Development of covalently cross-linked and composite perfluorosulfonic acid membanes

Y.M. Zang

L. Li

J.K. Tang

B. Bauer

W. Zhang

H.R. Gao

M. Taillades-Jacquin

D.J. Jones

J. Roziere

N.P. Lebedeva

R.K.A.M. Mallant

Presented at the 216th ESC Conference, October 2009, Vienna, Austria

ECN-L--09-180 December 2009

Development of Covalently Cross-linked and Composite Perfluorosulfonic Acid Membranes

Y. M. Zhang, L. Li (SJTU, China)
J. K. Tang (DY Group, China)
B. Bauer, W. Zhang (Fuma-Tech, Germany)
H. R. Gao, M. Taillades-Jacquin, D. J. Jones, J. Rozière (CNRS-UM2, France)
N. Lebedeva, R. K. A. M. Mallant (ECN, Holland)

shghr@sjtu.edu.cn ; Hong-rong.gao@etud.univ-montp2.fr

European Commission

SIXTH FRAMEWORK PROGRAMME

Characteristics of Perfluorosulfonic Acid (PFSA) membranes

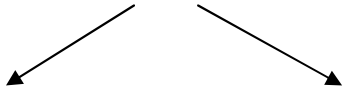
◆ **Advantages**

Excellent proton conductivity
High Chemical inertness
Good thermal stability
Good durability in fuel cell

Operation
High temperature and low relative humidity

Conductivity loss

Polymer with high IEC: Excessive swelling



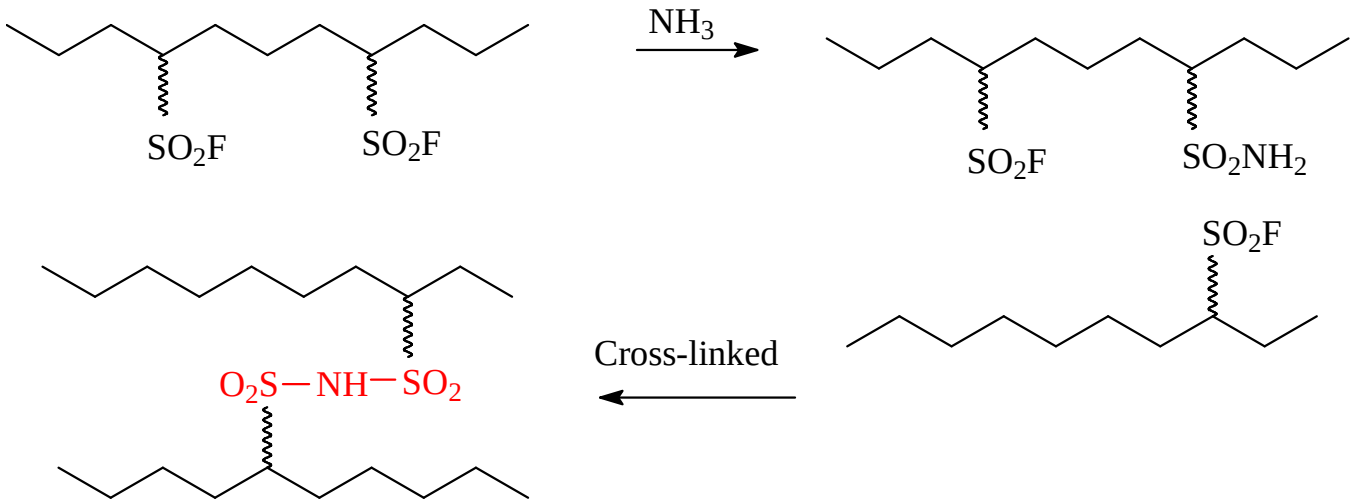
Cross-linking **Composite**

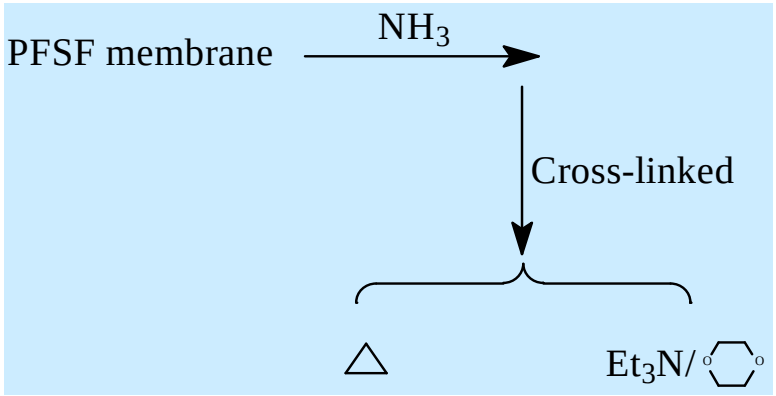
◆ **Two methods for cross-linking PFSA membranes**

- **Cross-linked PFSA membranes by formation of *sulfonimide***
- **Cross-linked PFSA membranes by formation of *perfluoroalkyl***

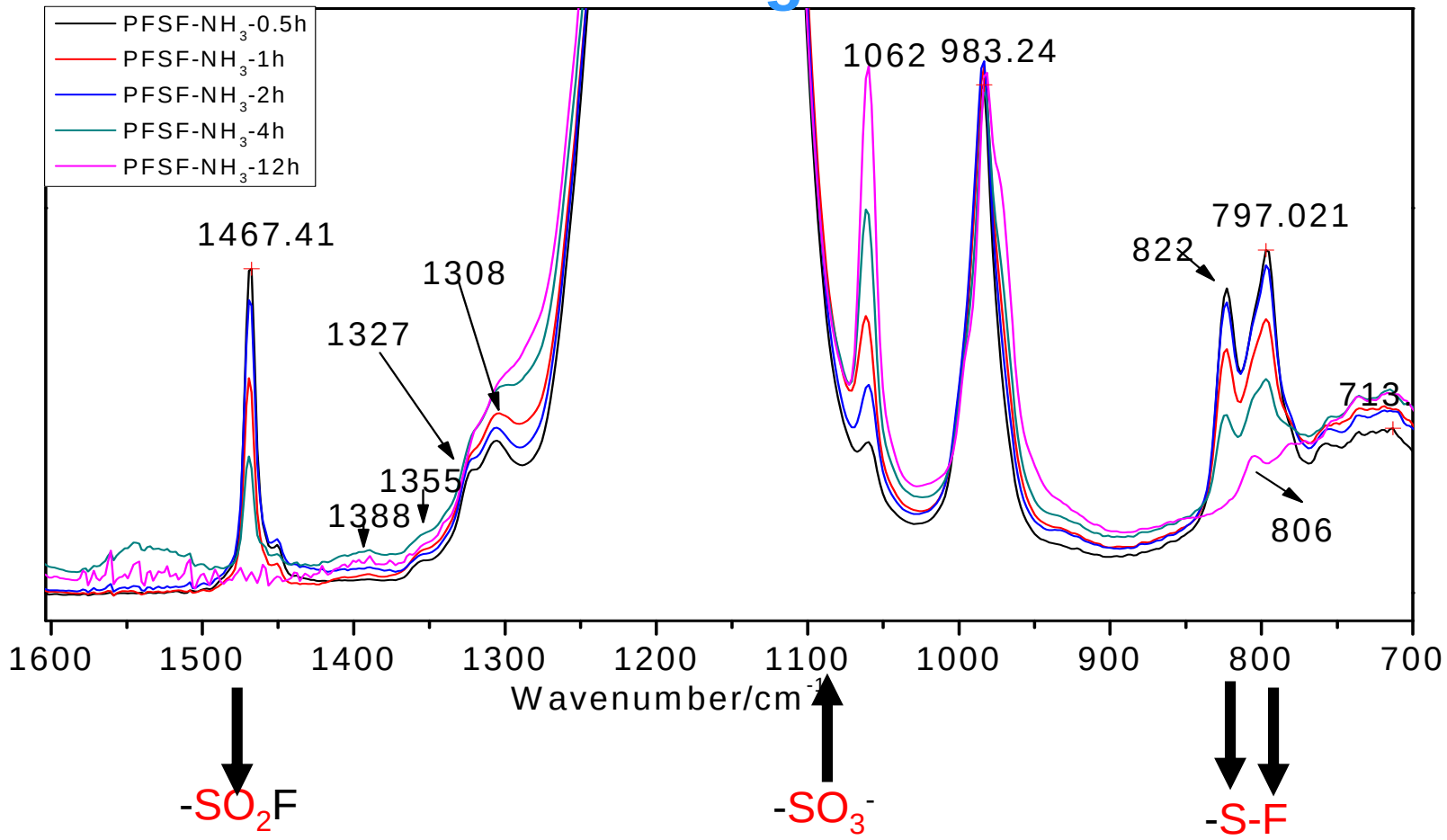
◆ **Inorganic component** : ***Zirconium phosphate (ZrP)***

◆ Cross-linked PFSA membranes by formation of Sulfonimide





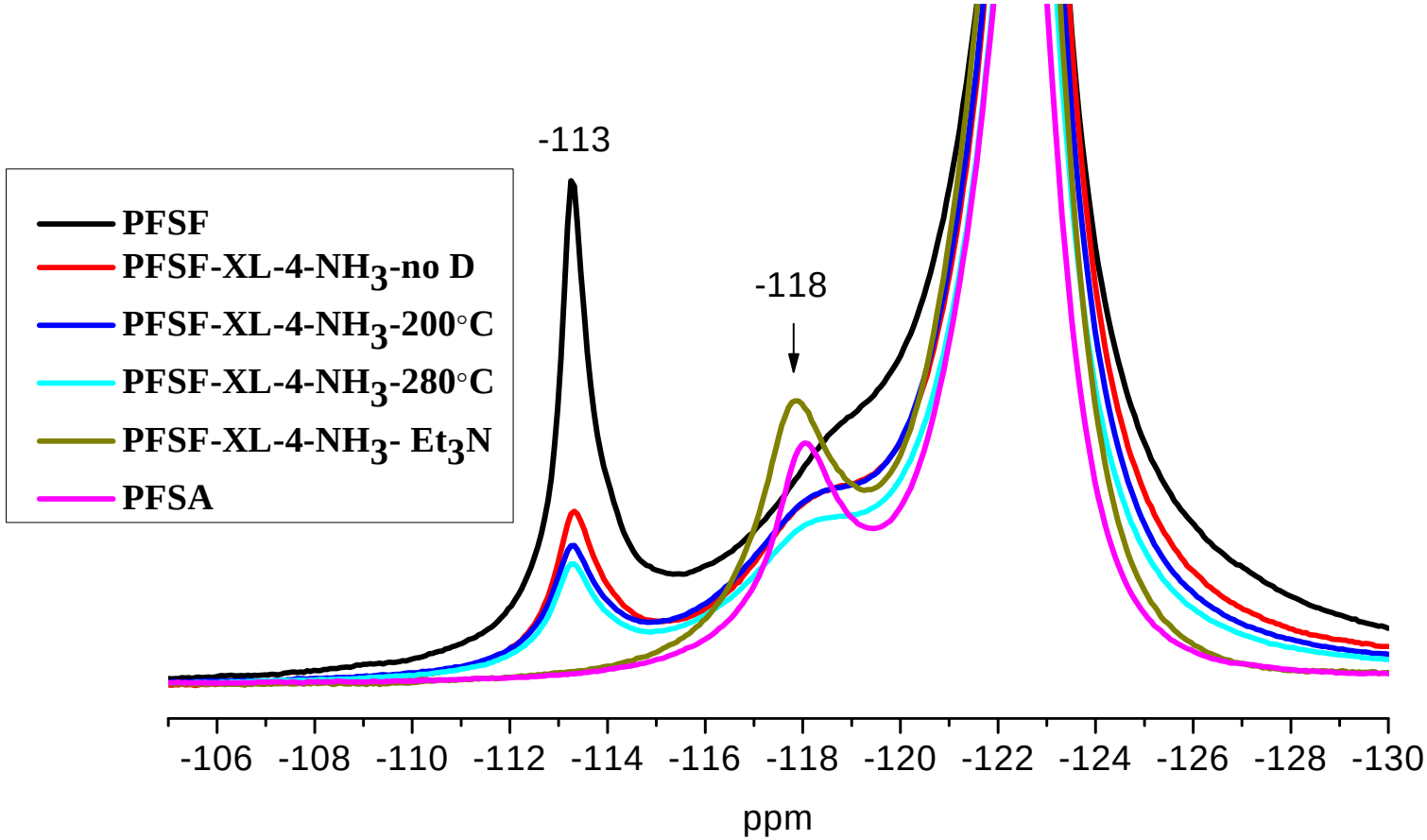
Evidence for Cross-linking from FT-IR/ATR



Reaction time ↑ **- SO_2F** ↓ **1467, 822 and 797 cm^{-1}**

$-SO_3^-$ ↑ **1062 cm^{-1}**

Evidence for Cross-linking from ^{19}F NMR

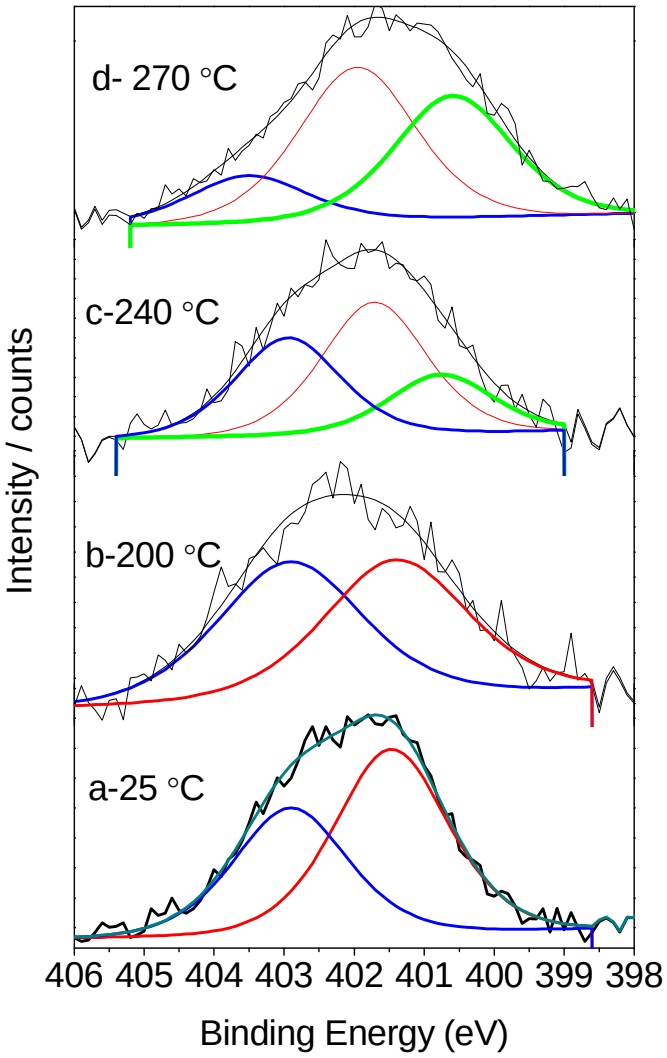


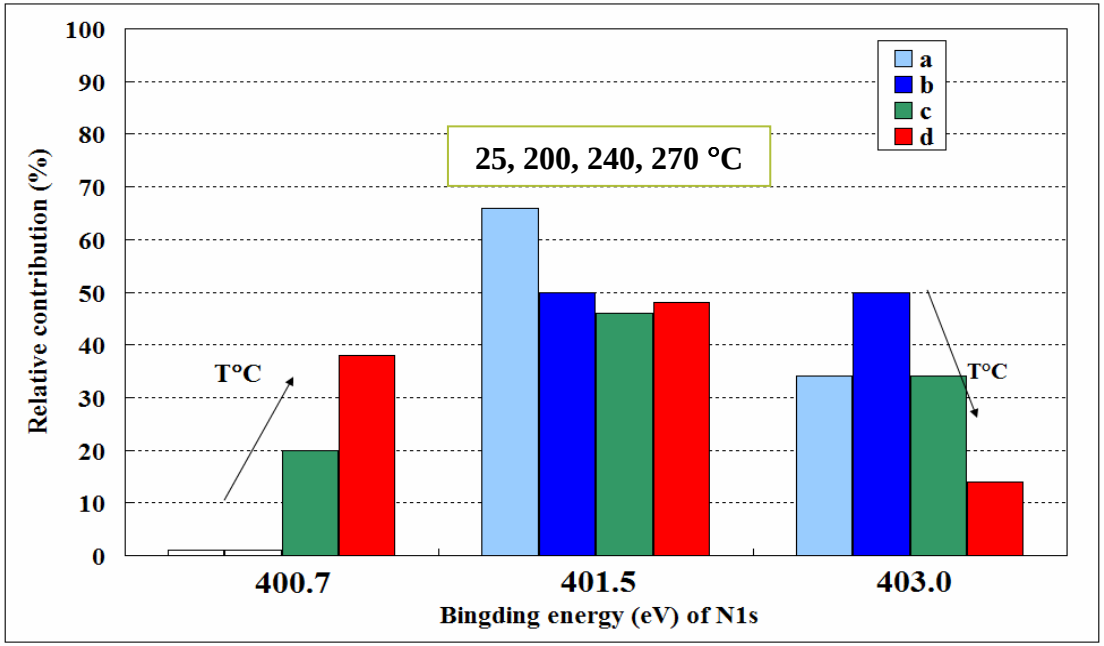
$-CF_2SO_2F$ $-CF_2SO_3H$

$-CF_2SO_2NH_2$

$-CF_2SO_2NHSO_2CF_2-$

Evidence for Cross-linking from XPS- N 1s

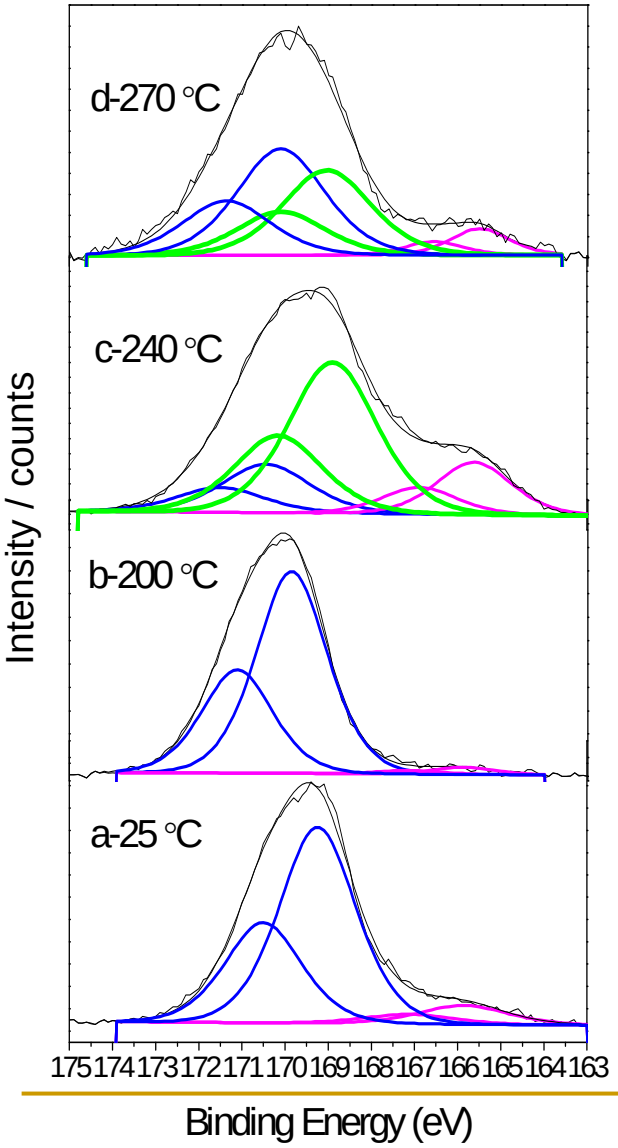


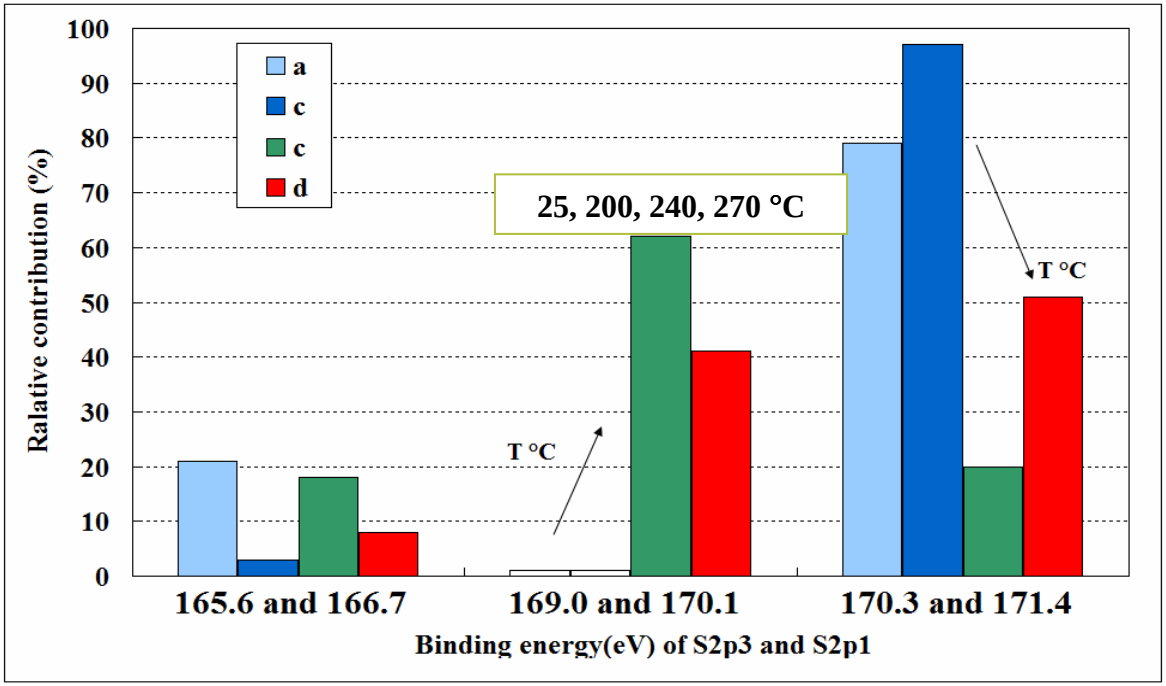


$-SO_2NHSO_2-$ $-SO_2NH_2$ $-SO_2NHNH_4$ $-SO_3NH_4$

S. Caporali et al. Journal of Electron Spectroscopy and Related Phenomena, 2006, V.151, 4~8.

Evidence for Cross-linking from XPS- S 2p



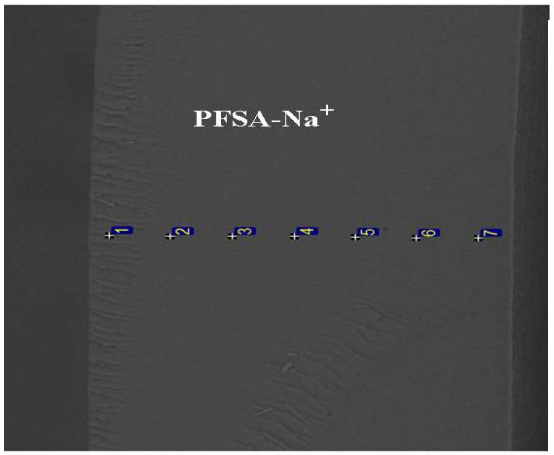


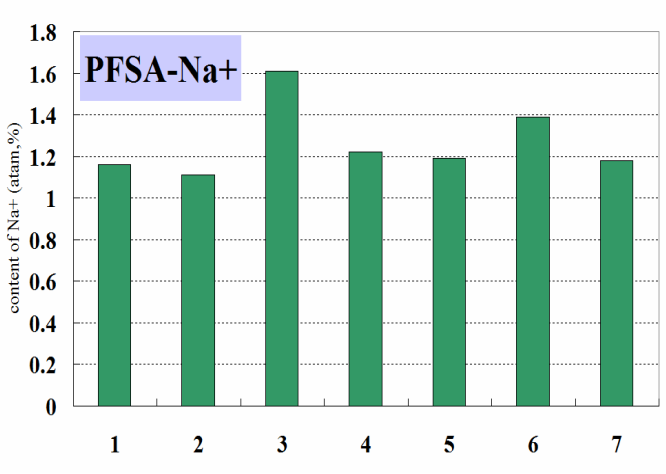
$-SO_2NH_2$ $-SO_2NHSO_2-$ $-SO_2F$

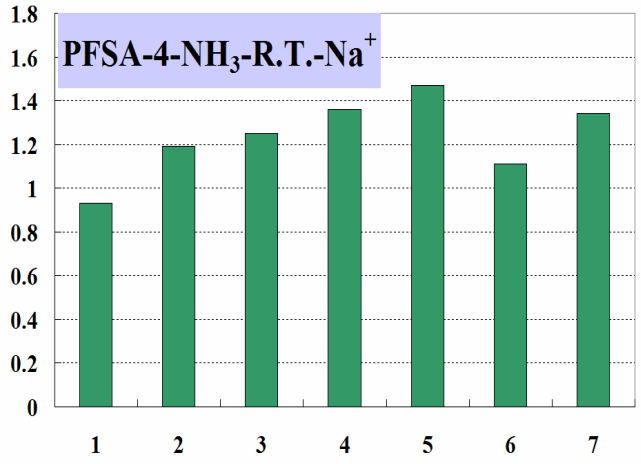
$-SO_2NHNH_4$

$2p_{1/2}$ $2p_{3/2}$

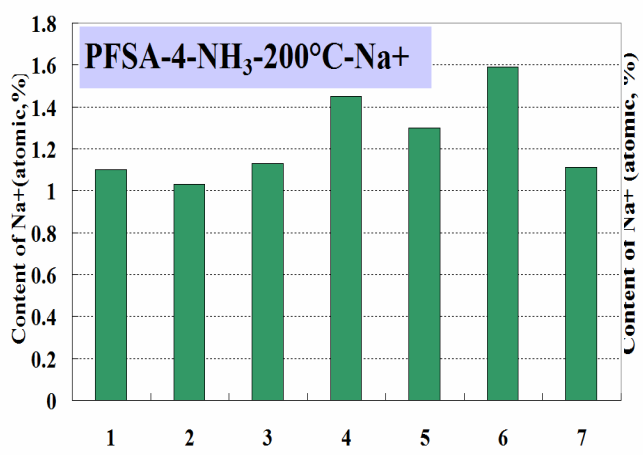
Evidence for Cross-linking - SEM-EDX

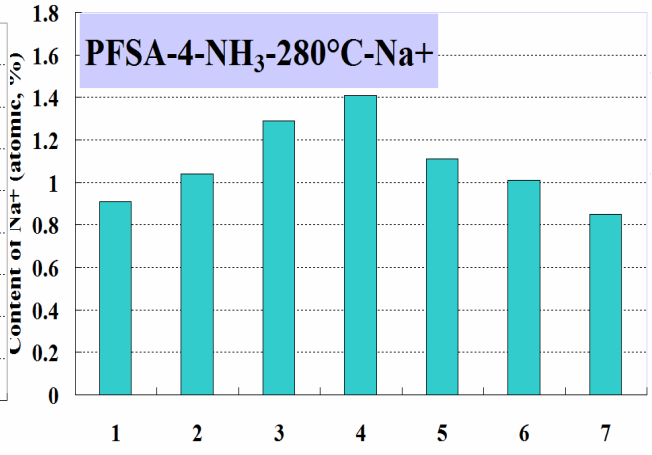


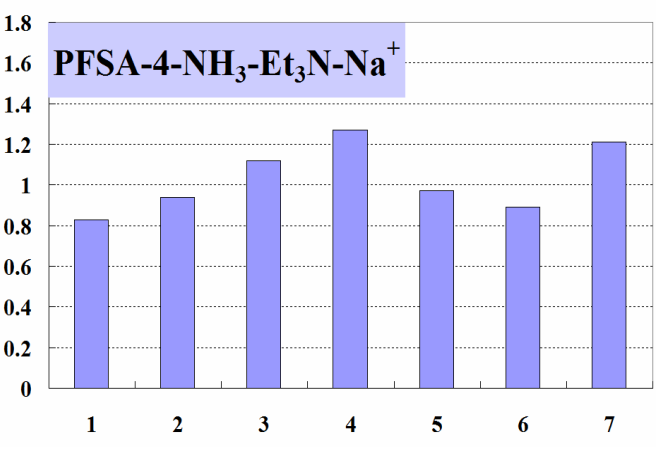




SEM micrograph of PFSA-Na^+ and its sketch map of 7 point analysis across the membrane thickness.



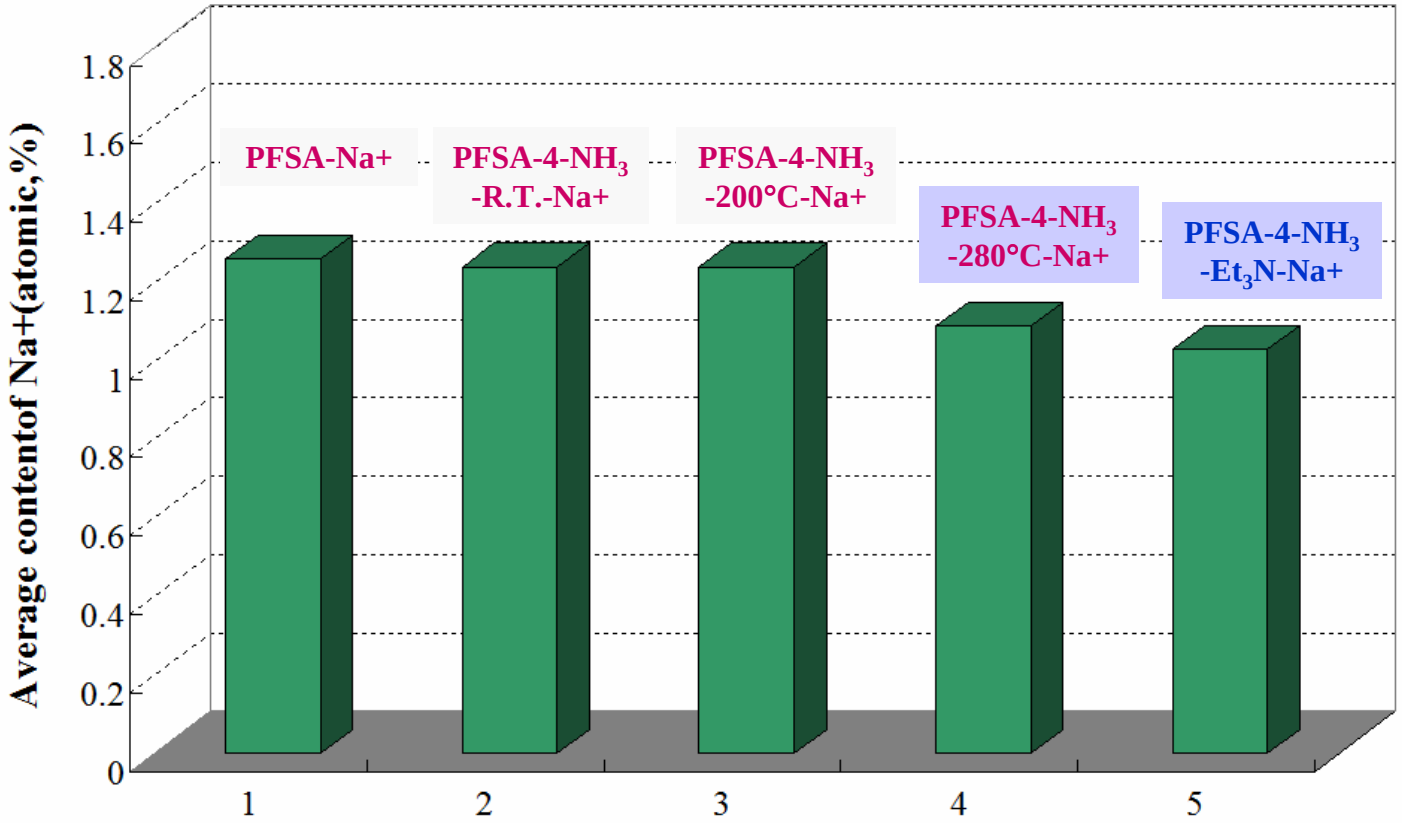




Evidence for Cross-linking from SEM-EDX

Na^+
$- SO_2-N^-SO_2-$

R_f-SO_3Na
$Rf-SO_2NHNa$

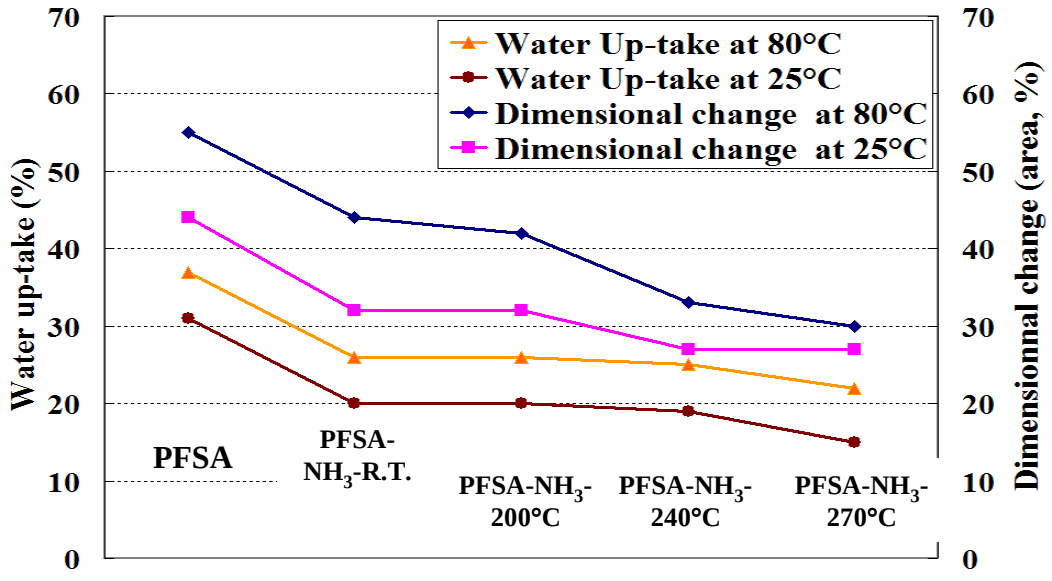


- Similar average Na^+ content in Na-PFSA , Na-PFSA-NH_3-without Δ and Na-PFSA-NH_3-200
- Lower average Na^+ content in membrane treated at 280 °C and Et_3N
- Gradient of Na^+ content between surface (lower) and centre (higher) of membrane → higher degree of cross-linking at the membrane surfaces

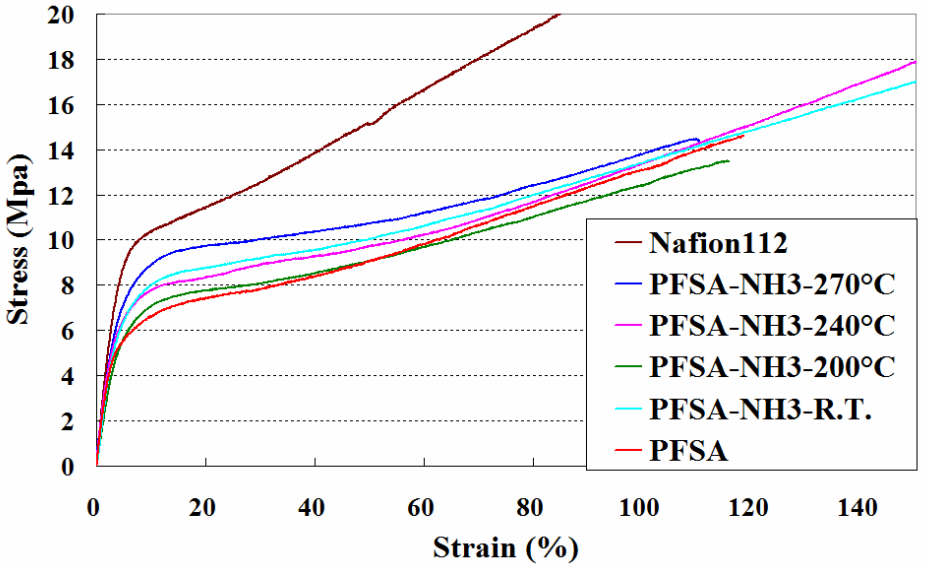
Properties of Cross-linked membranes

- *Water up-take and Dimensional chang*
- *Mechanical Property*
- *Proton Conductivity*

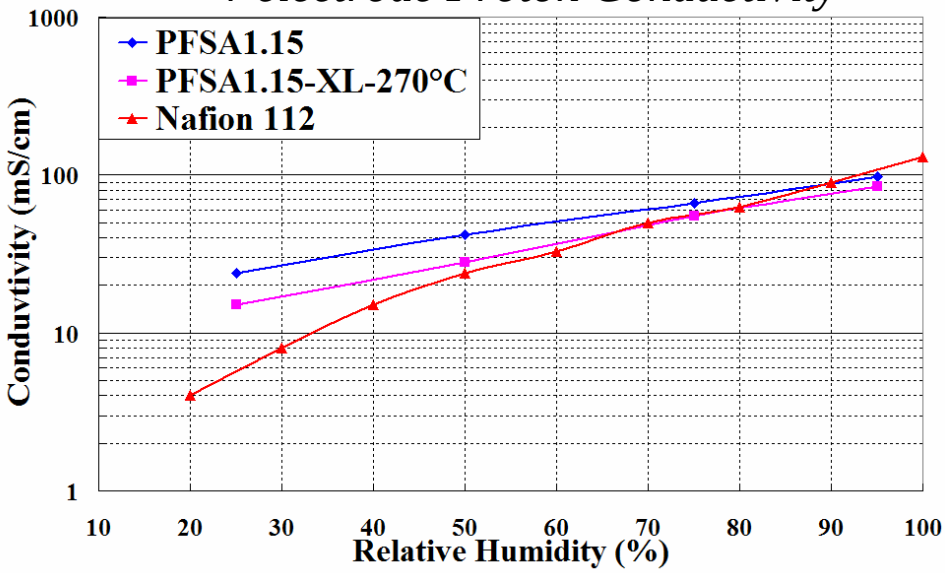
Water up-take and Dimensional change



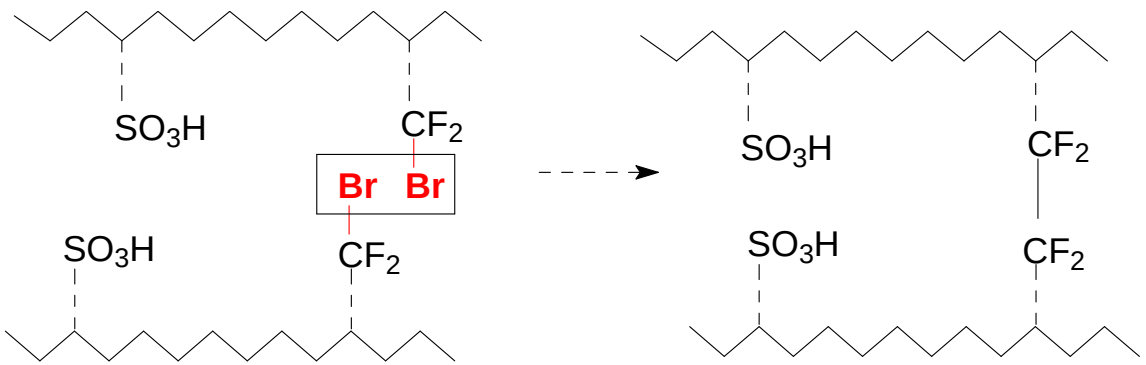
Mechanical Measurement



4-electrode Proton Conductivity



Cross-linked PFSA membranes by formation of perfluoroalkyl

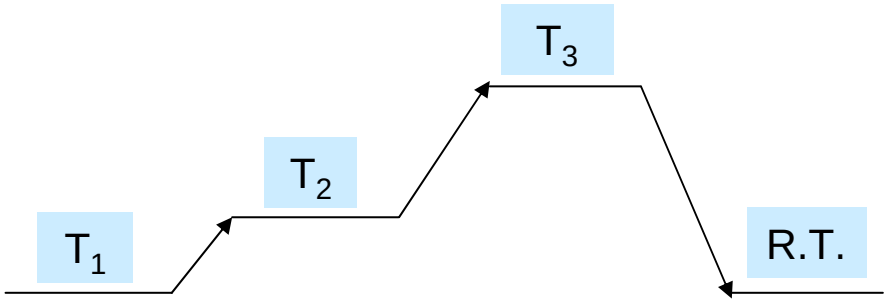


Cross-linking reaction: heat-induced **Bromoalkyl**

TGA of the resin

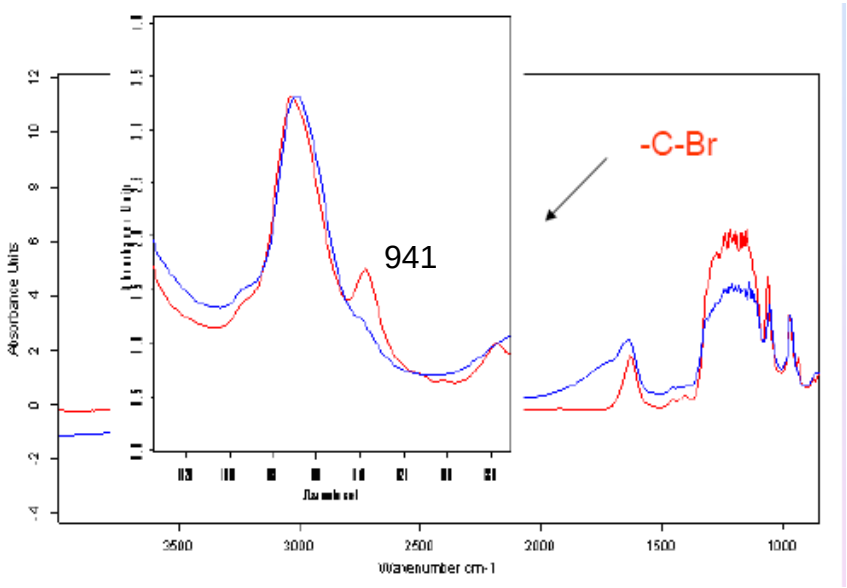
Temperature (°C)	Mass lost (w %)
20 ~ 100 (drying for 1h)	6.0 (water)
115 ~ 230	**2.8 (Br_2 +H_2O)**
256 ~ 600	Decomposition

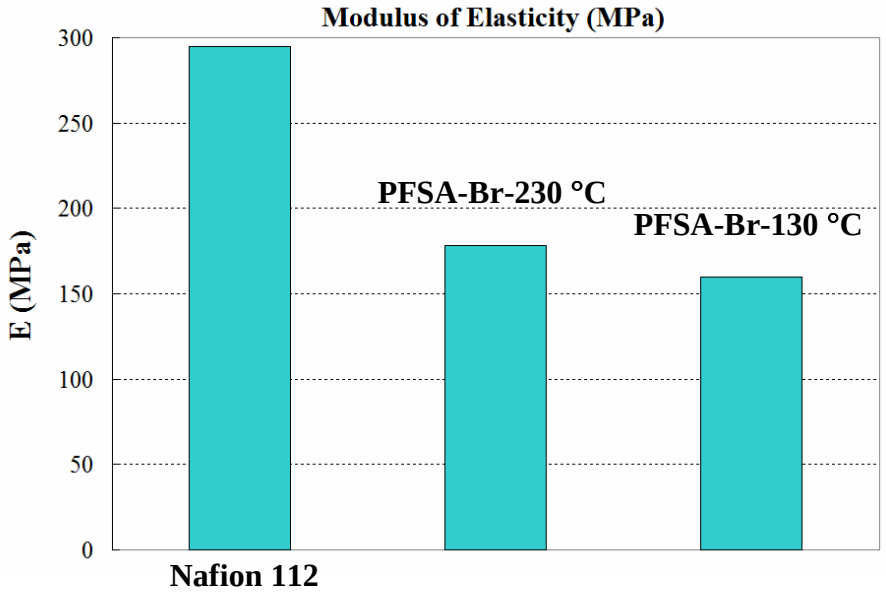
Process of thermal treatment by solution casting

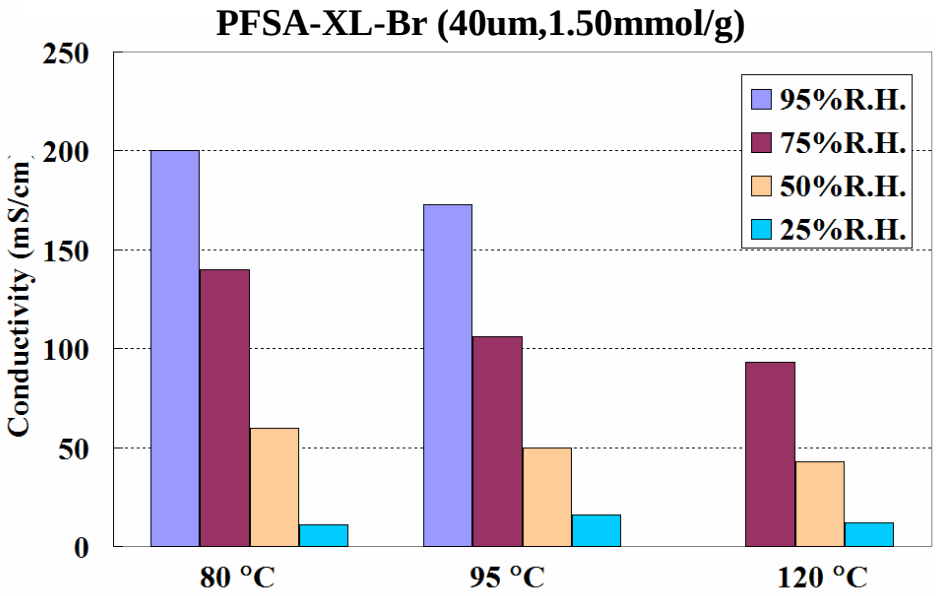


Characterisation of Cross-linked PFSA

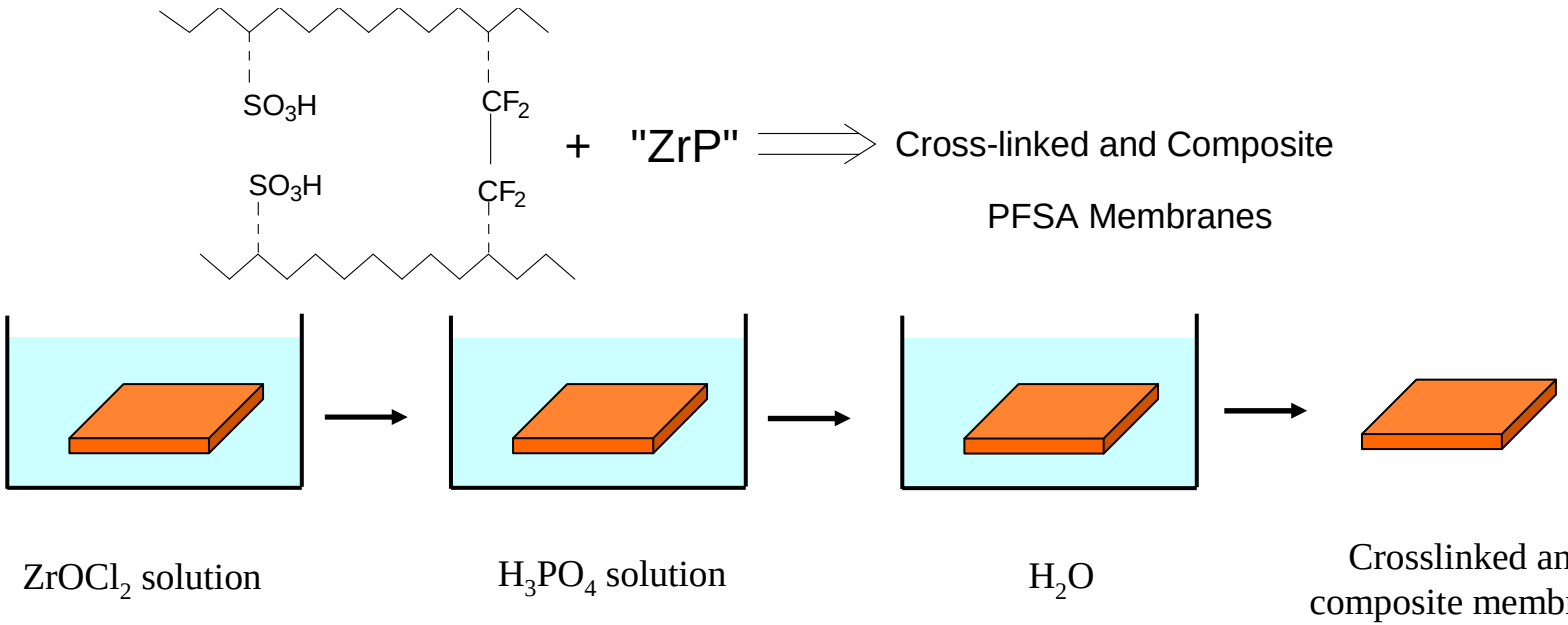
- *IR*
- *Modulus of Elasticity*
- *Proton Conductivity*







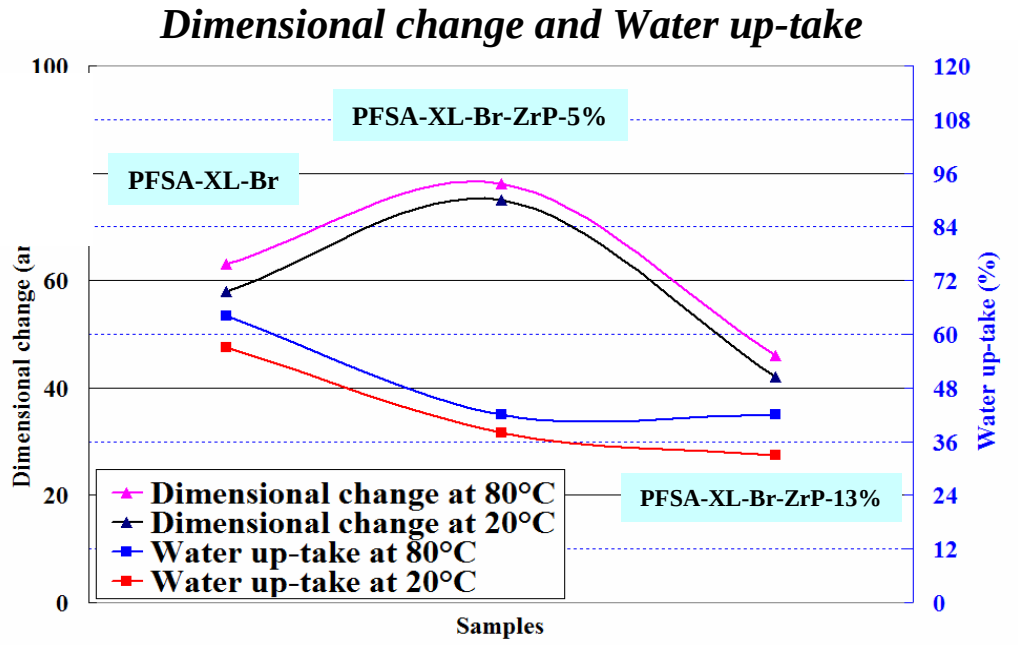
Preparation of composite membrane by ion-exchange/precipitation

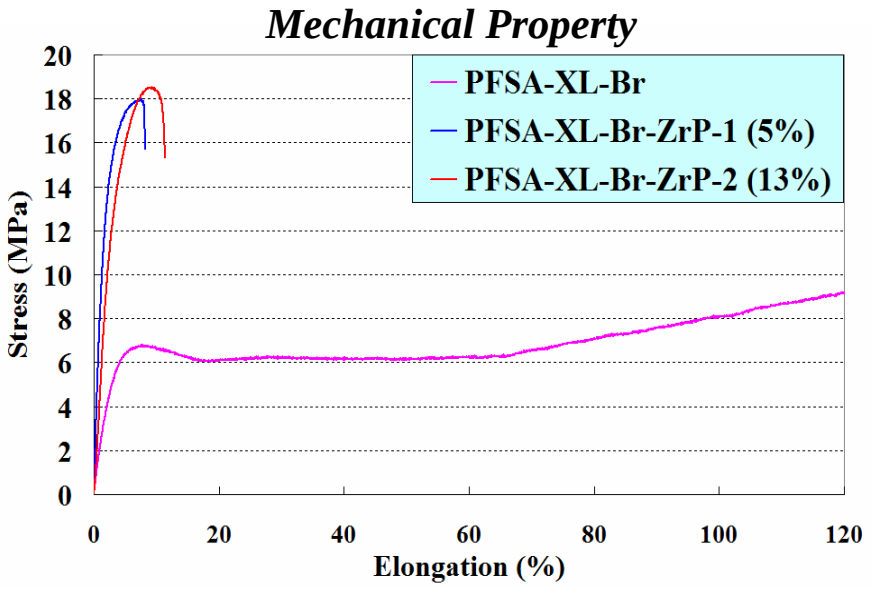


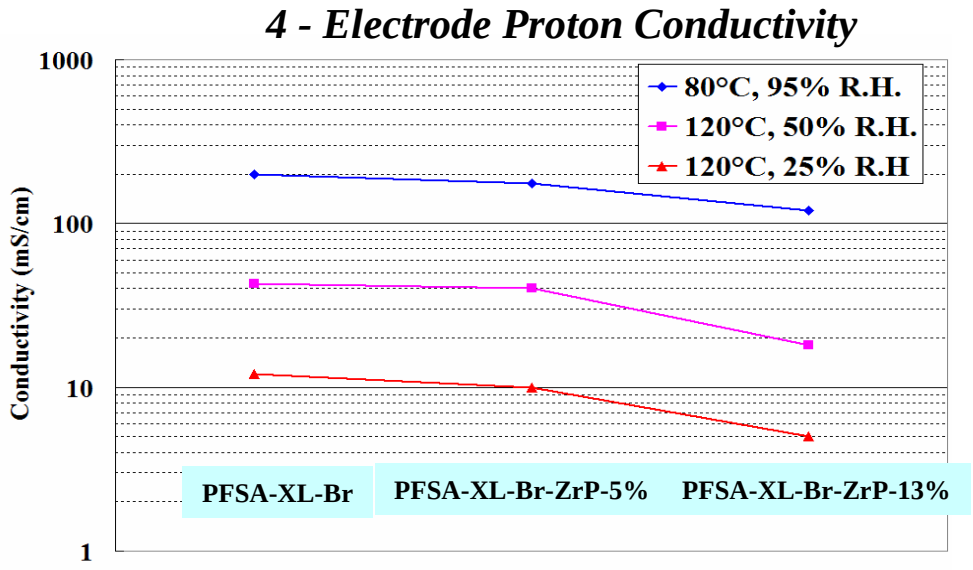
Samples	IEC (mmol/g)	Thickness (μm)	Content of "ZrP" (w%)
PFSA-XL-Br-ZrP-1	1.50	40	5
PFSA-XL-Br-ZrP-2	1.50	40	13

Properties of cross-linked and composite membranes

- *Water up-take and Dimensional change*
- *Mechanical Property*
- *Proton conductivity*

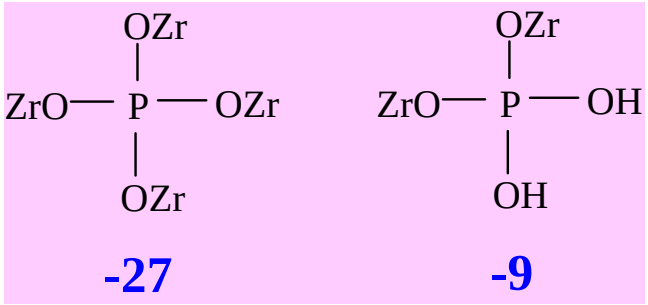




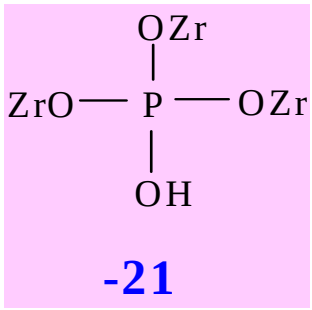


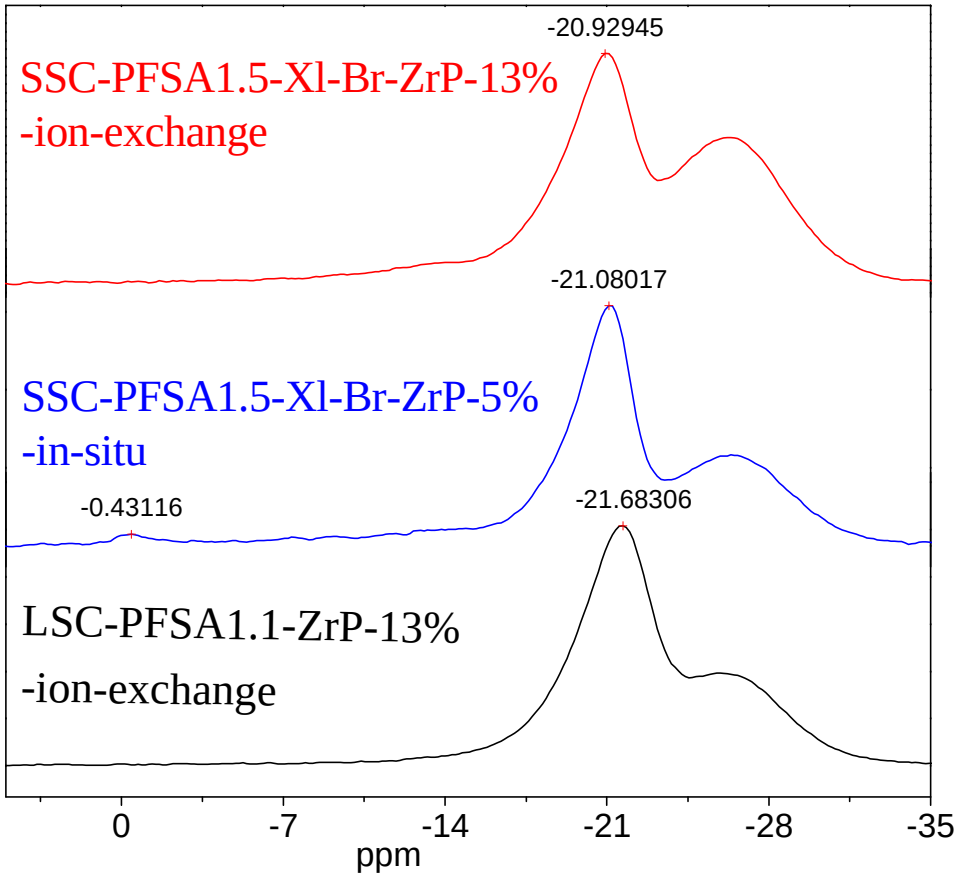
“ZrP” structure : ^{31}P NMR

γ-$Zr(H_2PO_4)(PO_4)$



α-$Zr(HPO_4)_2$





$Zr(HPO_4)_2 + Zr_3(PO_4)_4$

Hirokazu Nakayama, et al. J. Mater. Chem.,1997,7(6), 1063~1066

Single cell characterization

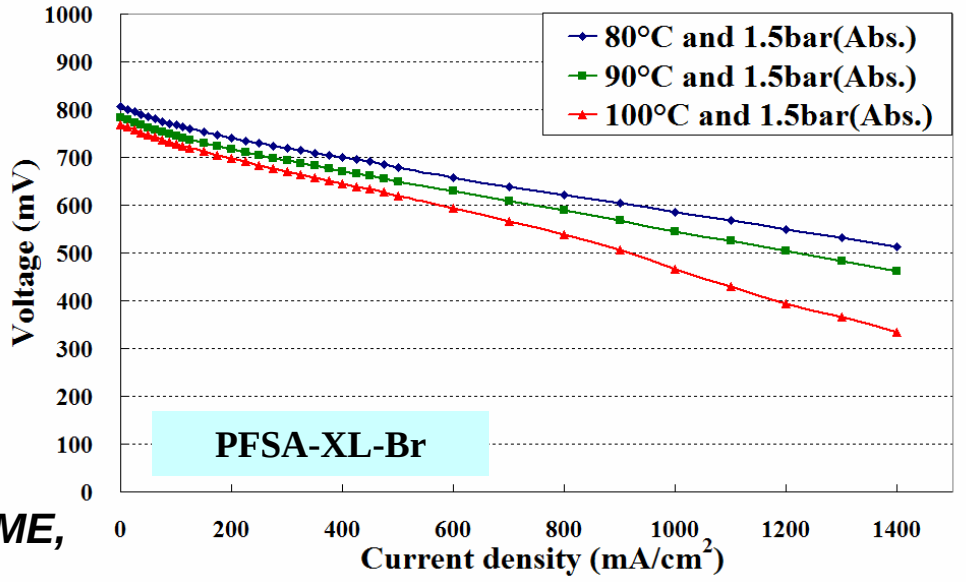
--- Electrodes: E-TEK

--- 30% Pt/C; 0.5 mg Pt/cm^2 ; 0.6 mg Nafion / cm^2

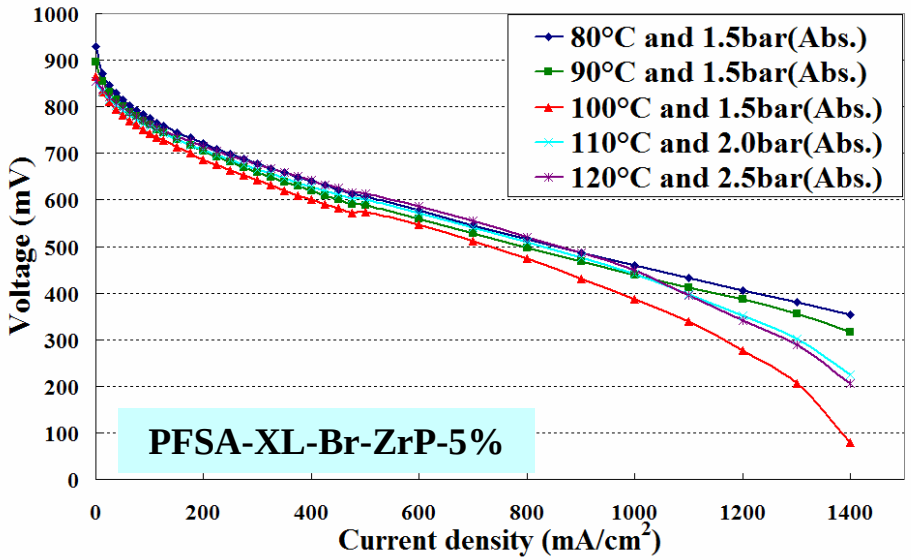
--- Humidified H_2, O_2

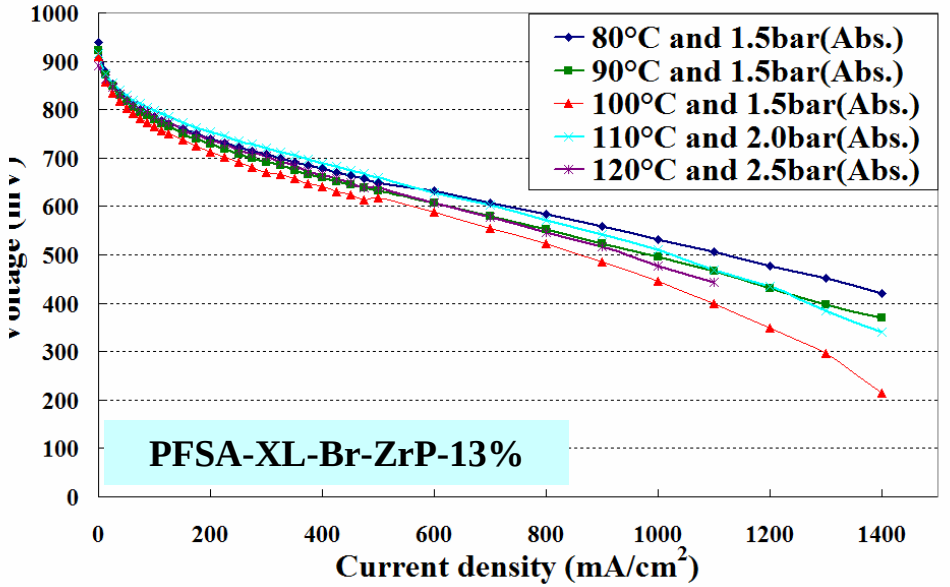
---Controlling temperature and Pressure

H2/O2 1.5 bar (Abs) with hydration (H2:80 °C - O2 : 64 °C)



MEA: made by Mr. Marc DUPONT, CNRS-AIME, Montpellier, France





Conclusions

- ***Two cross-linking approaches have been described for PFSA, with macroscopic and local characterisation of properties***

- ***Cross-linking stabilises high IEC/low EW membranes against excessive swelling***
  - ***lowers the water uptake and dimensional change***
  - ***improves the mechanical properties***

- ***High proton conductivity is maintained in cross-linked and composite membranes***

- ***Preliminary MEA characterisation shows that the presence of the ZrP component allows higher temperature operation, to 120 ℃***

Acknowledgements

Project no: *039016*

IPHE_GENIE: *International Partnership for a Hydrogen Economy for GENerationof New Ionomer membranEs*

Project partners

- *Energy Research Centre of the Netherlands, Holland*
- *Shanghai Jiao Tong University, China*
- *Dongyue Shenzhou New Materials, China*
- *Fuma –Tech GmbH, Germany*
- *CNRS-University of Montpellier 2, France*
- *Boreskov Institute of Catalysis, Russia*

Thank you
for your attention!