A. Albert, T. J. Schmidt, L. Gubler :: Paul Scherrer Institut :: Switzerland

Properties and Stability of Radiation Grafted Membranes for Water Electrolysis Cells

Pacific Polymer Conference 14, 9-13 December 2015, Kauai, Hawaii

Acknowledgments

NOVEL Novel materials and system designs for low cost, efficient and durable PEM electrolysers

SINTEF

New Energy World JTI

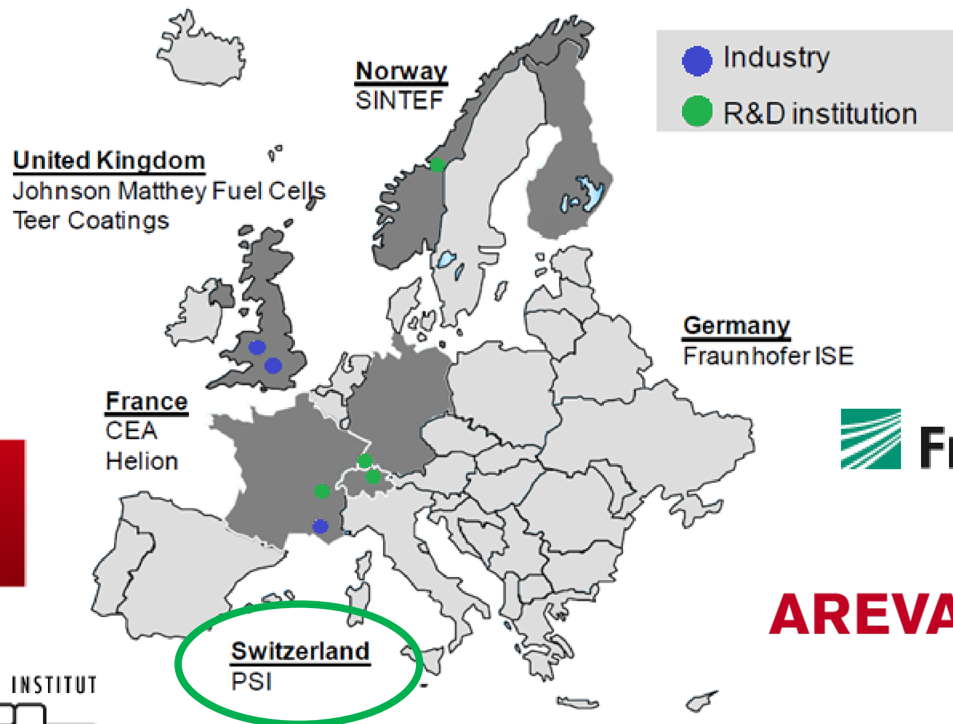
fuel cells & hydrogen for sustainability

SEVENTH FRAMEWORK PROGRAMME

Johnson Matthey Fuel Cells

the power within

Innovation in Motion Miba



Fraunhofer ISE

AREVA H_2Gen

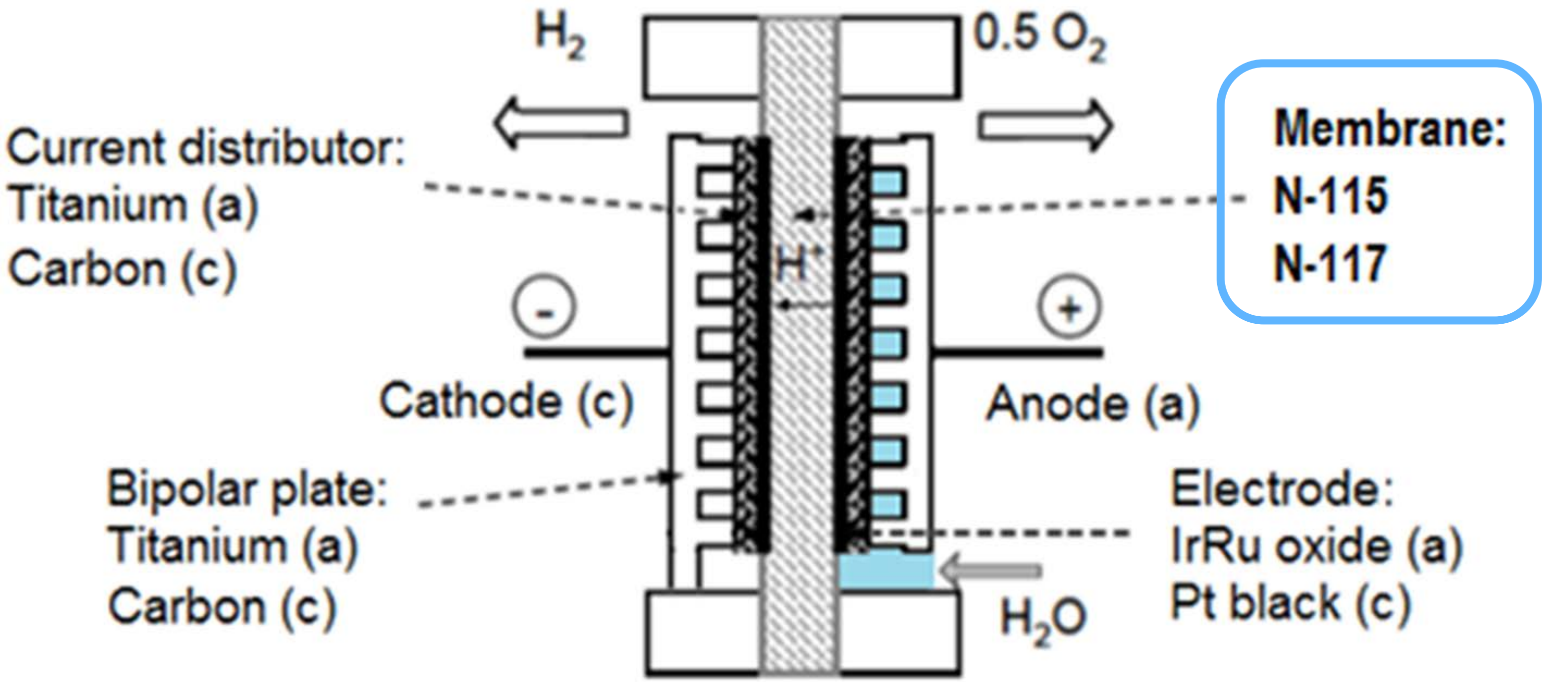
PAUL SCHERRER INSTITUT PSI

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n°303484.

Outline

- Introduction
  - Water Electrolyzer
  - Radiation Grafted Membranes
- Properties
- Stability
- Preliminary test
- Summary

Water Electrolyzer

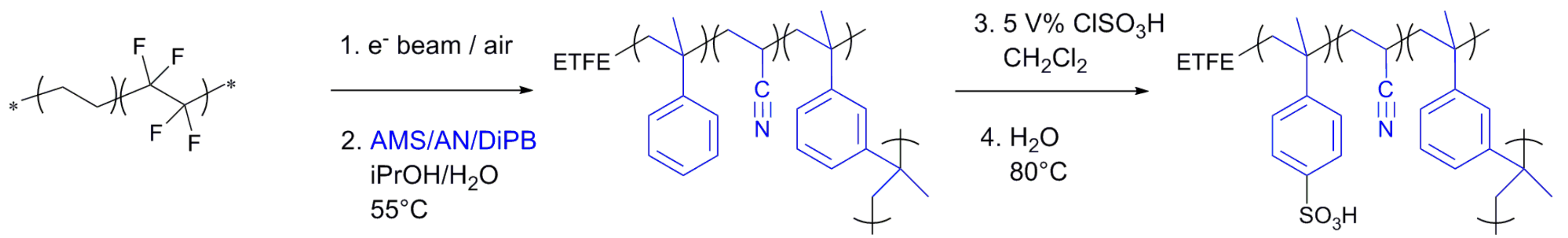


Nafion N-115 (127 µm) / N-117 (178 µm) :

- Low hydrogen crossover
- Stable
- High area resistance
- High cost

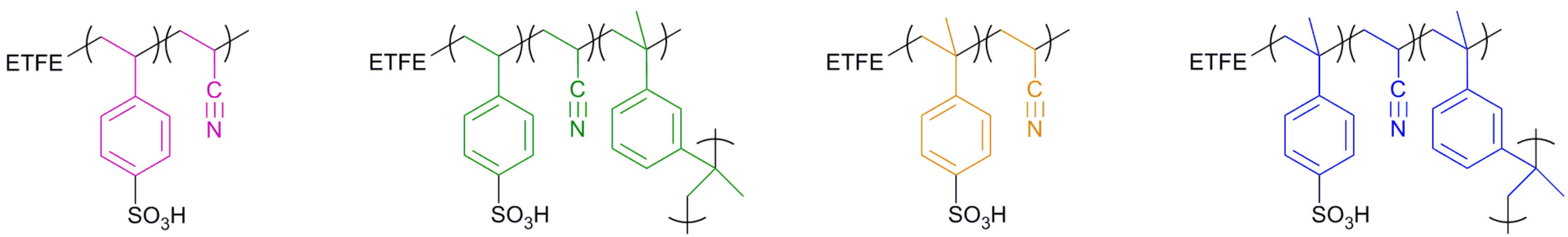
Alternative membrane ?

Radiation Grafted Membranes



Ethylene tetrafluoroethylene
(ETFE)
50 µm

Radiation grafted membrane



St/AN St/AN/DiPB AMS/AN AMS/AN/DiPB

St (Styrene) AMS (α-Methylstyrene) AN (Acrylonitrile) DiPB (1,3-Diisopropenylbenzene)

Radiation grafted membranes:

- Potentially low cost*

*L. Gubler and L. Bonorand, *ECS Trans.*, **2013**, 58, 149.

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Outline

- Introduction
- Properties
  - Hydrogen crossover
  - Area resistance
  - Mechanical properties
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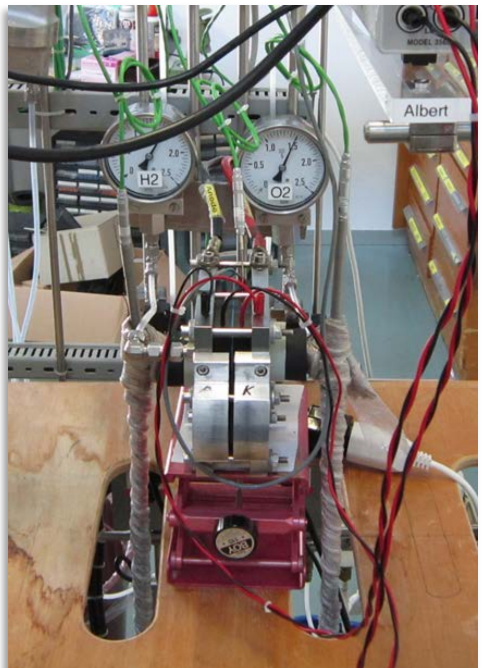
Properties - Experimental

H_2 Crossover & Area Resistance



Single Cell

$H_2/N_2(O_2)$

80 °C

2.5/2.5 bar

Humidity 100%

Mechanical Properties

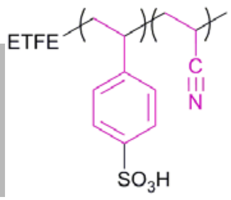
Materials Testing Machine

ASTM D 882

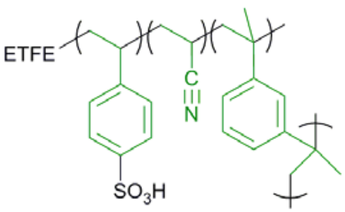
Room temperature

Fully hydrated condition

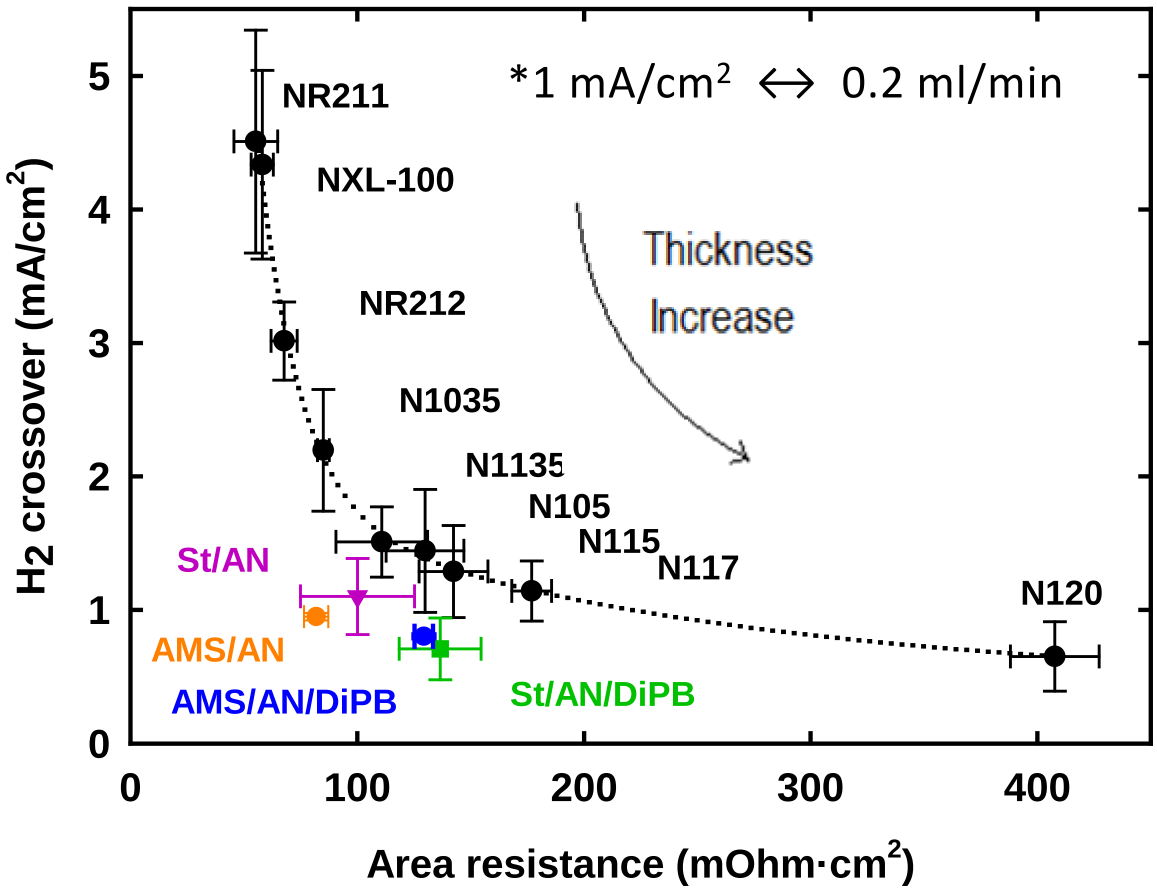
Hydrogen crossover vs. Area resistance

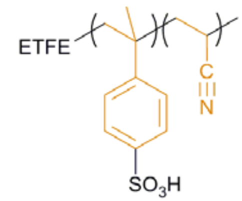


St/AN

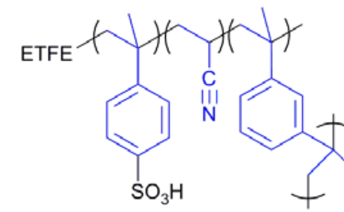


St/AN/DiPB





AMS/AN



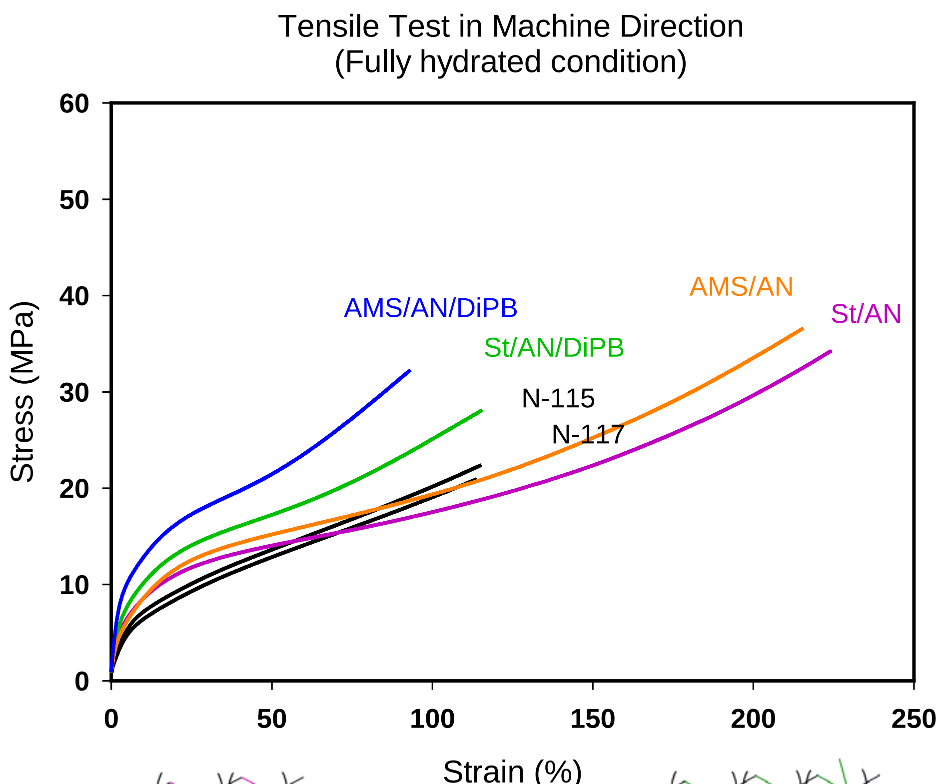
AMS/AN/DiPB

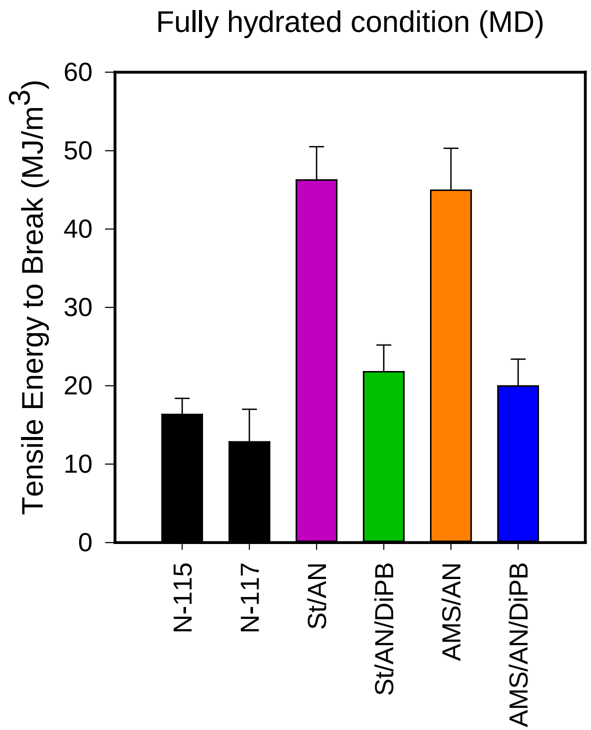
Radiation grafted membranes:

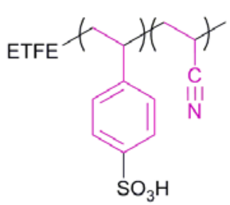
- Lower hydrogen crossover
- Lower area resistance

A. Albert, A. O. Barnett, M. S. Thomassen, T. J. Schmidt and L. Gubler, *ACS Appl. Mater. Interfaces*, **2015**, 7, 22203.

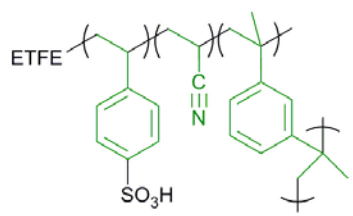
Mechanical Properties



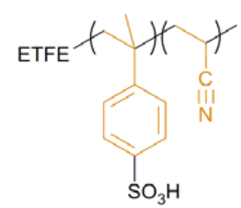




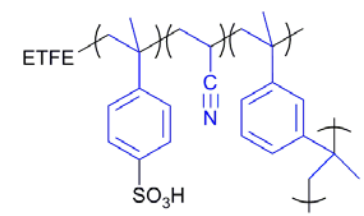
St/AN



St/AN/DiPB



AMS/AN



AMS/AN/DiPB

Radiation grafted membranes:

- Better Mechanical Properties

A. Albert, A. O. Barnett, M. S. Thomassen, T. J. Schmidt and L. Gubler, *ACS Appl. Mater. Interfaces*, **2015**, 7, 22203.

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Outline

- Introduction
- Properties
- Stability
  - Thermal Stress Test
    - Water
      - UV-Vis
      - IC
    - Membrane
      - IEC
      - FTIR
      - EDX
      - H_2 crossover & Area resistance
  - OCV Hold Test
    - H_2 crossover & Area resistance
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→ Degradation Mechanisms

Stability - Experimental

Thermal Stress Test (TST)

Membrane 30 cm²

100 ml deionized water

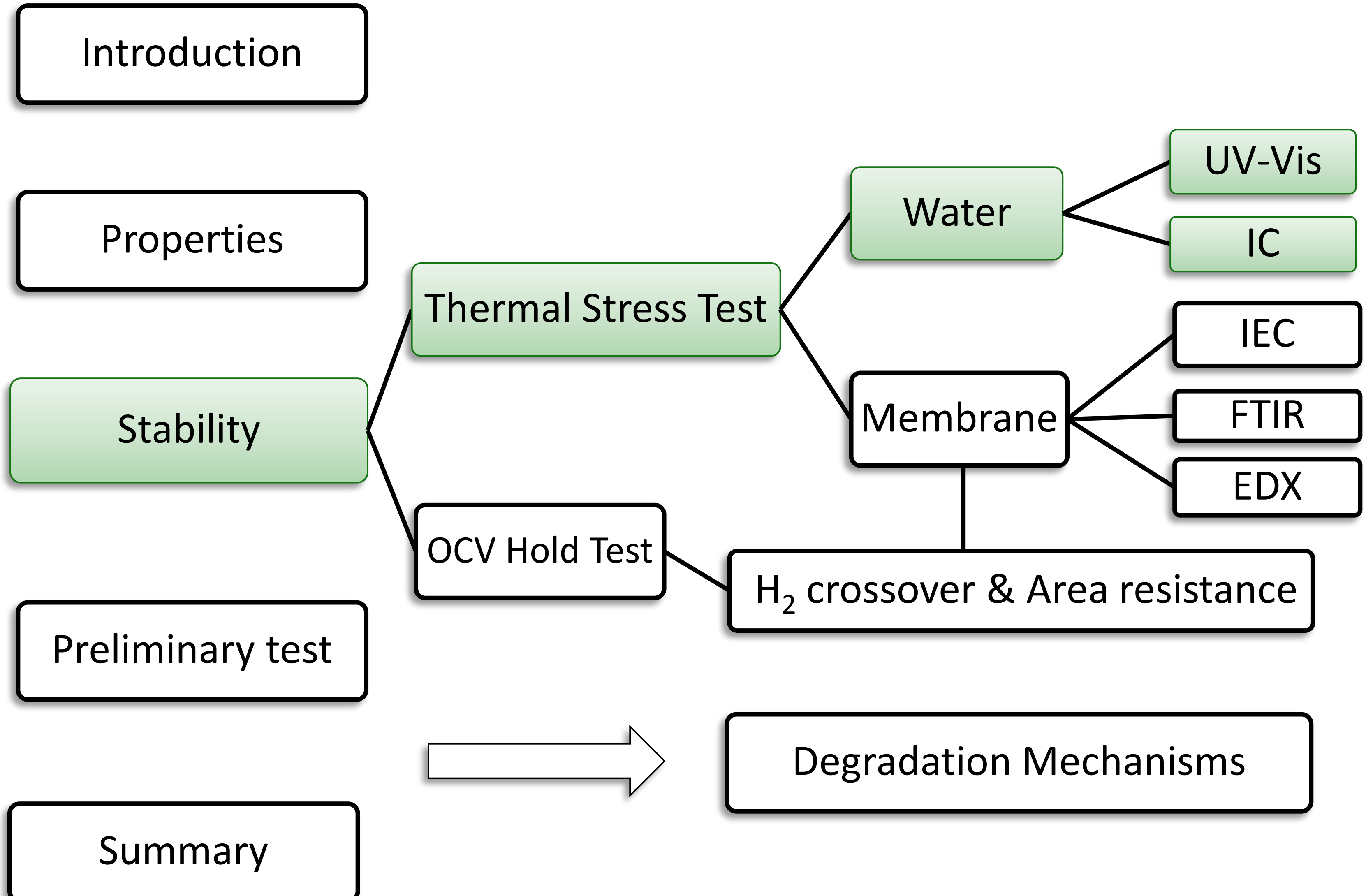
Air/Argon

90 °C

Under stirring

5 days

Outline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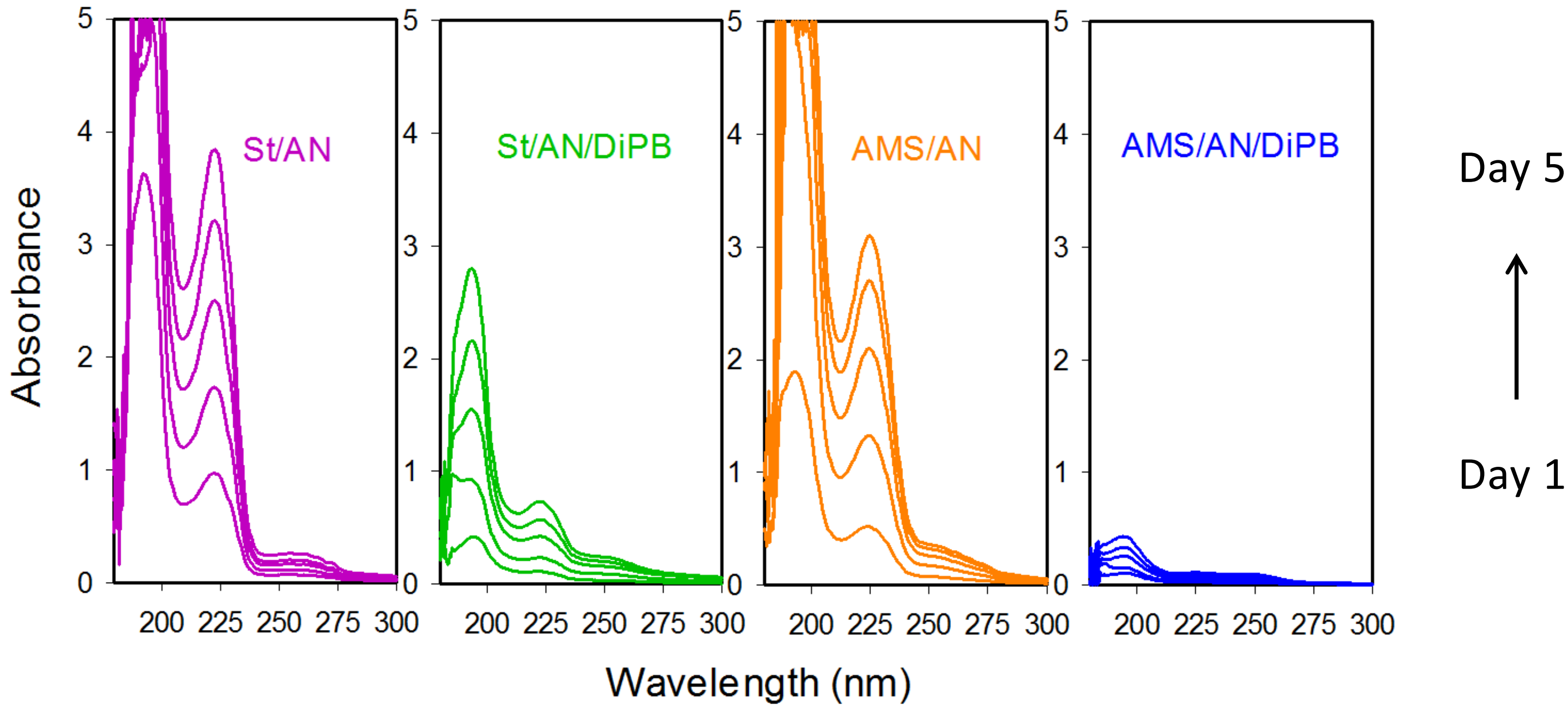
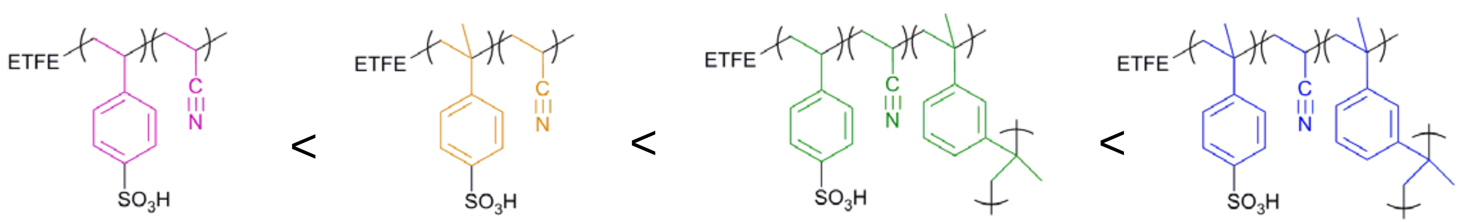
Degradation Mechanisms

Water (Air) - UV/Vis Spectroscopy



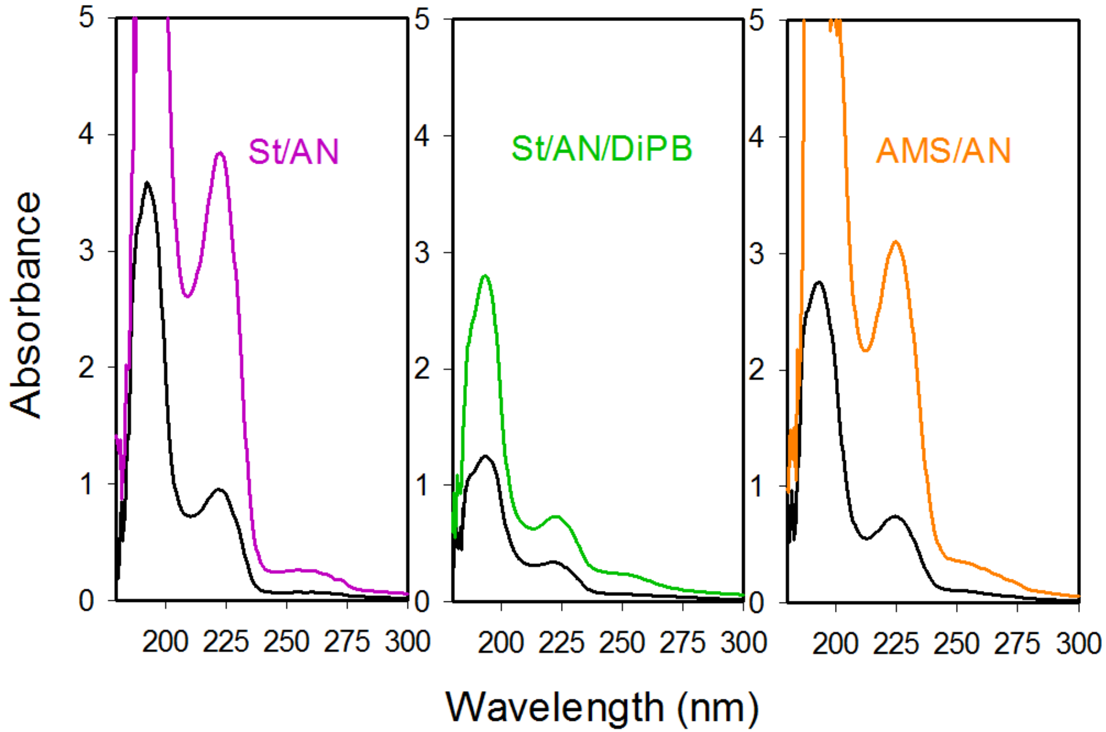
Stability



St/AN AMS/AN St/AN/DiPB AMS/AN/DiPB

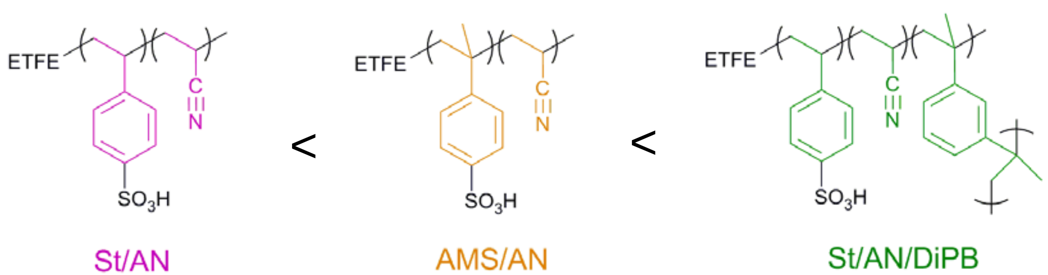
- Degraded species are in the form of polymer fragments
- Crosslinked membranes are more stable

Water (Argon)- UV/Vis Spectroscopy



UV-Vis after 5 days
Air (in color)
Argon (in black)

Stability



- Less scission of polymer chains, but not completely
- O_2 is somehow promoting

Water - Ion Chromatography (IC)

Sample	SO_4^{2-}	F^-	Cl^-	NO_3^-	PO_4^{2-}
Blank test	0.02	-	0.01	0.60	0.05
St/AN (Argon)	1.02 0.27 (0.17)	0.06 0.03 (0.03)	0.26 0.06 (0.08)	0.64 0.61 -	-
St/AN/DiPB (Argon)	3.64 2.02 (0.64)	0.14 0.05 (0.05)	0.53 0.47 (0.48)	0.85 0.62 (0.05)	-
AMS/AN (Argon)	0.64 0.71 (0.16)	0.09 0.07 (0.04)	0.21 0.19 (0.17)	0.13 0.16 (0.05)	-
AMS/AN/DiPB	1.20 1.62	0.02 0.05	0.24 0.24	0.04 0.12	-
N115	0.11	0.03	0.04	0.62	-
N117	0.14	0.04	0.10	0.71	-

*All in ppm ≈ mg/L (1 ppm ≈ 0.05 wt.% of the membrane)

- Very small extent of desulfonation

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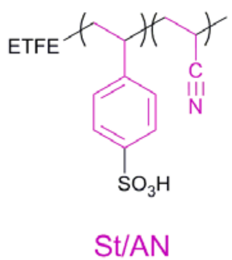
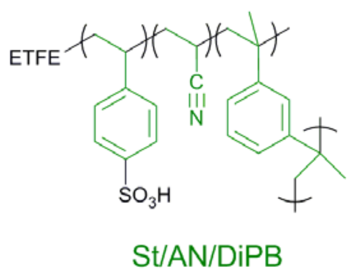
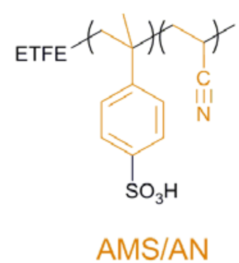
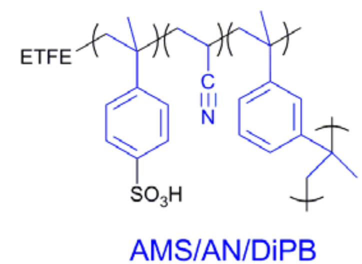
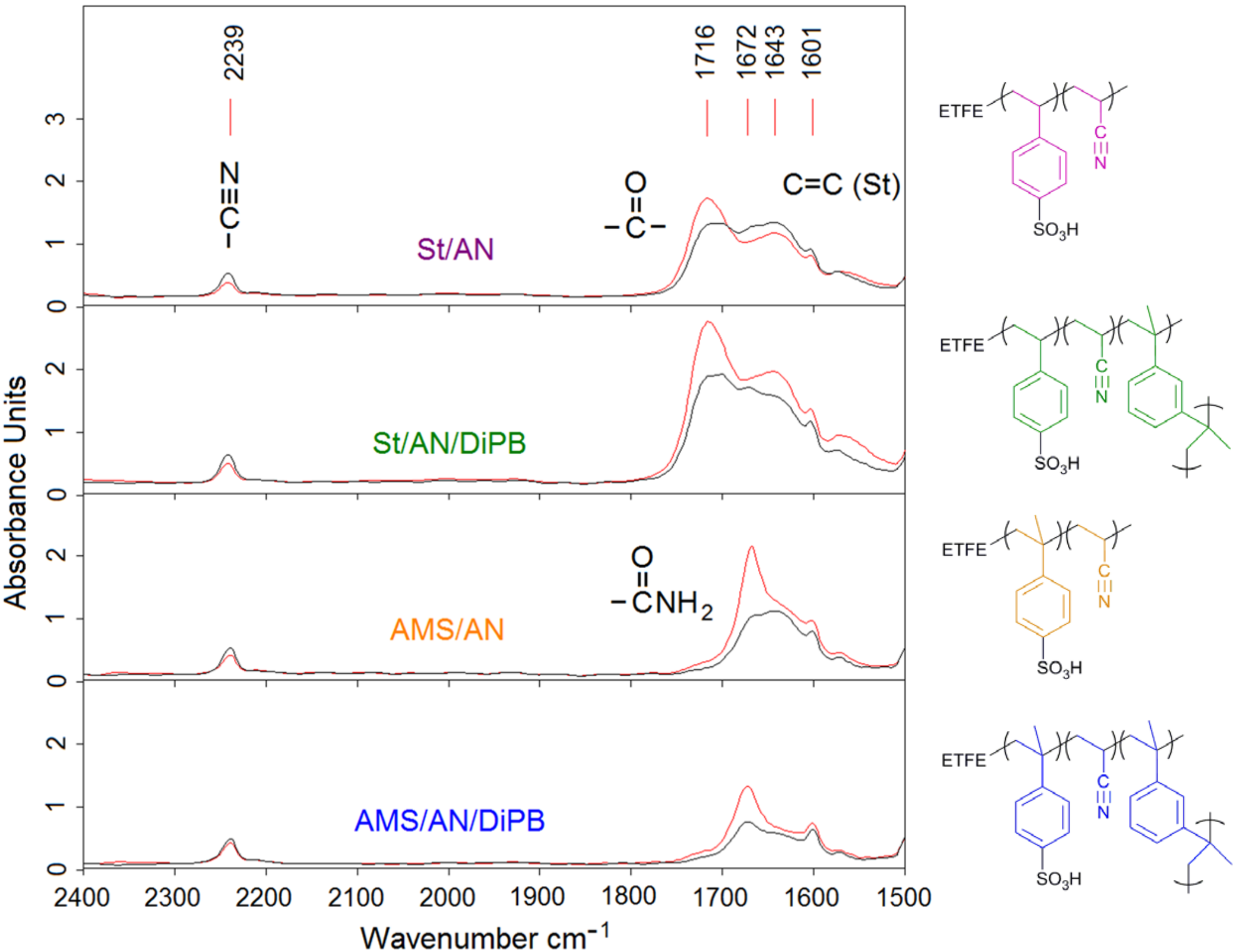
Membrane - IEC

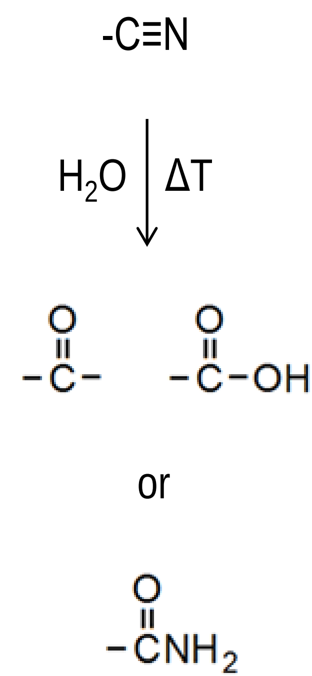
	Ion Exchange Capacity (mmol/g)		
Membranes	Before test	After test	% loss
St/AN (Argon)	1.24 ± 0.01 (1.25 ± 0.02)	0.82 ± 0.06 (0.82 ± 0.01)	34.1 ± 4.7 (34.4 ± 1.7)
St/AN/DiPB (Argon)	1.20 ± 0.00 (1.11 ± 0.02)	0.67 ± 0.01 0.57 ± 0.06	44.2 ± 0.8 (49.1 ± 5.9)
AMS/AN (Argon)	1.65 ± 0.03 (1.65 ± 0.01)	1.48 ± 0.00 (1.59 ± 0.03)	10.3 ± 0.0 (3.19 ± 2.0)
AMS/AN/DiPB	1.58 ± 0.00	1.52 ± 0.01	4.2 ± 0.5

Stability  ≈  <  < 

- Same IEC % loss of styrene based membranes under argon atmosphere
- Another degradation mechanism without any polymer chain scissions

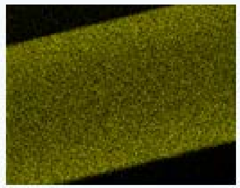
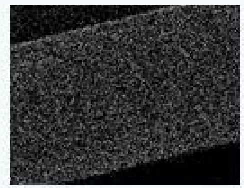
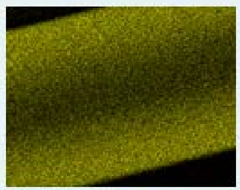
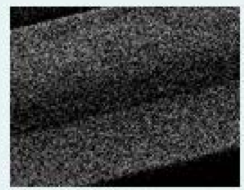
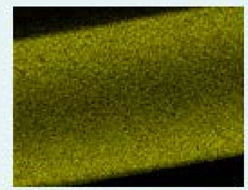
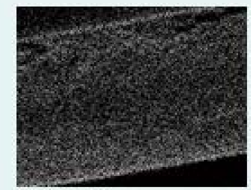
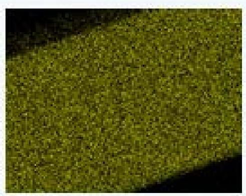
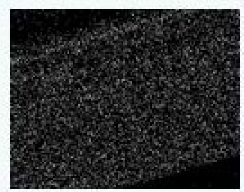
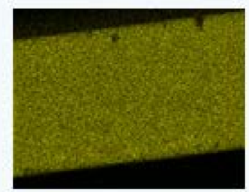
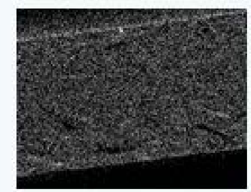
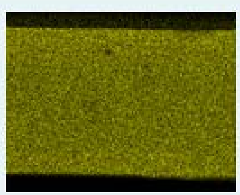
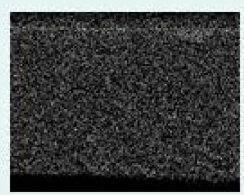
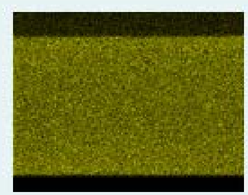
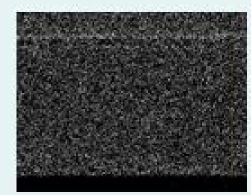
Membrane - FTIR





*Before (in black) and after (in red) 5 days Thermal Stress Test

Membrane - EDX Analysis

	Before		After	
EDX	**Sulphur**	**Nitrogen**	**Sulphur**	**Nitrogen**
St/AN				
St/AN/DiPB				
AMS/AN				
AMS/AN/DiPB				

- No localized degradation

* Energy-dispersive X-ray spectroscopy (EDX)

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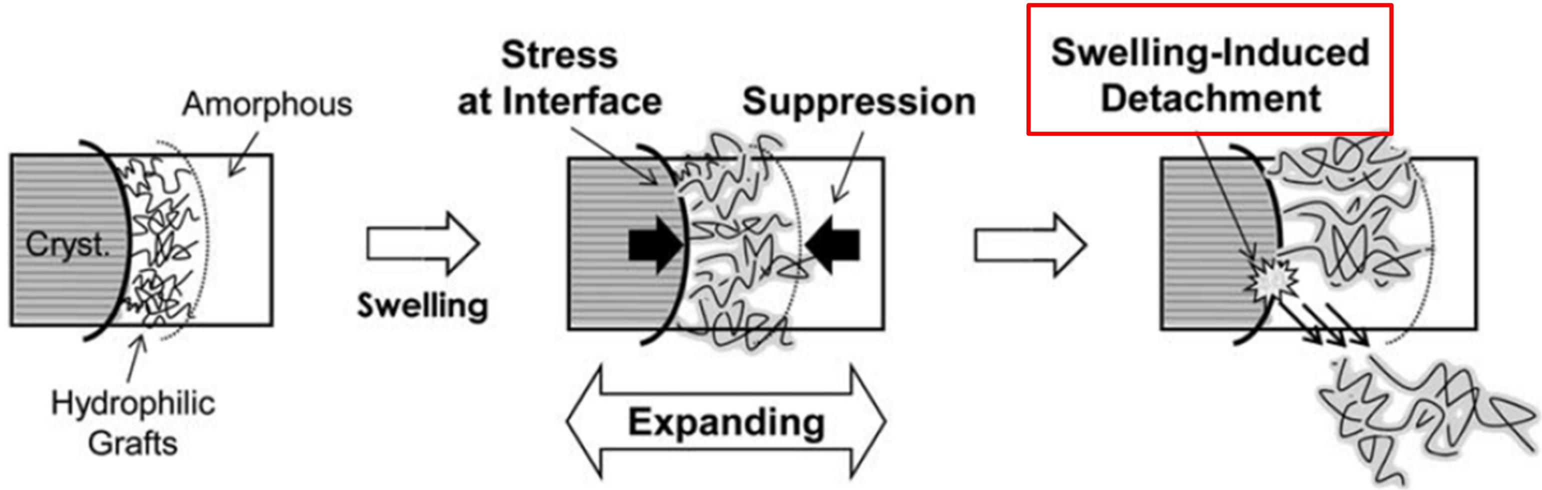
→ Degradation Mechanisms

Degradation Mechanisms in Hot Water

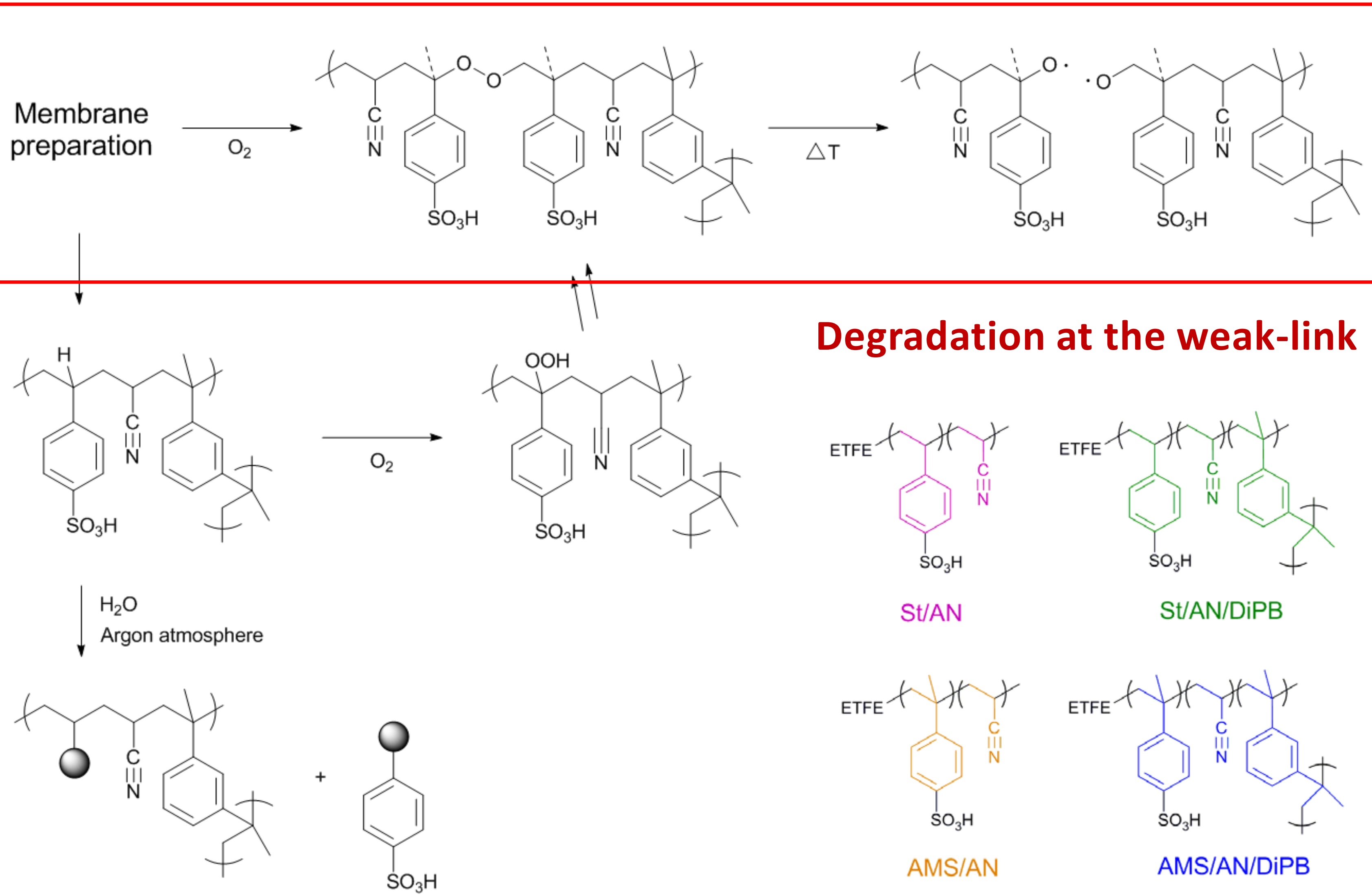


	Swelling (wt. %)		
Membranes	**Before test**	**After test**	**IEC % loss**
St/AN	66.6 ± 0.9	54.4 ± 3.0	34.1 ± 4.7
St/AN/DiPB	35.1 ± 3.2	40.9 ± 3.5	44.2 ± 0.8
AMS/AN	56.5 ± 0.5	60.0 ± 0.5	10.3 ± 0.0
AMS/AN/DiPB	31.7 ± 0.6	-	4.2 ± 0.5

➢ No correlation between swelling and degradation degree
Another degradation mechanisms ?

K. Enomoto, S. Takahashi, T. Iwase, T. Yamashita and Y. Maekawa, *J. Mater. Chem.*, **2011**, 21, 9343.

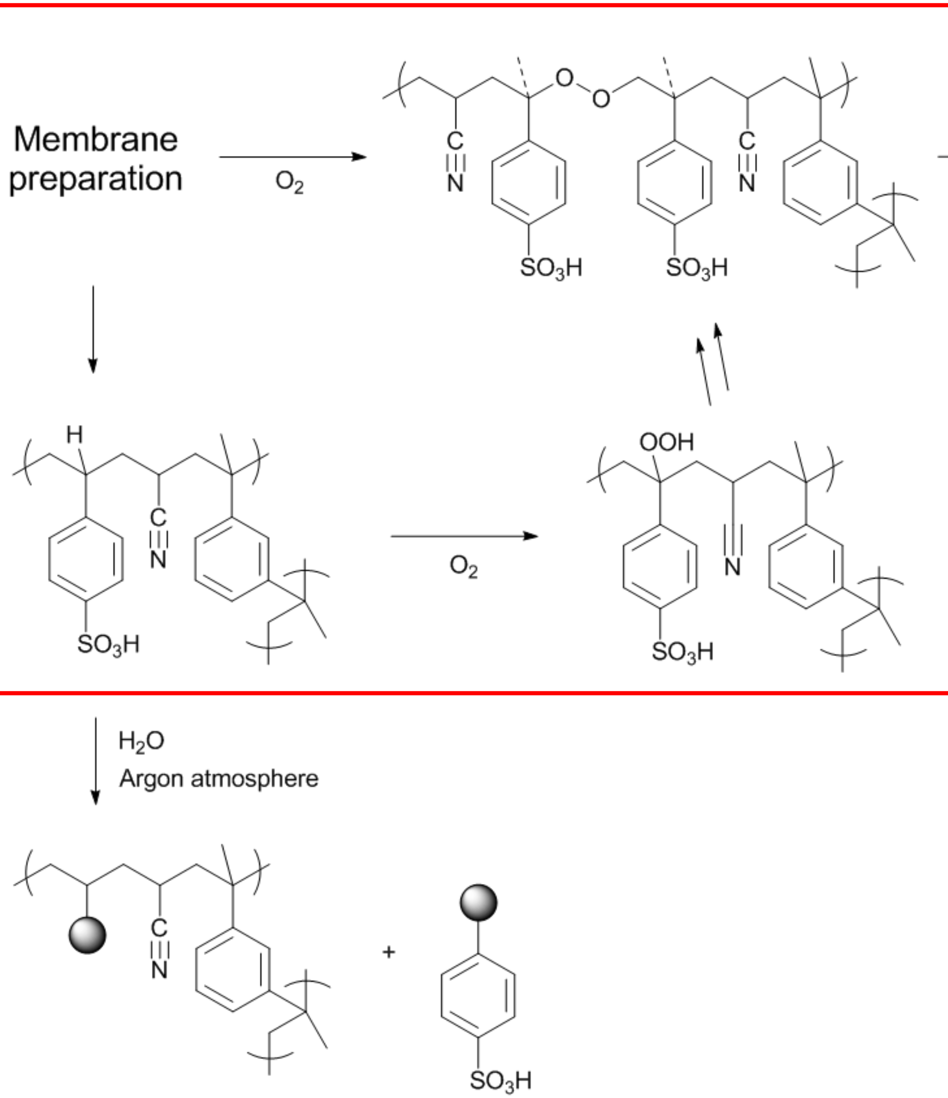
Degradation Mechanisms in Hot Water

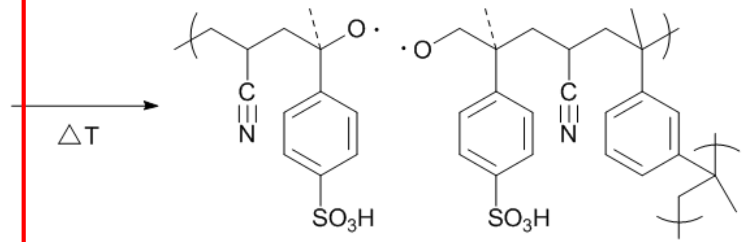


- Weak-links are formed during polymerization in the presence of O_2

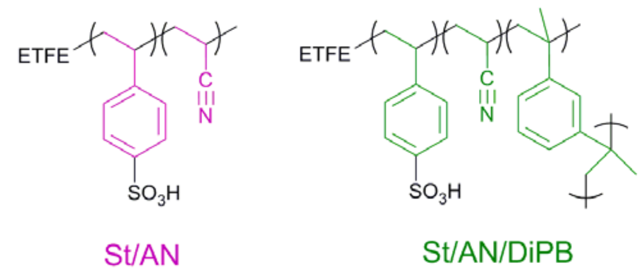
A. Albert, T. Lochner, T. J. Schmidt and L. Gubler, *Article in preparation; Proposed mechanisms.*

Degradation Mechanisms in Hot Water





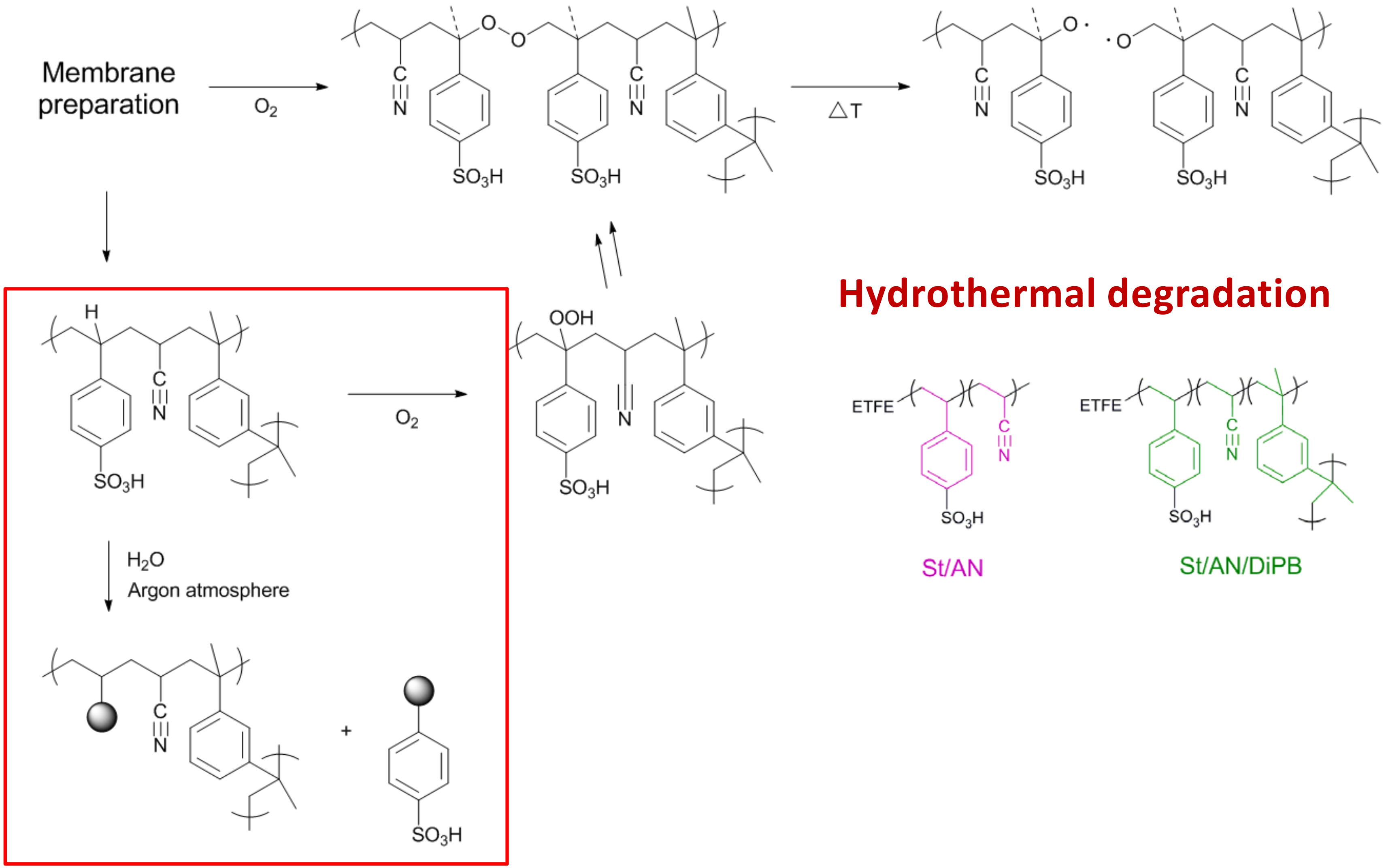
Oxygen-induced degradation



- O_2 leads to the formation of new weak-links

A. Albert, T. Lochner, T. J. Schmidt and L. Gubler, *Article in preparation; Proposed mechanisms.*

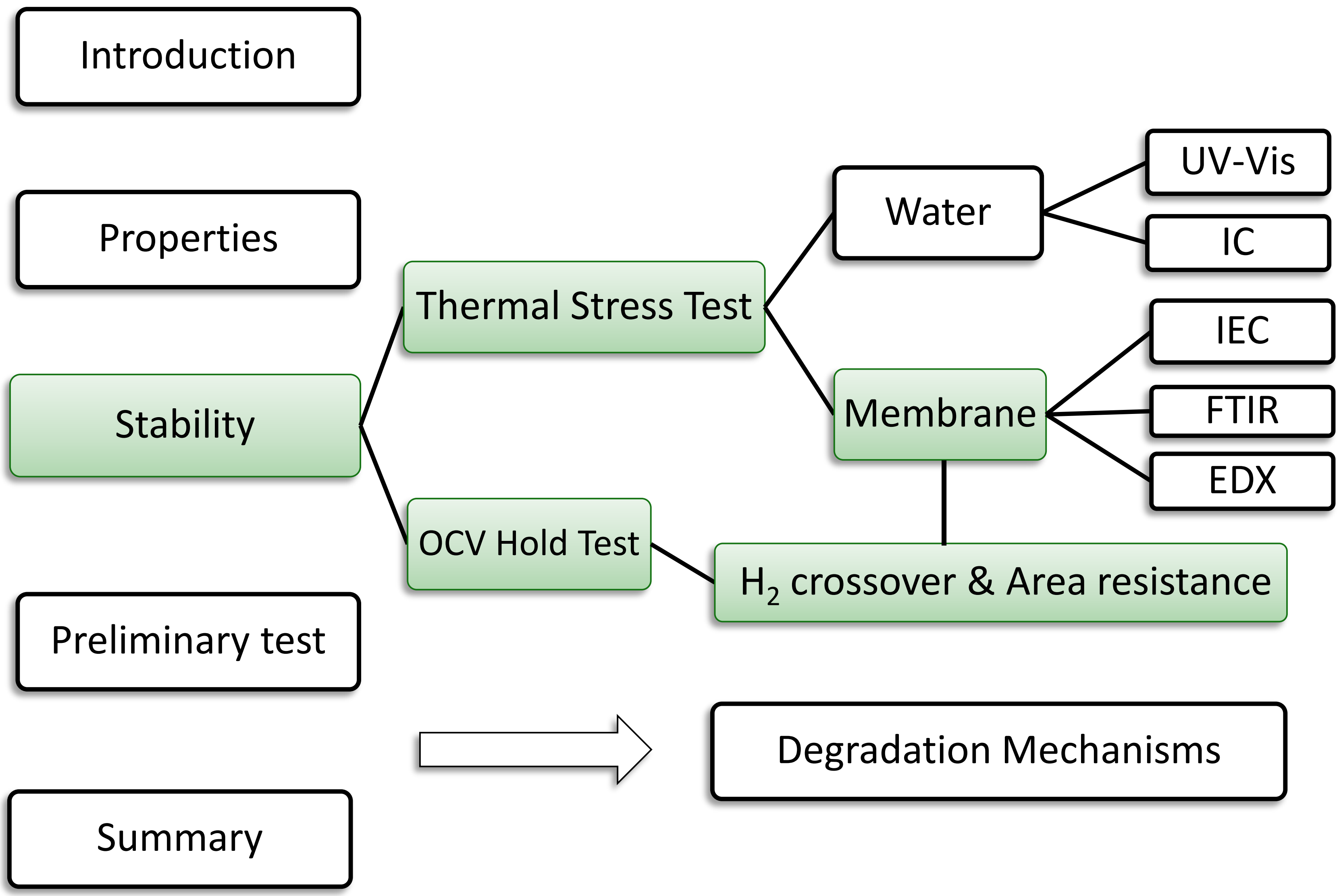
Degradation Mechanisms in Hot Water



- Loss of molecules containing sulphonic acid, but no chain scissions

A. Albert, T. Lochner, T. J. Schmidt and L. Gubler, *Article in preparation; Proposed mechanisms.*

Outline



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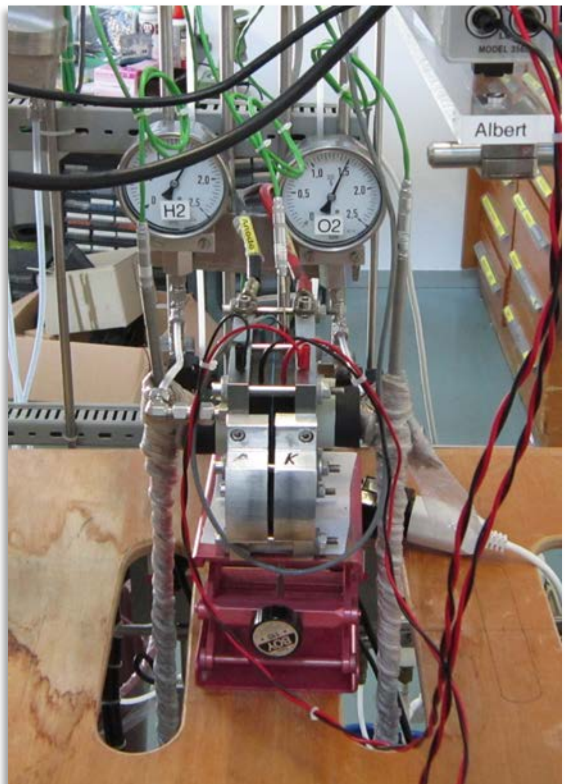
Stability - Experimental

Open Circuit Voltage (OCV) Hold Test



Fuel Cell

H_2/O_2

200 ml/min

80 °C

2.5/2.5 bar

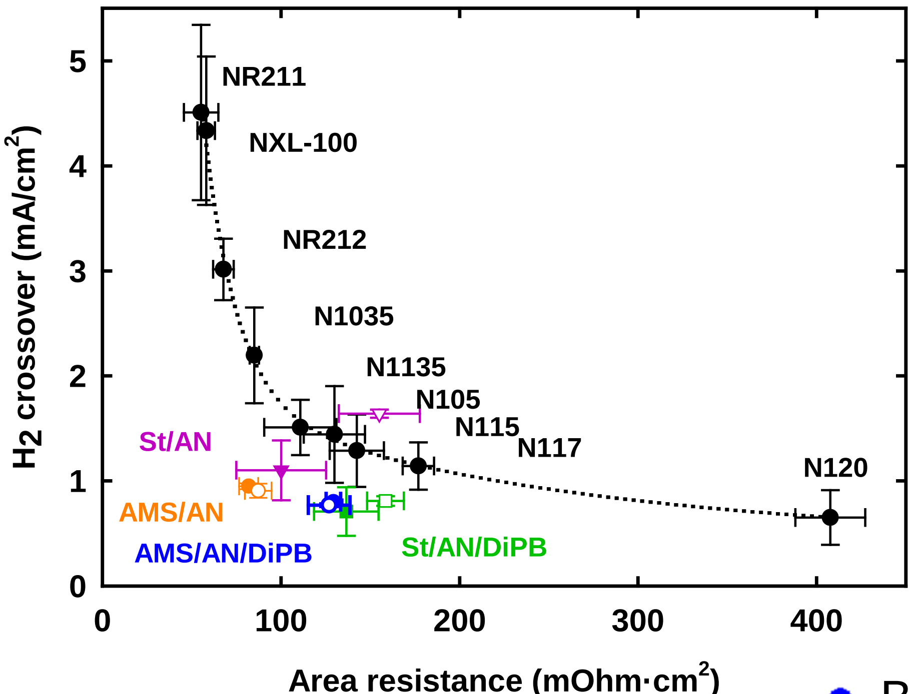
Humidity 100%

5 days

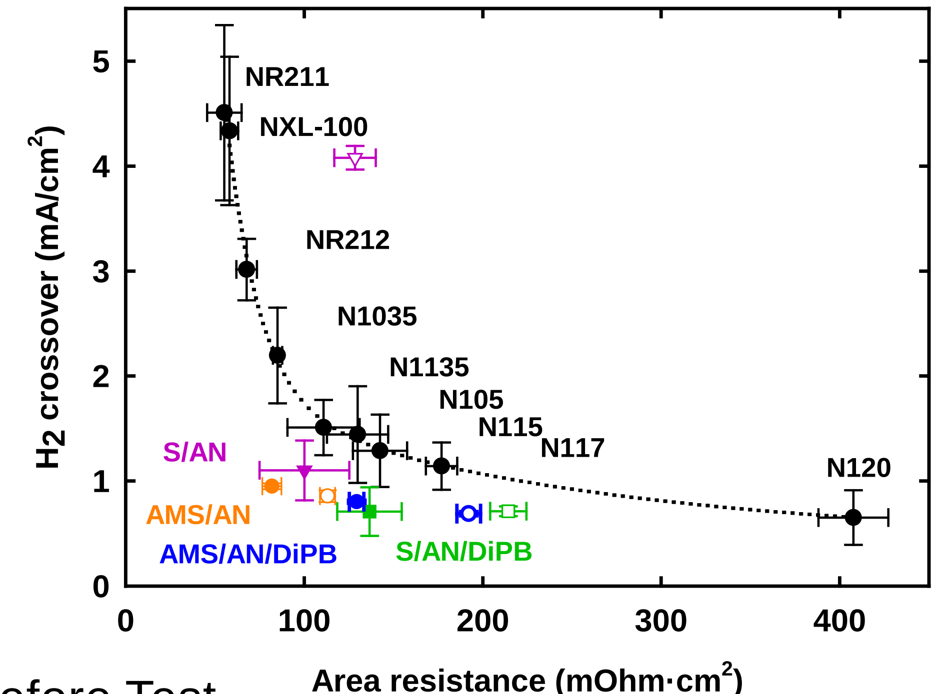
- Peroxide rich condition

Stability - H_2 crossover & Area Resistance

Thermal Stress Test



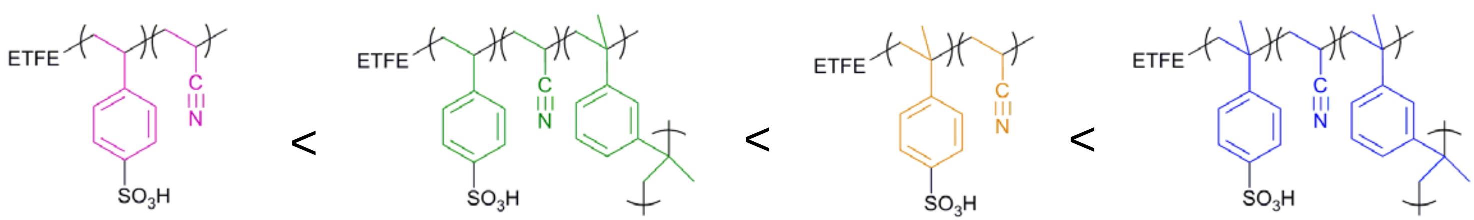
Open Circuit Voltage (OCV) Hold Test



● Before Test

○ After Test

Stability



St/AN < St/AN/DiPB < AMS/AN < AMS/AN/DiPB

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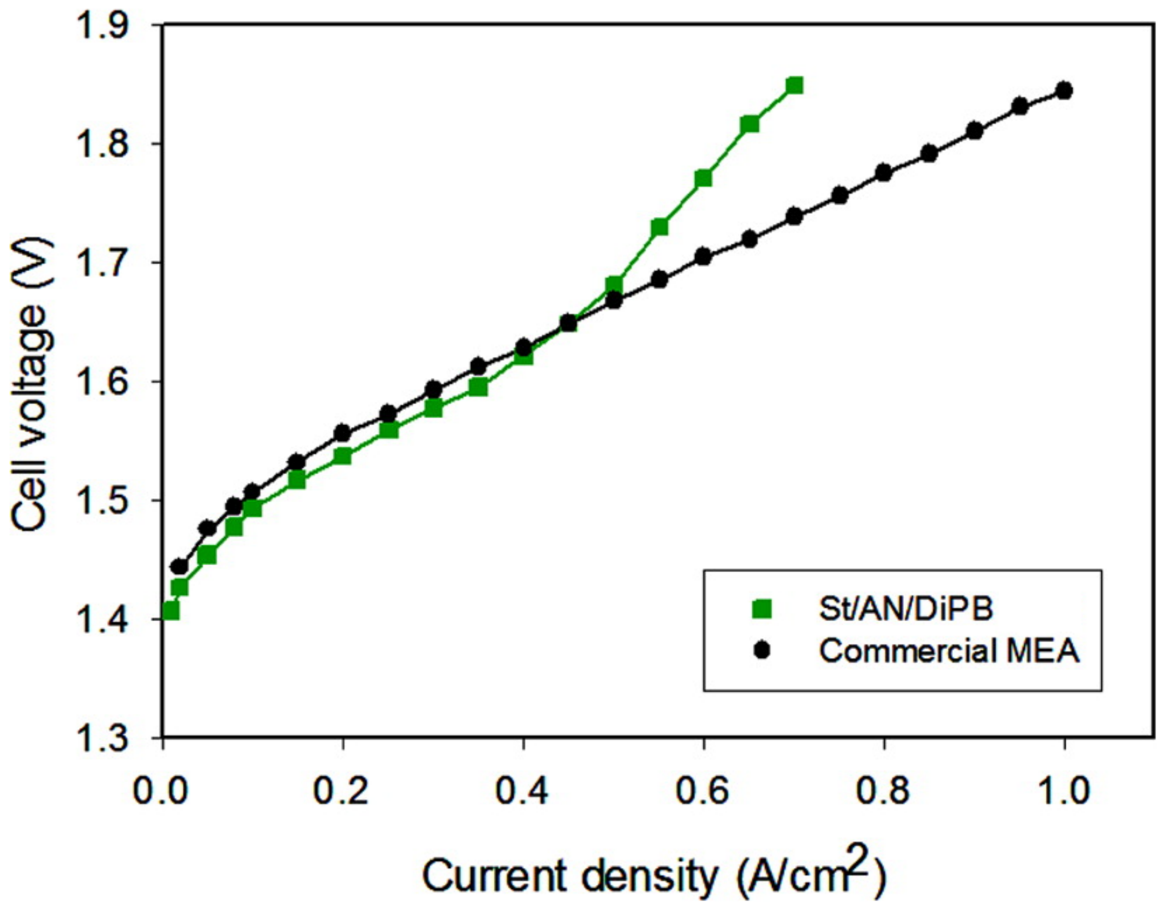
Preliminary test

Summary

Preliminary in-situ electrolyzer test



H_2O
500 ml/min
80 °C
25 cm^2
IrO_2/Pt
Ti/C

- Performance is comparable to commercial MEA at low current density (Homogeneity problem of St/AN/DiPB membrane)
- In-situ electrolyzer tests of other membranes will be perfomed

A. Albert, A. O. Barnett, M. S. Thomassen, T. J. Schmidt and L. Gubler, *ACS Appl. Mater. Interfaces*, **2015**, 7, 22203.

Outline

Introduction

Properties

Stability

Preliminary test

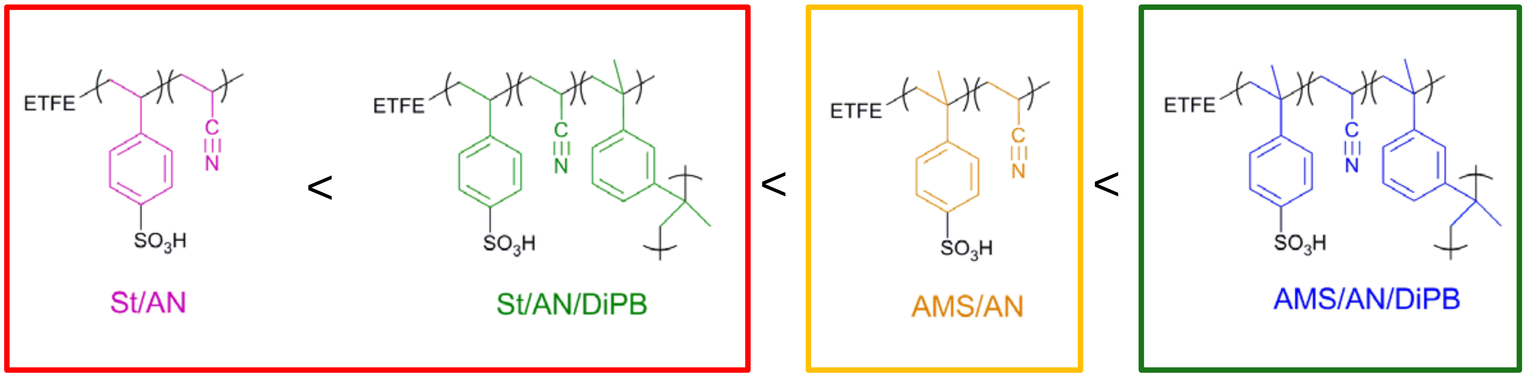
Summary

Summary

Properties of radiation grafted membranes:

- Lower hydrogen crossover
- Lower area resistance
- Better mechanical properties
- Potentially low cost*

Stability of radiation grafted membranes:



Degradation mechanisms in hot water:

- Degradation at the weak-link
- Oxygen-induced degradation
- Hydrothermal degradation

*L. Gubler and L. Bonorand, *ECS Trans.*, **2013**, 58, 149.

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Questions or comments ?

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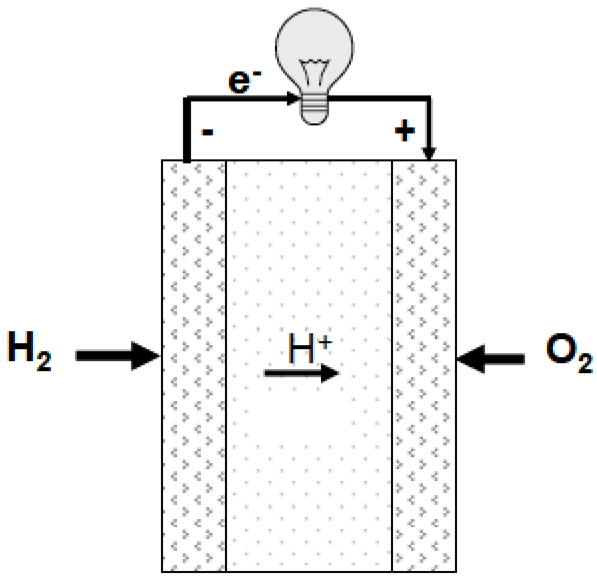
H2 crossover measurement principle

Normal Fuel Cell Operation

(−) $H_2 \rightarrow 2H^+ + 2e^-$

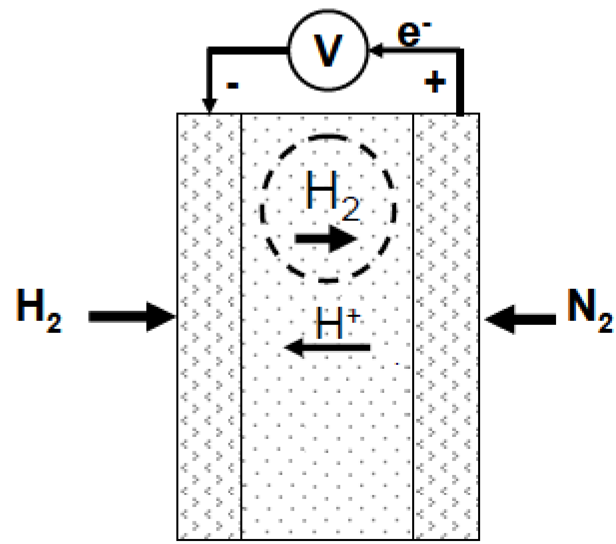
(+) $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$



Crossover Experiment

$2H^+ + 2e^- \rightarrow H_2$

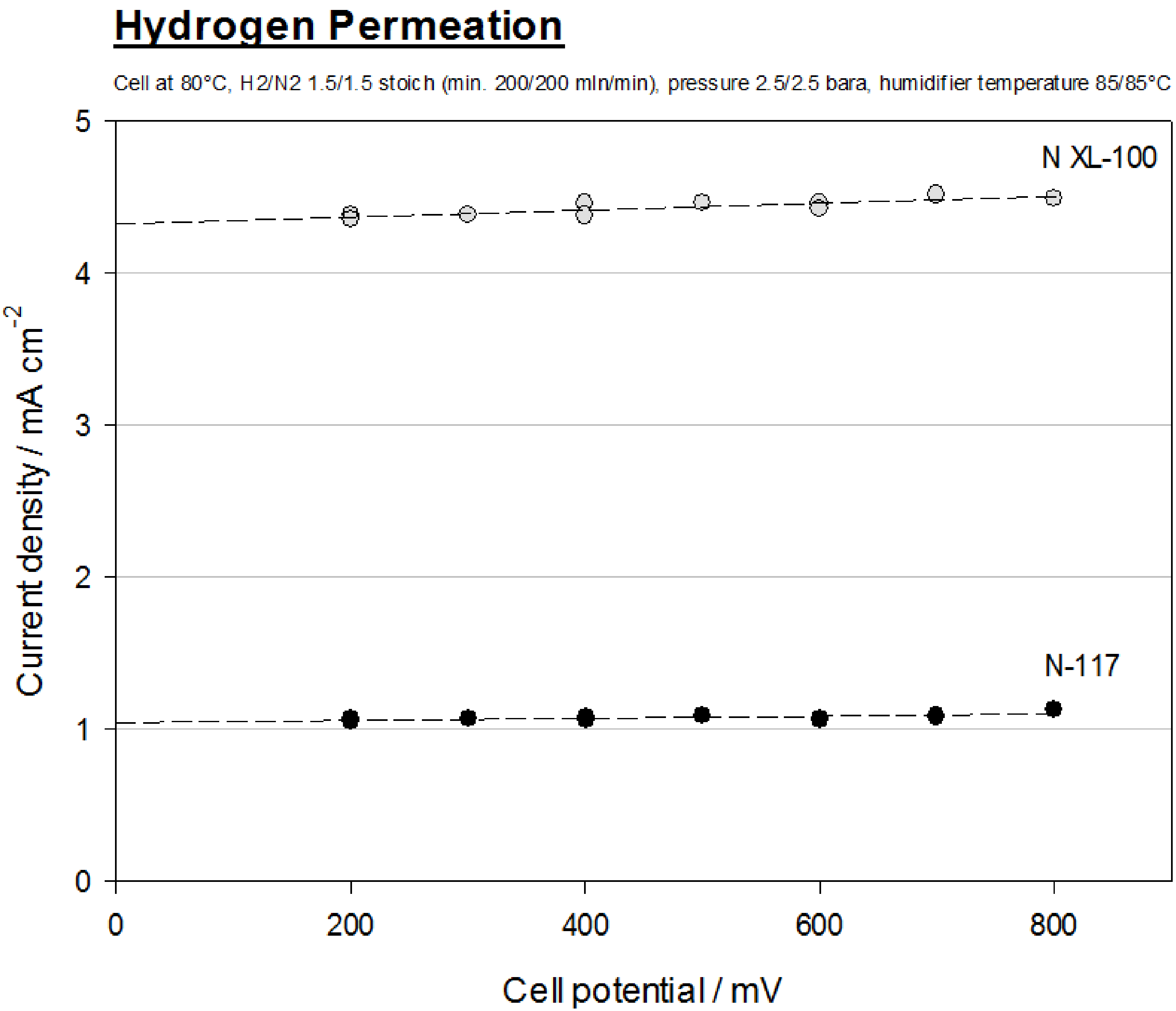
$H_2 \rightarrow 2H^+ + 2e^-$



Potential is set.

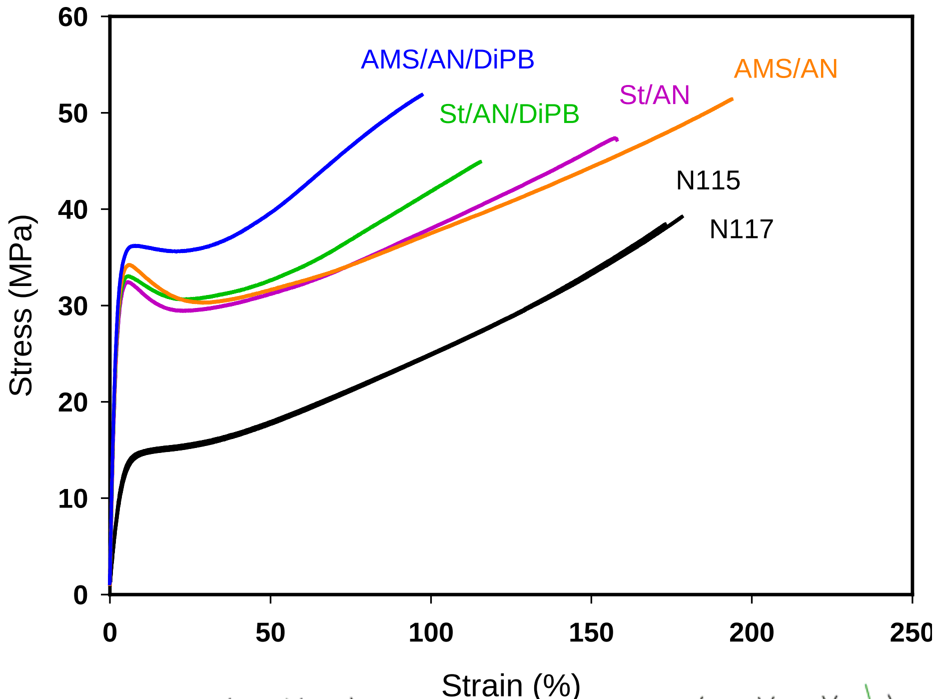
Current density is measured.

H2 crossover measurement principle

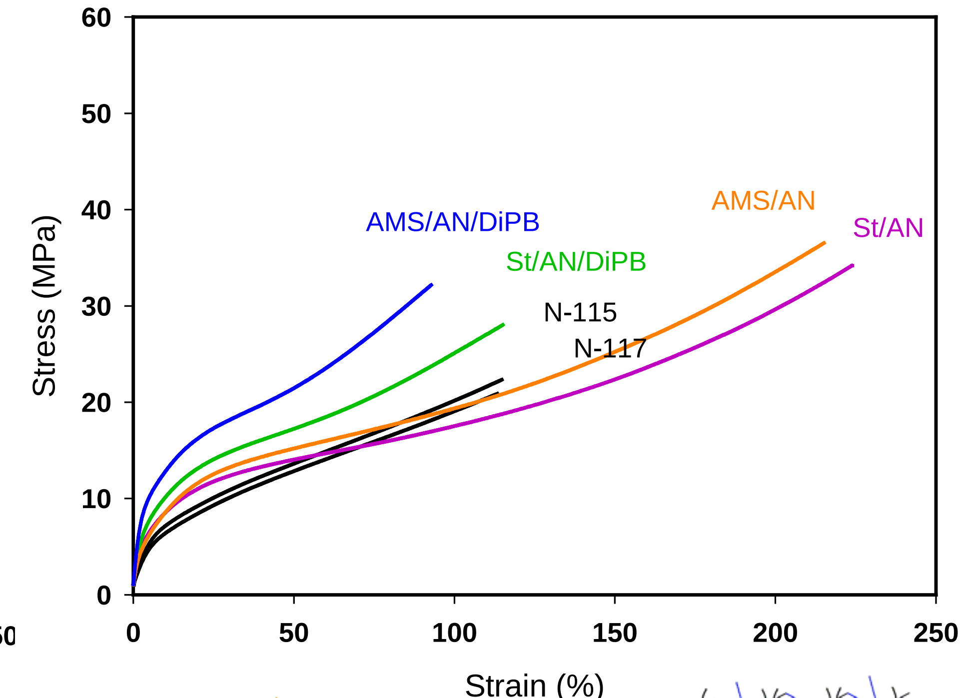


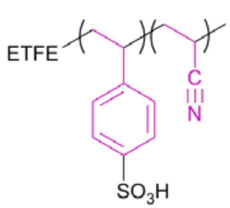
Mechanical Properties

Tensile Test in Machine Direction
(Ambient condition)

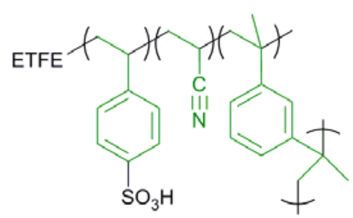


Tensile Test in Machine Direction
(Fully hydrated condition)

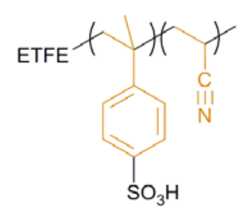




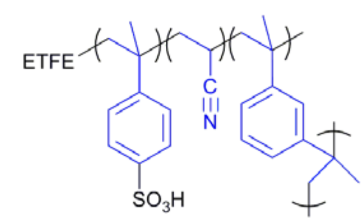
St/AN



St/AN/DiPB



AMS/AN

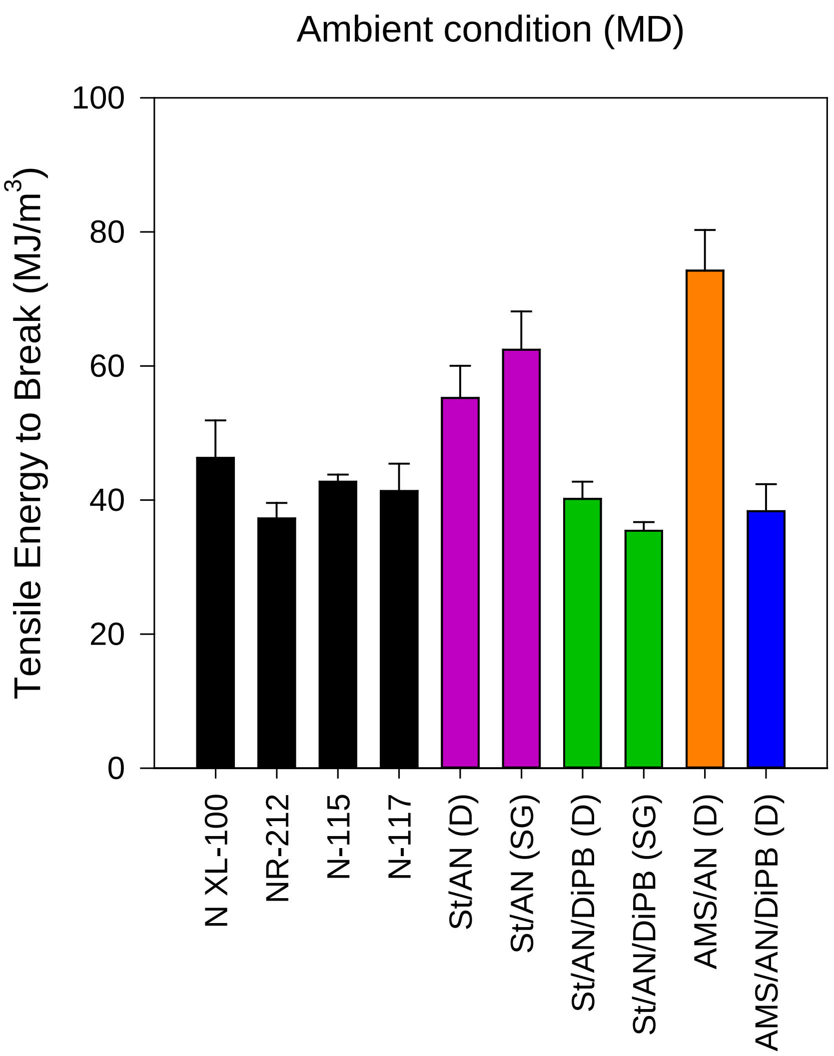


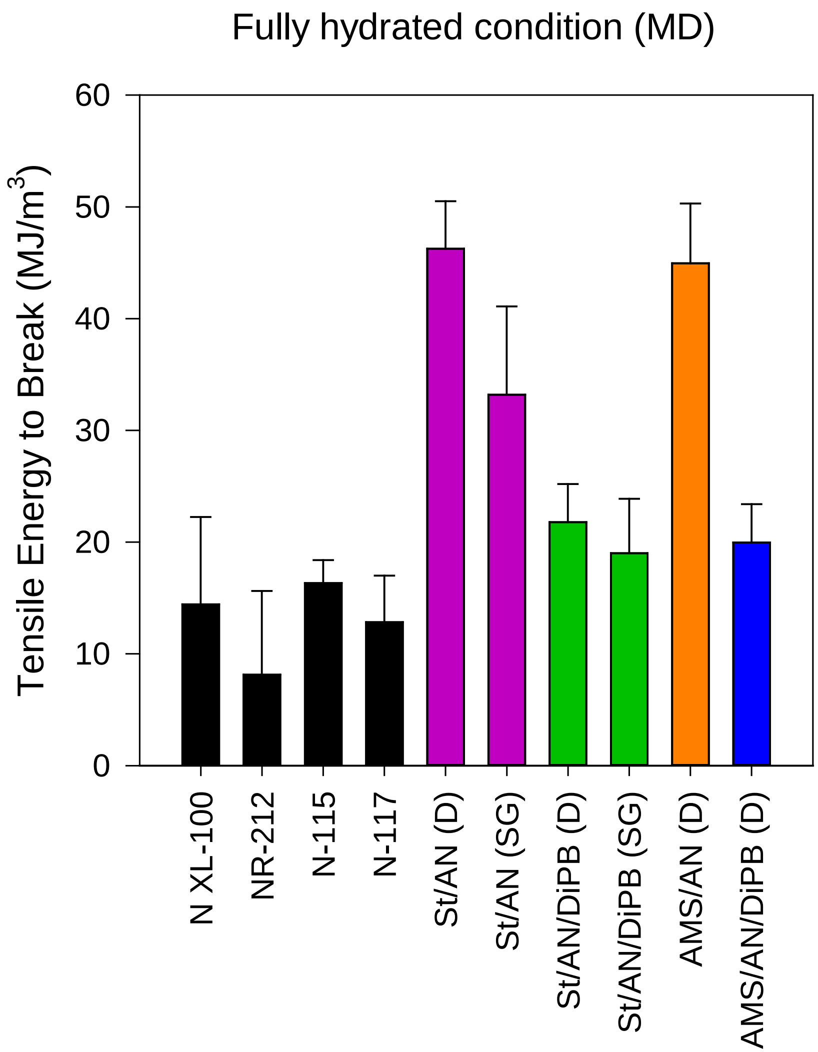
AMS/AN/DiPB

Radiation grafted membranes:

- Better Mechanical Properties

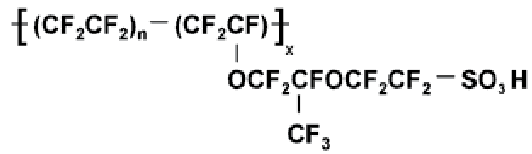
Tensile Energy to Break / Toughness



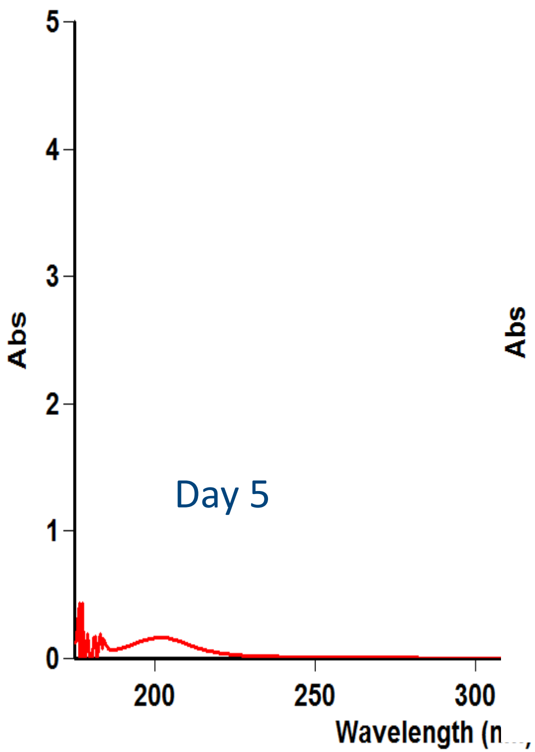


UV-Vis Spectroscopy - Nafion

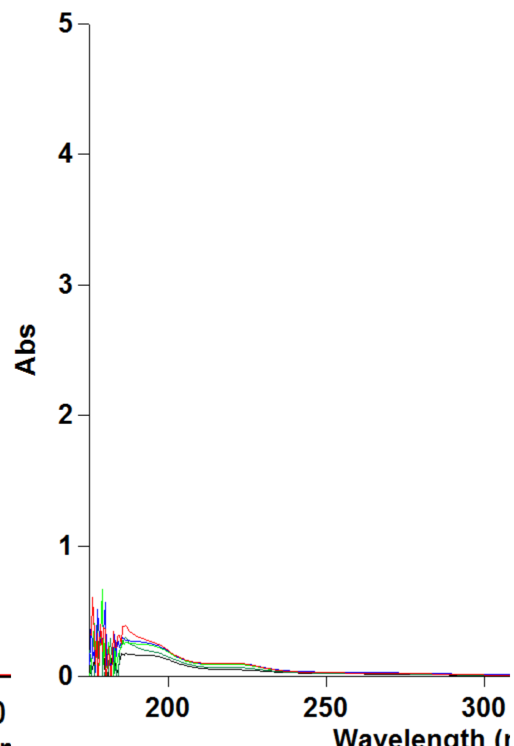
Nafion



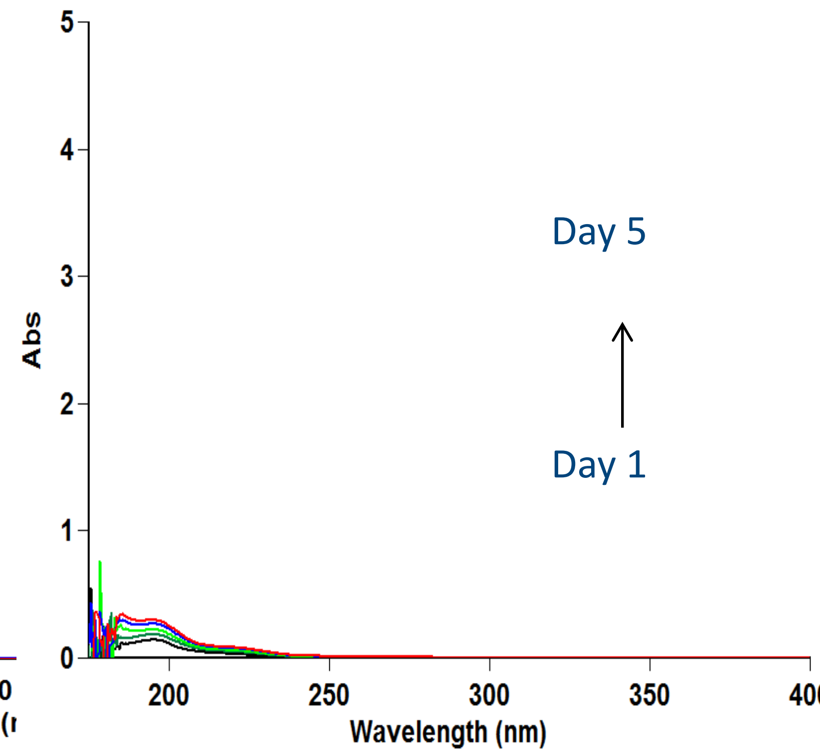
Blank Test



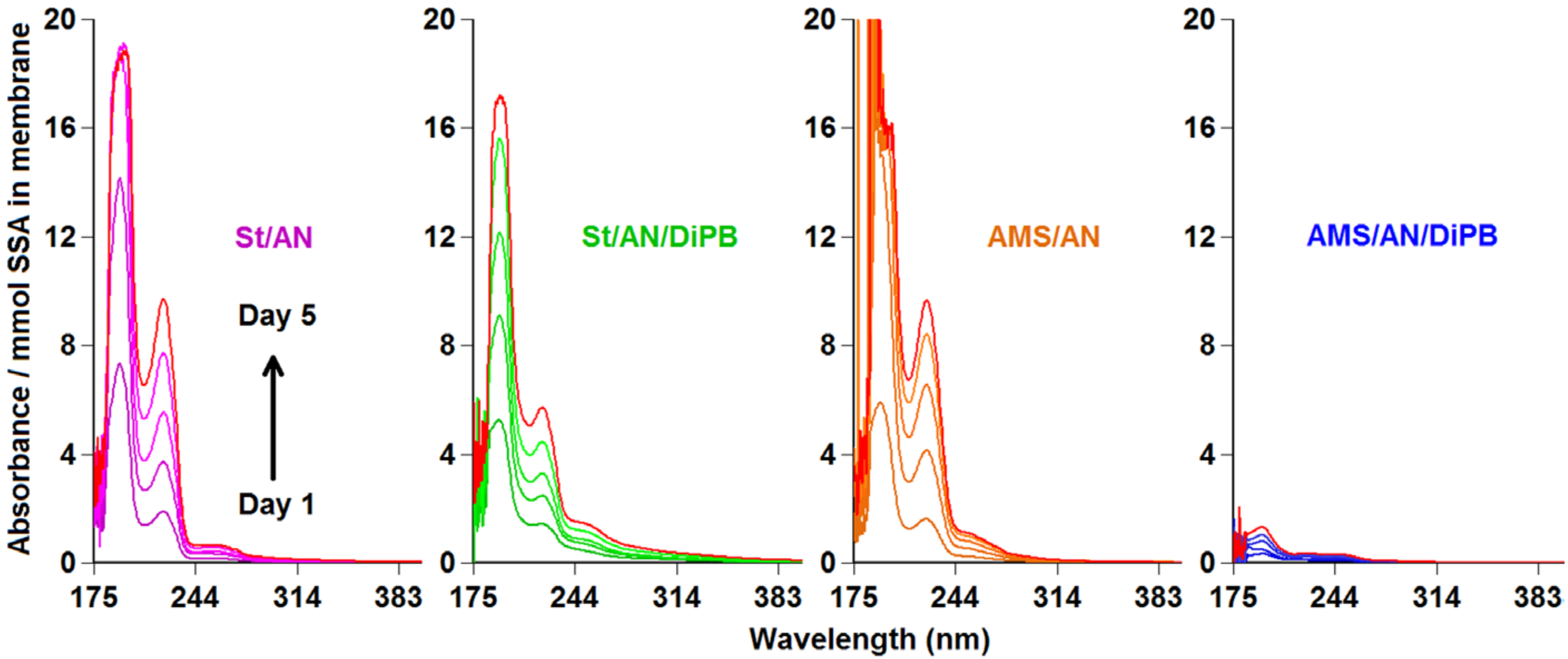
N115



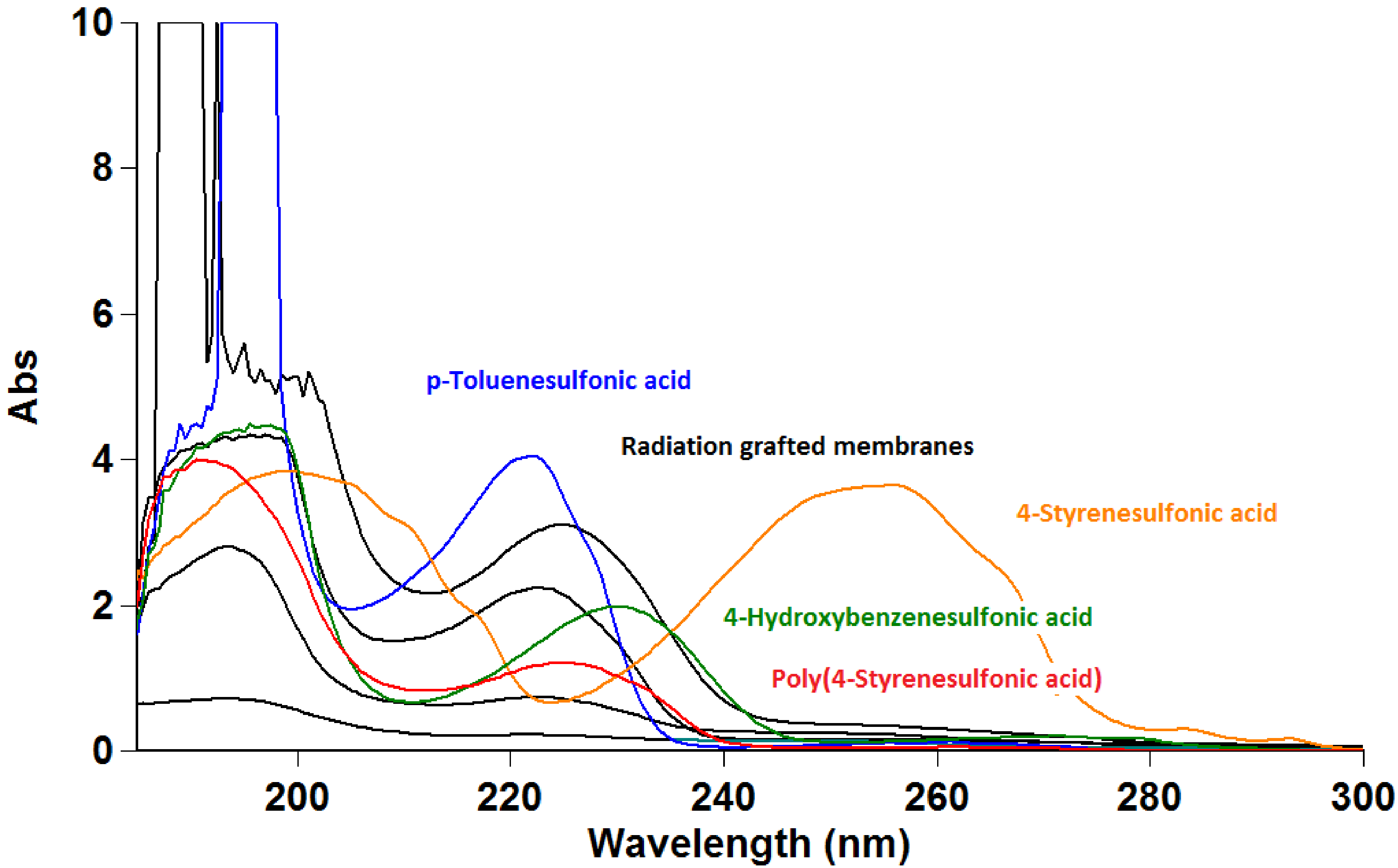
N117



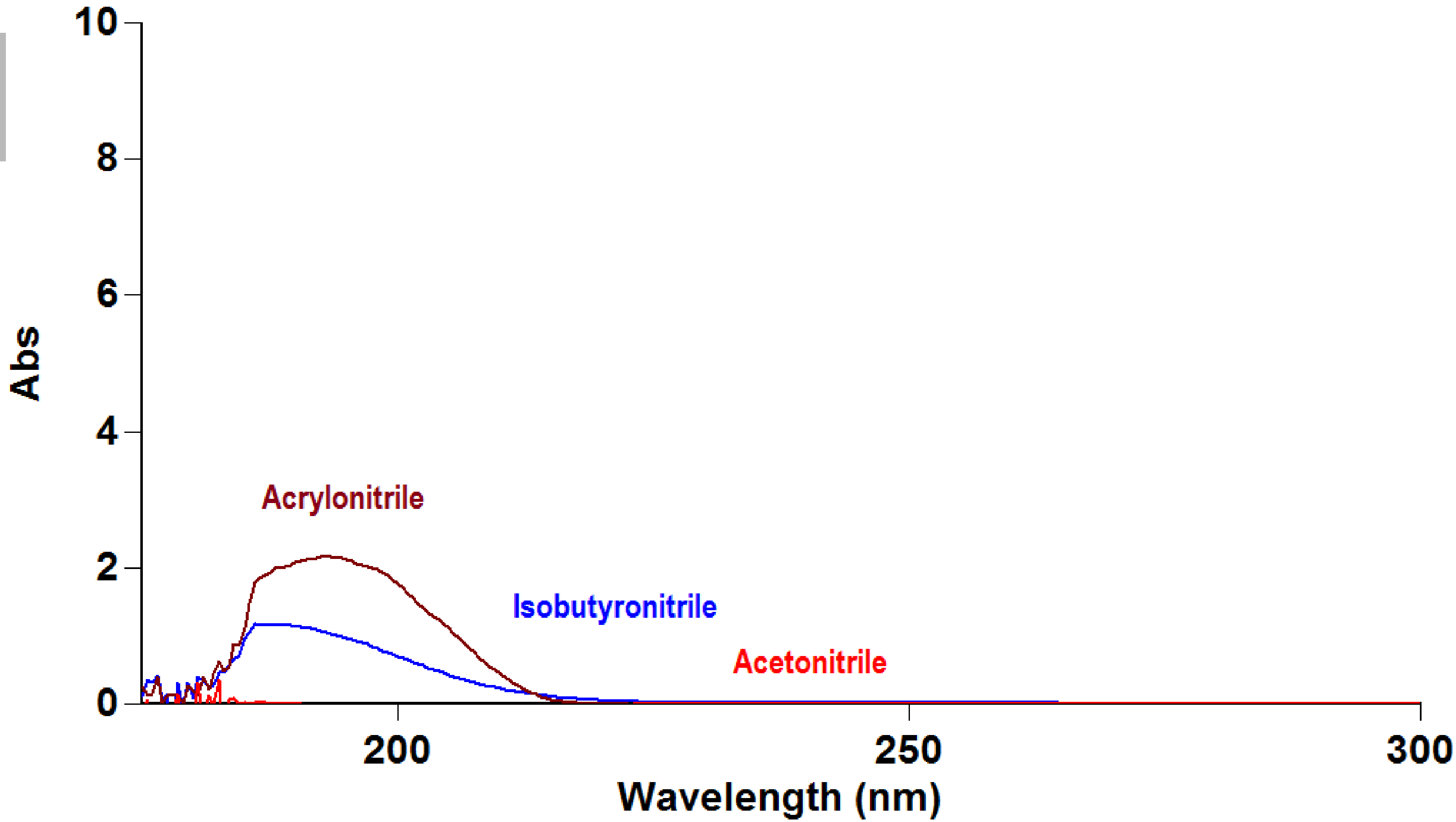
Normalized UV-Vis Spectroscopy



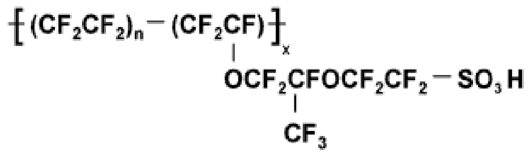
UV-Vis Spectroscopy - Degraded Species



UV-Vis Spectroscopy - Degraded Species

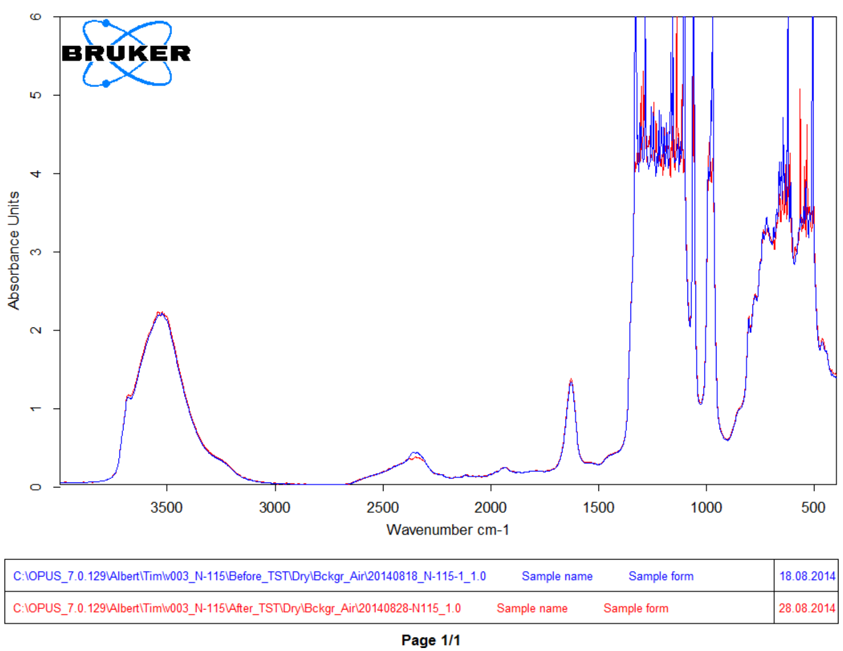


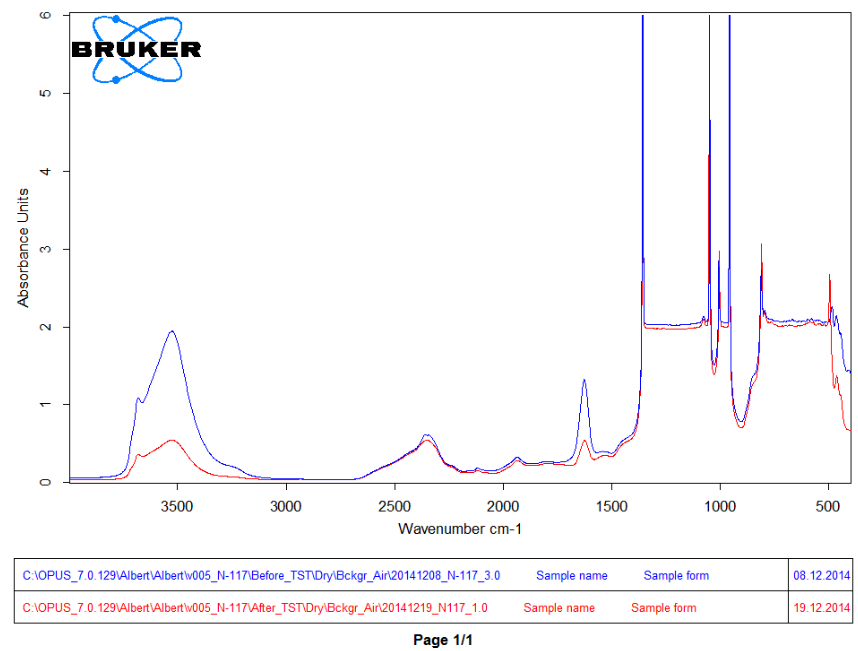
FTIR - Nafion



N115

N117





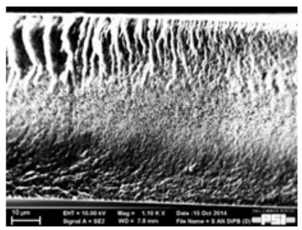
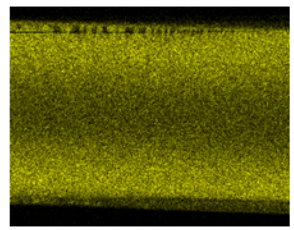
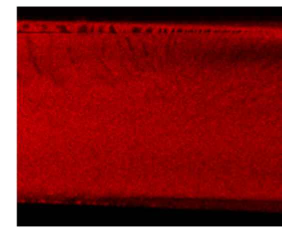
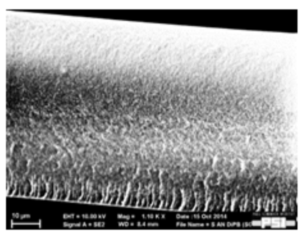
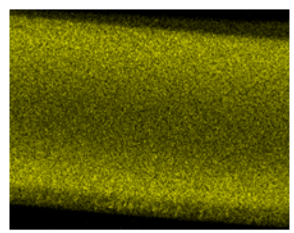
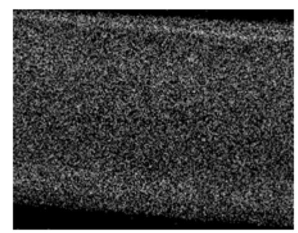
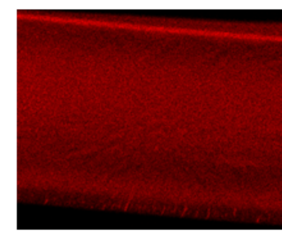
Swelling under Argon Atmosphere

	Swelling (wt. %)		
Membranes	**Before test**	**After test**	**IEC % loss**
St/AN (Argon)	66.6 ± 0.9 (67.8 ± 2.4)	54.4 ± 3.0 (63.2 ± 1.6)	34.1 ± 4.7 (34.4 ± 1.7)
St/AN/DiPB (Argon)	35.1 ± 3.2 (34.9 ± 1.5)	40.9 ± 3.5 (31.7 ± 6.3)	44.2 ± 0.8 (49.1 ± 5.9)
AMS/AN (Argon)	56.5 ± 0.5 (53.0 ± 1.3)	60.0 ± 0.5 (58.5 ± 1.3)	10.3 ± 0.0 (3.19 ± 2.0)
AMS/AN/DiPB	31.7 ± 0.6	-	4.2 ± 0.5

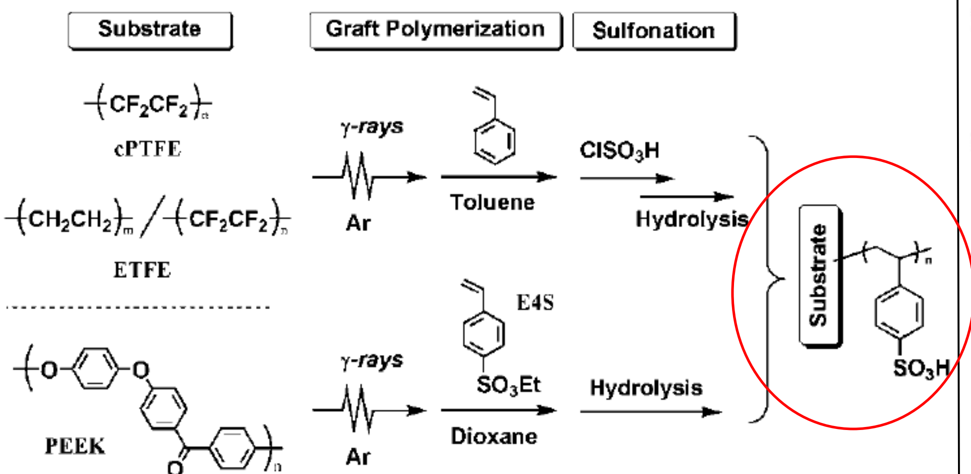
Raw Datas

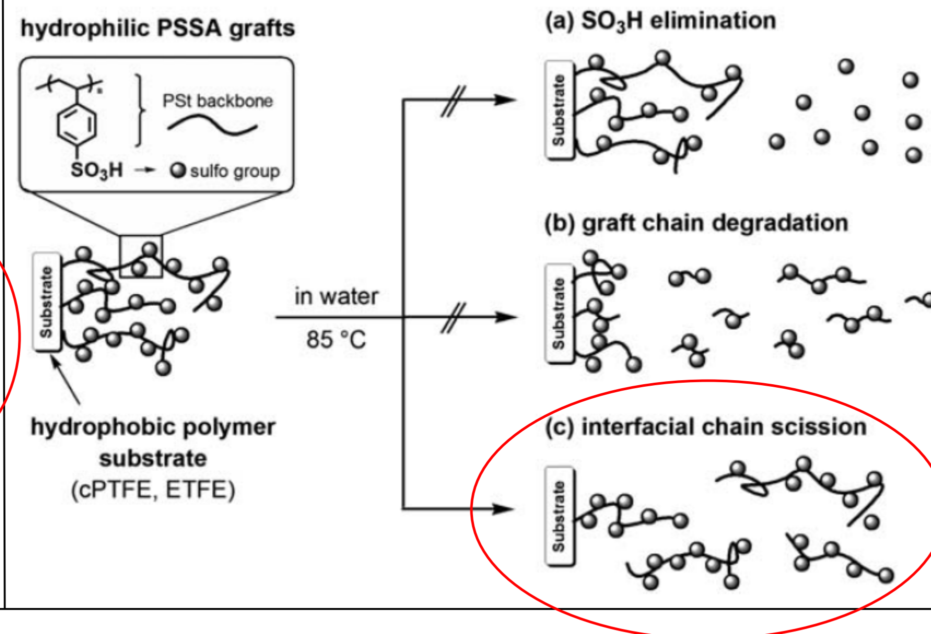
Membrane	Graft level (%)	Wet thickness (µm)	IEC (mmol/g)	Swelling (m%)	Hydration (H_2O/SO_3H)
S/AN (D)	41	86.0 ± 1.0	1.25 ± 0.02	67.8 ± 2.4	30.1 ± 0.9
S/AN (SG)	40	95.3 ± 1.1	1.29 ± 0.02	68.6 ± 1.7	29.6 ± 0.3
S/AN/DiPB (D)	41	79.5 ± 0.7	1.20 ± 0.00	33.1 ± 1.0	15.3 ± 0.5
S/AN/DiPB (SG)	39	79.5 ± 0.5	1.15 ± 0.02	34.4 ± 1.9	16.6 ± 1.1
AMS/AN/DiPB (SG)	42	74.5 ± 3.5	1.59 ± 0.01	30.1 ± 0.5	10.5 ± 0.1
NR211	-	30.5 ± 0.0	1.22 ± 0.01	28.1 ± 13.6	12.7 ± 6.1
NXL-100	-	37.3 ± 0.3	1.01 ± 0.04	29.3 ± 4.7	16.1 ± 2.1
NR212	-	61.7 ± 1.3	1.16 ± 0.01	38.6 ± 6.8	18.6 ± 3.3
N1035	-	114.2 ± 3.8	1.15 ± 0.00	46.1 ± 3.8	22.3 ± 1.9
N1135	-	103.8 ± 1.5	1.05 ± 0.02	39.3 ± 2.4	20.8 ± 1.0
N105	-	152.3 ± 1.5	1.10 ± 0.00	47.9 ± 0.3	24.1 ± 0.1
N115	-	153.0 ± 1.0	1.04 ± 0.02	39.9 ± 2.9	21.2 ± 1.2
N117	-	202.7 ± 1.0	1.04 ± 0.00	39.9 ± 0.1	21.4 ± 0.0
N120	-	293.0 ± 8.2	0.83 ± 0.00	27.2 ± 0.3	18.3 ± 0.2

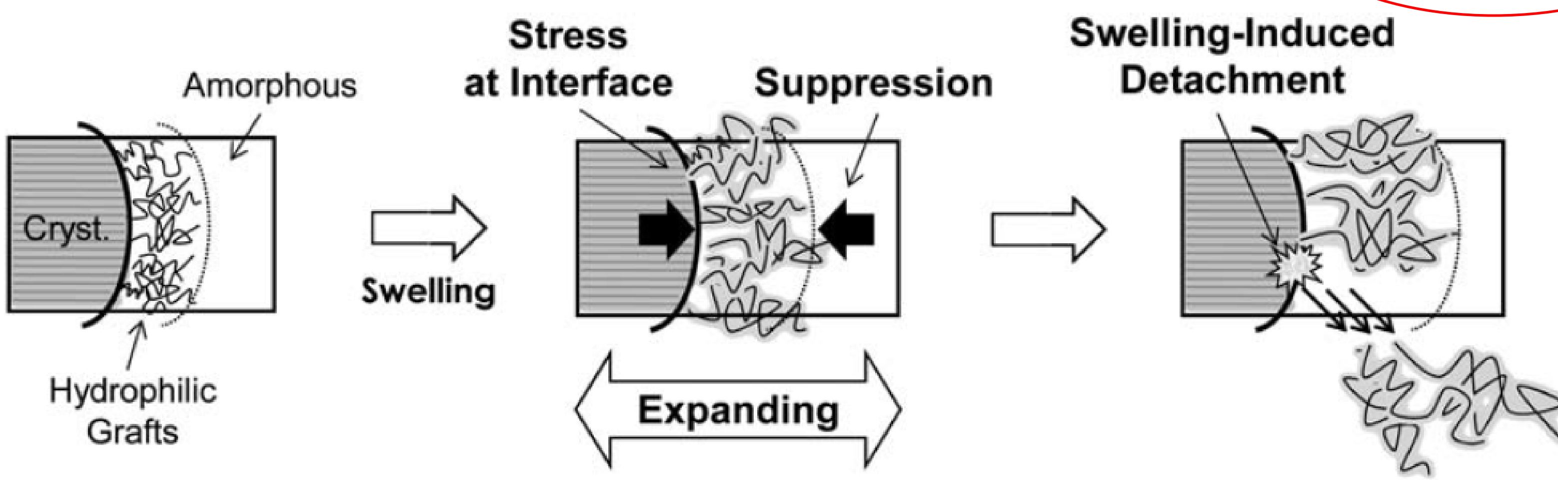
SEM/EDX

Membrane	SEM-EDX	Sulphur	Nitrogen	Carbon
S/AN/DiPB (DuPont)				
S/AN/DiPB (Saint-Gobain)				

Swelling-Induced Detachment

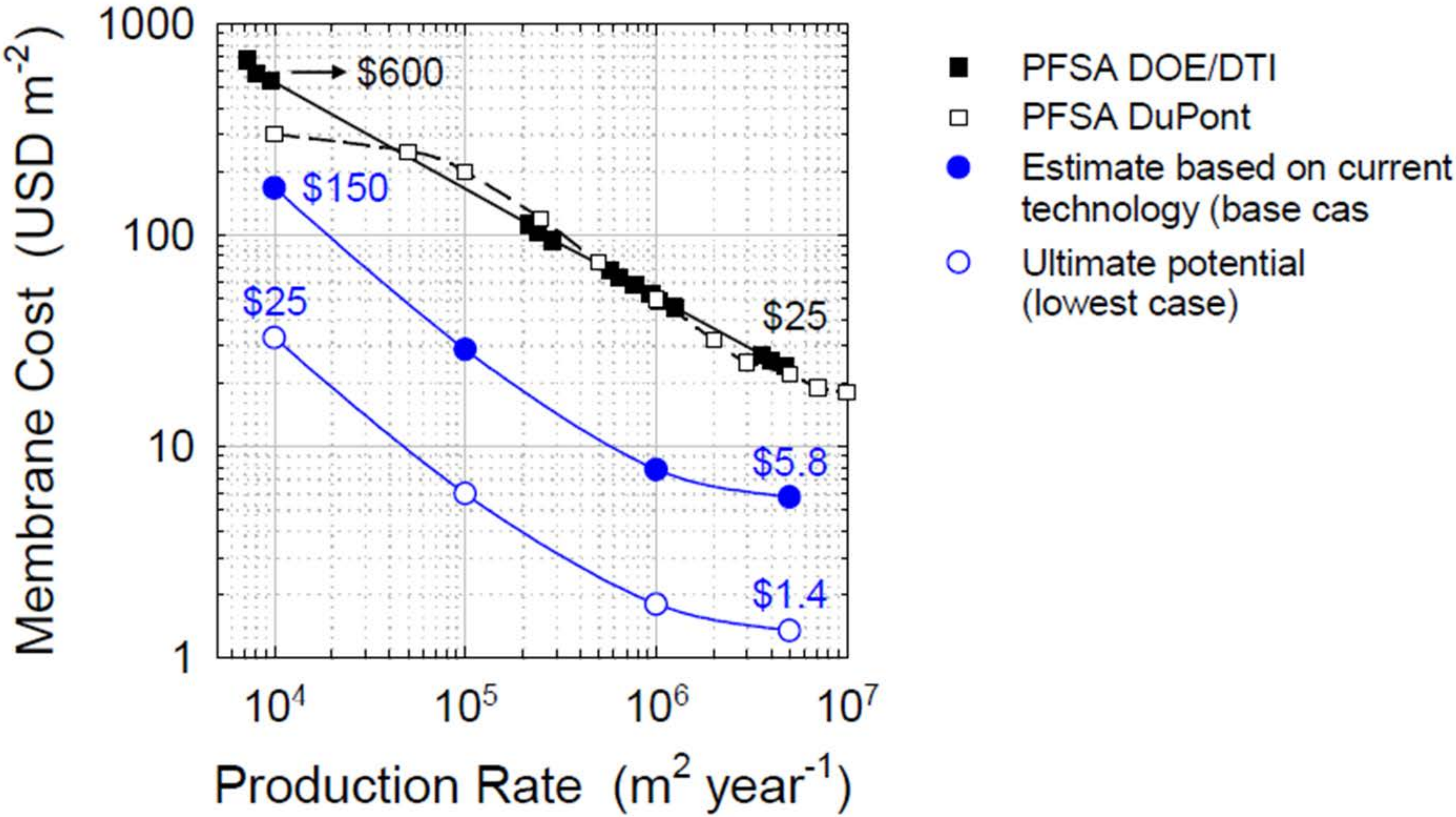






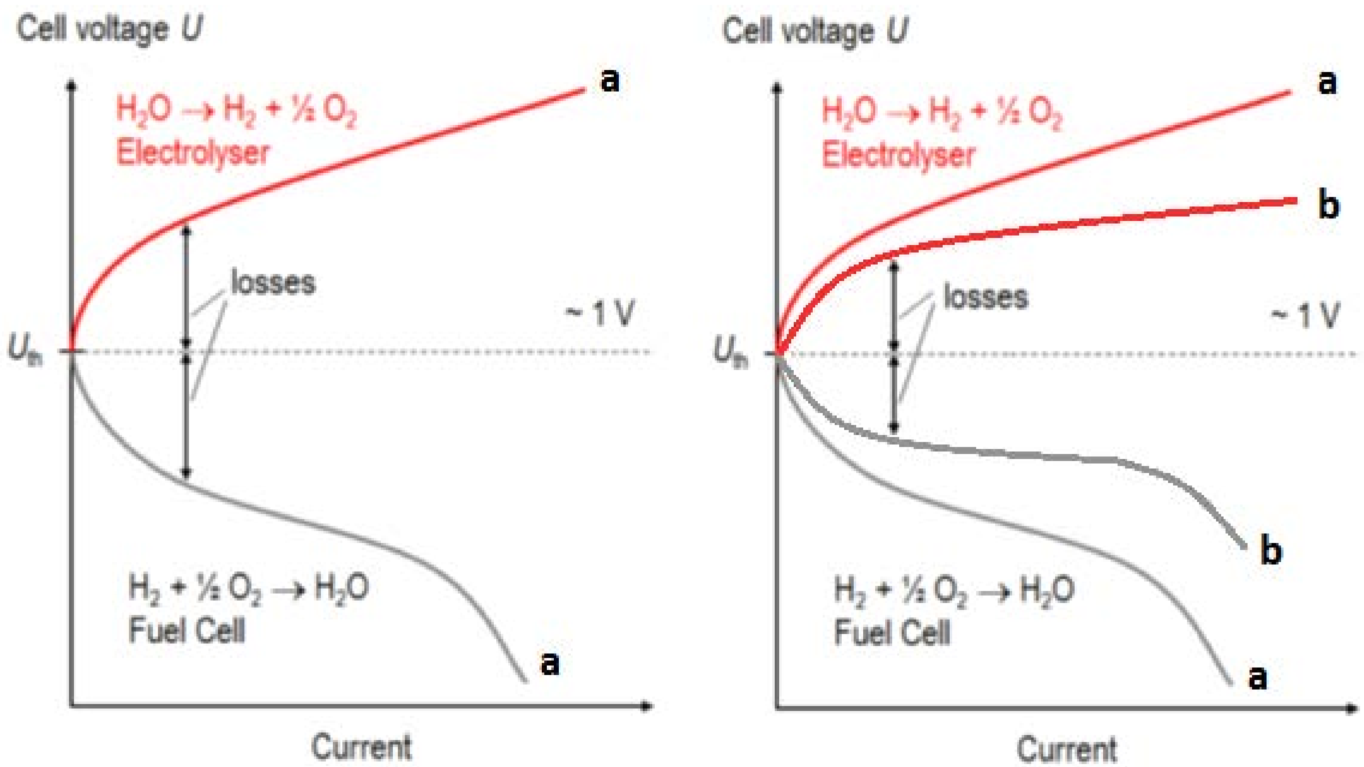
K. Enomoto, S. Takahashi, T. Iwase, T. Yamashita and Y. Maekawa, *J. Mater. Chem.*, **2011**, 21, 9343.

Estimated cost of radiation grafted membranes



*L. Gubler and L. Bonorand, *ECS Trans.*, **2013**, 58, 149.

I/U curves



Cell voltage U
$H_2O \rightarrow H_2 + ½ O_2$
Electrolyser
a
losses
~ 1 V
U_{th}
$H_2 + ½ O_2 \rightarrow H_2O$
Fuel Cell
a
Current
Cell voltage U
$H_2O \rightarrow H_2 + ½ O_2$
Electrolyser
a
b
losses
~ 1 V
U_{th}
b
$H_2 + ½ O_2 \rightarrow H_2O$
Fuel Cell
a
Current