content varies between 14 and 19 %-mole in the EW range of 700-900.

DIFFERENTIAL SCANNING CALORIMETRY

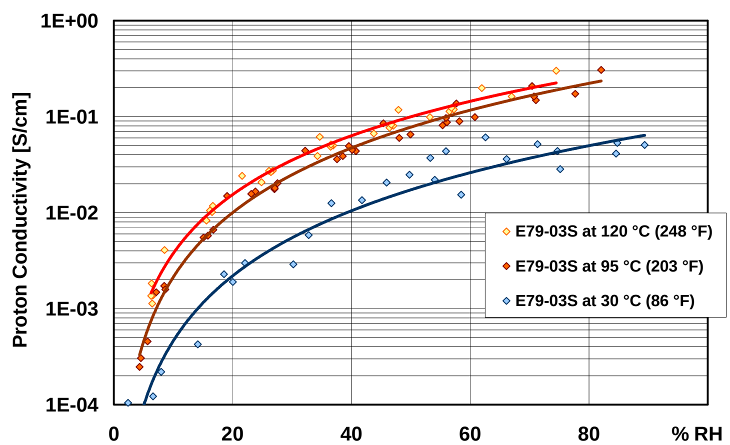
Aquivion™ ionomer membranes exhibit a higher level of crystallinity compared to PFSA ionomers with longer side chains. This is observed through comparison of the heat of fusion determined from DSC analyses. Additionally, Solvay Solexis Ionomer retains crystallinity down to approximately EW 600.



PROTON CONDUCTIVITY

High proton conductivity not only at ambient conditions but especially with hot gaseous reactants of low relative humidity (RH) is an essential element of Aquivion™'s characteristics. Though conductivity declines with decreasing gas humidity, the membranes maintain higher absolute values compared to other commercial materials. This is critical during the high T / low RH operation of fuel cells or for construction of energy efficient electrolyzers.

The following graphs show ex-situ measurements of proton conductivity of E87-05 and E79-03S at three different temperatures, generated via the pressure-decay method in a closed chamber. The setup is a four-probe in-plane measurement.



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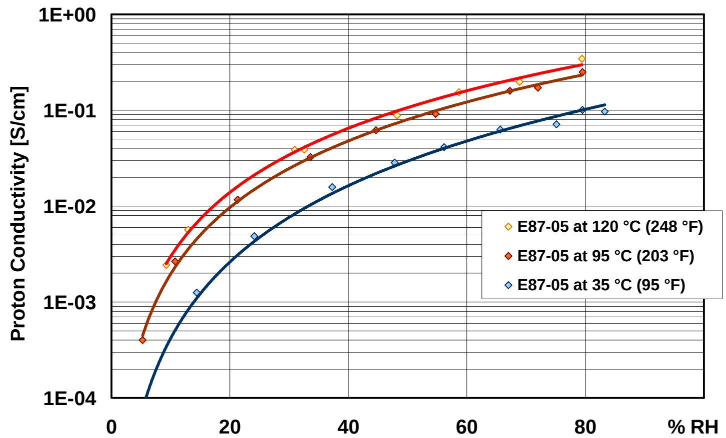
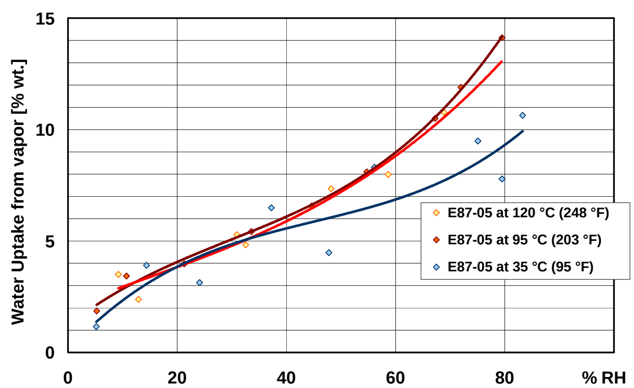
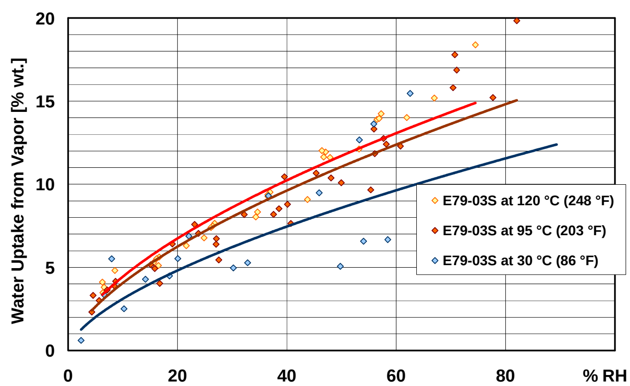


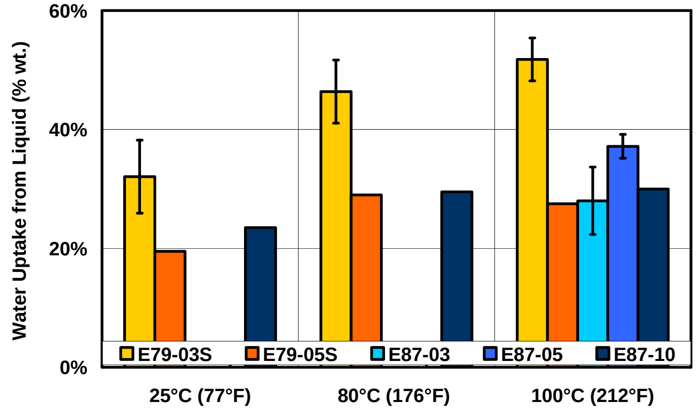
WATER ABSORPTION ISOTHERM

Good water retention especially upon exposure to hot and dry gases is a mostly desirable property. It is helpful to minimize water absorption to limit mechanical stress on the material during alternation of wet and dry states. Tests performed in humid gases and liquid water give different results as shown in the following graphs. All specimens were vigorously dried at 105 °C (220 °F) under vacuum for reference before measuring the equilibrium point in atmospheres of defined moisture.



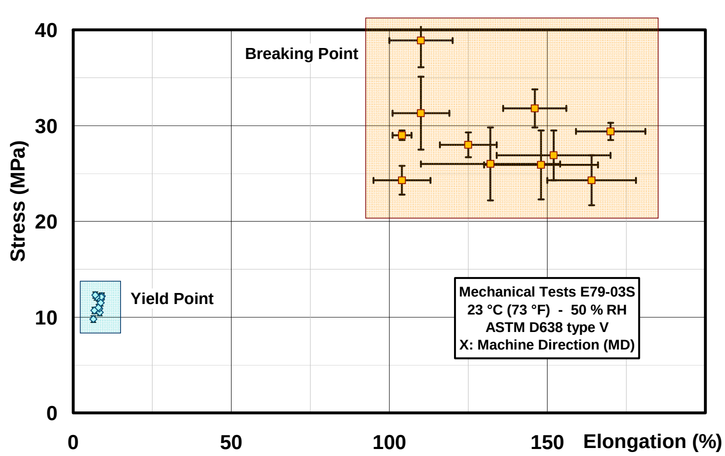


In most PEFC applications, water uptake from liquid has a practical relevance near ambient temperature when product water still condensates. As an *ex-situ* characterization of membranes, water uptake after several hours of immersion in boiling water is used as a theoretical reference value – whether as a weight increase or as λ value, i.e. moles of H_2O per mole SO_3H.



MECHANICAL PROPERTIES

Tensile data of Aquivion™ ionomer membranes are typically controlled via ASTM D638 protocol in multiple specimens (typically 3-5). Also data on D882 is available. For both production and operational purposes such mechanical properties are of interest: The yield point position indicates the transition area from elastic to plastic deformation imposed either during MEA fabrication or via exposure to cycling changes of certain operation conditions. Stress and strain at break describe intrinsic mechanical stability of the thin films. Charts reflect measurements in both machine and transverse direction (MD, TD) and reveal a minor level of mechanical anisotropy.



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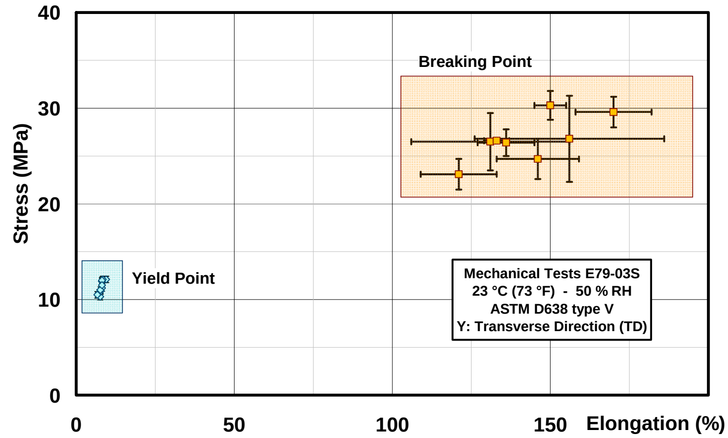
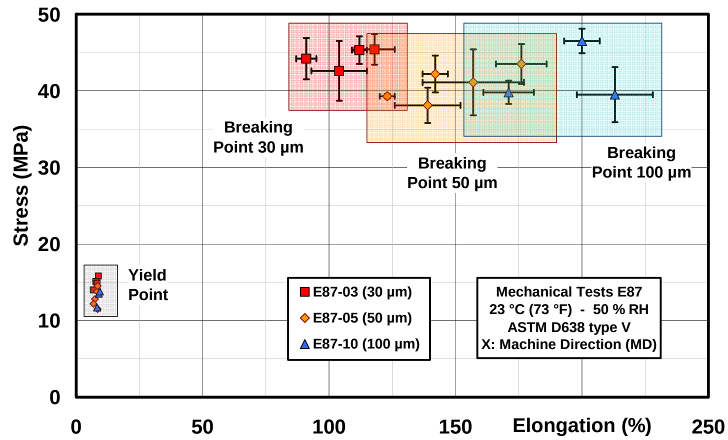
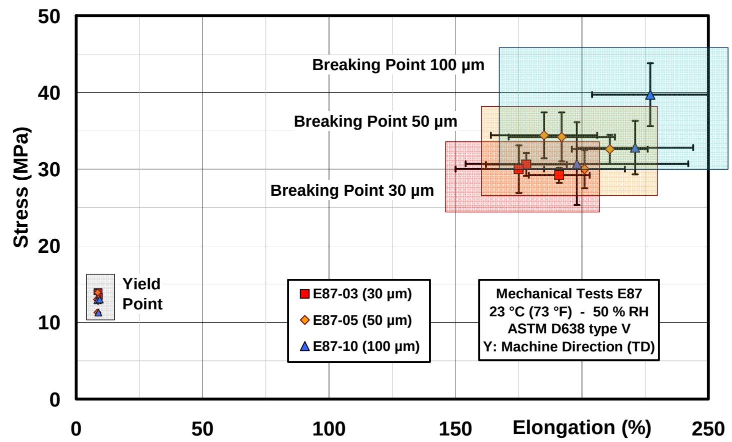
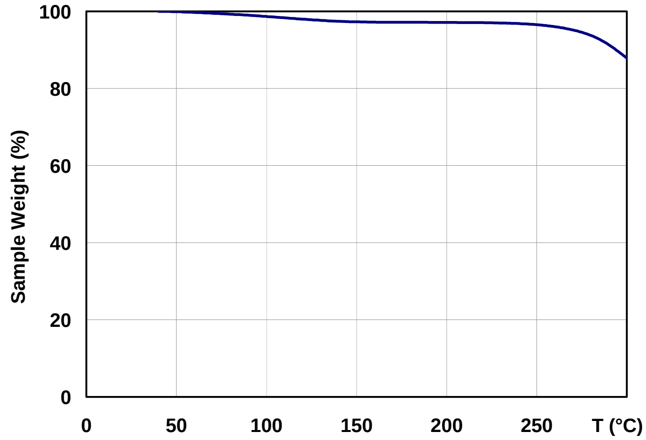




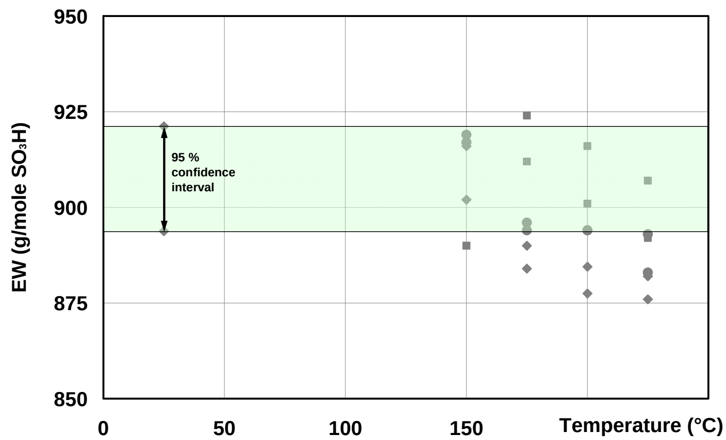


THERMAL PROPERTIES

TGA was performed in air (oxidative environment) at a slow temperature ramp of 1 °C/min. The sample was preconditioned for 24 hours at 40 °C to equilibrate the corresponding water content. The TGA chart reveals a continuous loss of water up to around 140 °C (285 °F), value above which no more osmotic water leaves the system. An initial onset of structural degradation can be estimated at around 220 °C (430 °F), or even higher.



Exposure to excessive temperatures could also decompose the functional SO_3H group and release SO_2, be it via a radical or ionic mechanism (Wilkie CA 1991, Samms SR 1996). The result should yield an EW increase, but a study involving heat treatments up to 250 °C (482 °F) for two hours revealed that no loss in functional groups did occur on any specimen. Titrated values were consistently within the analytical error - or slightly below due to some weight loss through reduction of the residual water content (λ).

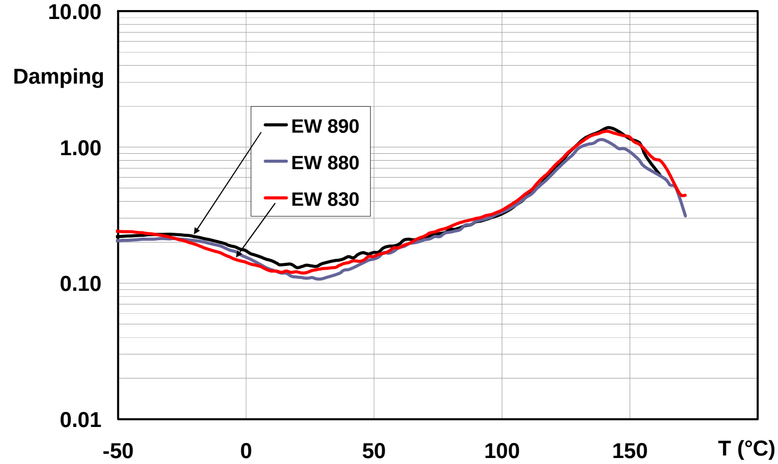


HYDRO-THERMO-MECHANICAL PROPERTIES

Dynamo-Mechanical Spectroscopy (DMS) according to ASTM D4065 was performed on three membrane lots of Equivalent Weights between 830 and 890. The damping curves indicate a glass-transition temperature T_G around 140 °C (285 °F) for all films tested under the following process parameters:

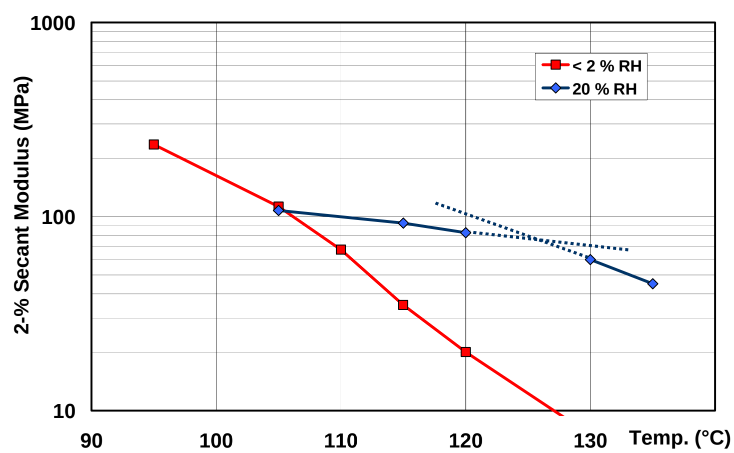
- Spectrometer Rheometric ARES, rectangular torsion mode
- Sample thicknesses > 1 mm

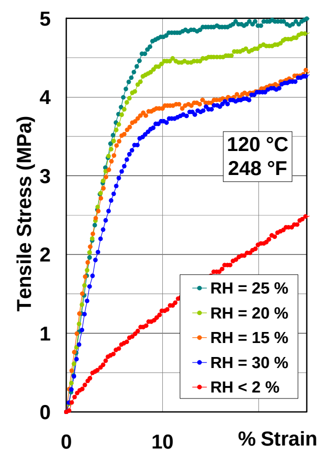
- Initial drying: 45 min at 150 °C under nitrogen
- Dynamic temperature ramp of 2 °C/min
- Frequency of 6.28 rad/s



Standard DMS tests on very hygroscopic materials such as Solvay Solexis Ionomer deliver only limited information on the material under real application conditions. To maintain some level of good ionic conductivity a certain level of humidity in the environment is maintained, equaling typically some 10 to 30 % RH also at operation temperatures above 100 °C (212 °F). The influence of water under these conditions is such that very low H_2O amounts do first act as stabilizers inside the polymeric system before higher absorption levels rather plasticize the material.

To illustrate this effect tensile tests at both < 2 % and 20 % RH were performed on E79-03S at various temperatures. When plotting the modulus as a function of temperature it can be easily seen how the slope changes below and above some 125 °C (257 °F) under 20% RH. Dry material such as the one tested in DMS exhibits instead a constant decrease.



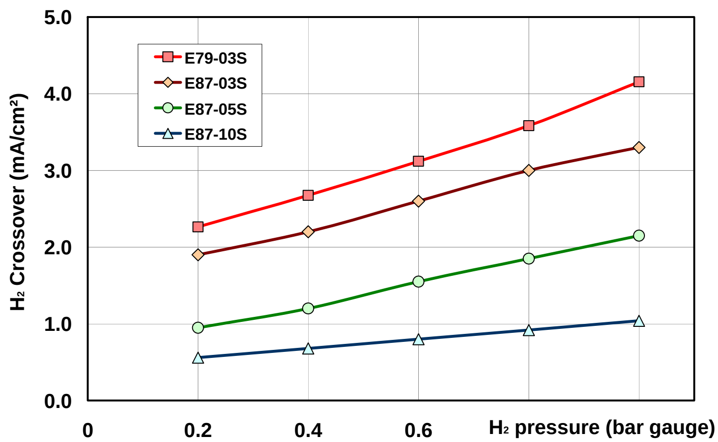


Comparing tests at 120 °C (248 °F) and various relative humidity it can be seen easily how humidity between 15 and 25 % RH increases the modulus. In exchange, virtually dry material or humidity around 30 % and above lead to a lower modulus.

HYDROGEN CROSSOVER

H_2 crossover analysis is best performed in single cells where anode and cathode are flushed with humidified hydrogen and nitrogen, respectively. A potential of 420 mV is imposed to let all permeating H_2 directly react on the cathode side, delivering a measurable electrical current density that quantifies the crossover. The experiment (75 °C, 167 °F) starts at a low overpressure of H_2 then increased up to 1 bar gauge (14.5 psig) i.e. 2 bar abs (H_2) on the anode and 1 bar abs (N_2) on the cathode side.

Statistical analysis of various different Aquivion™ lots indicates a standard deviation of around 1 mA/cm^2 meaning, for example, that typical values for E79-03S are below 6 mA/cm^2.



NITROGEN PERMEABILITY

N_2 permeation is measured *ex-situ* in a closed chamber monitoring reduction of a pre-imposed pressure difference over time. The mounted sample is carefully dried under vacuum (105 °C / 220 °F, 1 hour) before pressurizing one side of the permeometer to some 1.3 bar abs (19 psia). Pressure increase of the evacuated side is then recorded. The following values were calculated from measurements performed on twin specimens of two different EW membranes (135±5 µm thick).

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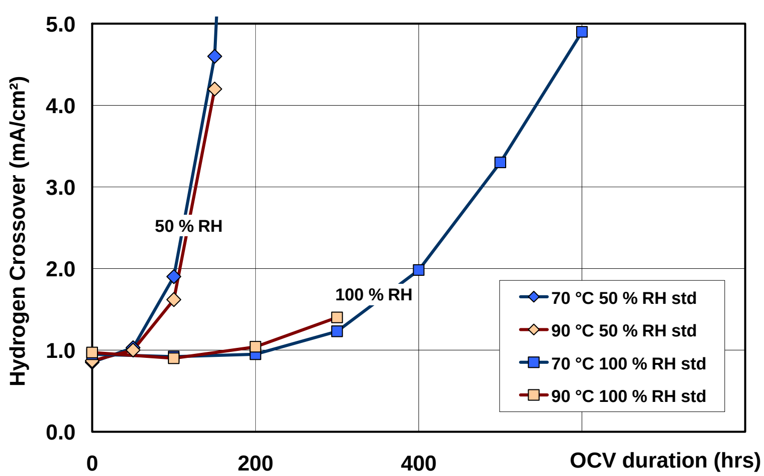
EW	Temperature	P [$cm^3 \cdot mm/m^2 \cdot atm \cdot d$]	
E87 (855)	80 °C (176 °F)	*110*	**110**
		110	
	120 °C (248 °F)	*450*	**455**
		460	
E79 (795)	80 °C (176 °F)	*70*	**65**
		60	
	120 °C (248 °F)	*410*	**430**
		450	

OPEN-CIRCUIT VOLTAGE (OCV) LIFETIME

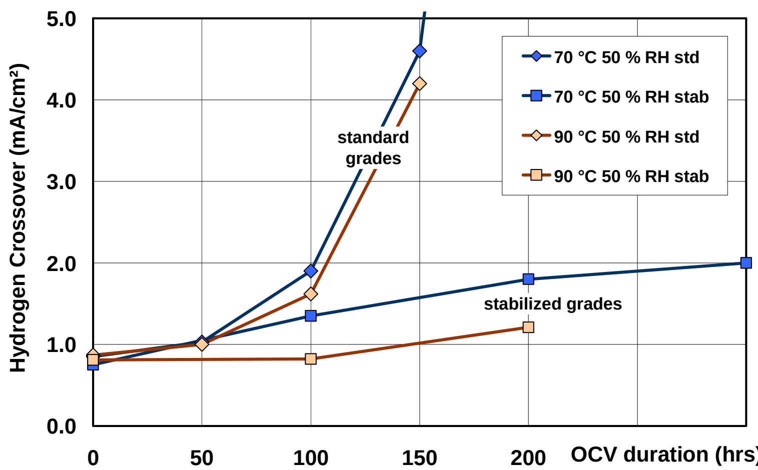
Pure OCV testing can easily accelerate and evidence membrane degradation that leads to an increase of (hydrogen) permeability. H_2 crossover current is used as indicator, measured periodically between the OCV test periods. A standard E87-05 membrane (EW 870, 50 µm) underwent testing at both 70 °C and 90 °C (158 and 194 °F, respectively) at both 50 and 100 % RH.

Thanks to a high glass-transition temperature T_G of Aquivion™ a higher operation temperature of at 90 °C has limited influence provided humidification is kept at high level. Under reduced humidification (curves at 50 % RH), however, the test duration is shortened for both 70 and 90 °C.

Stabilized membrane grades (suffix S) confirm to withstand over longer OCV periods compared to the standard grades as illustrated by the example at 50 % RH.



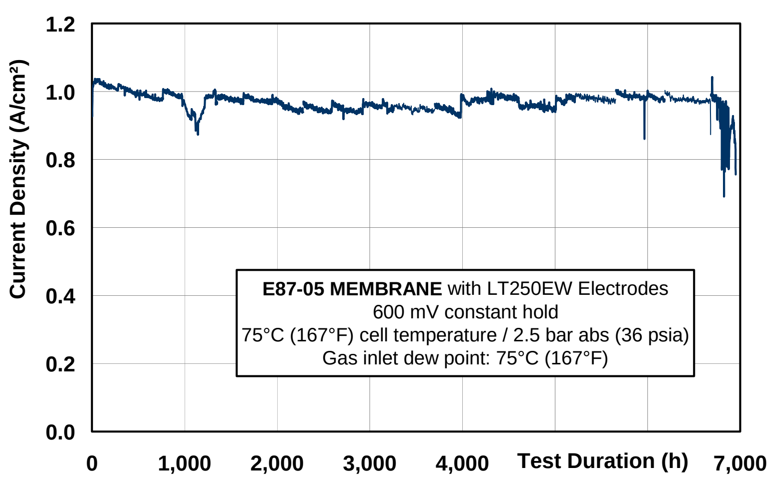
AQUIVION™ IONOMER MEMBRANE



POTENTIOSTATIC LIFETIME

Sample testing at a constant voltage of 600 mV is conducted at 25 cm^2 cell scale with both standard and stabilized membrane types E87-05 (EW 870, 50 µm) and E87-05S. This long-term testing (75 °C / 167 °F, 2.5 bar abs / 36 psia, humidified H_2/air flows) revealed that stabilized grades can not only reach longer absolute lifetimes but experience also a reduced degradation in terms of their specific current loss rate.

Aquivion™ E87-05 turned out to have a current loss < 1 % per 1,000 hours (test stopped beyond 6,500 hours) whereas the corresponding stabilized grade had a current loss of around 1.6 % per 1,000 hours (test ongoing beyond 10,500 hours).



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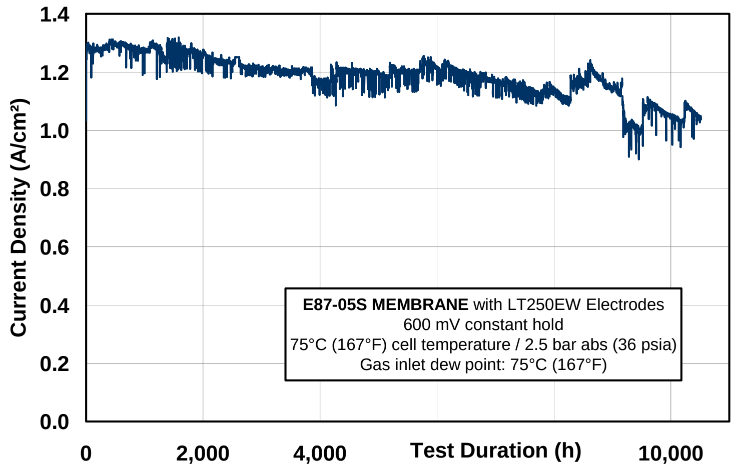
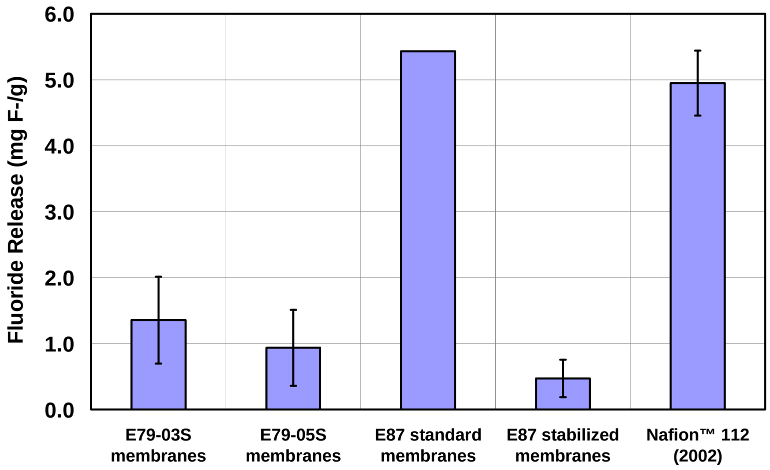


EX-SITU CHEMICAL STABILITY (FENTON REAGENT)

Chemical integrity of perfluorosulfonic acid (PFSA) materials can be verified by Fenton-type reactants where a certain concentration of ferrous ions Fe^{2+} generates reactive species from hydrogen peroxide (·OH and ·OOH). The radicals incur polymer degradation producing fluoride ions as decomposition indicators. Various protocols for the so-called Fenton testing exist in public literature; along with theoretical background.

For comparative purposes, Solvay Solexis applies a public protocol where membrane specimens are degraded in a Mohr Salt solution with 36 ppm of ferrous ions and 15 % H_2O_2 solution for six hours at 55 °C. Temperature has been chosen moderate to avoid a too fast decomposition of hydrogen peroxide. A precise quantitative analysis of the solution's F^- content (ppm/mg levels) via ion chromatography follows.

The chart gives a comparison of test results obtained on the commercial Aquivion™ membrane grades also involving a commercial 50 µm (2 mil) Nafion® material purchased in 2002. Material improvements on Nafion® could be expected in a way such that test results on recent material are similar to Aquivion™'s stabilized S-grades.



GENERAL PROCESSING REMARKS

Absence of air during hot-pressing phases can be of importance. It is favorable to decrease the temperature before e.g. opening the press. Reduction to around 120 °C (250 °F) is generally recommended. This may require 1 to 2 minutes of cooling time or be realized via active cooling. Membranes are delivered in acid form (>99,9 % SO_3H). A cleaning with H_2SO_4 or HNO_3 and H_2O_2 can be helpful but is not necessary in general.

PROCESSING VIA CCM ROUTES

When building MEA via catalyst-coated membrane (CCM) intermediates the application of Decal routes has evolved as state of the art. To combine the material in a way such that intense contact with low resistance is developed between membrane and catalyst layers, we recommend the following baseline parameters as a starting point for individual optimization of the transfer process:

a) <u>for E87 series membranes</u>
- Temperature 200 °C (390 °F)
- Press pressure between 1 and 5 MPa (150-700 psi)
- Hot-pressing times between 2 and 5 minutes
- Higher temperatures can require shorter hot-pressing times

b) <u>for E79 series membranes</u>
- Temperature 200 °C (390 °F)
- Press pressure between 1 and 5 MPa (150-700 psi)
- Hot-pressing times between 2 and 3 minutes
- Higher temperatures can require shorter hot-pressing times

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PROCESSING VIA GDE ROUTES

If, however, internal customer processes foresee lamination of gas-diffusion electrodes (GDE) together with the ionomer membrane, slightly different parameters are preferable:

a) for E87 series membranes
- Temperature 150-160 °C (300-320 °F)
- Pressure limitation by GDL/microporous layer to be respected
- Hot-pressing times between 0.5 and 2 minutes
- Higher temperatures can require shorter hot-pressing times

b) for E79 series membranes
- Temperature 150-160 °C (300-320 °F)
- Pressure limitation by GDL/microporous layer to be respected
- Hot-pressing times between 1 and 2 minutes
- Higher temperatures can require shorter hot-pressing times

AQUIVION™ IONOMER MEMBRANE

AQUIVION™ E87 IONOMER MEMBRANES - TYPICAL PROPERTIES

	Test Method	Typical Values			
		SI Units		US Customary Units	
Physical-Chemical Properties					
Density (extrapolated to 0 % water adsorption)	ASTM D 0792	~ 2.06	g/cm^3	~ 129	lb/ft^3
Equivalent Weight (eq = mol SO_3H)	PF 87/21e	850-890	g/eq	850-890	g/eq
Total Acid Capacity	PF 87/21e	> 1.12	meq/g	> 1.12	meq/g
Mechanical Properties					
Tensile @ 23 °C (73 °F) and 50% RH	ASTM D0638				
Stress at Break (MD / TD)		> 25/20	MPa	> 3.6/2.9	10^3 psi
Elongation at Break (MD / TD)		>140/180	%	> 140/180	%
Modulus	50 mm/min				
Yield Stress (MD / TD)		> 11/11	MPa	> 1.6/1.6	10^3 psi
Yield Strain (MD / TD)		> 8/8	%	> 8/8	%
Electrochemical Properties					
Power Output @ 0.8 A/cm^2	PF87-22e (*)	> 0.50	W/cm^2	> 0.50	W/cm^2
Water Uptake Properties (in liquid)					
Uptake by Weight (4 hr soak @ 100°C / 212°F)	PF 87/23e	< 40	%	< 40	%
Elongation (MD / TD) @ 100 °C	PF 87/23e	< 15/25	%	< 15/25	%

MD = Machine Direction; TD = Transverse Direction; PF = Solvay Solexis Internal Test Method

(*) T_{cell} = 75 °C, $T_{gas\ humidification}$ = 80 °C, P (Air, H_2) = 2.5 bar abs
LT250EW E-Tek electrodes w/ 0.5 mg Pt/cm^2 and 0.7 mg Nafion™/cm^2

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AQUIVION™ IONOMER MEMBRANE

AQUIVION™ E79-03S IONOMER MEMBRANES - TYPICAL PROPERTIES

	Test Method	Typical Values	
		SI Units	**US Customary Units**
Physical-Chemical Properties			
Density (extrapolated to 0 % water adsorption)	ASTM D792	~ 2.06 g/cm^3	~ 129 lb/ft^3
Equivalent Weight (eq = mol SO_3H)	PF 87/21e	770-810 g/eq	770-810 g/eq
Total Acid Capacity	PF 87/21e	> 1.23 meq/g	> 1.23 meq/g
Mechanical Properties			
Tensile @ 23 °C (73 °F) and 50% RH	ASTM D638		
Stress at Break (MD)	(50 mm/min)	20-40 MPa	2.9-5.8 10^3 psi
Stress at Break (TD)	(Type V)	20-35 MPa	2.9-5.0 10^3 psi
Elongation at Break (MD)		90-180 %	90-180 %
Elongation at Break (TD)		100-200 %	100-200 %
Yield Stress (MD and TD)		9-13 MPa	1.3-1.9 10^3 psi
Yield Strain (MD and TD)		6-10 %	6-10 %
Electrochemical Properties			
Power Output @ 0.8 A/cm²	PF87-22e (*)	> 0.57 W/cm²	> 0.57 W/cm²
Water Uptake Properties (in liquid)			
Uptake by Weight (4 hr soak @ 100°C / 212°F)	PF 87/23e	< 55 %	< 55 %
Elongation (MD / TD) @ 100 °C	PF 87/23e	< 15/25 %	< 15/25 %

MD = Machine Direction; TD = Transverse Direction; PF = Solvay Solexis Internal Test Method

(*) T_{cell} = 75 °C, $T_{gas\ humidification}$ = 80 °C, P (Air, H_2) = 2.5 bar abs,
LT250EW E-Tek electrodes w/ 0.5 mg Pt/cm² and 0.7 mg Nafion™/cm²

*For any further information on Aquivion™ contact your regional Solvay Solexis representative, send us an email directly to solexis.ionomers@solvay.com or go to **www.solvaysolexis.com***

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