

PFSA Aquivion® membranes: general features and degradation mechanisms

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Agenda

- PFSA ionomers
- Aquivion® general features
- PFSA degradation mechanisms
- Different behavior in different operating conditions
- Aquivion® short side chain structure effects
- Conclusions



- **PFSA ionomers**

Examples of ionomers currently being synthesized

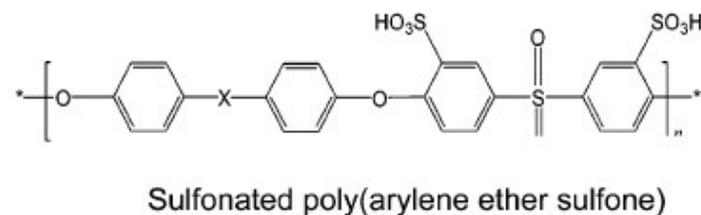
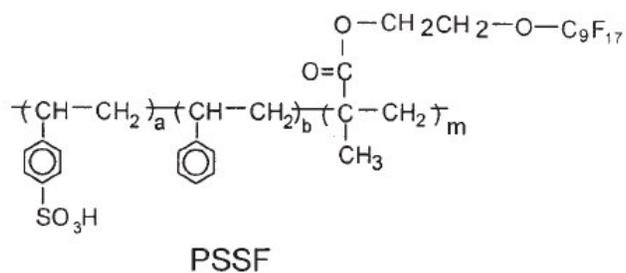
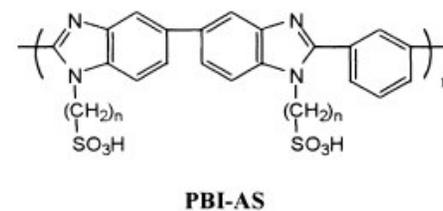
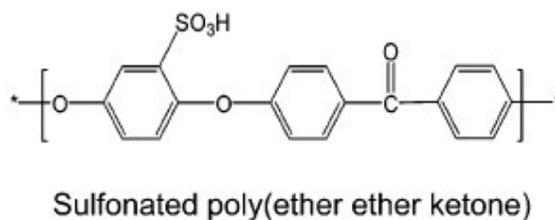
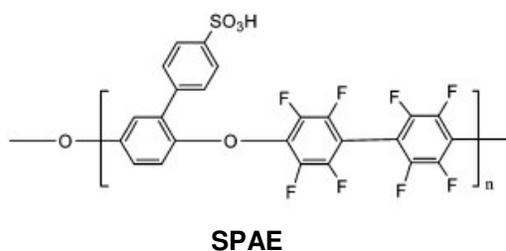
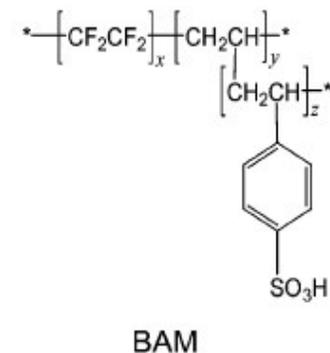
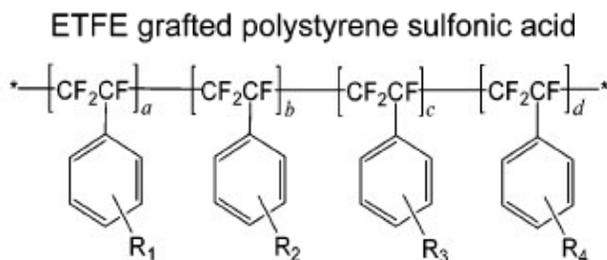
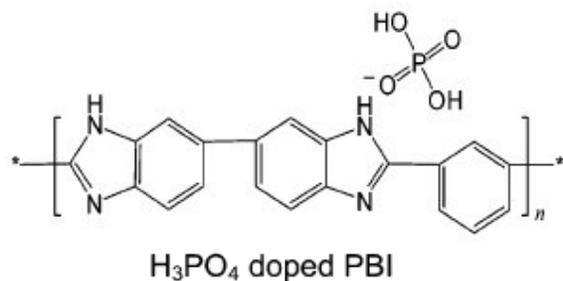
What are the distinguishing features of PFSA ionomers ?

Intrinsic advantage of the PFSA technology

PFSA structures available on the market

PFSA ionomers

Different options of proton conductive membranes:



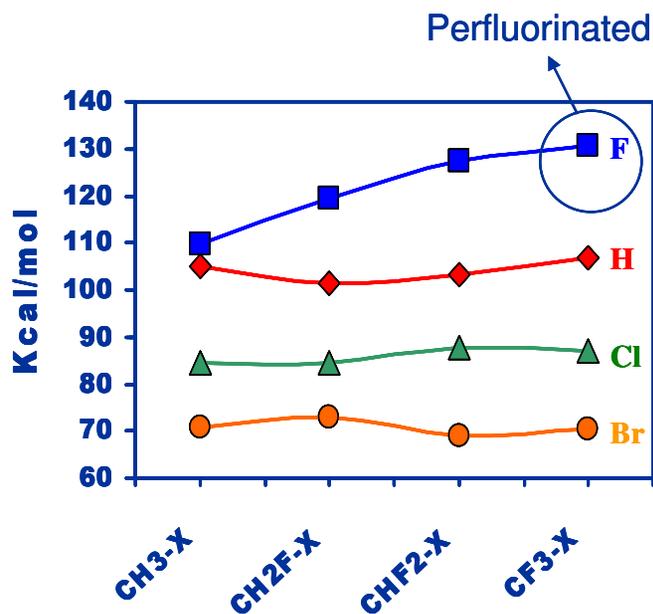
Chem. Rev. 2007, 107, 3904–3951

PFSA ionomers



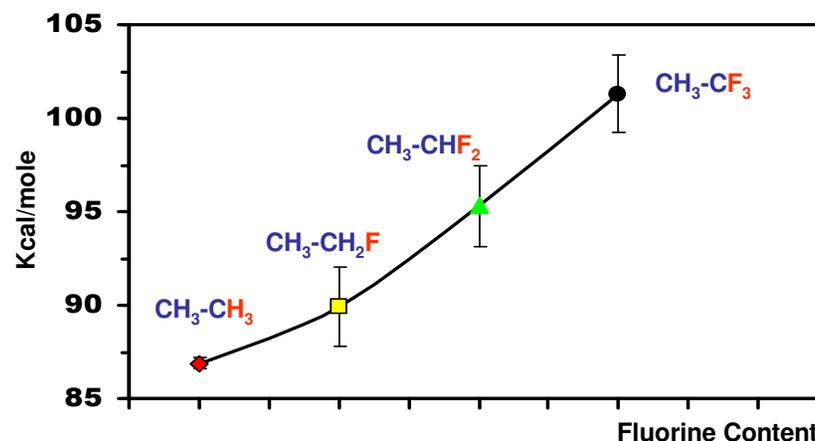
Why are PFSA ionomers preferable ?

1 – Intrinsic chemical stability



The C-F bond is the strongest bond.

The effect induced by higher fluorine substitution results in C-F bond strength increase



The strength of the C-C bond is also influenced by the fluorine substitution

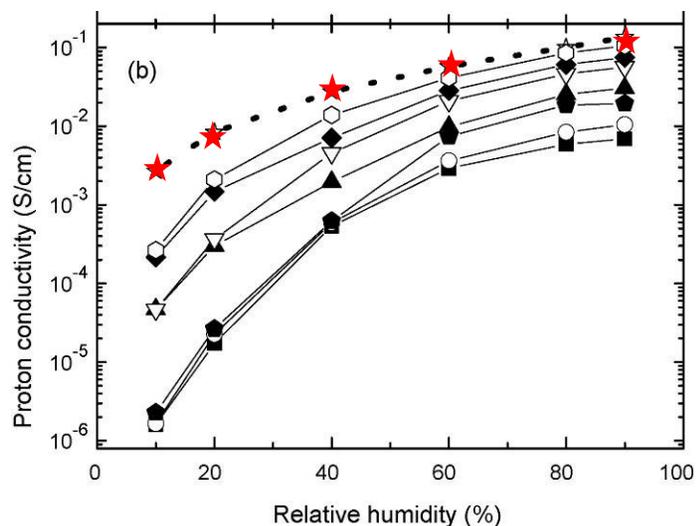
PFSA ionomers



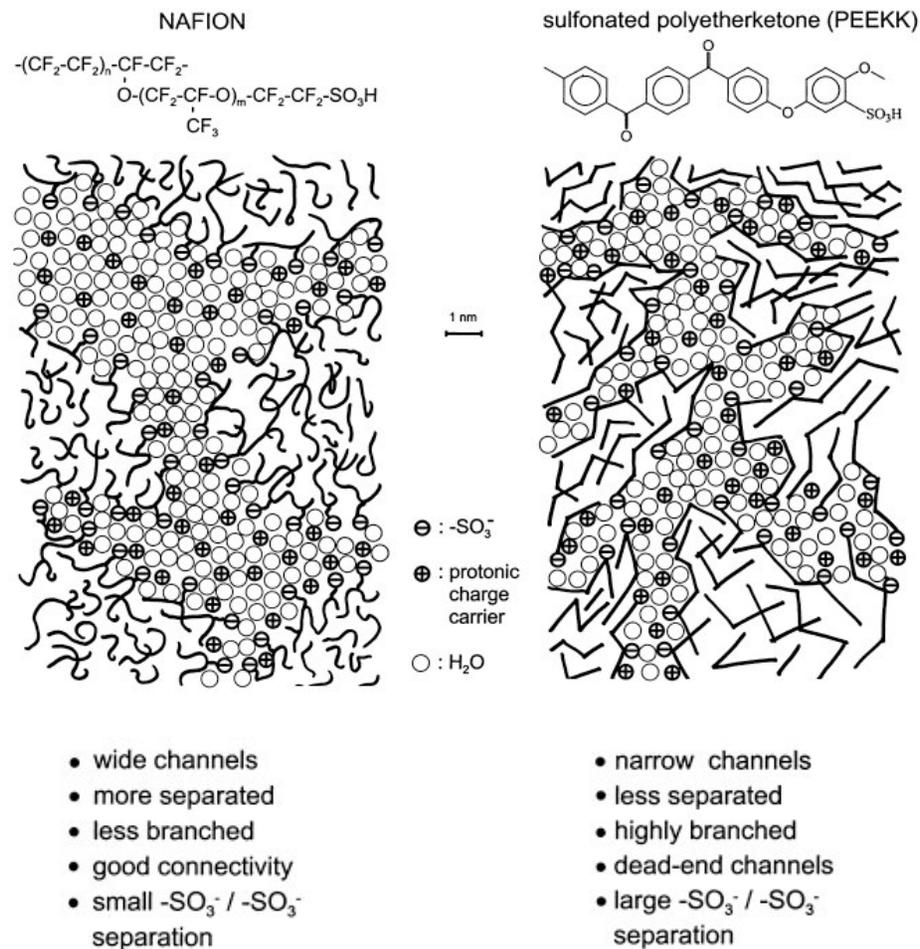
Why are PFSA ionomers preferable ?

3 – ionic cluster nanostructure

PFSA structures ★ gives ‘flatter’ conductivity curve decreasing RH

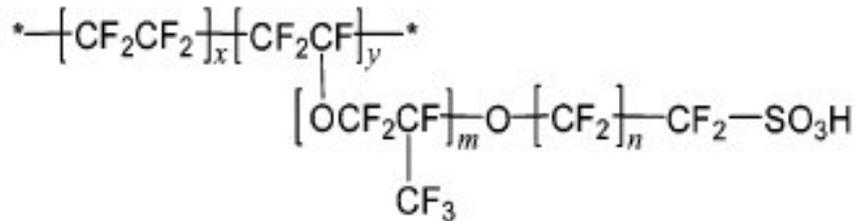


K.D. Kreuer / Journal of Membrane Science 185 (2001) 29–39





PFSA ionomers



Available (or described) PFSA:

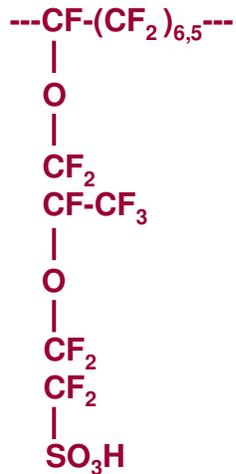
Nafion®: m=1 n=1 x=5-13.5

Flemion®: m=0,1 n=1-5 x=?

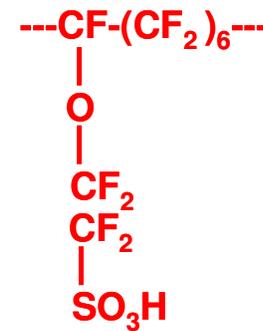
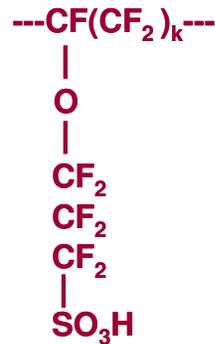
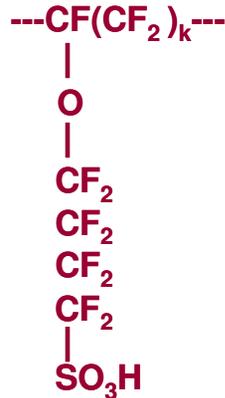
Aciplex®: m=0,3 n=2-5, x=1,5-14

Aquivion®: m=0 n=1 x=3-7

-----> From LSC to SSC ionomers...



Nafion 1100 g/eq



Aquivion 870 g/eq

This "slight" difference...

... allows higher crystallinity and/or conductivity
 ... allows higher working temperatures (> Tg)



- Aquivion® general features

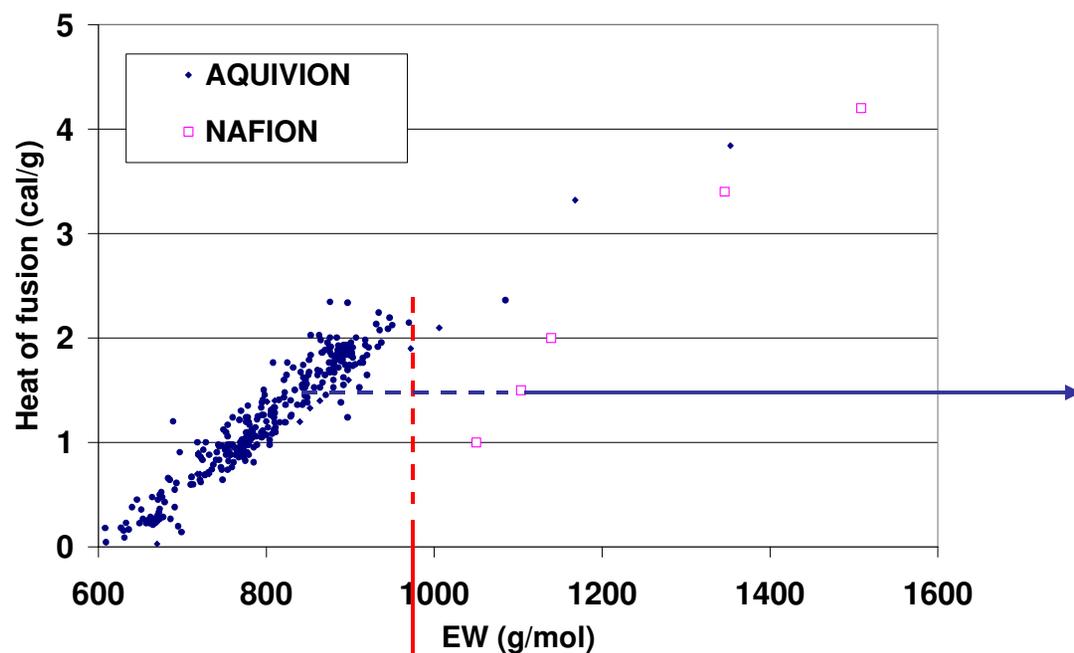
Short side chain structure advantages in terms of:

crystallinity

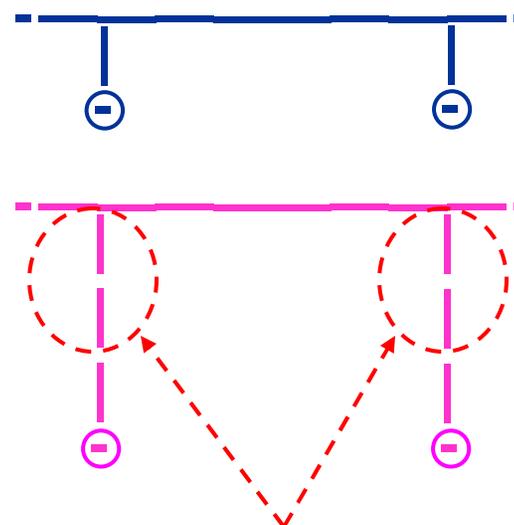
ionic conductivity

and glass transition temperature

Aquivion® general features

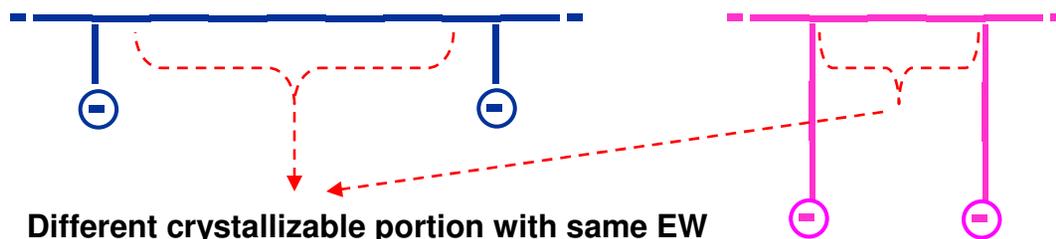


Models of **Aquivion** and **Nafion** with similar crystallinity:



Gives increase of EW without increase of crystallinity

Models of **Aquivion** and **Nafion** with similar EW:



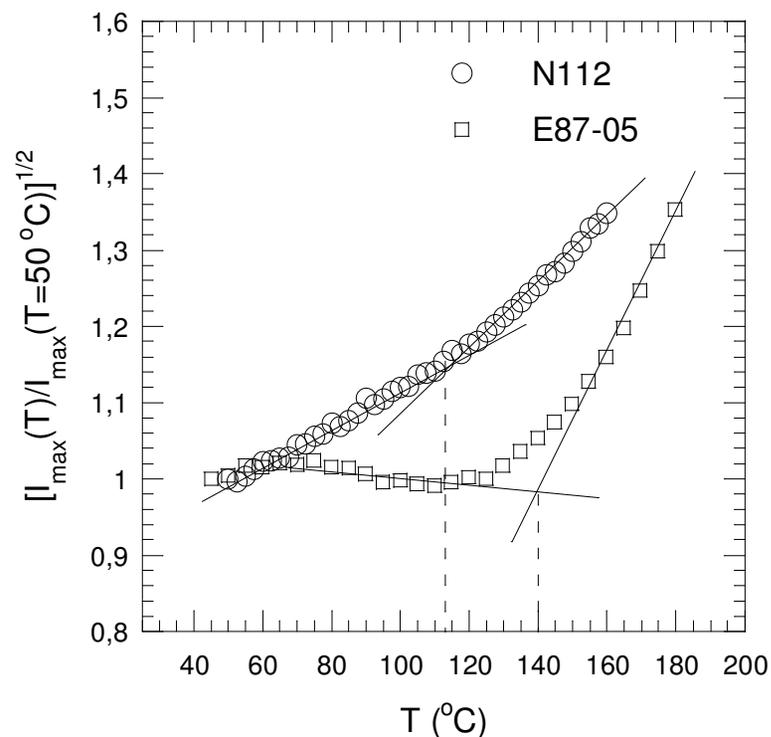
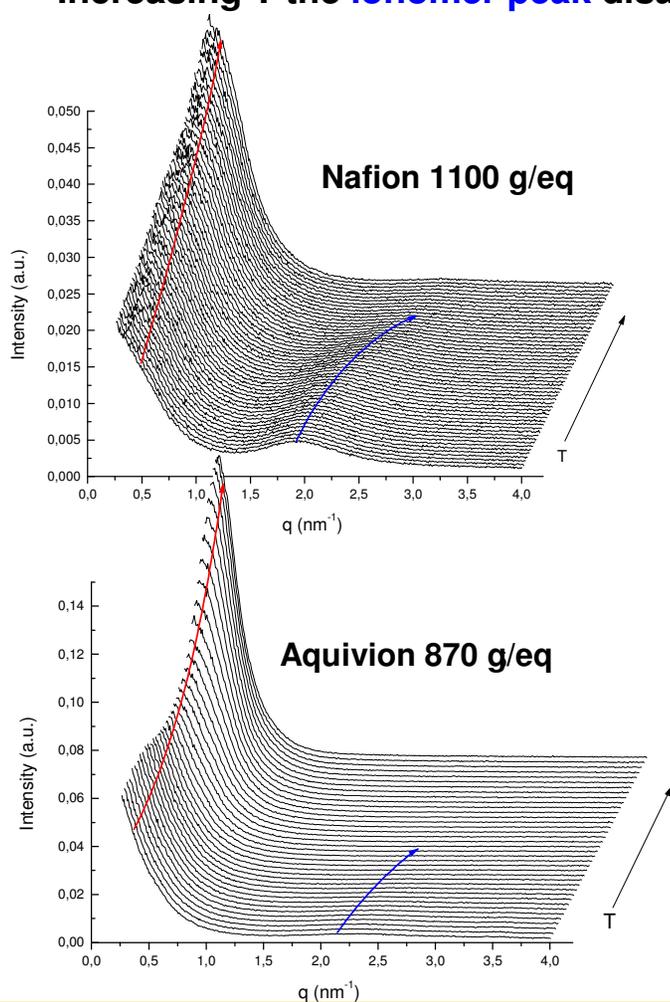
Different crystallizable portion with same EW

Nafion data: Tant et al., ACS Symp. Ser. 395 (1989), 370

Aquivion® general features

SAXS scan temperature resolved:

Increasing T the **ionomer peak** disappears (water evaporation) while the **matrix peak** increases



Change in slope of I_{\max} is associated to the T_g of the material (=mobilization of the chains increases crystallinity)



- **PFSA degradation mechanisms**

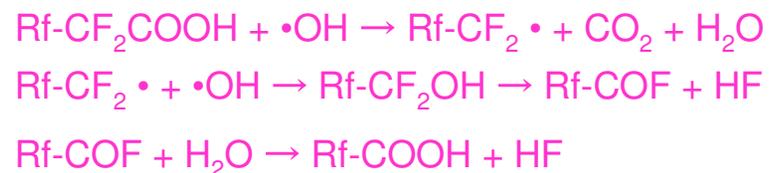
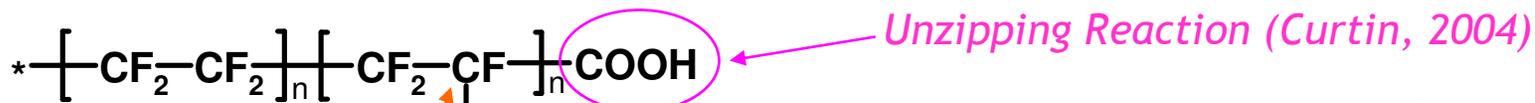
Degradation mechanism described in the literature

Fenton test, is it a good simulation of fuel cell environment?

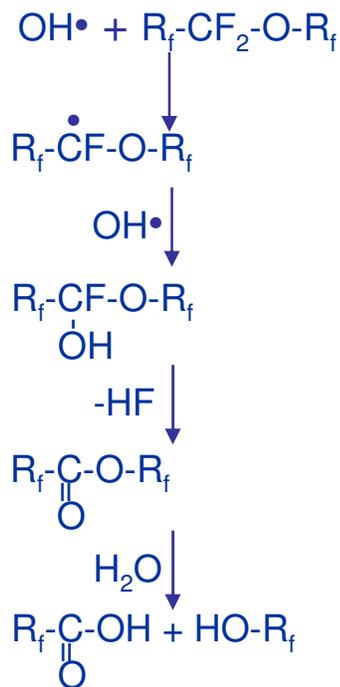
Role of H₂O₂ and radicals / kinetic models

Role of gas crossover in membrane degradation

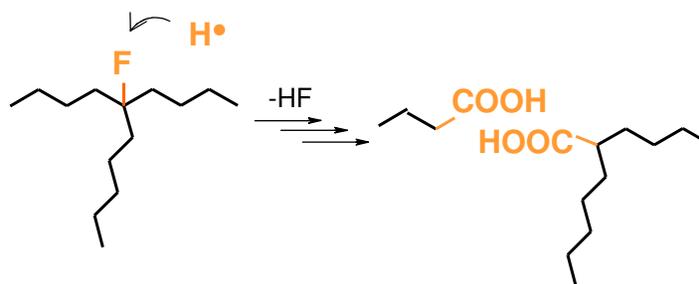
PFSA degradation mechanisms



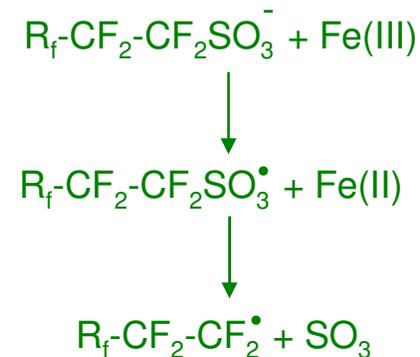
Secondary carbon (vic. O₂)



Tertiary carbons



Sulfonic group

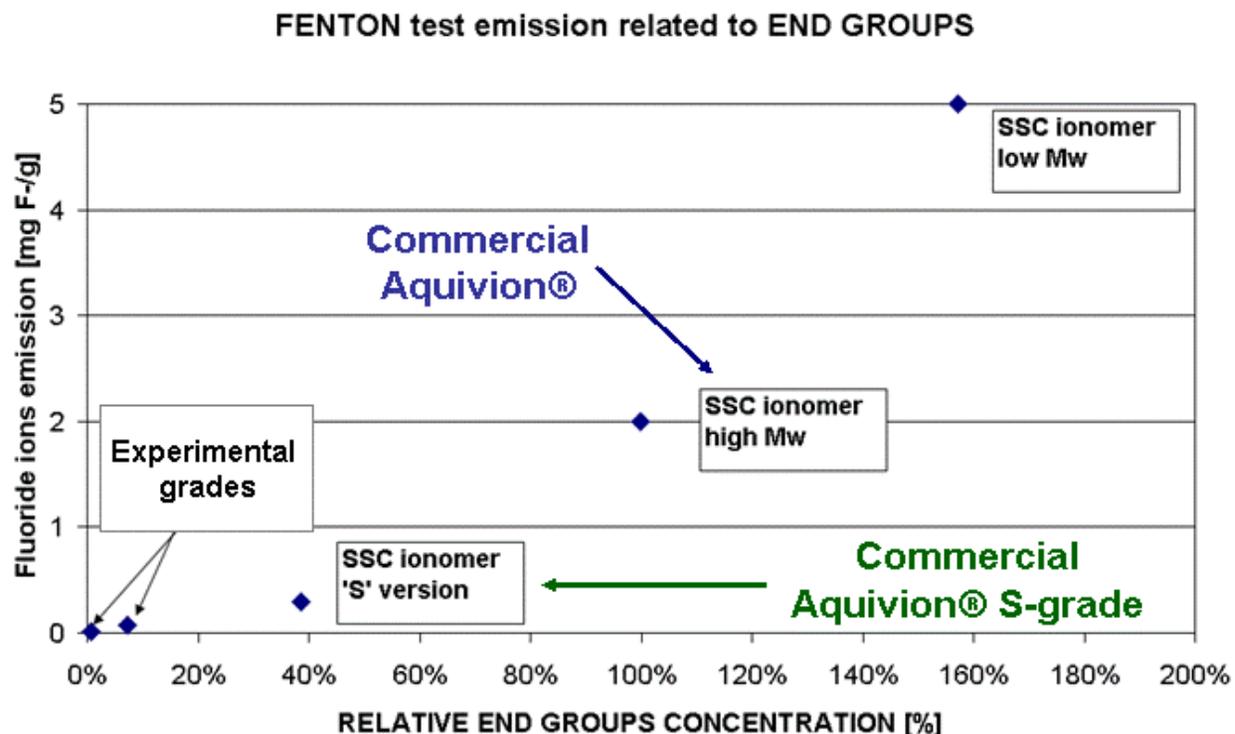


J. *ECS Trans.* 2007, 11, 1083
 J. *Electrochem. Soc.* 2011, 158, B175
Macromolecules 2007, 40, 8695-8707
 J. *Phys. Chem. B* 2005, 109, 7664-7670
S. Macromolecules 2010, 43, 3352-3358

PFSA degradation mechanisms



There is common agreement on the prevalence of 'end groups' driven degradation (unzipping).

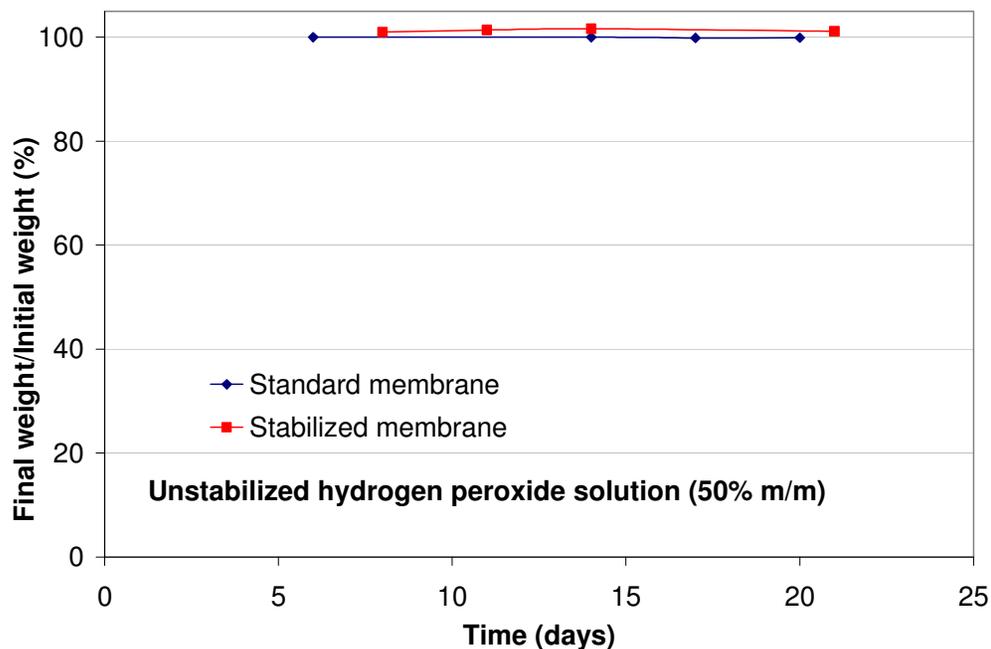


In Fenton test environment (water, $\cdot\text{OH}$ radicals, presence of Fe^{n+} ions) when **end groups concentration is very low, degradation** (measured by HF release) **is close to zero** in Aquivion structure.

PFSA degradation mechanisms



Both in case of stabilized and unstabilized (containing -COOH end groups) membranes, **contact with H_2O_2 is not sufficient to initiate degradation**. Radical species are necessary.



Key questions that scientific community is trying to answer are:

- where are the radicals coming from ?
- which kind of radicals are formed?
- Are other improvements necessary to chemically stabilized PFSA membranes?

PFSA degradation mechanisms



Journal of The Electrochemical Society, 159 (2) B211-B218 (2012)

#	Reaction	Rate constant	unit
1	$\text{HO}^\bullet + \text{R}_f\text{CF}_2\text{COOH} \rightarrow \text{products}$	$<10^6$	$\text{M}^{-1}\text{s}^{-1}$
2	$\text{HO}^\bullet + \text{PSSA}^{\text{a}} \rightarrow \text{products}$	$4 \cdot 10^8$	$\text{M}^{-1}\text{s}^{-1}$
3	$\text{H}_2\text{O}_2 \rightarrow 2 \text{HO}^\bullet$	$1.2 \cdot 10^{-7}$	s^{-1}
4	$\text{HO}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{HOO}^\bullet + \text{H}_2\text{O}$	$2.7 \cdot 10^7$	$\text{M}^{-1}\text{s}^{-1}$
5	$\text{HOO}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{HO}^\bullet + \text{H}_2\text{O} + \text{O}_2$	≤ 1	$\text{M}^{-1}\text{s}^{-1}$
6	$\text{HO}^\bullet + \text{H}_2 \rightarrow \text{H}^\bullet + \text{H}_2\text{O}$	$4.3 \cdot 10^7$	$\text{M}^{-1}\text{s}^{-1}$
7	$\text{H}^\bullet + \text{O}_2 \rightarrow \text{HOO}^\bullet$	$1.2 \cdot 10^{10}$	$\text{M}^{-1}\text{s}^{-1}$
8	$2 \text{HOO}^\bullet \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$8.6 \cdot 10^5$	$\text{M}^{-1}\text{s}^{-1}$
9	$\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{HO}^\bullet + \text{H}_2\text{O}$	63	$\text{M}^{-1}\text{s}^{-1}$
10	$\text{Fe}^{2+} + \text{HO}^\bullet + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}$	$2.3 \cdot 10^8$	$\text{M}^{-1}\text{s}^{-1}$
11	$\text{Fe}^{2+} + \text{HOO}^\bullet + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2$	$1.2 \cdot 10^6$	$\text{M}^{-1}\text{s}^{-1}$
12	$\text{Fe}^{3+} + \text{HOO}^\bullet \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+$	$2 \cdot 10^4$	$\text{M}^{-1}\text{s}^{-1}$
13	$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HOO}^\bullet + \text{H}^+$	$4 \cdot 10^{-5}$	$\text{M}^{-1}\text{s}^{-1}$

Decomposition of H_2O_2 is negligible in absence of Fenton metals

...but presence of 1 ppm of Fe ions causes dramatic increment of $\bullet\text{OH}$ generation

Decomposition of $\bullet\text{OH}$ even in presence of Fe has comparable rate with polymer attack

Generation of $\bullet\text{H}$ is reasonable in presence of hydrogen

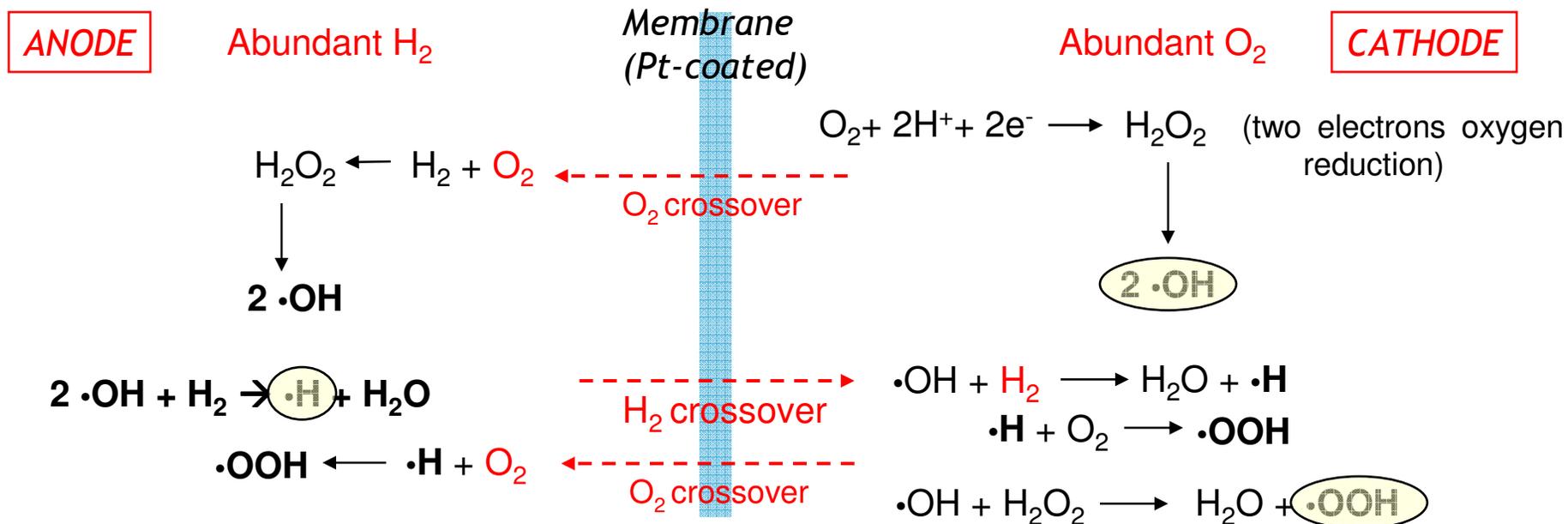
...but $\bullet\text{H}$ is fastly decomposed in presence of oxygen

$\bullet\text{OOH}$ is generally considered less aggressive than $\bullet\text{OH}$ and $\bullet\text{H}$

PFSA degradation mechanisms



Trying to schematized the fuel cell environment...



H₂O₂ can be generated of cathode side by electrochemical reaction and on anode side as a consequence of oxygen crossover

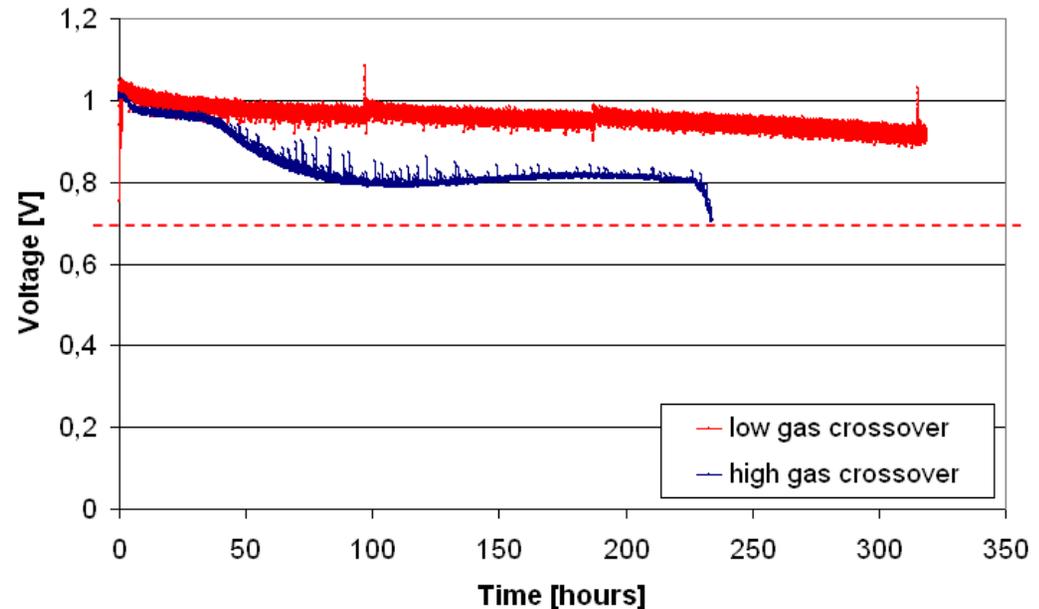
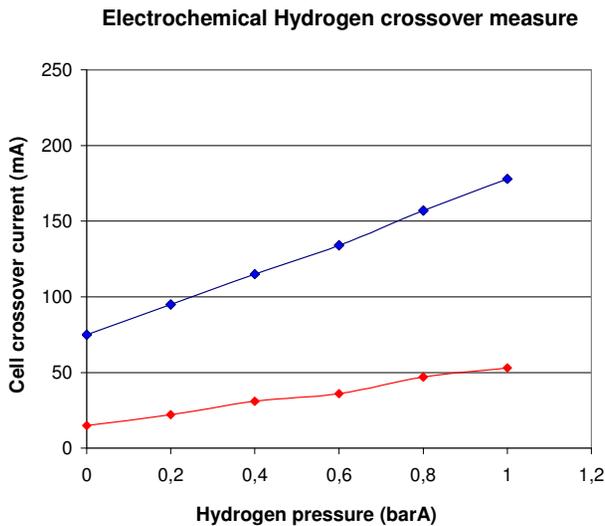
Traces of metals (but also Pt catalyst surface!) can promote ·OH generation

- OH can evolve faster to ·H on anode side (then decomposed to ·OOH in presence of O₂ crossover)
- OH can evolve to ·H on cathode side (for H₂ CO) but then fastly converted to ·OOH, or, more probably, react with H₂O₂ to form ·OOH

PFSA degradation mechanisms



Is gas crossover really a relevant factor for chemical degradation?



Two similar membranes (same thickness and chemistry, but largely different permeability) evidenced **fairly different OCV (dry) durability**.

This sounds like an important influence of gas crossover contribution to radical generation ($\cdot\text{H}$ on anode side according to the previously described scheme)



- Different behavior in different operating conditions

**High humidity level of gas reactants, a good environment for
stabilized PFSA membranes**

Dry gas OCV test, what is really happening?

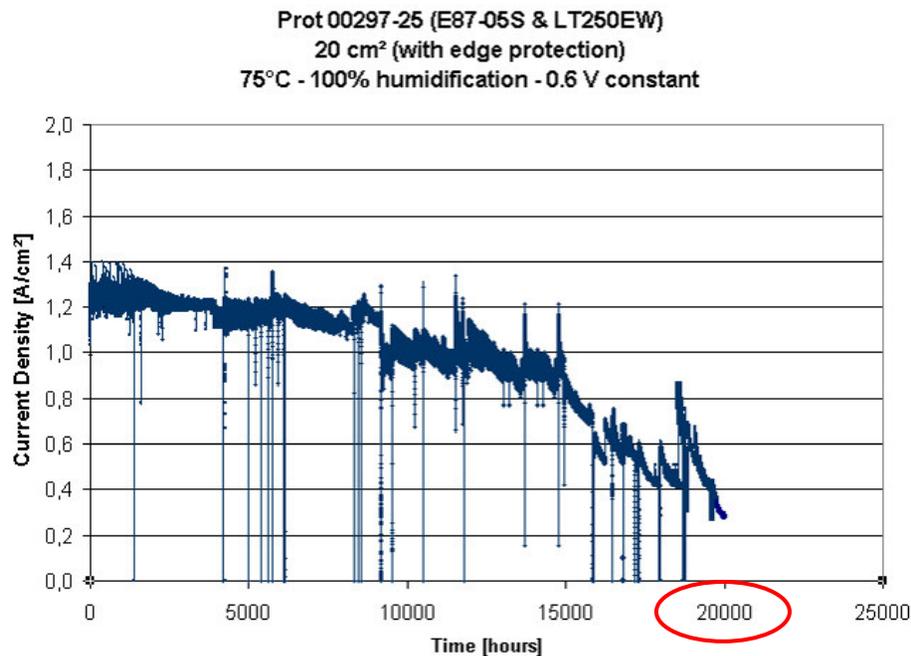
**Humidity cycles, when durability is linked with mechanical
stability**

Different behavior in different operating conditions

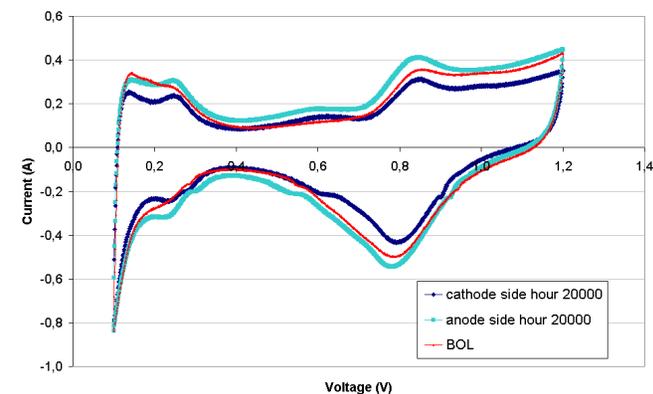
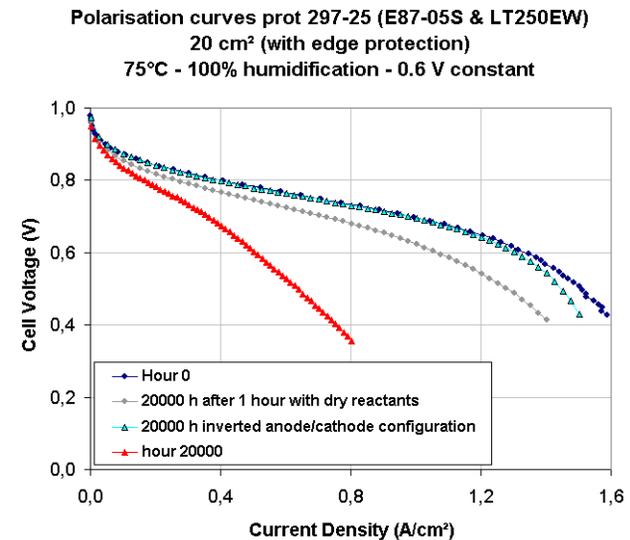


Different operating conditions evidences different degradation mechanisms.

Example 1: full humidification operating conditions



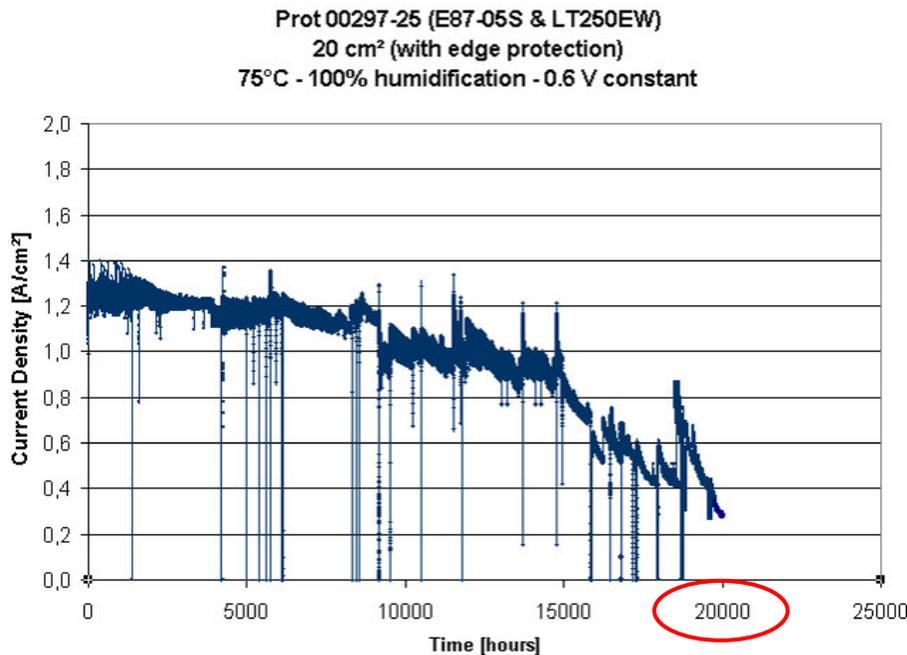
After **20000 h** operation the performance loss is apparently concentrated in the the GDL, **the membrane is substantially not degraded.**



Different behavior in different operating conditions

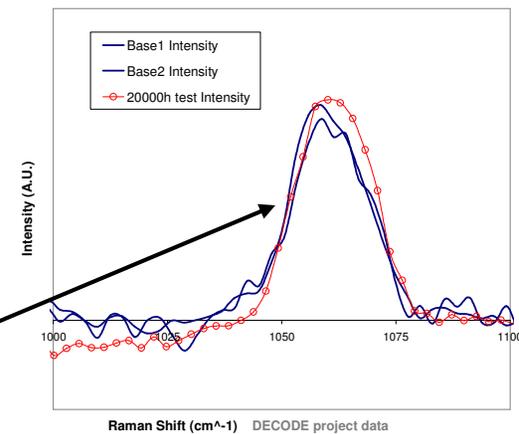
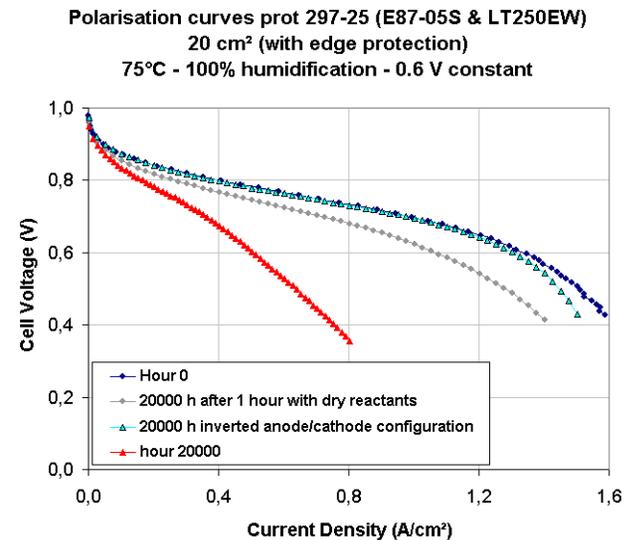
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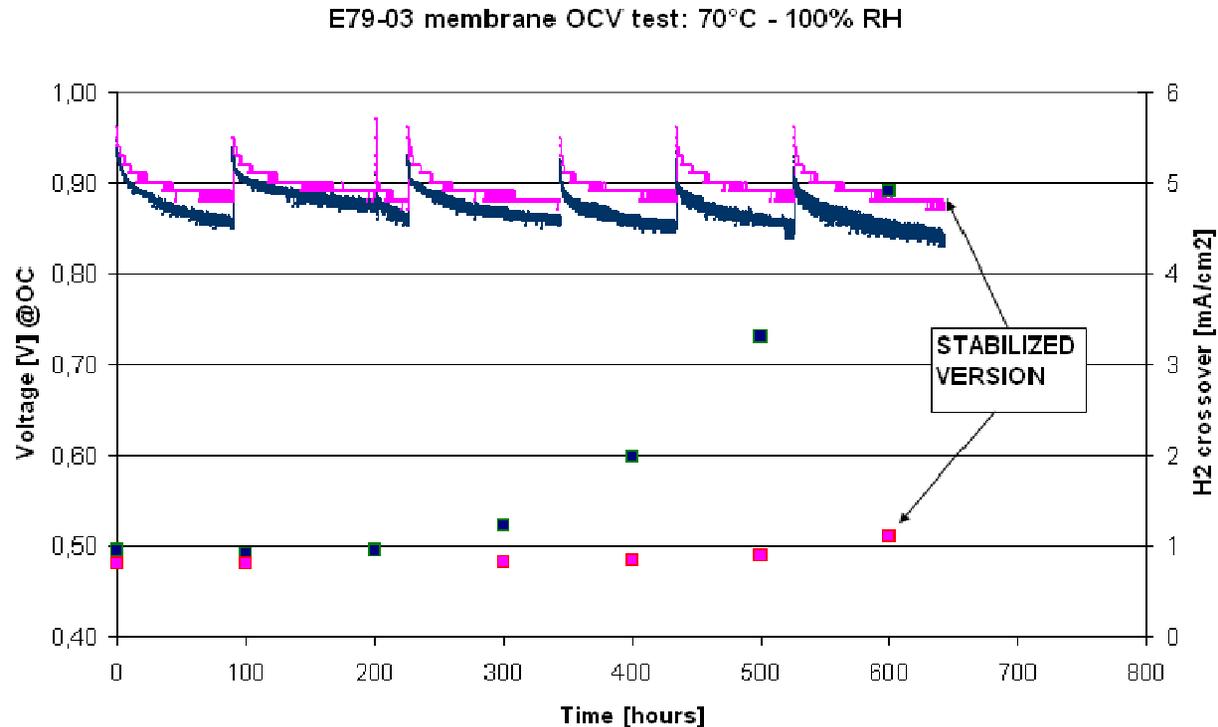
Raman confirmed unchanged -SO₃H content





Different behavior in different operating conditions

Example 1: full humidification operating conditions

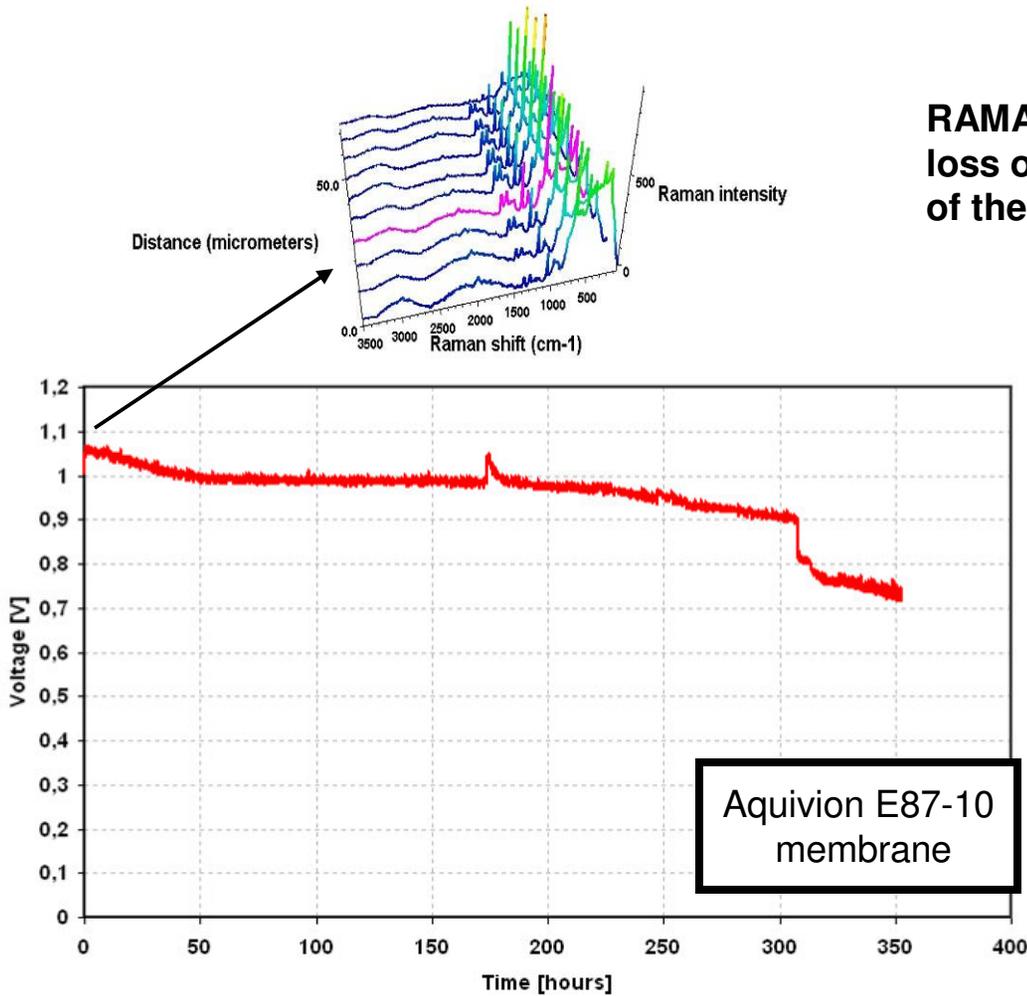


Relevant durability difference (in OCV) between standard and chemically stabilized polymers
= **unzipping reaction** is the dominant degradation mechanism

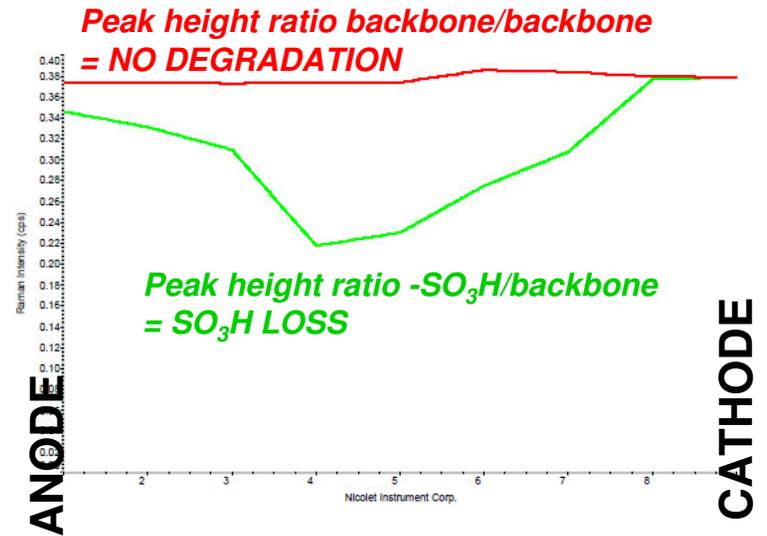
Different behavior in different operating conditions



Example 2: OCV with dry (30% RH) reactants



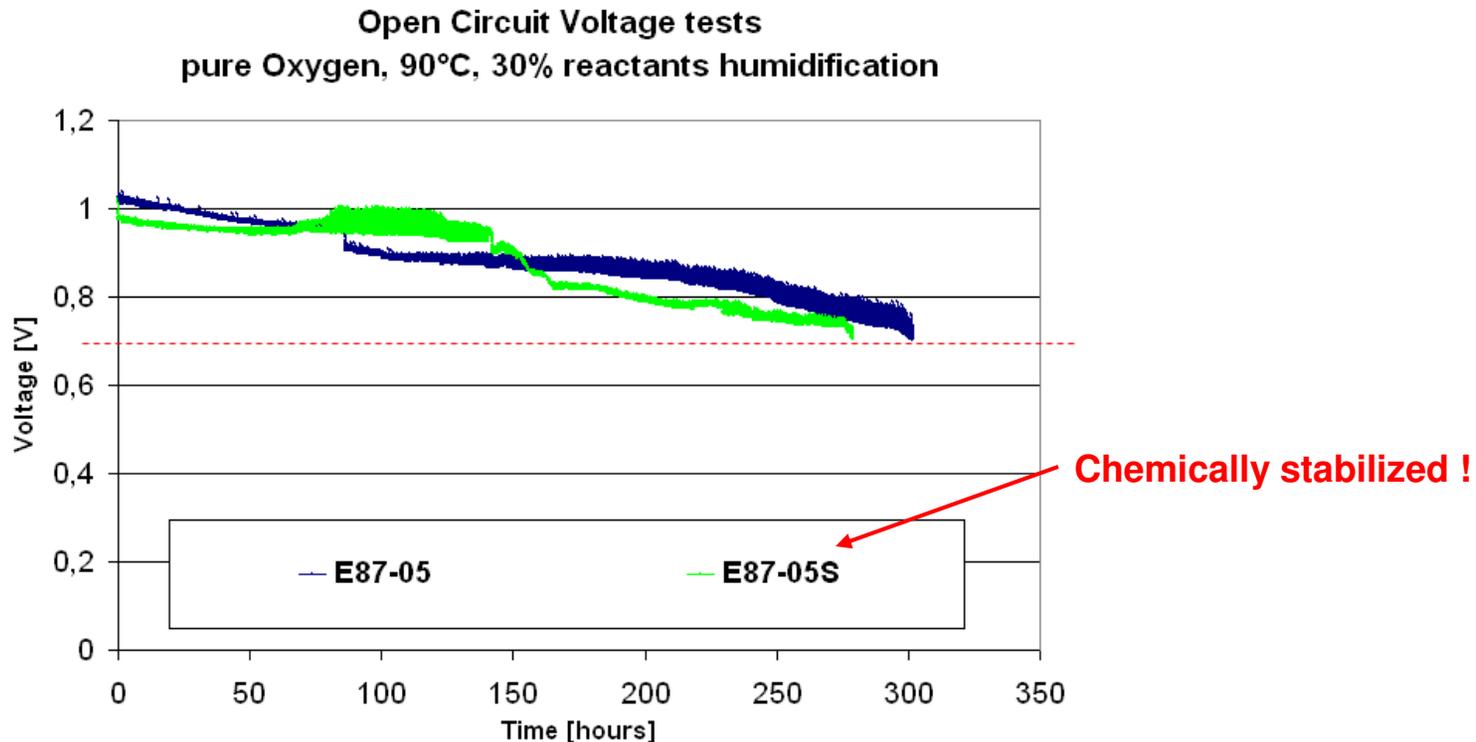
RAMAN spectroscopy evidences at end of life loss of -SO₃H groups concentrated in the middle of the membrane



Different behavior in different operating conditions



Example 2: OCV with partially dry reactants



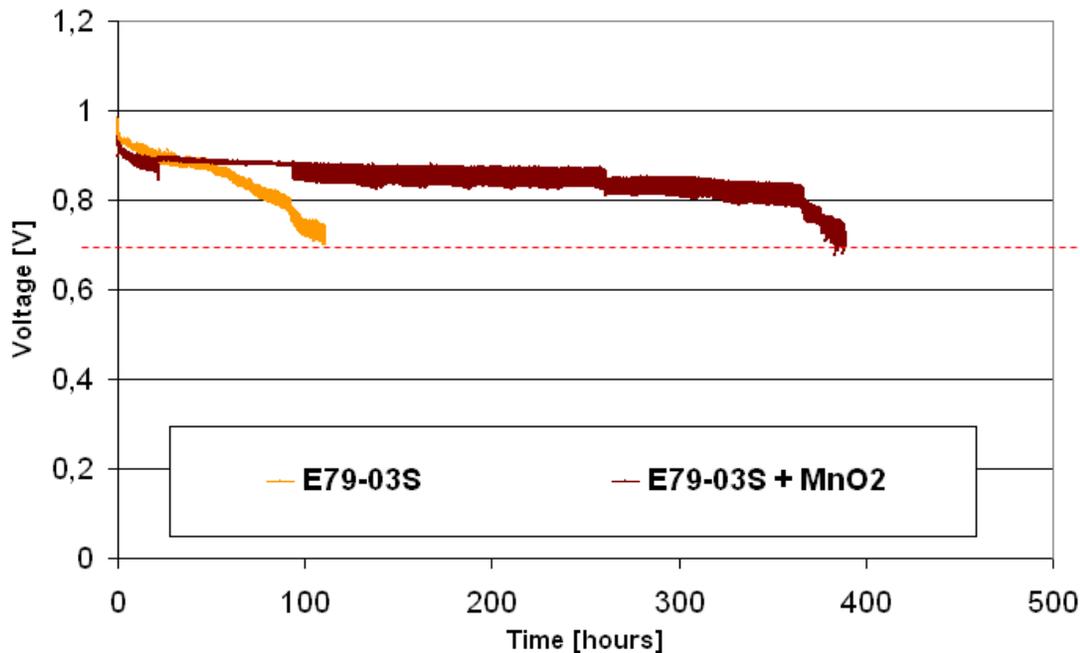
In this operating conditions the difference between standard and chemically stabilized ionomers (-COOH free) is not relevant
= degradation mechanism **is NOT the unzipping reaction**

Different behavior in different operating conditions



Example 2: OCV with partially dry reactants

Open Circuit Voltage tests
pure Oxygen, 90°C, 30% reactants humidification



Journal of The Electrochemical Society, 159 (2) B211-B218 (2012)

Reaction	Rate constant ($M^{-1}s^{-1}$)
$Mn^{2+} + HO^{\bullet} + H^{+} \rightarrow Mn^{3+} + H_2O$	$3 \cdot 10^7$
$Mn^{2+} + HOO^{\bullet} \rightarrow MnO_2^{+} + H^{+}$	$1.8 \cdot 10^6$
$MnO_2^{+} + H^{+} \rightarrow Mn^{2+} + HOO^{\bullet}$	$2.1 \cdot 10^7$
$MnO_2^{+} + HOO^{\bullet} \rightarrow Mn^{2+} + H_2O_2 + O_2$	10^7
$Mn^{2+} + H^{\bullet} \rightarrow Mn^{+} + H^{+}$	$2 \cdot 10^8$
$Mn^{+} + O_2 \rightarrow MnO_2^{+}$	$6 \cdot 10^6$
$Mn^{3+} + HOO^{\bullet} \rightarrow Mn^{2+} + O_2 + H^{+}$	$< 10^5$
$Mn^{3+} + H_2O_2 \rightarrow MnO_2^{+} + 2 H^{+}$	$3 \cdot 10^3$

Presence of 'chemical scavenger' is relevant for lifetime increase in these operating conditions

Different behavior in different operating conditions



Example 3: current cycles causing humidification/drying

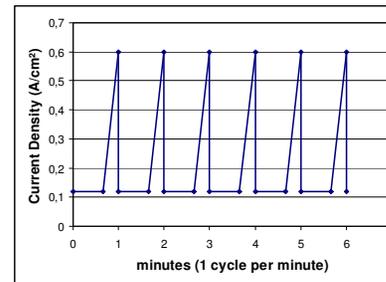
Cell T: 80° C

gas pressure: 1.5 BarAbs

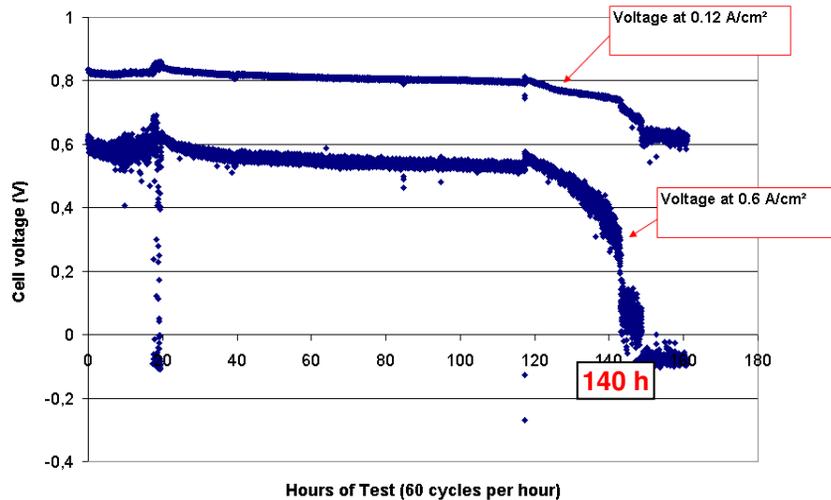
H₂: 40% humid, 1.5 stoich

Air: 60% humid, 1.8 stoich

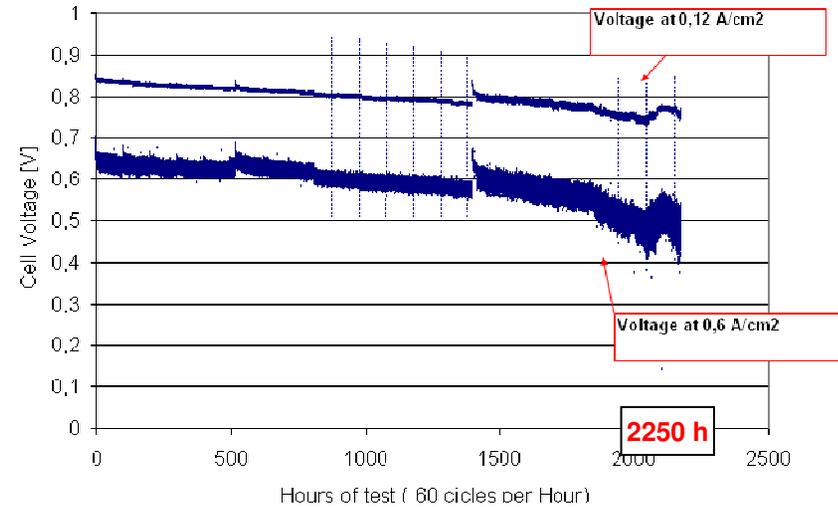
Current regulated like 1 minutes cycles



Cyclic test 130-A37 (E79-03S with GDE, **no edge protection**)



EXP REINF membrane with GDE **no edge protection**

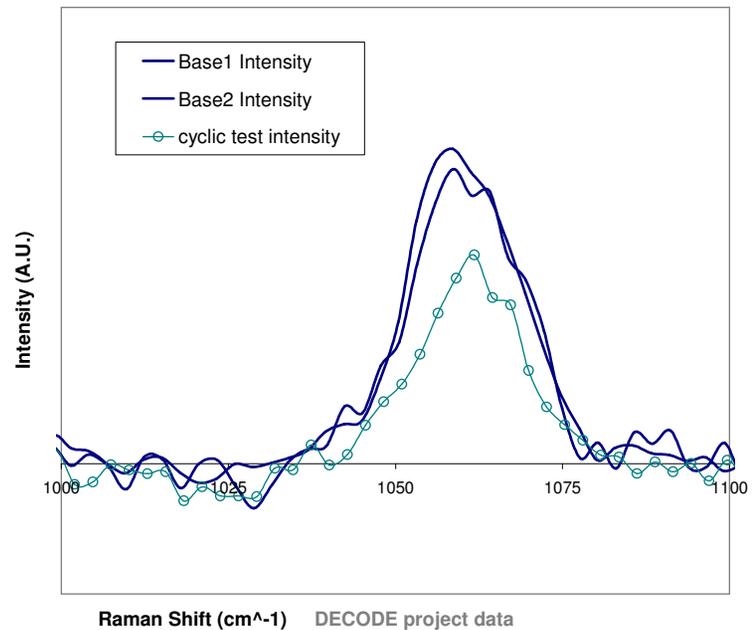
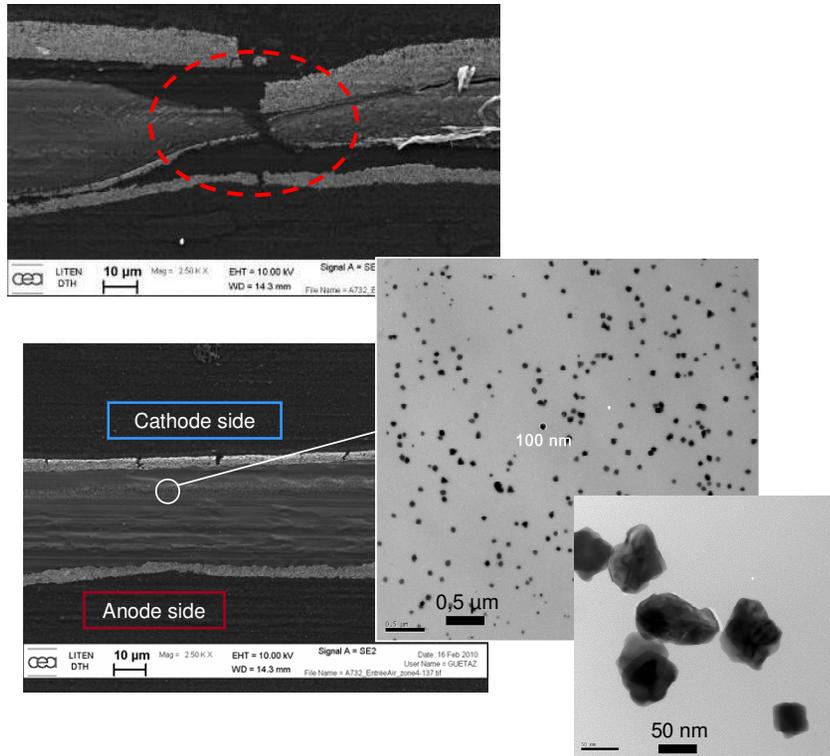


In absence of edge protection, the presence of a mechanical reinforcement **extends dramatically the membrane lifetime**

Different behavior in different operating conditions



Example 3: current cycles causing humidification/drying



The membrane aged with humidification cycles shows an internal Pt band, some thinning that caused holes and a general reduction of -SO₃H group signal

DECODE FP 7th Project data



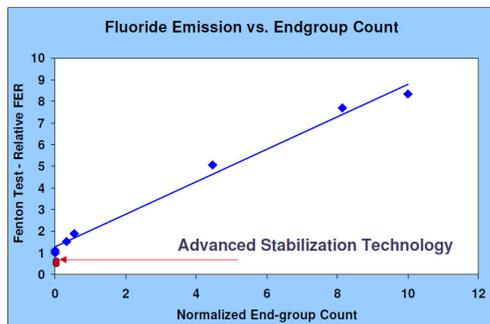
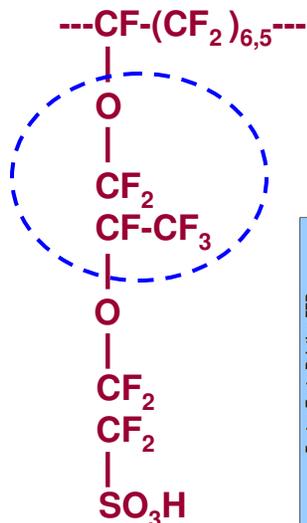
- Aquivion® short side chain structure effects

Advantage of not-branched side chain

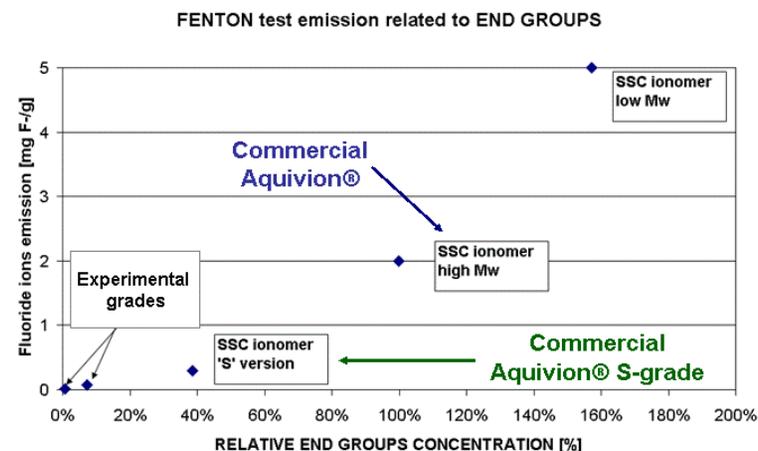
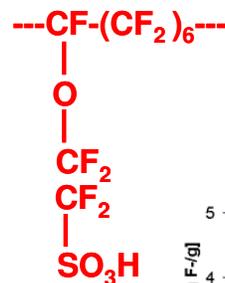
Evidence of higher stability in certain operating conditions

Aquivion® short side chain structure effects

Minor difference in side chain structure **may constitute a difference in chemical stability**



B. Choudhury - ISHE - Nov. 12-15, 2007



The presence of non-zero intercept of Nafion (branched) structures in Fenton test studies **seems to indicate** that the side chain is more subject to $\cdot\text{OH}$ radicals attack.

Anyway, the existence of different radical species in fuel cell environment is probable and the equation: **NO end groups = NO degradation** can be only partially correct.

Aquivion® short side chain structure effects

Different studies on **model compounds** turned to results with difficult interpretation:

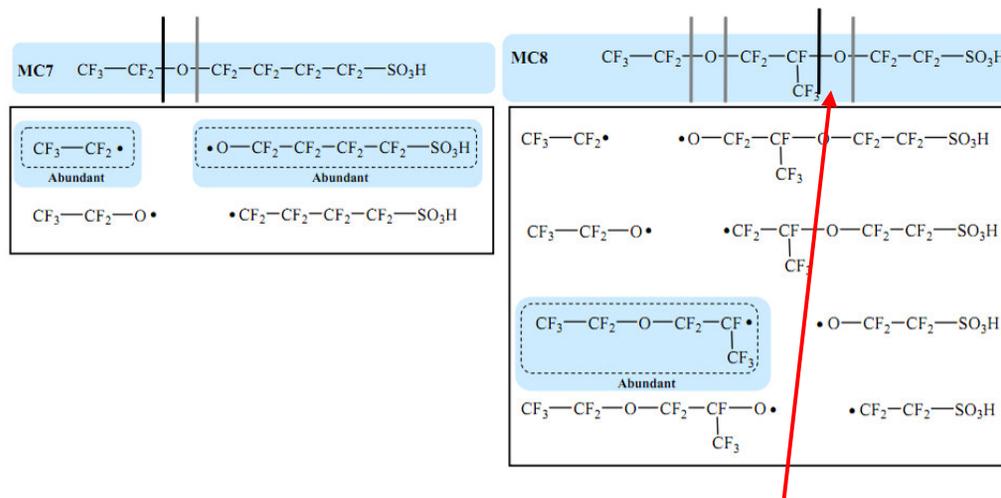
Model Compound	F ⁻ Release (% of total in MC)	Relative F ⁻ Release
3M ionomer: [(CF ₂ CF ₂)(CF ₂ CF(R ₁))]	0.01 (0.1)	1.5 (14)
Nafion ionomer: [(CF ₂ CF ₂)(CF ₂ CF(R ₂))]	0.03 (0.26)	4.3 (37)
CO ₂ HCF(CF ₃)OC ₃ F ₇	0.08	11
CO ₂ HCF(CF ₃)OC ₄ F ₈ SO ₃ H	0.28	40
C ₇ F ₁₅ CO ₂ H	0.02	2.8
C ₄ F ₉ SO ₃ H	0.008	1.1
C ₈ F ₁₇ H	0.007	1
C ₂ F ₅ OC ₃ F ₈ SO ₃ H	0.002	0.3
C ₂ F ₅ OC ₂ F ₃ (CF ₃)OC ₂ F ₄ SO ₃ H	0.001	0.15

R₁ = OC₄F₈SO₃H

R₂ = OCF₂CF(CF₃)OC₂F₄SO₃H

Numbers in parenthesis based on side chain only

Evidence of some advantage of the non-branched structure of the side chain



Collection of radicals species evidences that the weakest ether bond is the closest to tertiary carbon (but the model compound does not have the 'other' tertiary carbon...)

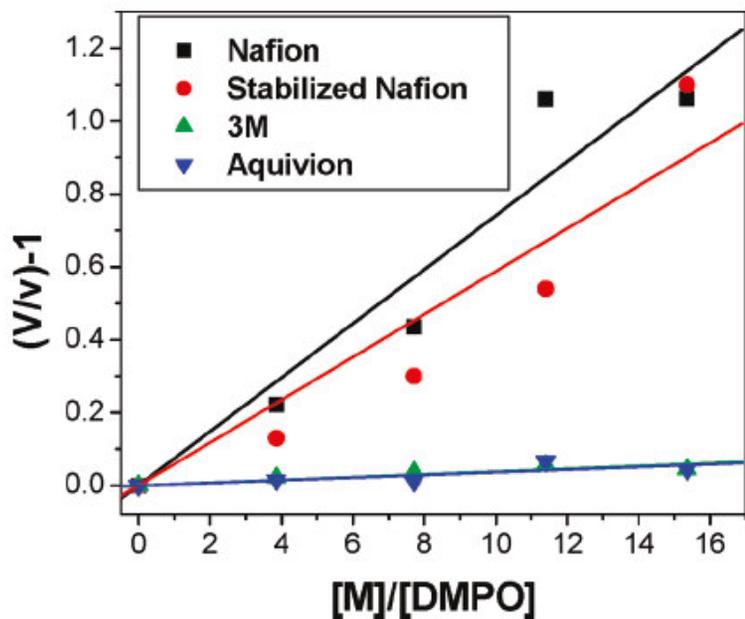
DOE, Cooperative Agreements Nos. DE-FC36-03GO13098 and DE-FG36-07G017006

Aquivion® short side chain structure effects

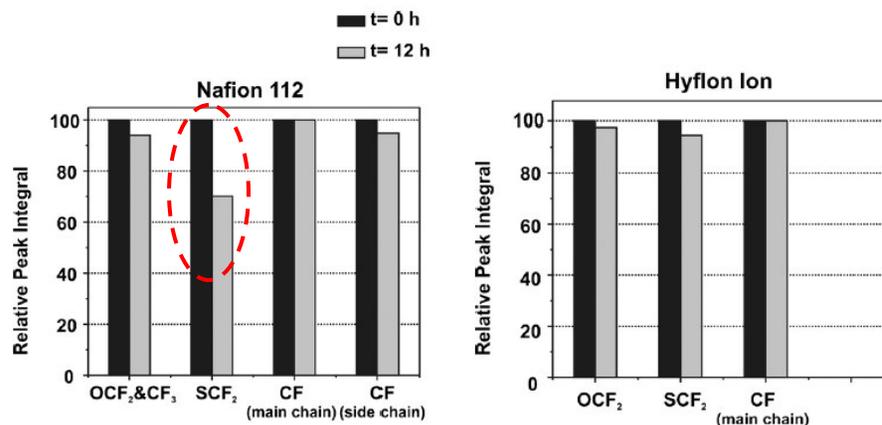
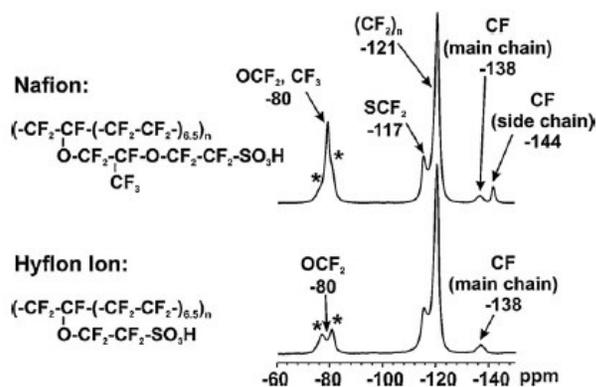
Otherwise, studies exist that gives indication of a **clear advantage of the short side chain structure:**

Journal of Power Sources 196 (2011) 2490–2497

Macromolecules, 2010, 43 (7), pp 3352–3358



V: rate of formation of the DMPO/OH adduct
v: rate of formation of the DMPO/OH adduct in presence of competitor (ionomer)





- Conclusions

Conclusions



- **PFSA** polymers **are preferable** in terms of performance and chemical resistance among other ionomers
- **chemical stabilization** (conversion of end groups) **inhibits the unzipping reaction** giving a large improvement in membrane durability (particularly in stationary operating conditions)
- **low level of 'Fenton' metals is important** to limit the aggressive radical species (utility of 'zero' level is questionable since radical species generate also on catalyst surface)
- **gas crossover reduction** can be one route to inhibit the formation of certain radical species (but not all of them)
- in some operating conditions the use of **scavenger** or a **mechanical reinforcement** are useful to increase substantially membrane lifetime
- **short side chain** structures appears **intrinsically less exposed to certain degradation mechanisms** compared to branched ones

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