CARISMA 2012

3 – 5 September 2012

Recent Development of Acid Doped PBI Membranes in Denmark

- Polymer Chemistry and Durability Issues

Qingfeng Li, J. O. Jensen, L.N. Cleemann, D. Aili, J.S. Yang, N. J. Bjerrum

Department of Energy Conversion and Storage

Technical University of Denmark

Thomas Steenberg, Carina Terkelsen, Hans Aage Hjuler

Danish Power Systems ApS

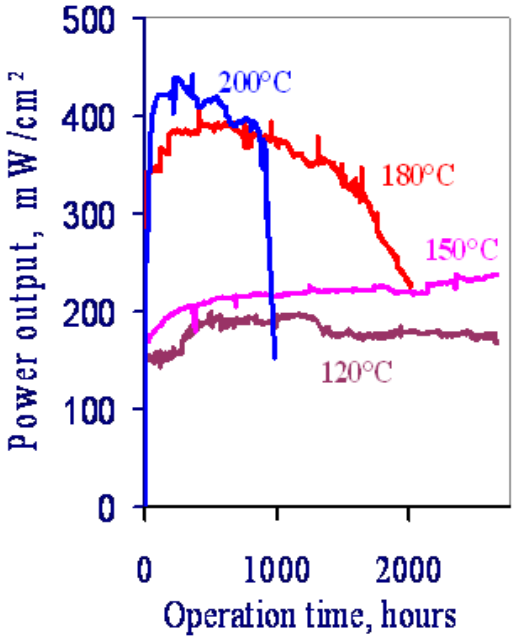
Outline

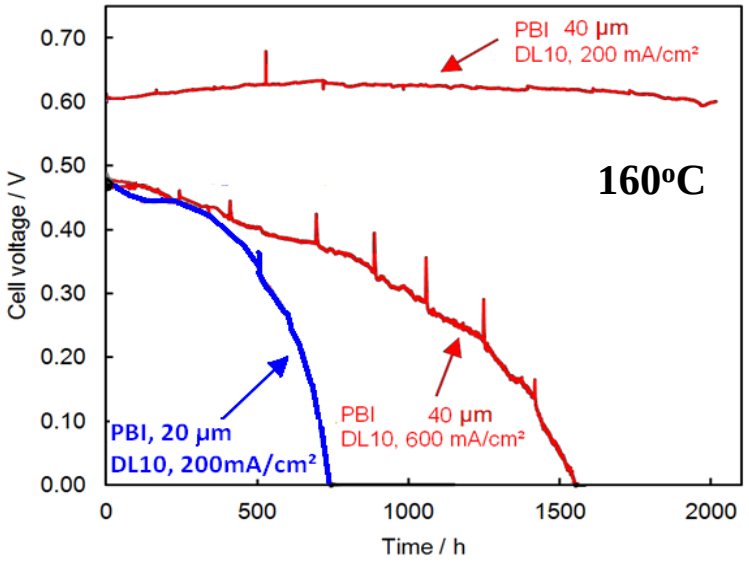
- Durability issues for PBI cells
- Membrane degradation
  - Thermal and radical oxidations
  - Effects of Fe^{2+} and phosphoric acid
  - Polymer chemistry
- Newest development
  - High Mw PBI
  - PBI blends
  - PBI variants
  - Cross-linking
- Conclusions

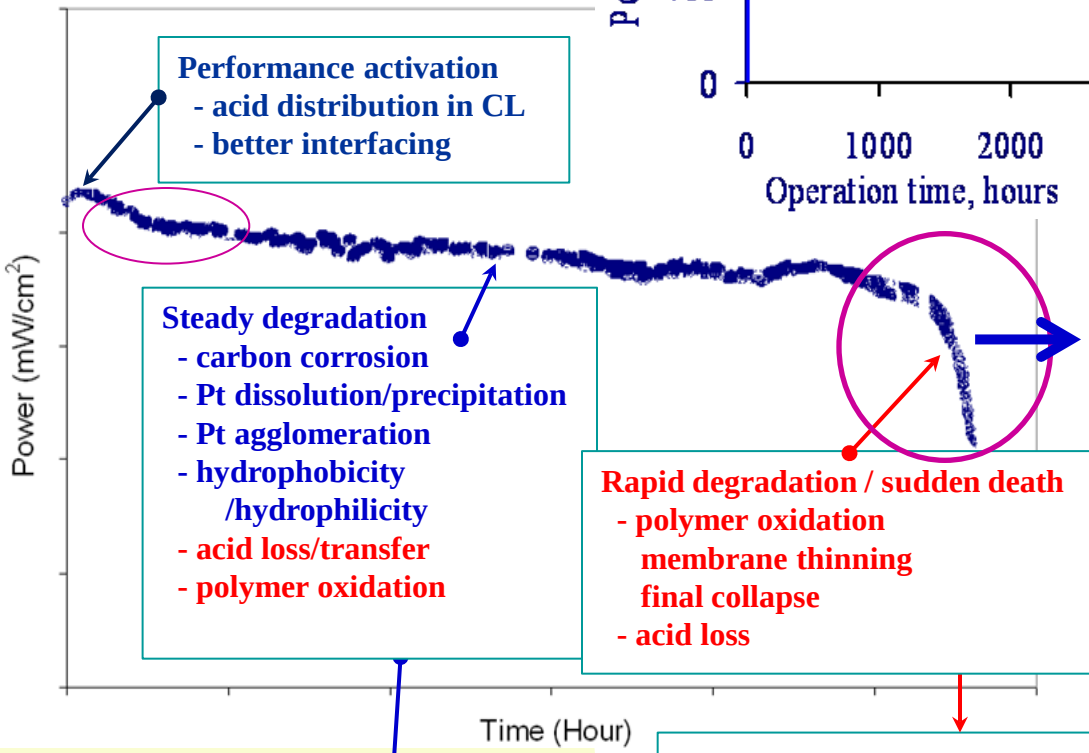
Durability issues

Steady state operation

Dynamic operation







Performance activation
- acid distribution in CL
- better interfacing

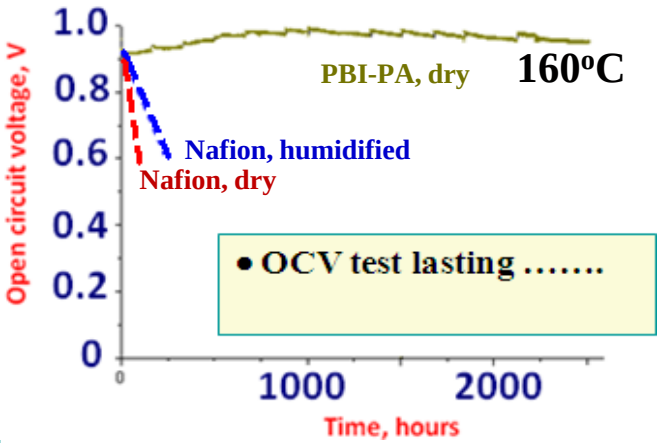
Steady degradation
- carbon corrosion
- Pt dissolution/precipitation
- Pt agglomeration
- hydrophobicity /hydrophilicity
- acid loss/transfer
- polymer oxidation

Rapid degradation / sudden death
- polymer oxidation
  membrane thinning
  final collapse
- acid loss

- **Significant membrane degradation**
  - thinner membranes
  - at high loads (currents)
  - at high temperatures

Significant at higher potentials
- worse under dynamic operation
  severe C corrosion
  high Pt solubility

Significant at higher currents
- more water formation
  acid loss
- more radical formation
  polymer oxidation
- locally higher tempearture?

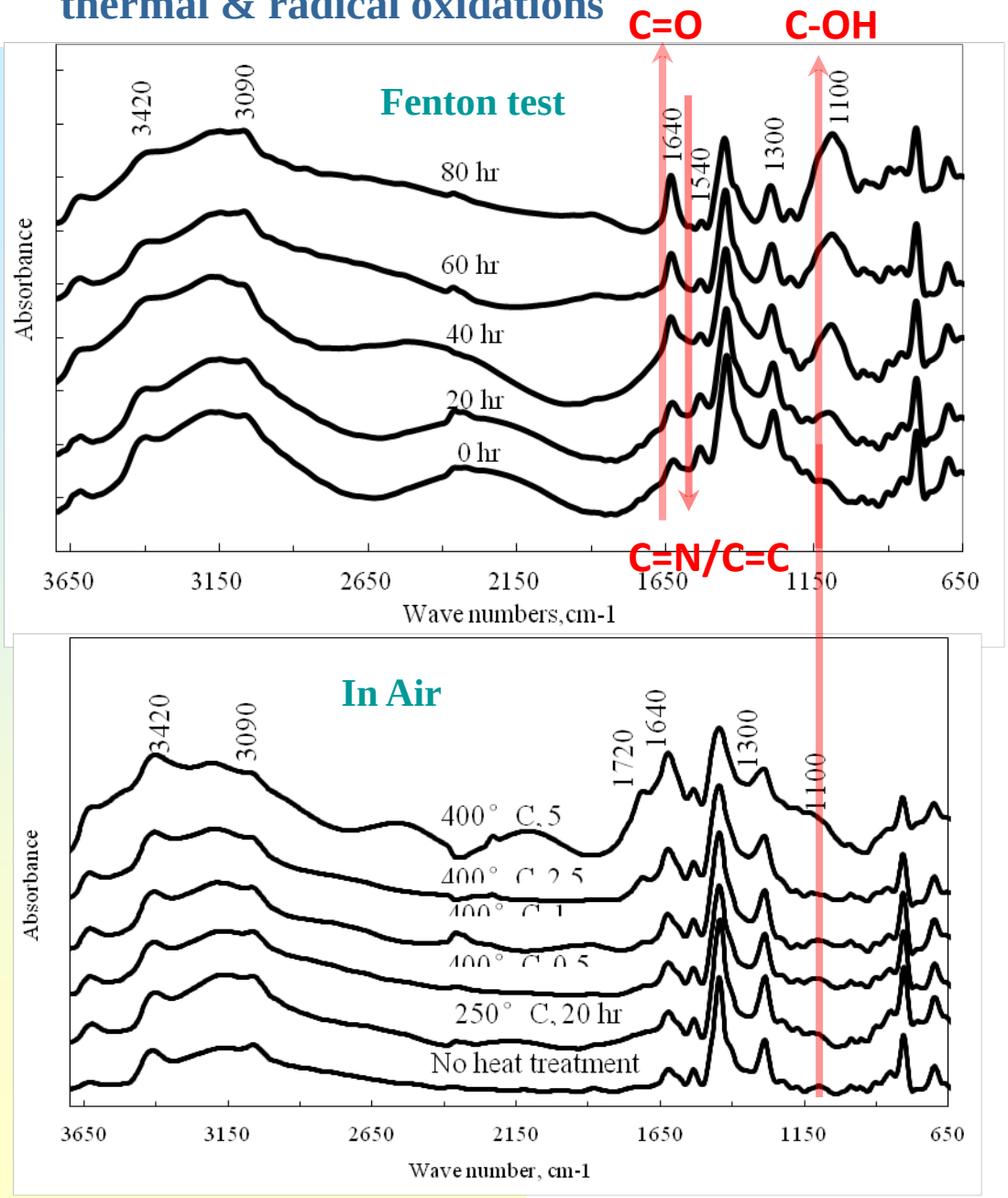


- **OCV test lasting …….**

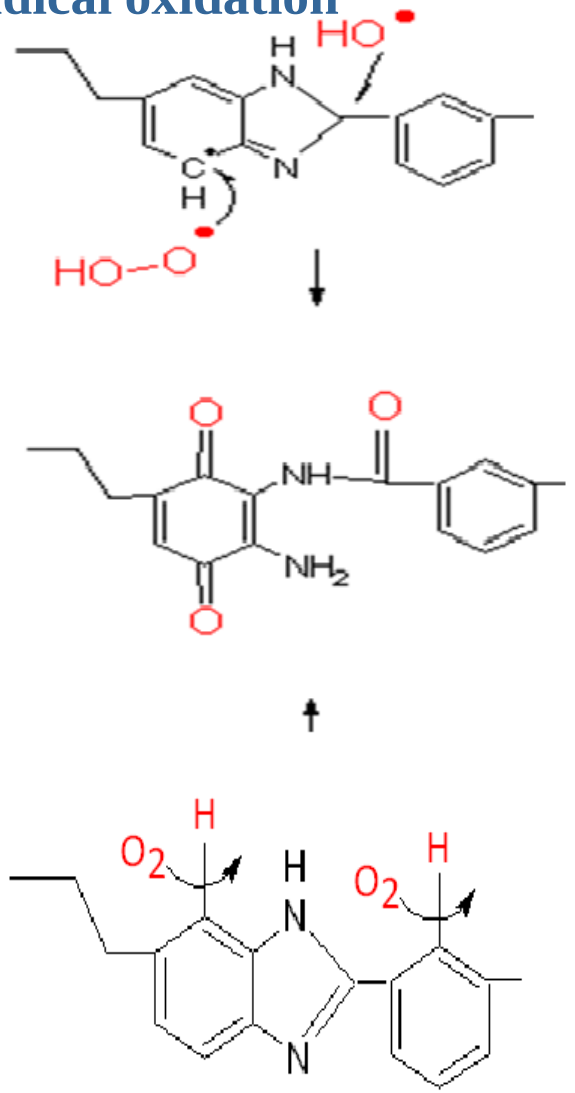
Polymer degradation

Liao et al. Fuel Cells, 11, 745 (2011)

thermal & radical oxidations



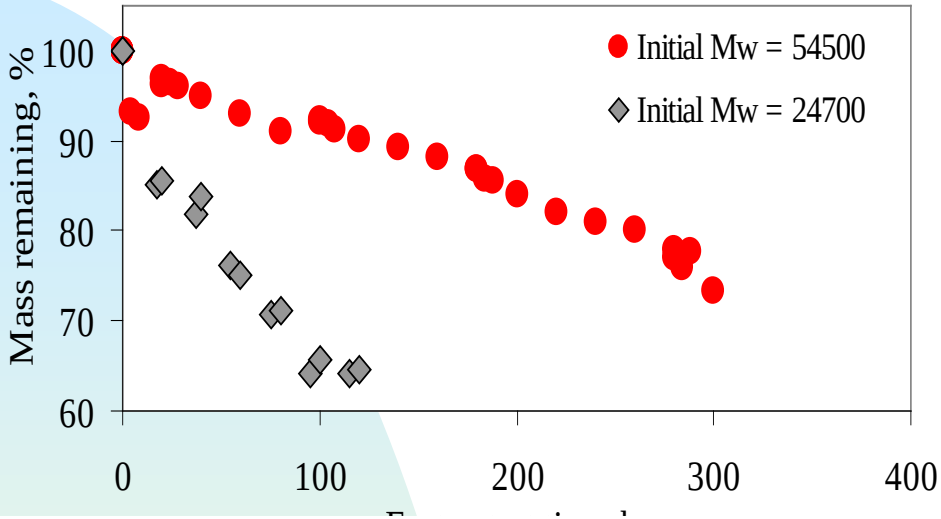
radical oxidation



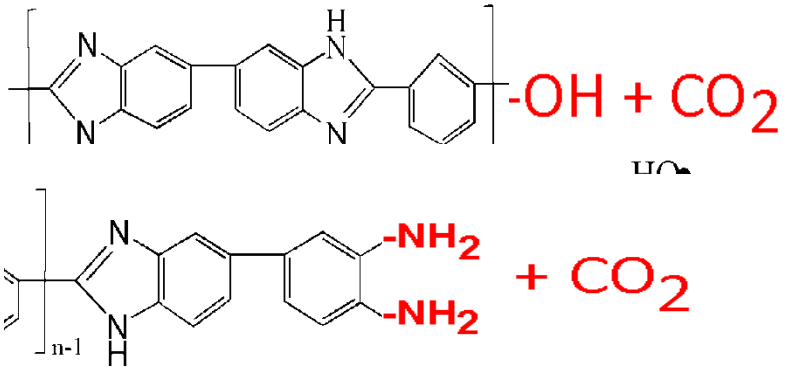
dioxygen oxidation

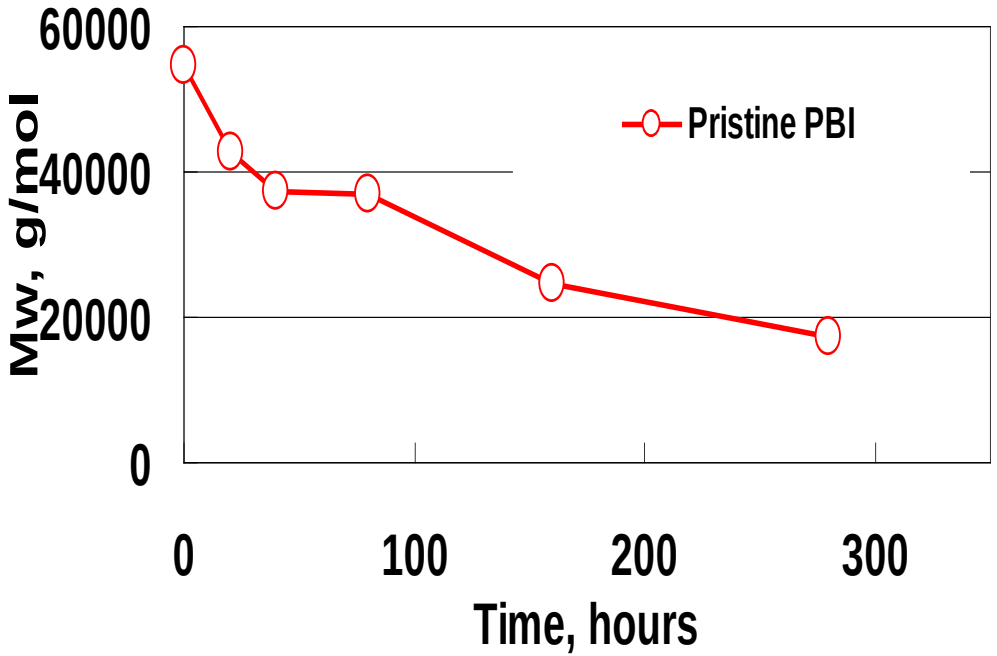
Polymer degradation

Weight loss of pristine PBI



- **Weight loss depedent of M_W**
  - **importance of terminal groups**

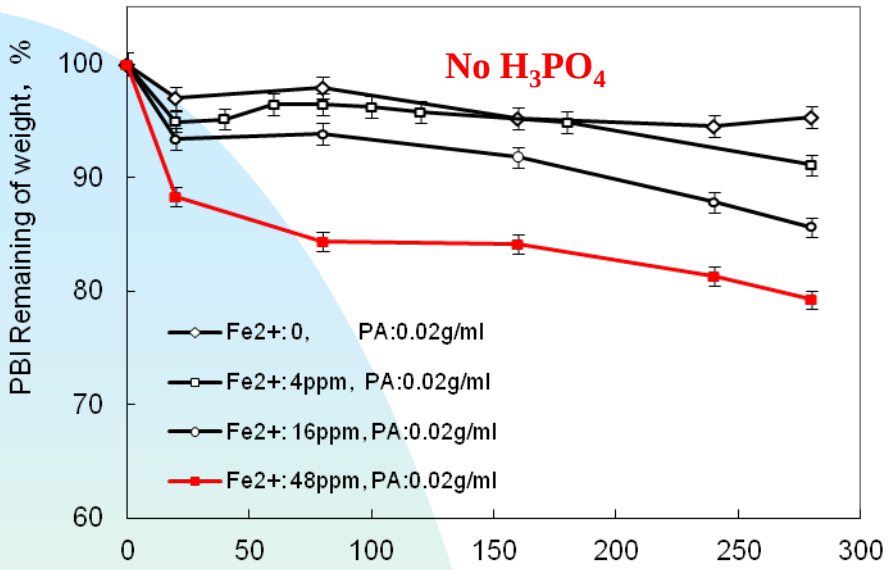


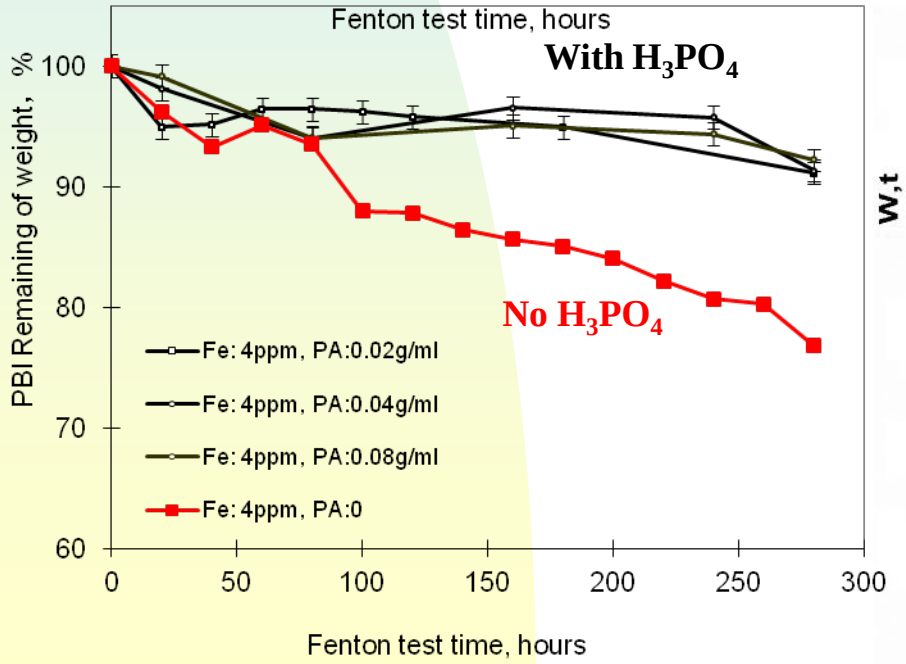


- **Mw decrease from 54,500 to 20,000 - ca. 1½ cuts while weight loss of 20%**
  - **chain scission and further weight loss**

Polymer degradation

Effect of Fe^{2+}

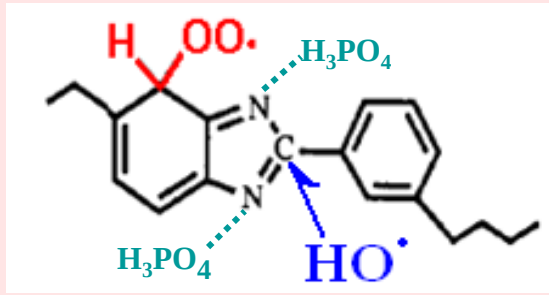




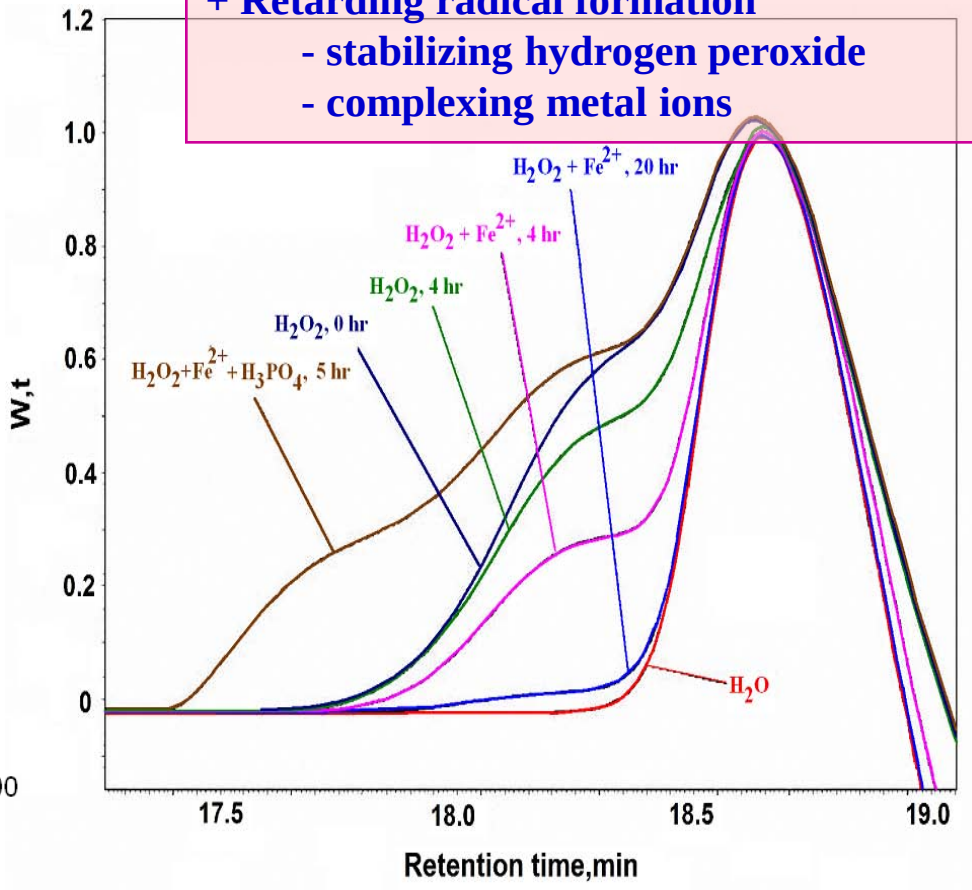
Effect of H_3PO_4

÷ Swelling polymer chains
- access for radicals

+ Stabilizing the heterocyclic rings
- through acid-base interaction



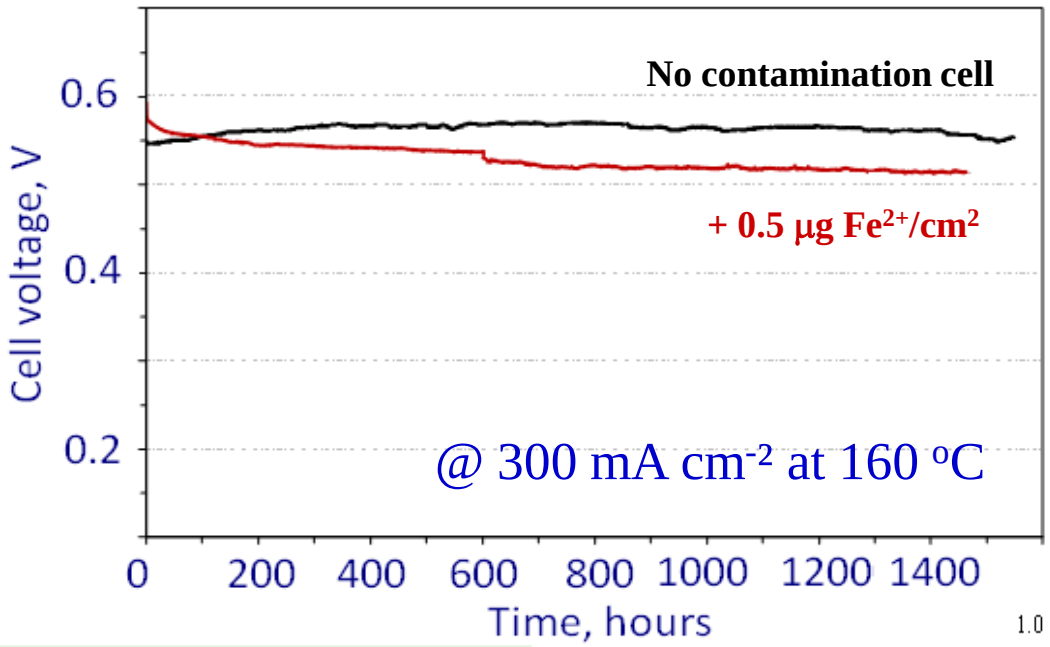
+ Retarding radical formation
- stabilizing hydrogen peroxide
- complexing metal ions

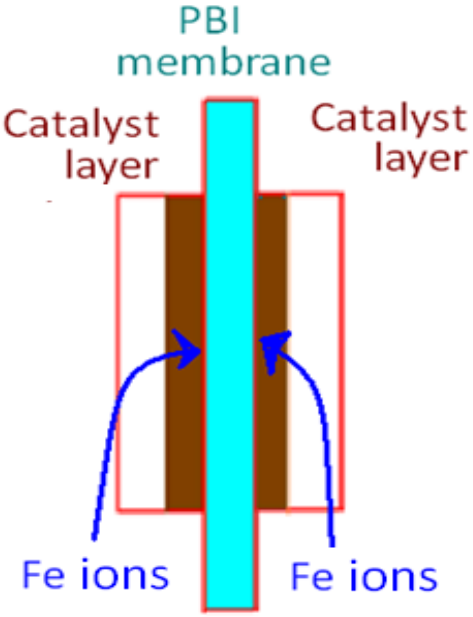


Polymer degradation

Liao et al. J. Power Sources (2012)

Effect of Fe^{2+} in presence of H_3PO_4



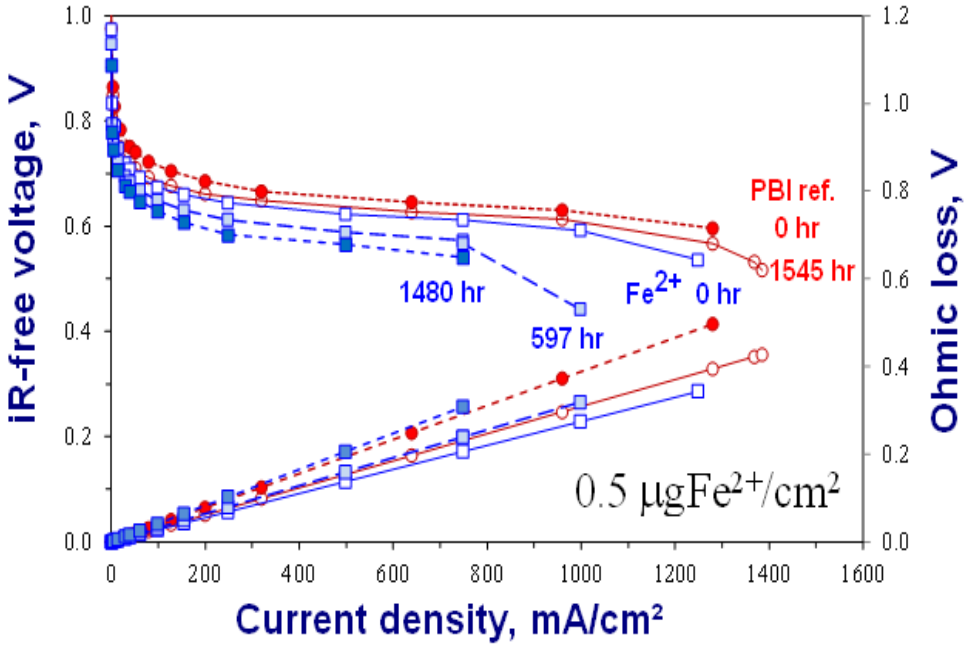


The metal contamination in PBI MEAs

… causes no additional OCV or iR changes

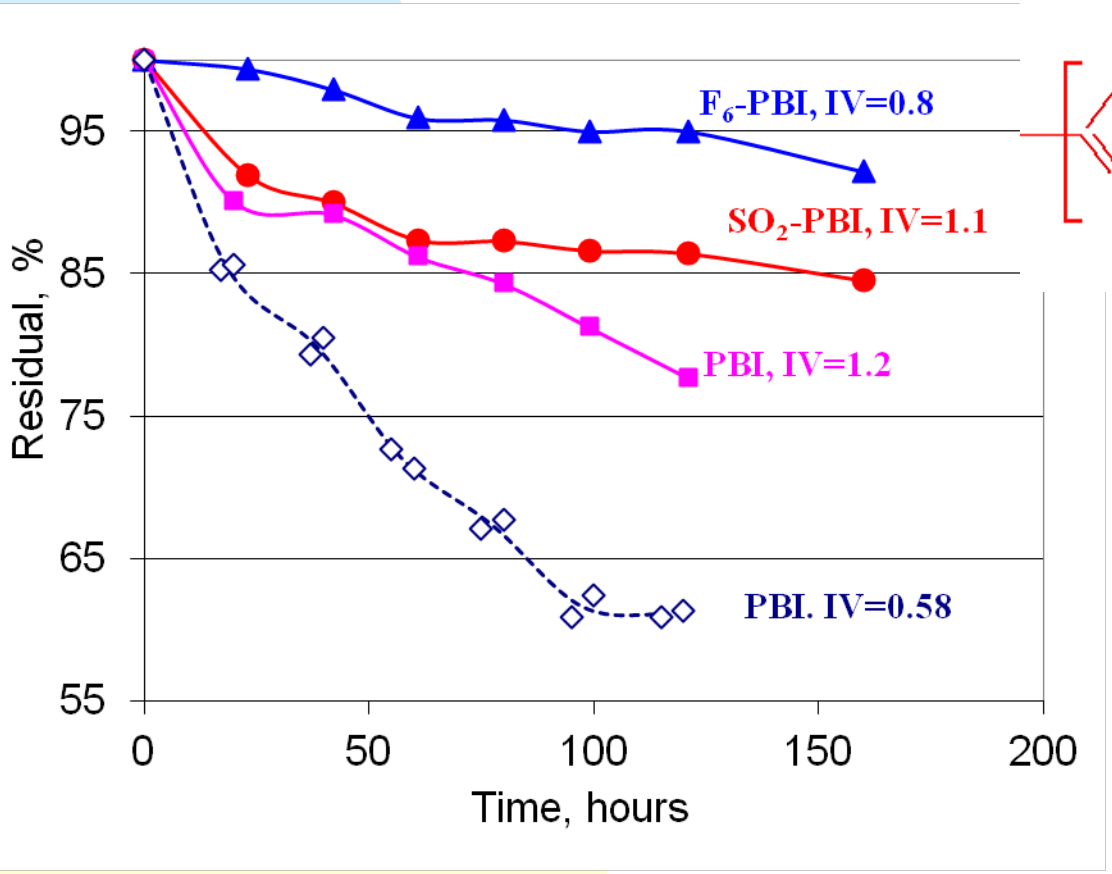
… but more catalyst degradation

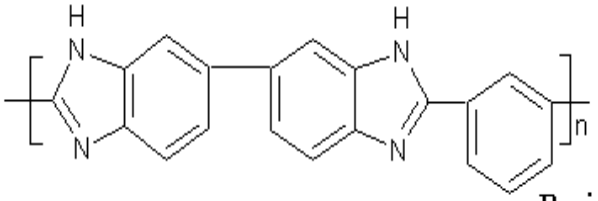
… during the first 1500 hours



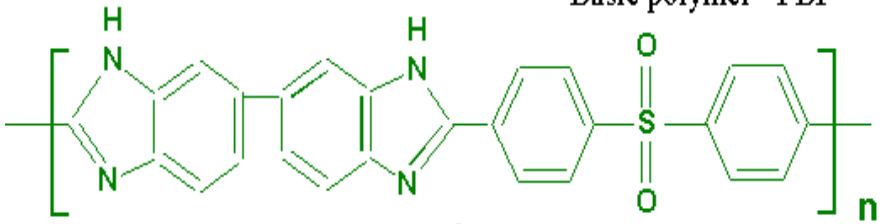
Polymer degradation

Effect of PBI chemistry

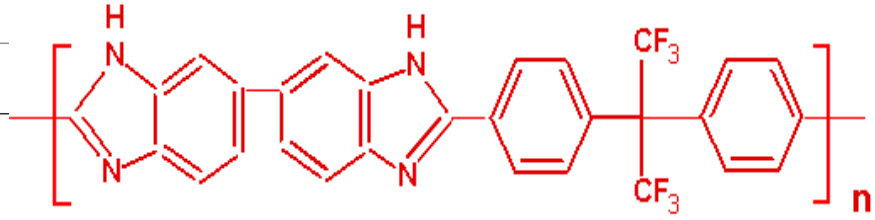




Basic polymer - PBI



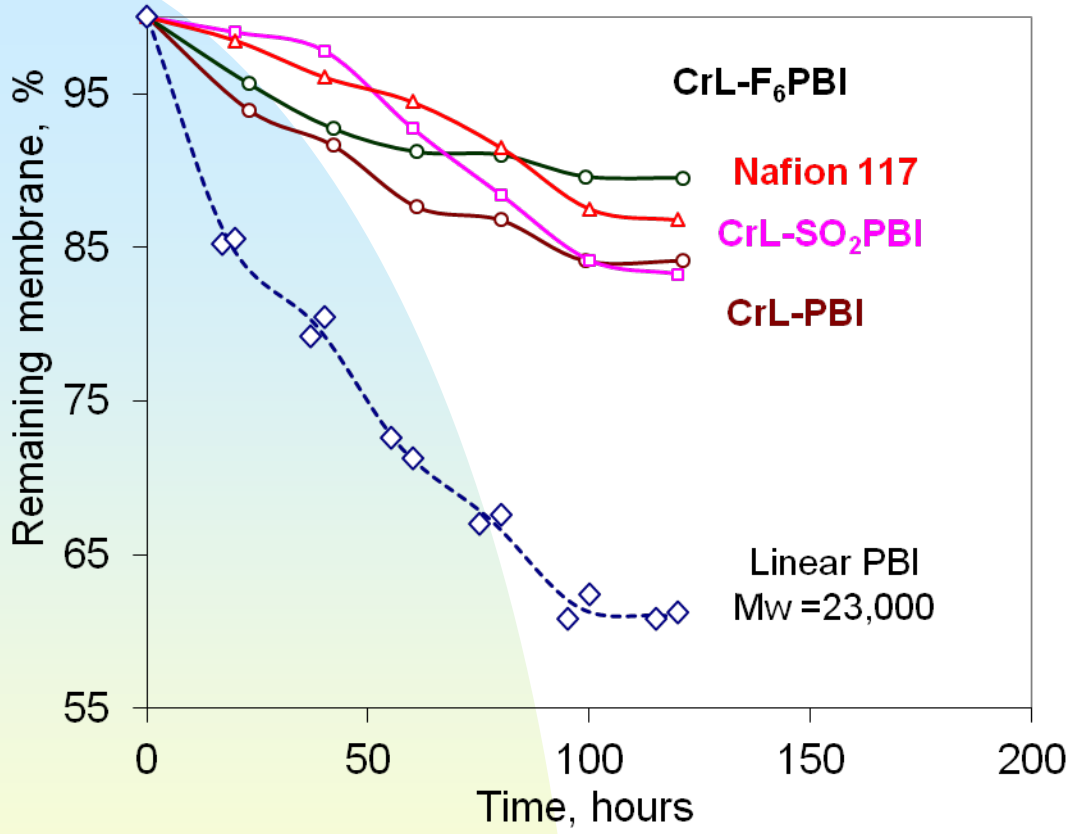
Basic polymer – SO_2-PBI

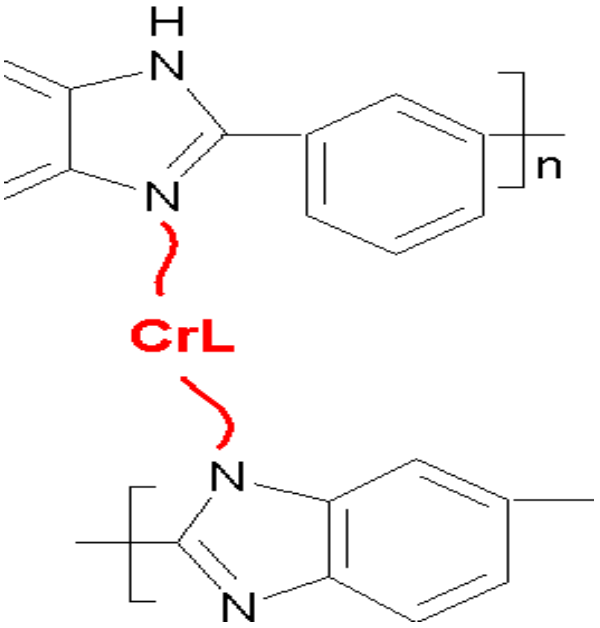


Basic polymer – F_6-PBI

Polymer degradation

Cross-linking



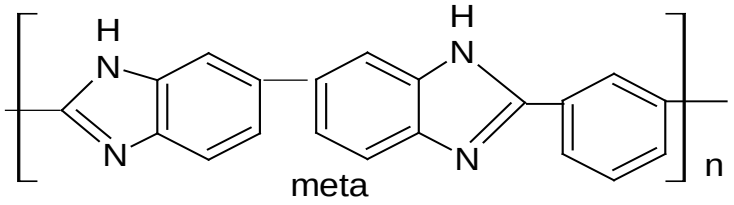


The weak link of PBI is nitrogen-containing heterocyclic rings

- **cross-linking occurs an amide linkage through imidazole groups**
- **the network structure holds the membrane from being falling into pieces**
- **Compatible to Nafion**

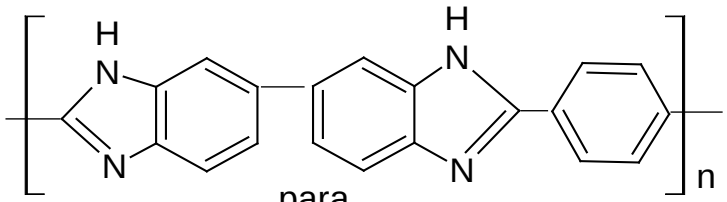
Recent development at DTU/DPS

- *m*PBI – ~~High Mw~~
  - Cross-linking
  - Thermal curing
  - Further blends



meta

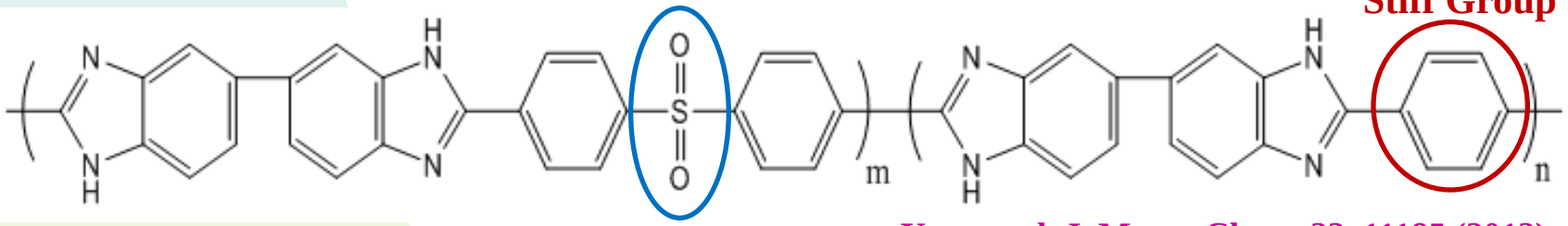
- *p*PBI – stiff & strong but less soluble
  - co-polymer with SO_2PBI



para

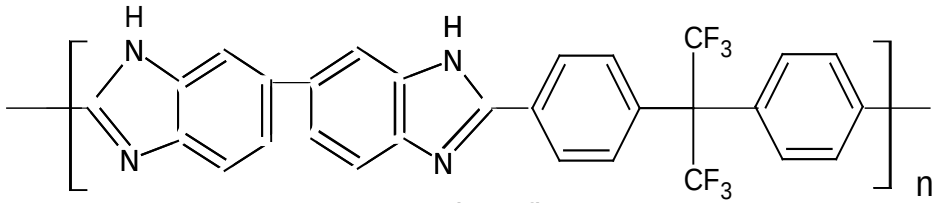
Flexible Group

Stiff Group



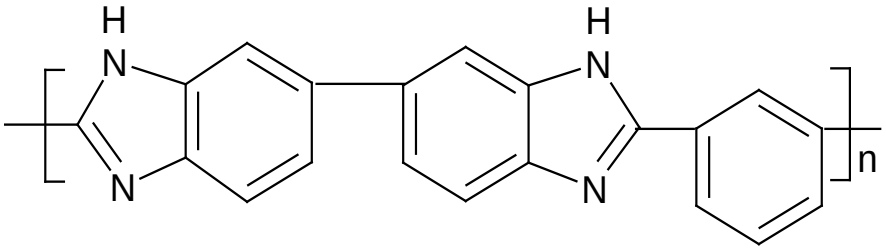
Yang et al. J. Mater. Chem. 22, 11185 (2012)

- F_6PBI – chemically very stable
  - easy to process (solubility)
  - poor mechanical stability (at ~~high~~ ADL/temp)
  - cross-linking

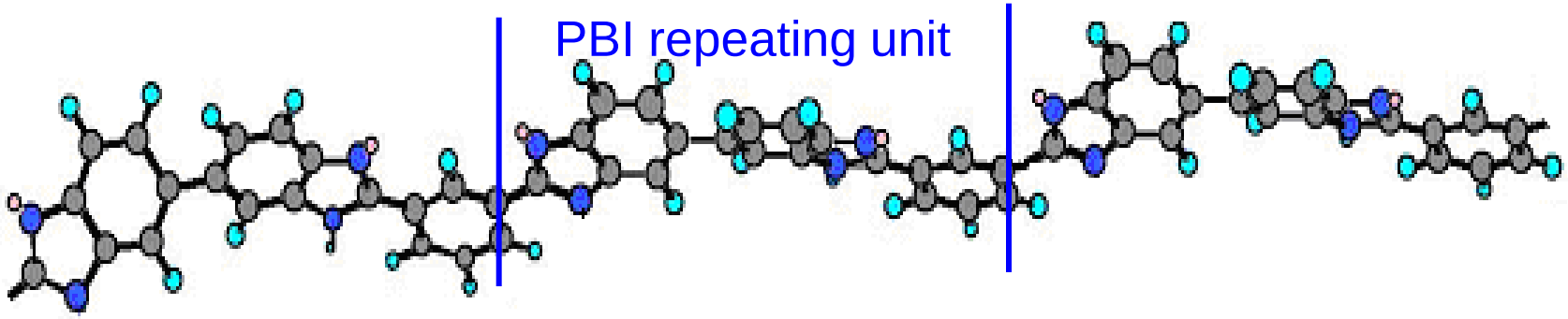


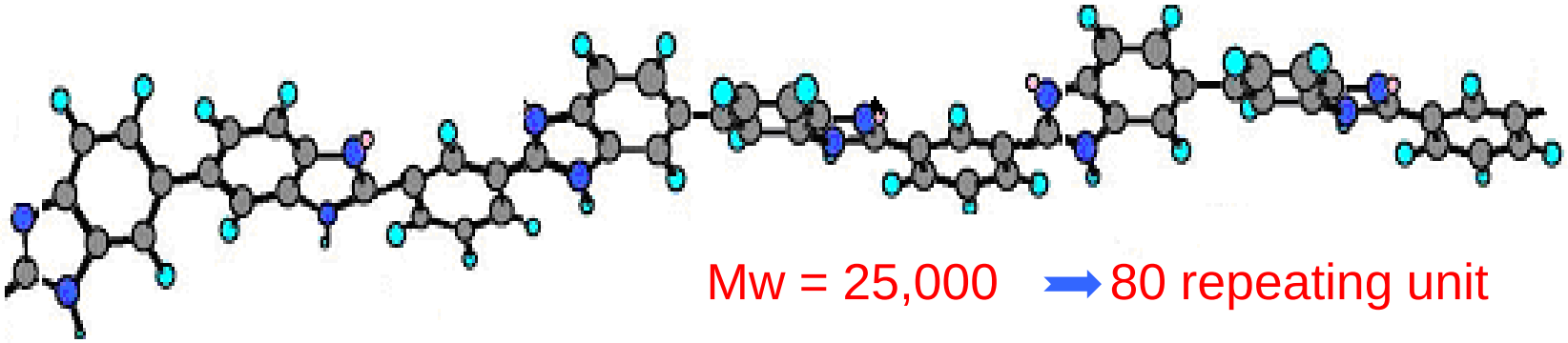
hexafluoro-PBI

High molecular weight PBI



PBI Mw <18,000



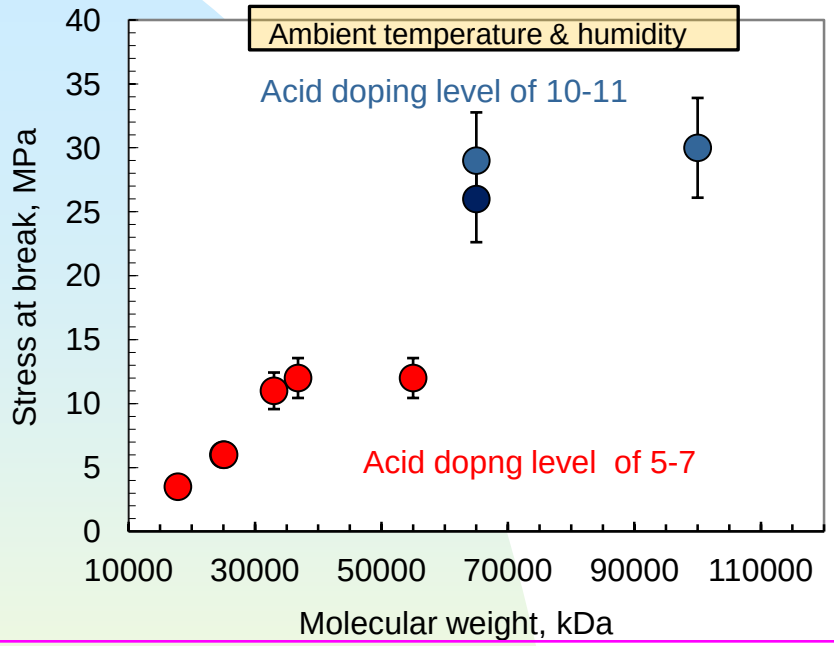


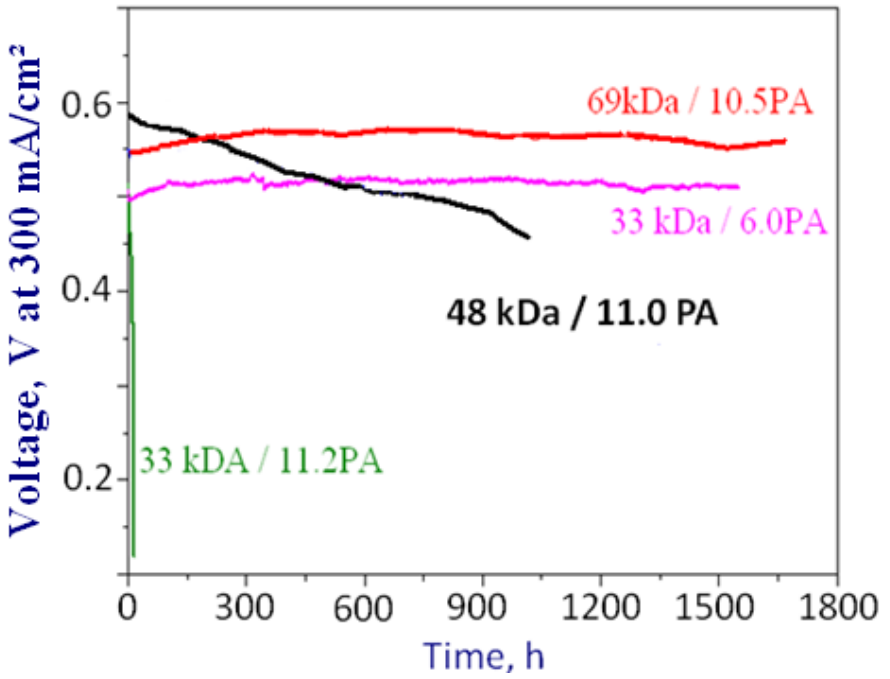
Mw = 25,000 ➡ 80 repeating unit

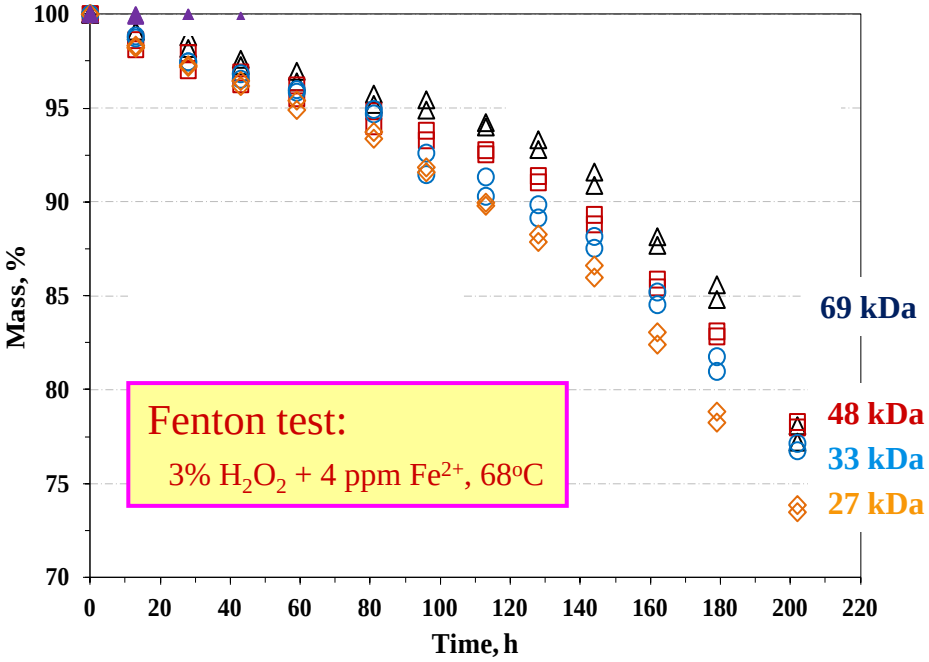
High M_W PBI

– high M_W PBI (up to 100,000 kDa)

synthesized with sufficient organo solubility







High M_W PBI

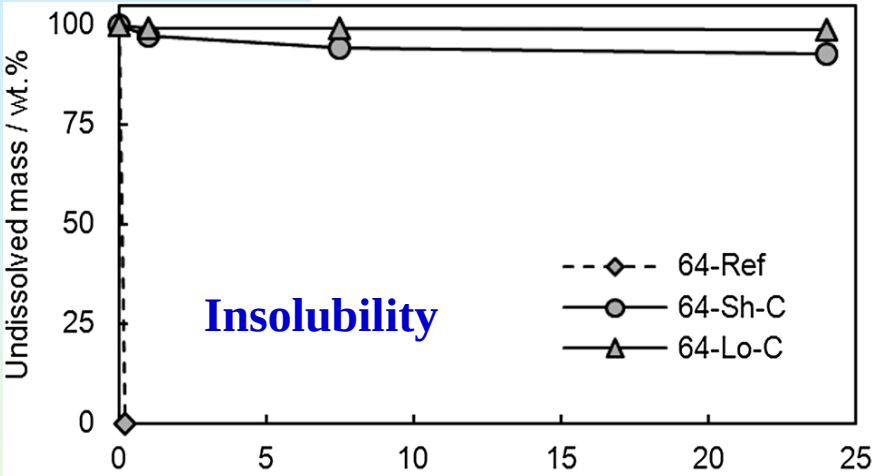
- slow acid doping
  - high doping temperatures
  - high doping acid concentration
  - less membrane swelling
- better mechanical strength
  - allowing for high doping levels and hence high conductivity
- better stability
  - resistance to radical oxidations (Fenton test)

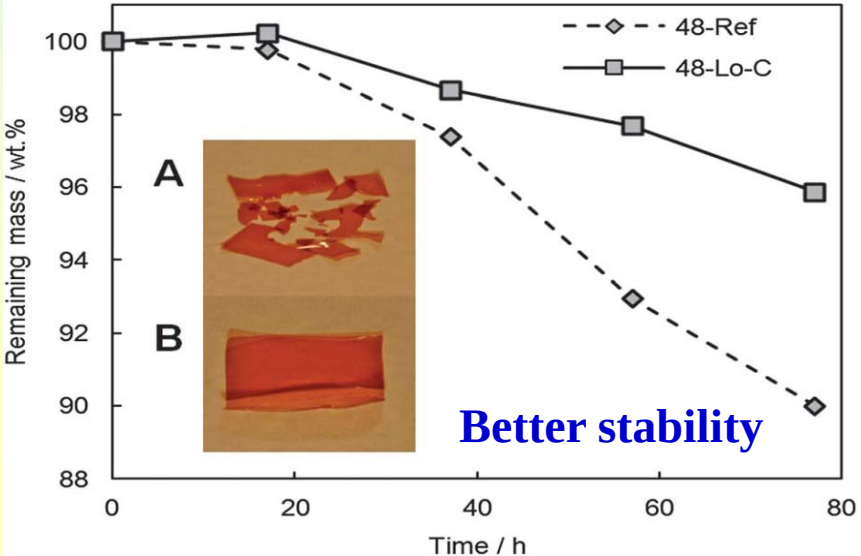
Thermal curing PBI

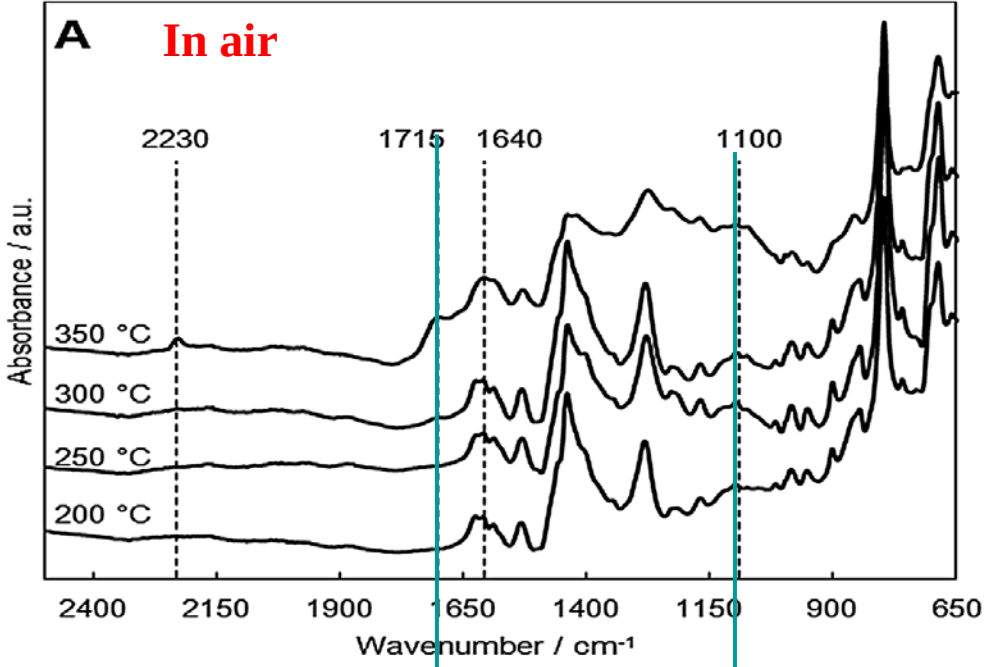
Curing PBI membranes in an inert atmosphere

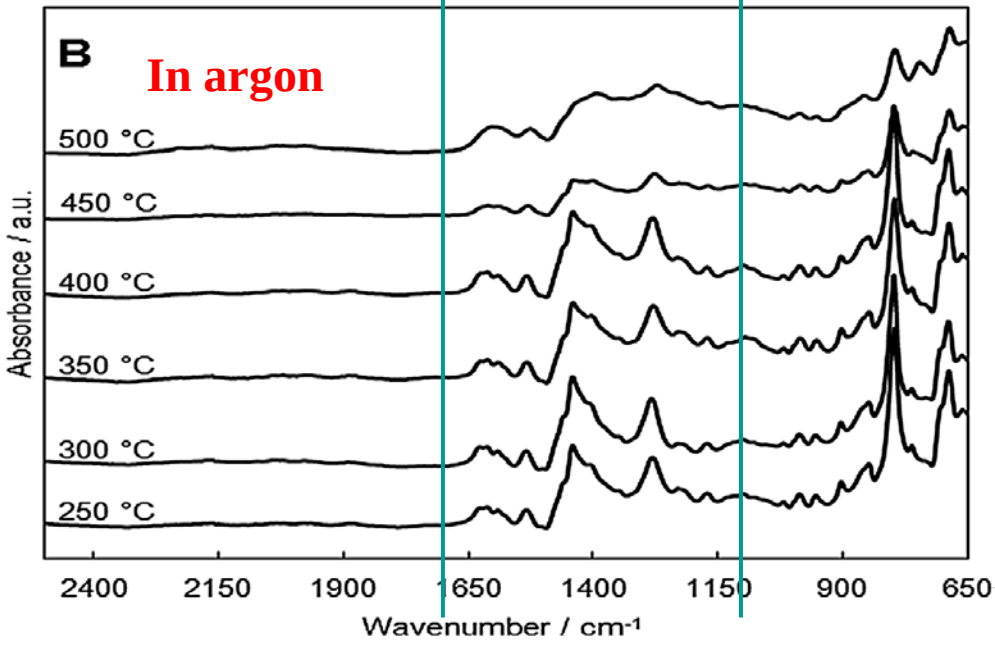
leading to little degradation

but effective cross-linking / branching …







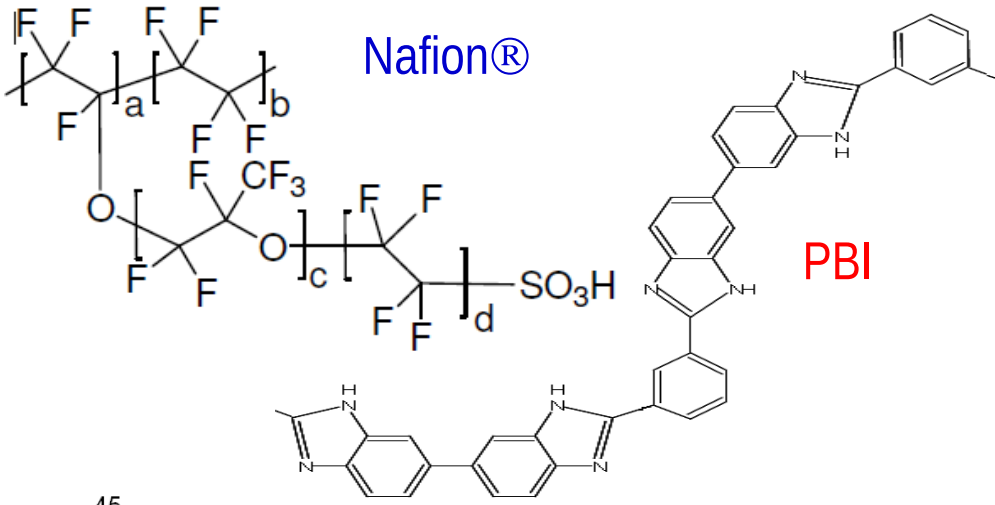


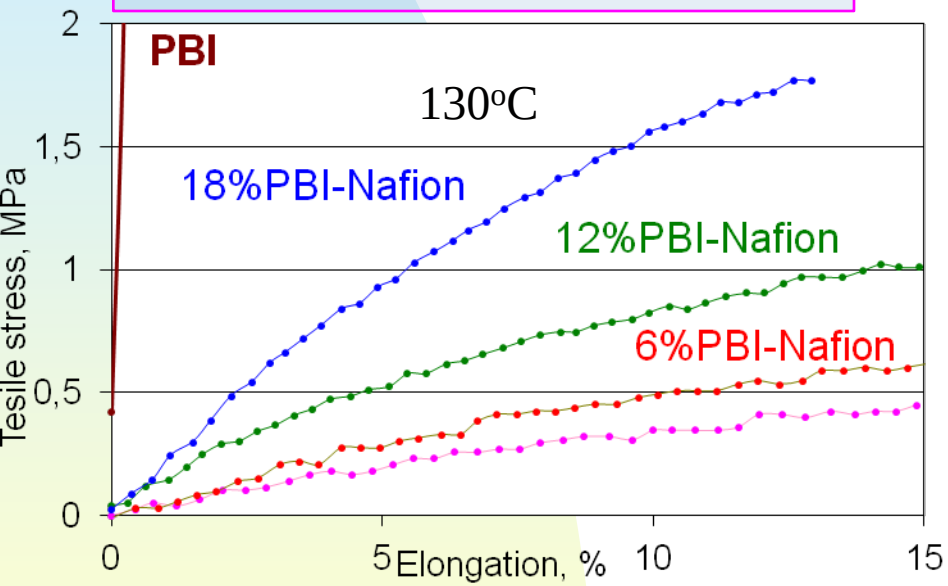
Aili et al. J. Mater. Chem. 22, 5444 (2012)

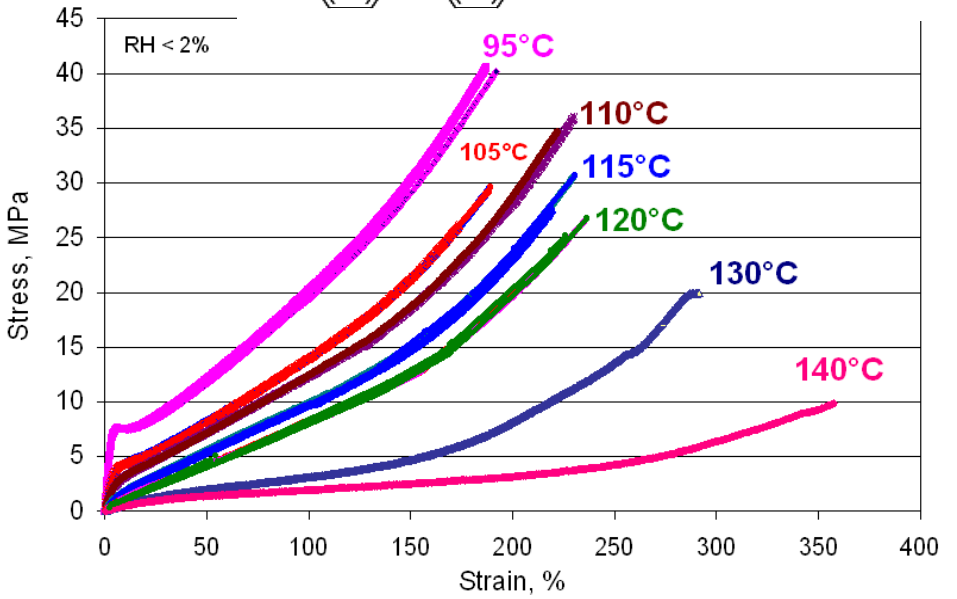
PBI blends

- Acid-base chemistry and miscibility

NH_4^+ Nafion – PBI
homogenous membranes
through entire composition range
- exchanging cations
acidity (cation size)
possible hydrogen bonds



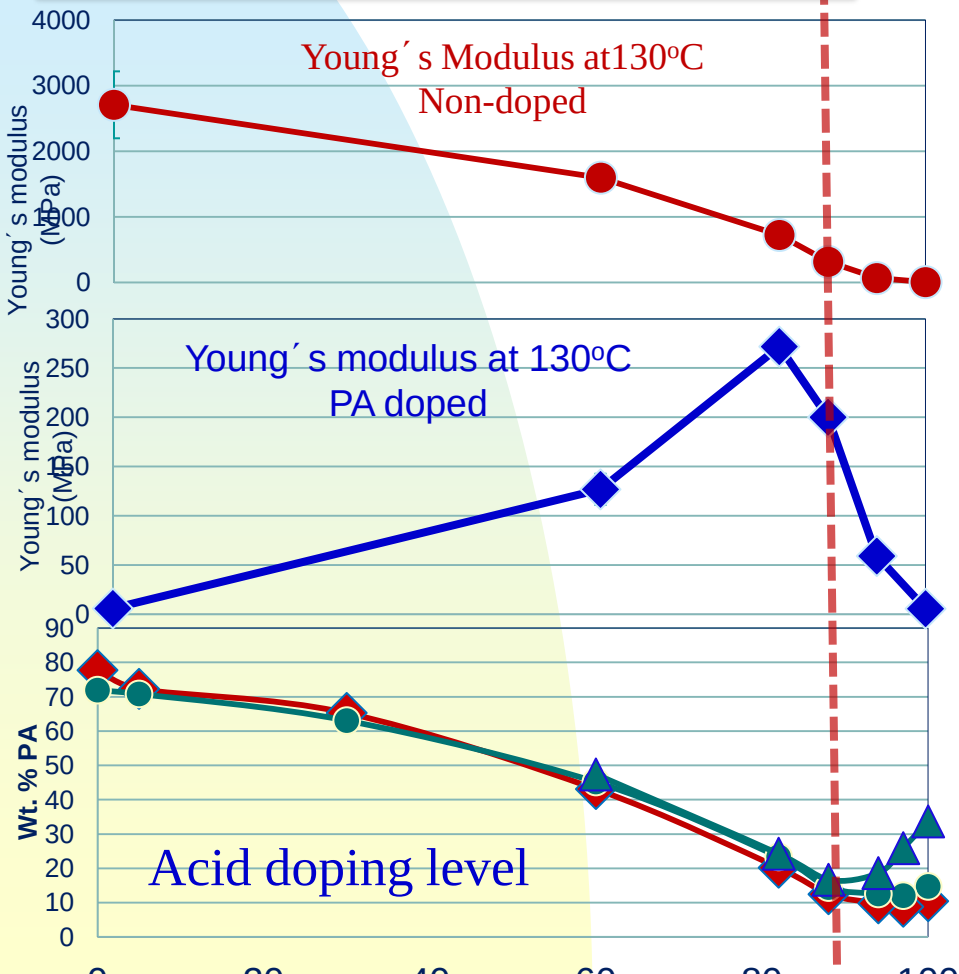


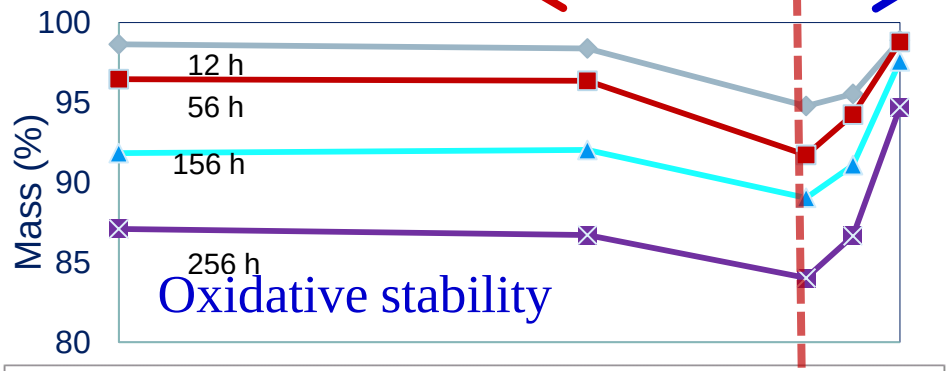


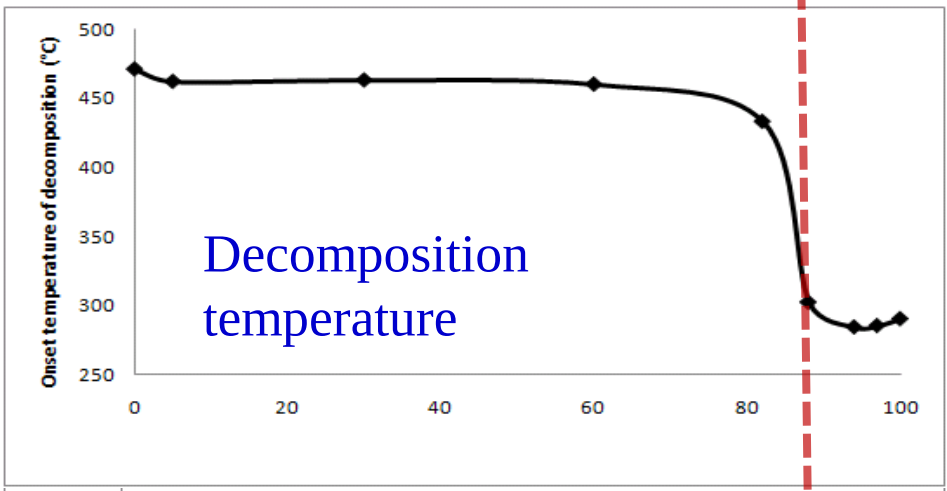
Cation exchanged Nafion and its blends with PBI

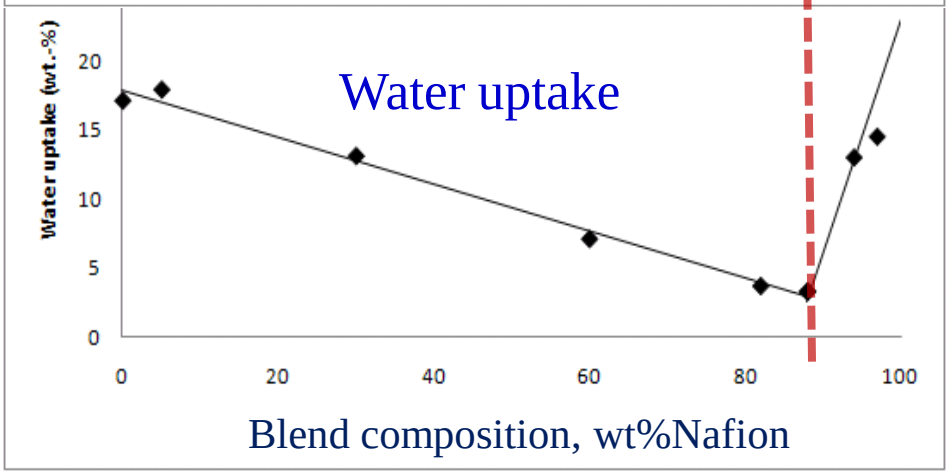
PBI blends - Acid-base chemistry

Neutralization at 88%Nafion-12%PBI
- minimum water uptake /acid doping
- transit in thermal stability
- minimum chemical stability (!)
- best mechanical strength





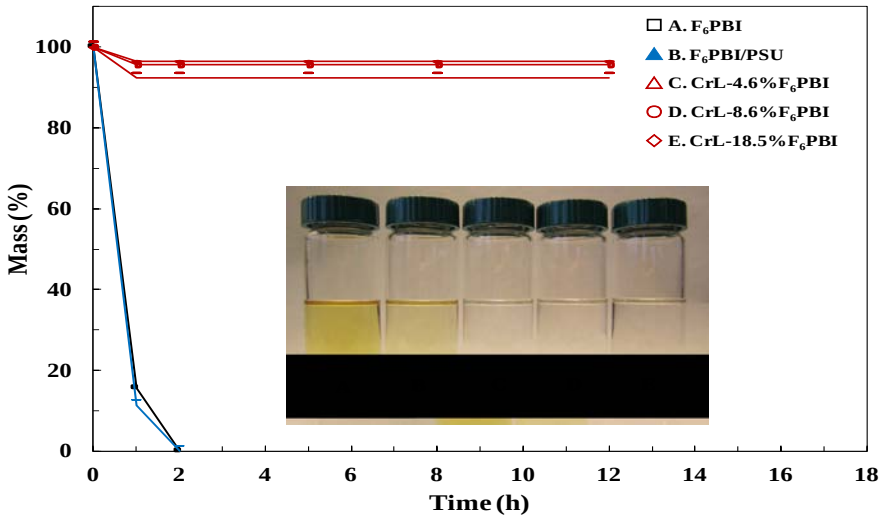




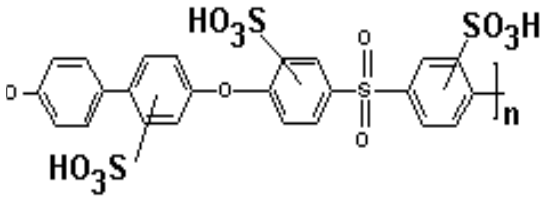
D. Aili et al. Inter. J. Hydrogen Energy, 36 (2011) 6985

Ionic or covalent crosslinking

C.Hasiotis et al. J. Electrochem. Soc. (2001)

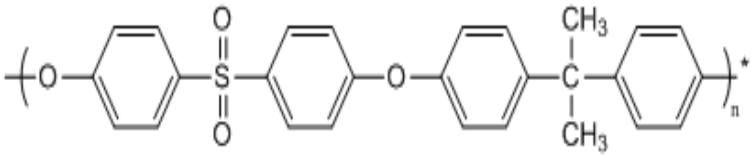


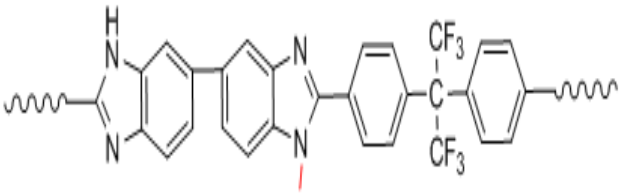
Sulphonated polysulfone

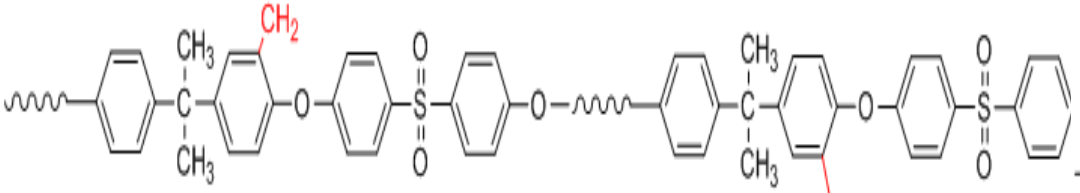


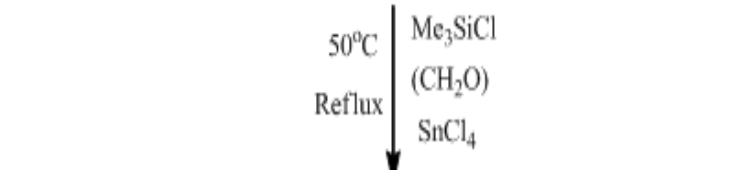
PBI

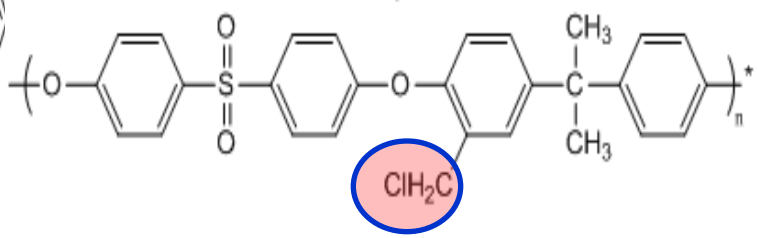
Ionically cross-linked





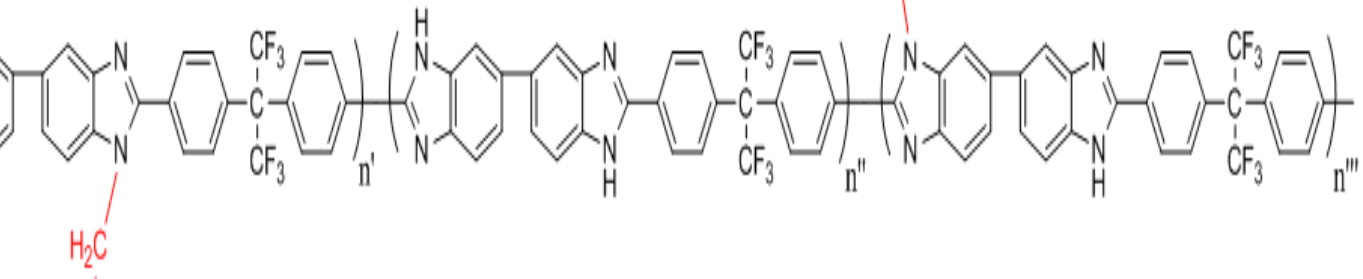




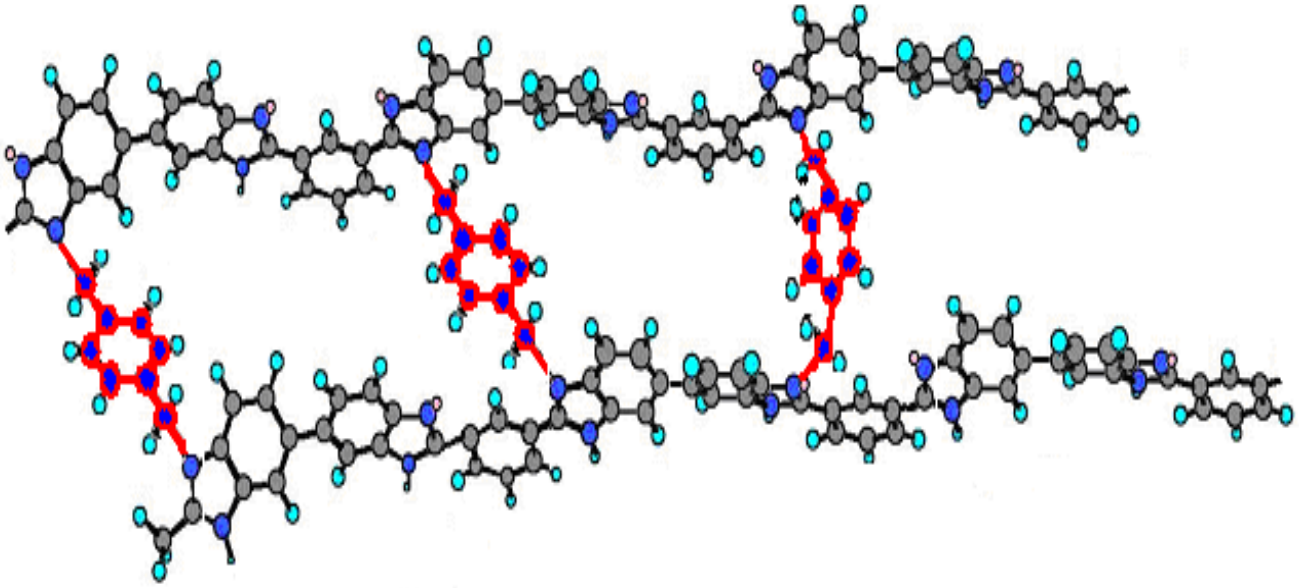


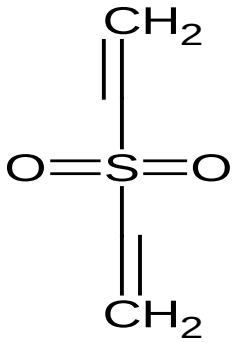
Chloromethylated PSU

Polymerically covalent cross-linking



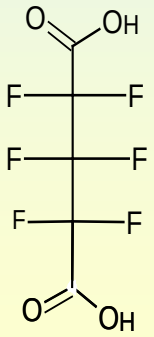
PBI Cross-linking



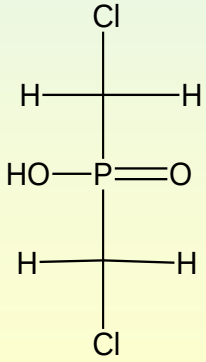


Aili et al., Polymer Intern. 60, 1201 (2011)

Perfluoroglutaric acid

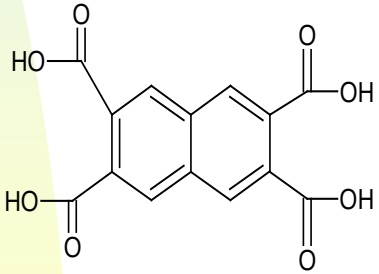


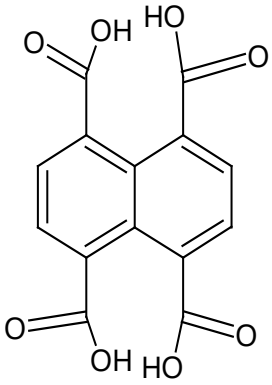
di(chloromethyl)phosphinic acid

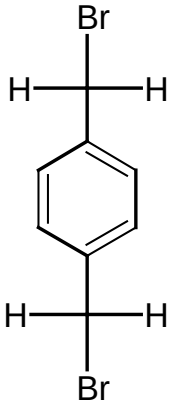


Noyé et al., Polym. Adv. Techn. 19, 1270 (2008)

naphthalenetetracarboxylic acids



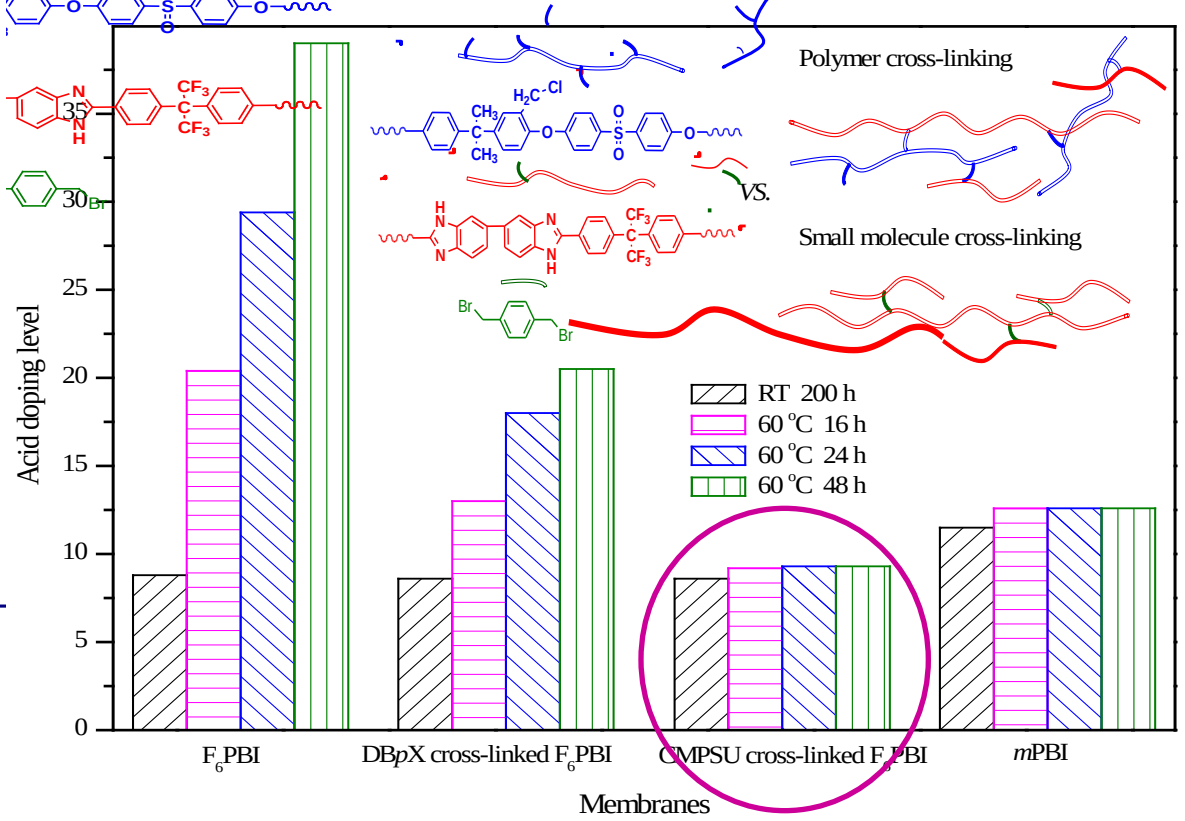


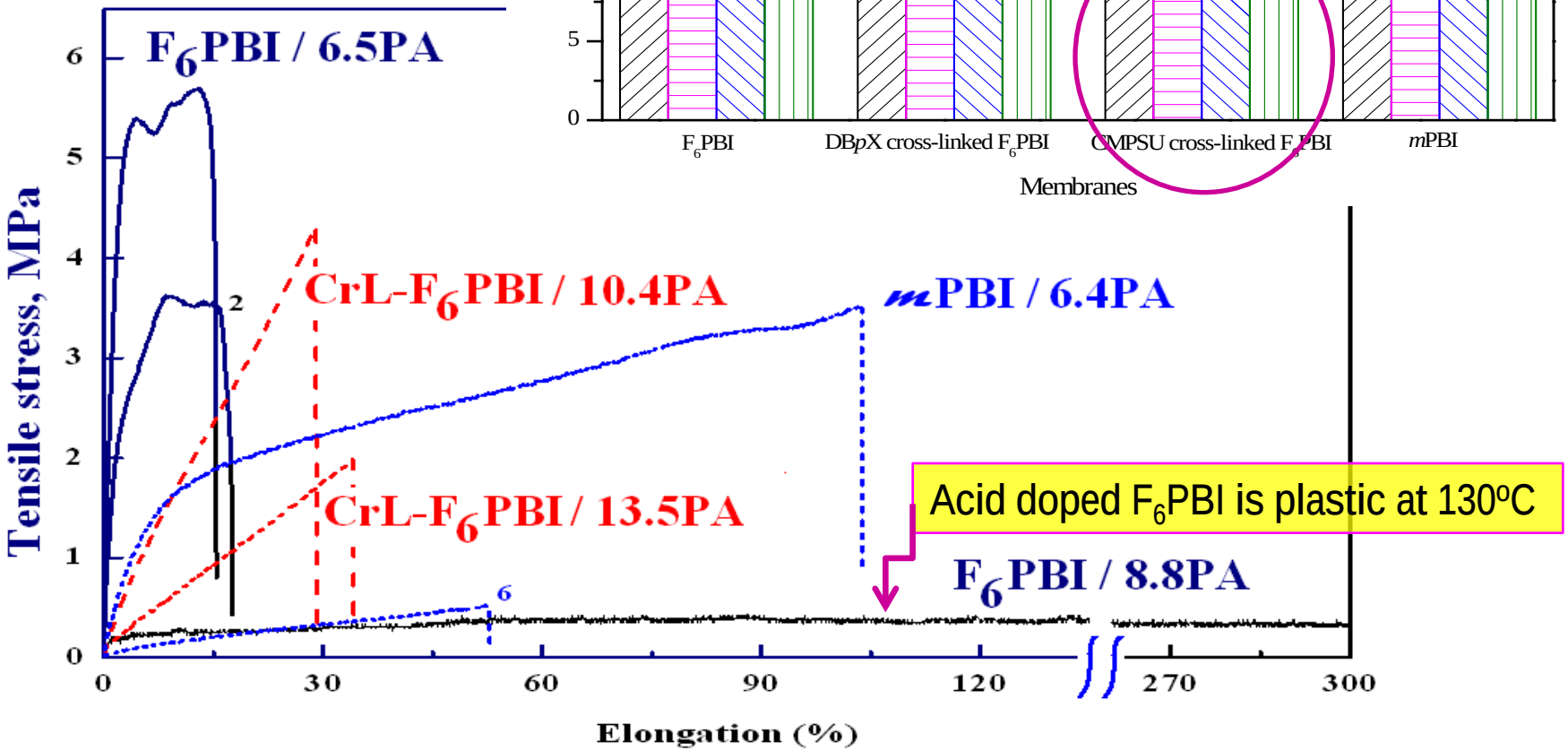


Li et al., Chem. Mater. 19, 350 (2007)

PSU-CrL F_6PBI

- insolubility
- high doping levels
- better stability
- stiffer membranes
  at elevated temperatures

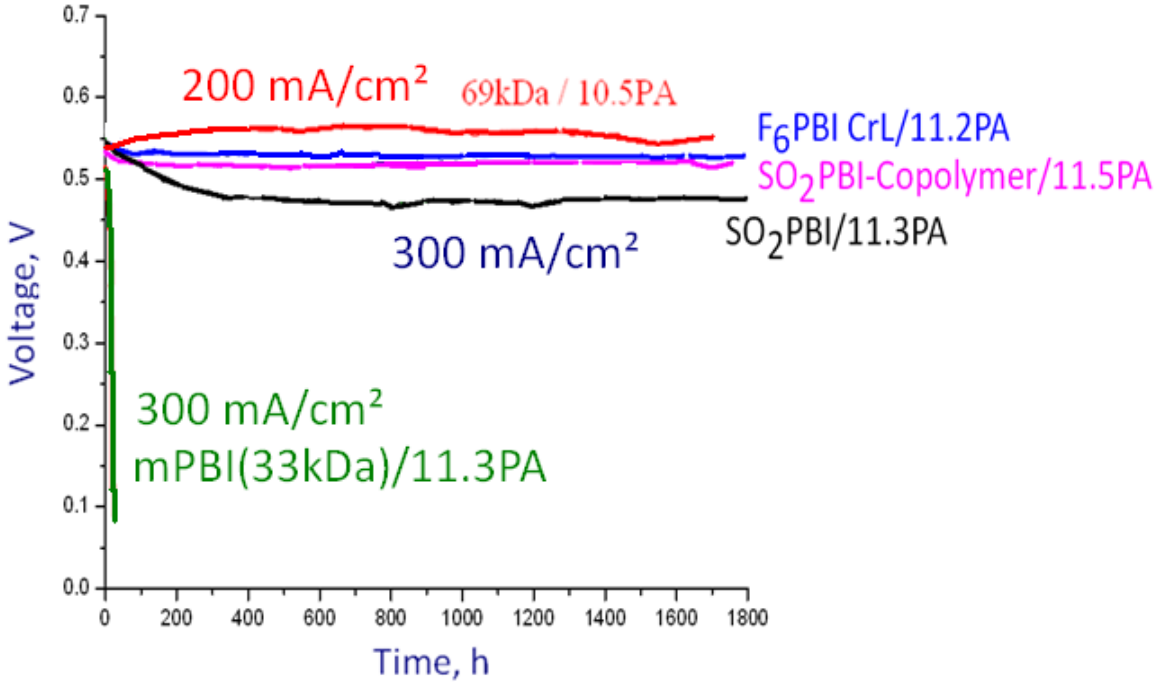


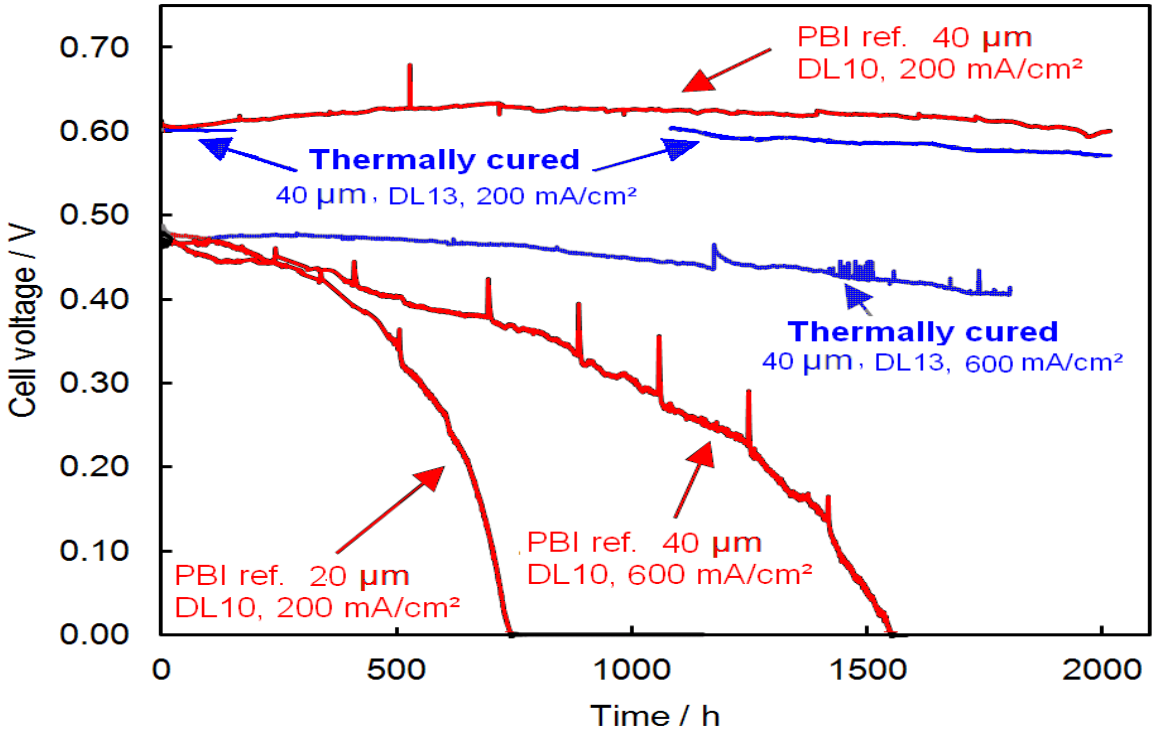


Acid doped F_6PBI is plastic at 130°C

Performance and durability tests

- Better performance
  due to high doping levels
  and hence high conductivity
- Better durability
  chemical stability
  high load currents
- More durability evaluation
  in progress …





Acknowledgements

Financial supports from

- the Public Service Obligations (the ForskEL programme)
  - HOT-MEA Consortium
  - PEM Fuel Cell Durability
  - High performance MEAs
  - Quantify and Improve PEM Fuel Cell Durability
  - CATBOOSTER
- the Danish Energy Authorities (the EUDP programme)
  - Commercial Breakthrough of Advanced FC
- Danish National Advanced Technology Foundation
  - HT-FUMA