Ionomer and Ionomer Membrane Development for Fuel Cells and Electrolysis

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**HySA, Chemical Resource Beneficiation, North-West University, Potchefstroom, South Africa*
***ZSW-BW, GB03, Ulm, Germany*

Layout

1. New aryl monomers and –(co)polymers

2. Membrane concepts I:
   Cation-exchange acid-excess blend membranes for fuel cells and electrolysis

3. Membrane concepts II:
   Intermediate T fuel cell blend membranes

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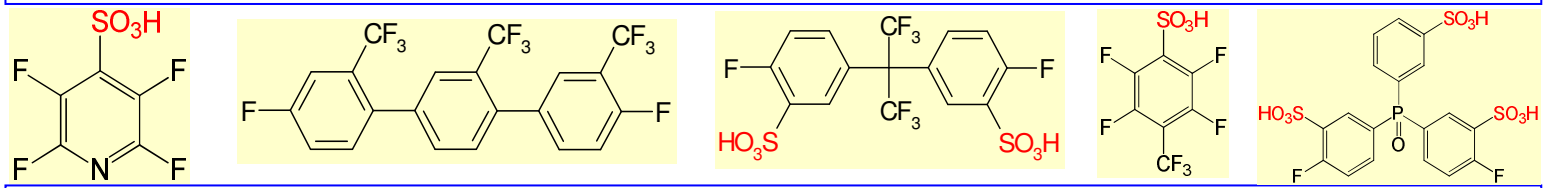
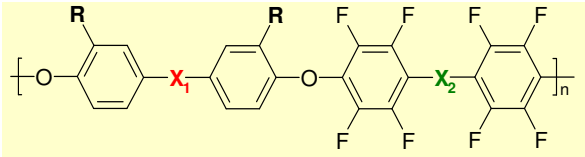
Polymer Strategies

Cross-linking

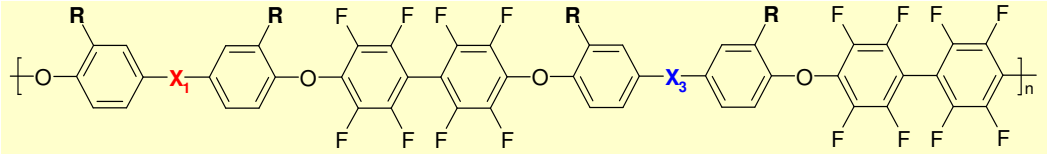
Evaluation – New Monomers



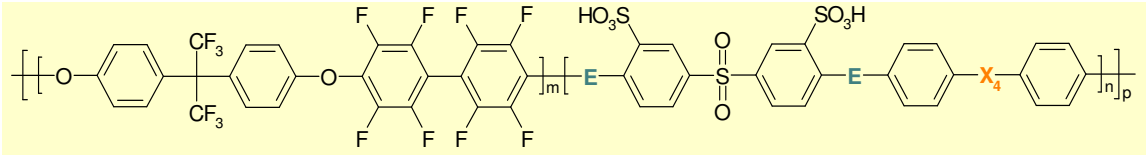
Evaluation – AB-Type Homo-Ionomers



Chemical Tailoring – ABCB-Type Statistical Co-Ionomers

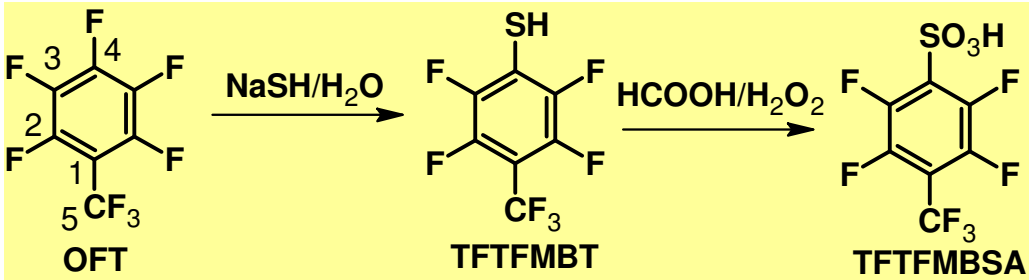


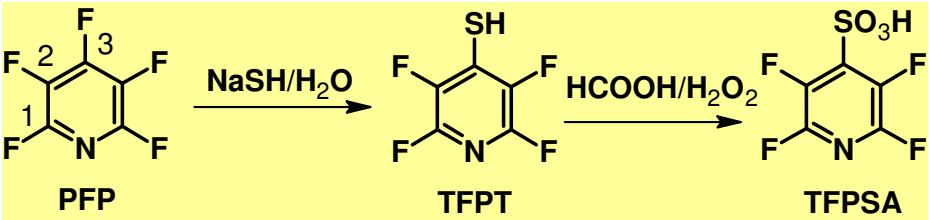
Chemical + morphological Tailoring - $[AB]_m[CD]_n$ Typ Block-*co*-ionomers



Tailoring of the properties

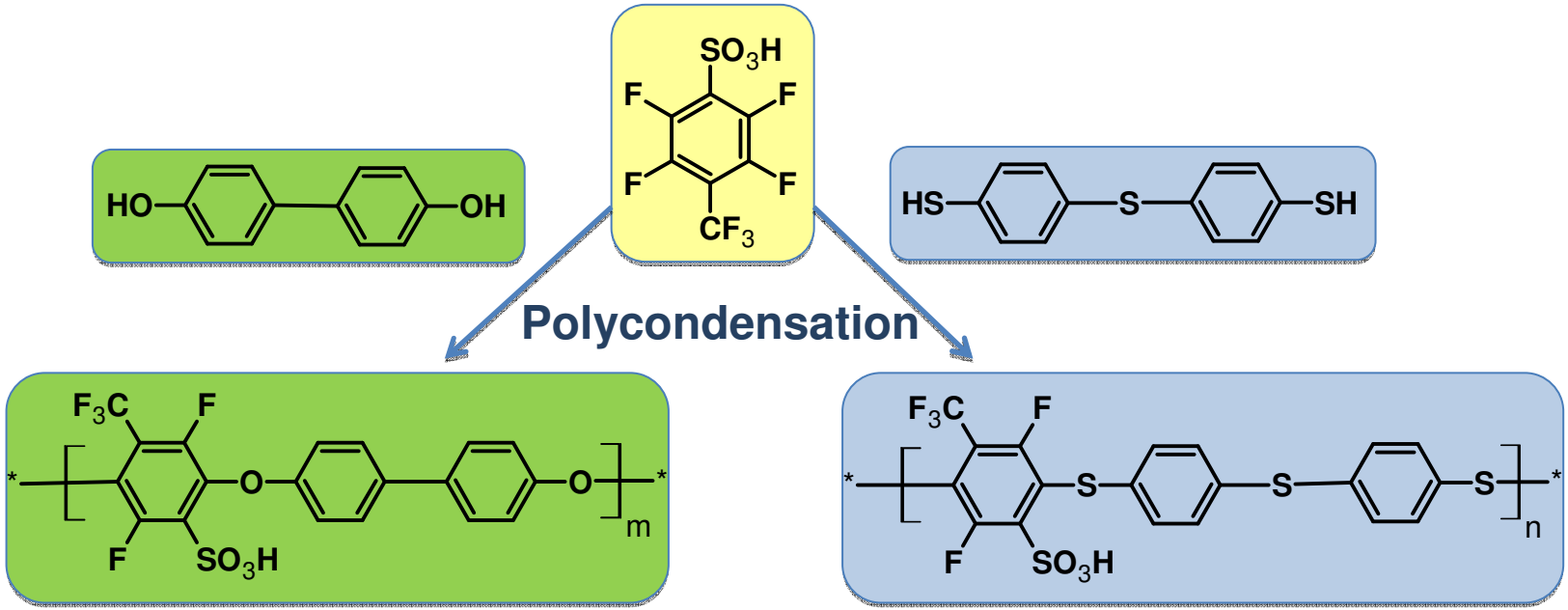
Novel Perfluorinated and Sulfonated Arylene Monomers





Advantage of perfluorinated aromatic sulfonic acids:
Strong acidity and high chemical stability of SO_3H groups

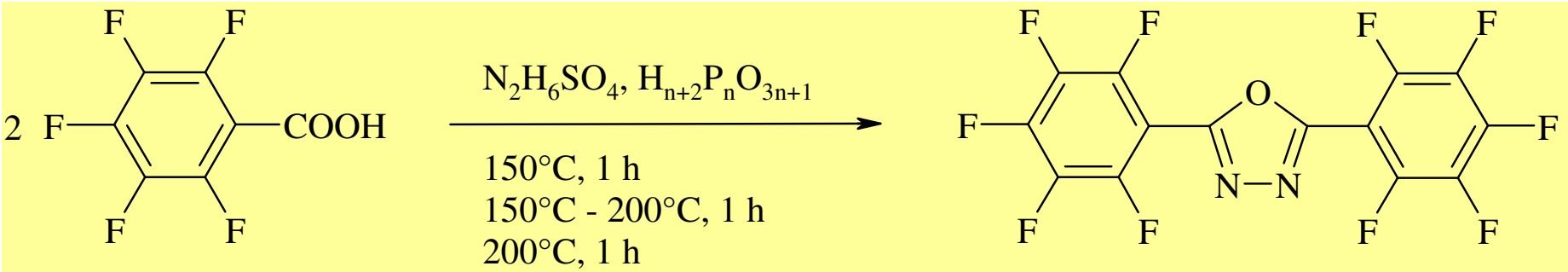
Polymers From TFTFMBSA



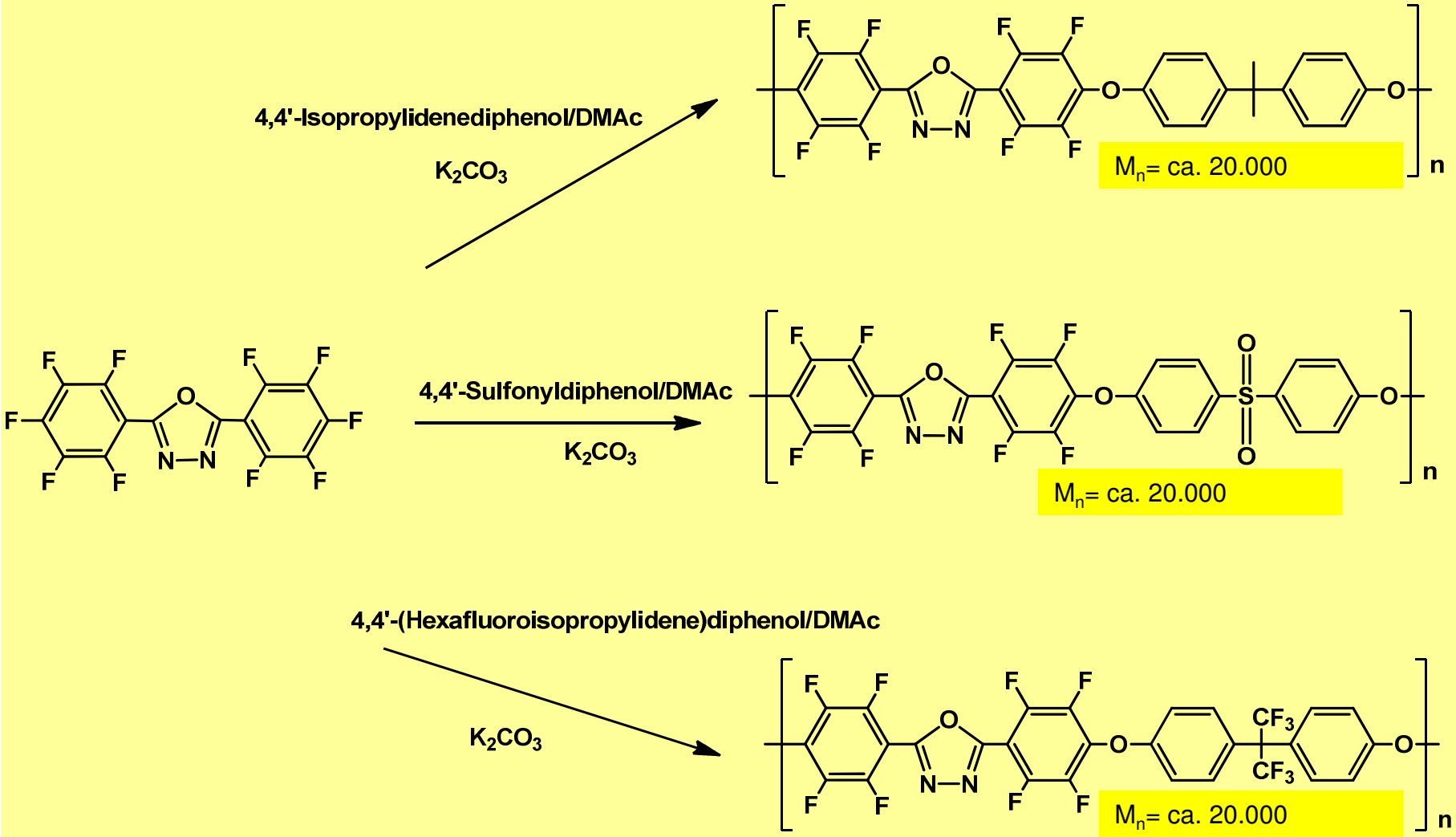
Analytics	
GPC	M_n: 30 000 g/mol M_w: 39 000 g/mol PDI: 1,3
Yield	80%
IEC_{direct}/IEC_{theo}	2,2 /2,2 mmol/eq

Analytics	
GPC	M_n: 29 000 g/mol M_w: 73 000 g/mol PDI: 2,5
Yield	80%
IEC_{direct}/IEC_{theo}	1,6 /1,9 mmol/eq

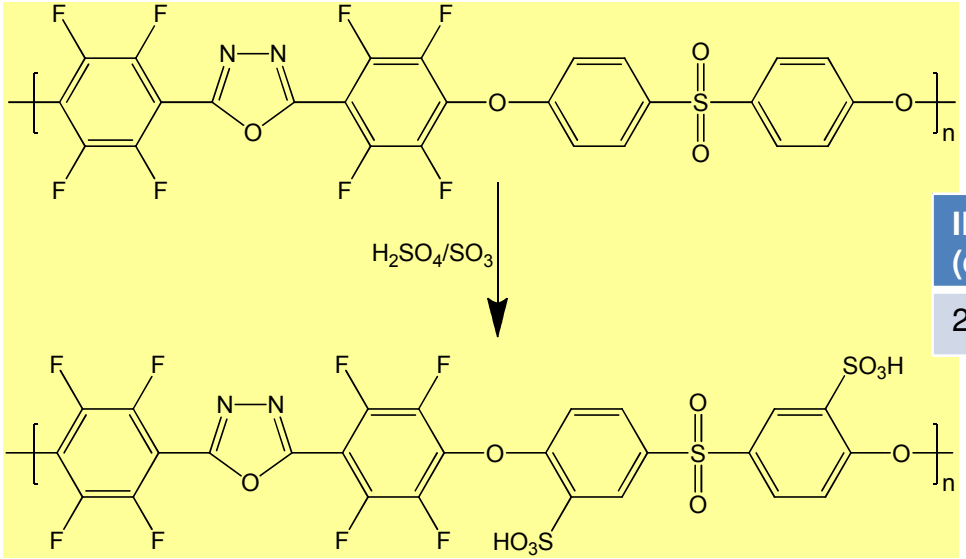
Preparation of a Oxadiazole Monomer



Preparation of Oxadiazole Polymers

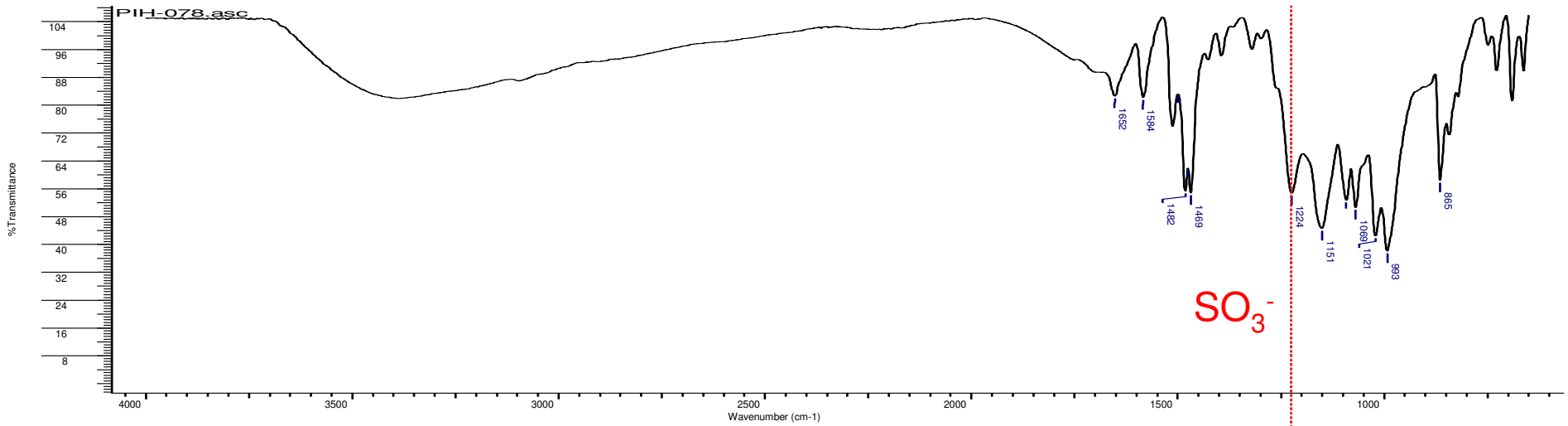


Sulfonation of the Poly(oxadiazole) From Bisphenol S

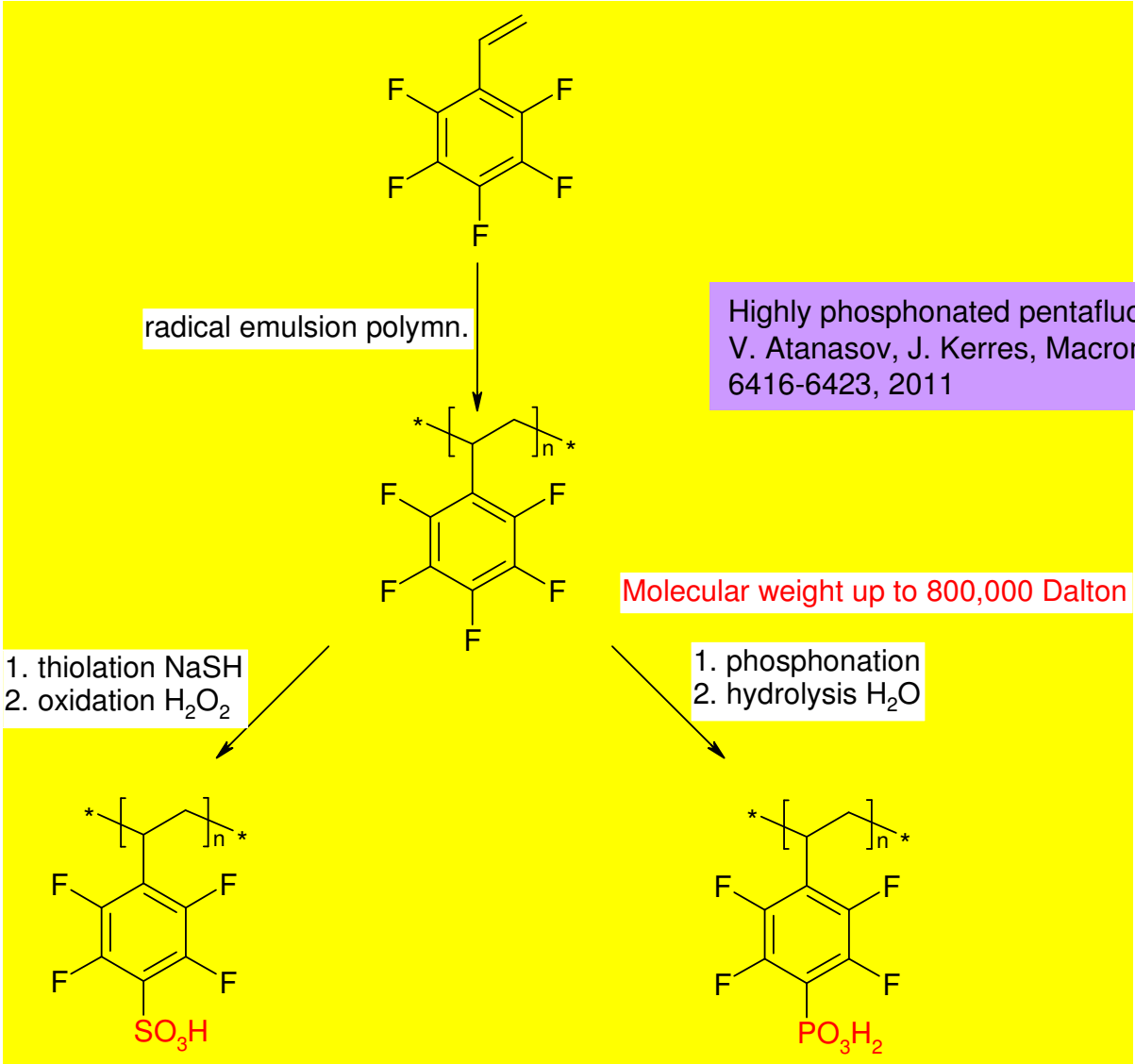


IEC_{direct} (calc/exp)	IEC_{back} (calc/exp)
2.59/2.83	6.19/6.21

DS ≈ 2 SO_3H/RU



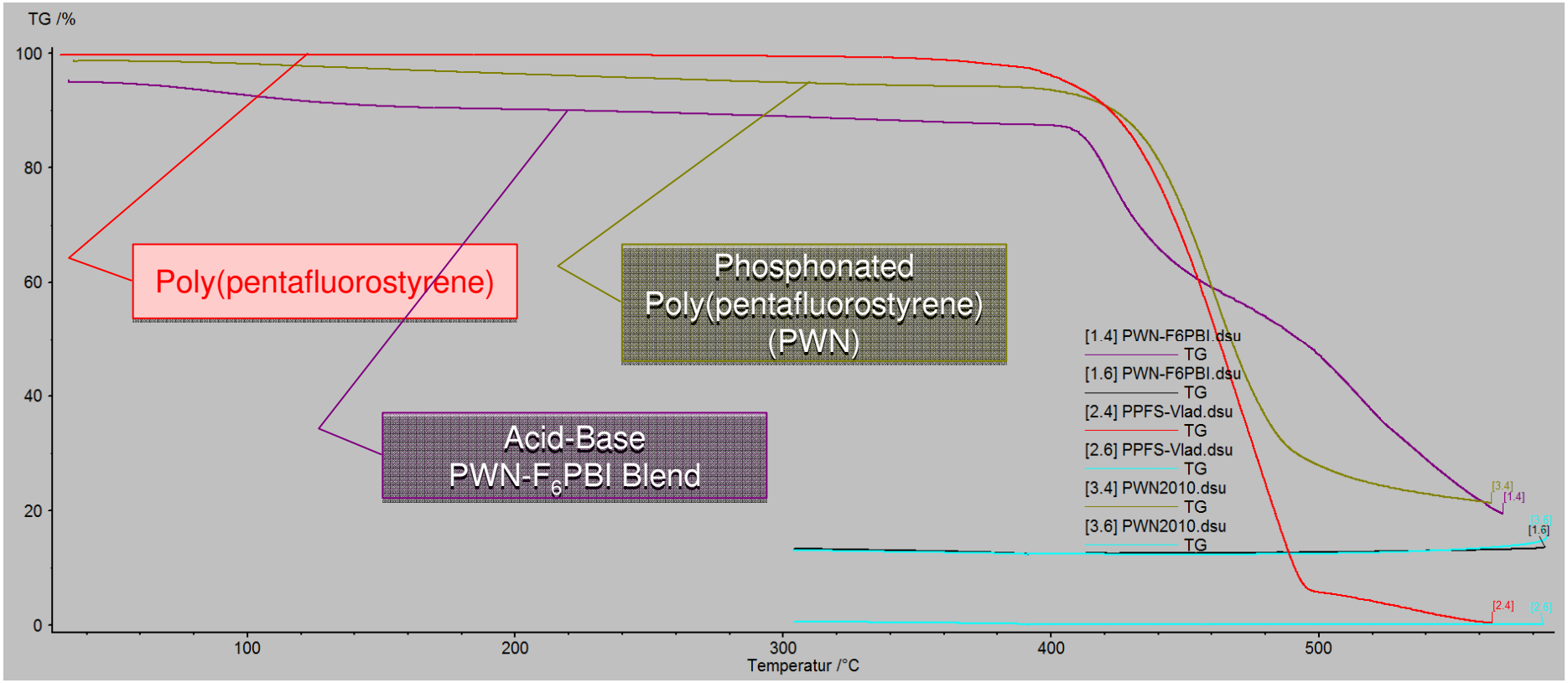
Poly(pentafluorostyrene) (PPFS) Ionomers



Highly phosphonated pentafluorostyrene
V. Atanasov, J. Kerres, Macromolecules, 44 (16), 6416-6423, 2011

Molecular weight up to 800,000 Dalton

Thermal Stability of PPFS-Ionomers



Talk of Vladimir Atanasov today evening:

Talk 11	17h30-17h50	Vladimir ATANASOV	*Phosphonated poly(pentafluorostyrene): synthesis, characterization & application as PEMs*	ICVT, University of Stuttgart, DE

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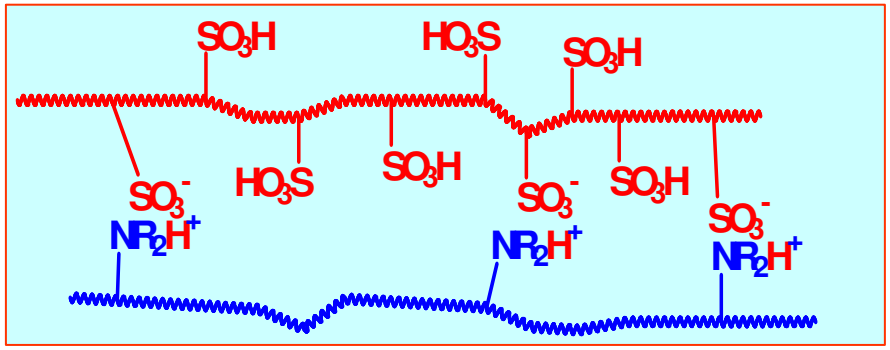
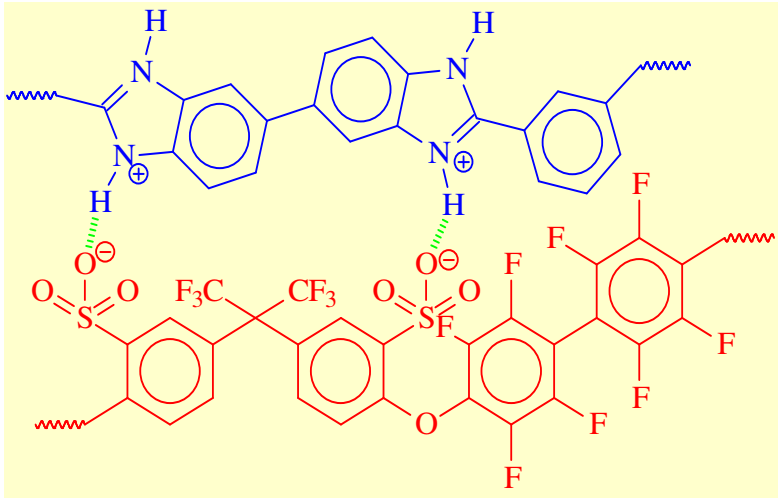
1. New aryl monomers and –(co)polymers

2. **Membrane concepts I:**
   Cation-exchange acid-excess blend membranes for fuel cells and electrolysis

3. Membrane concepts II:
   Intermediate T fuel cell blend membranes

Ionically Cross-Linked Blend Membranes





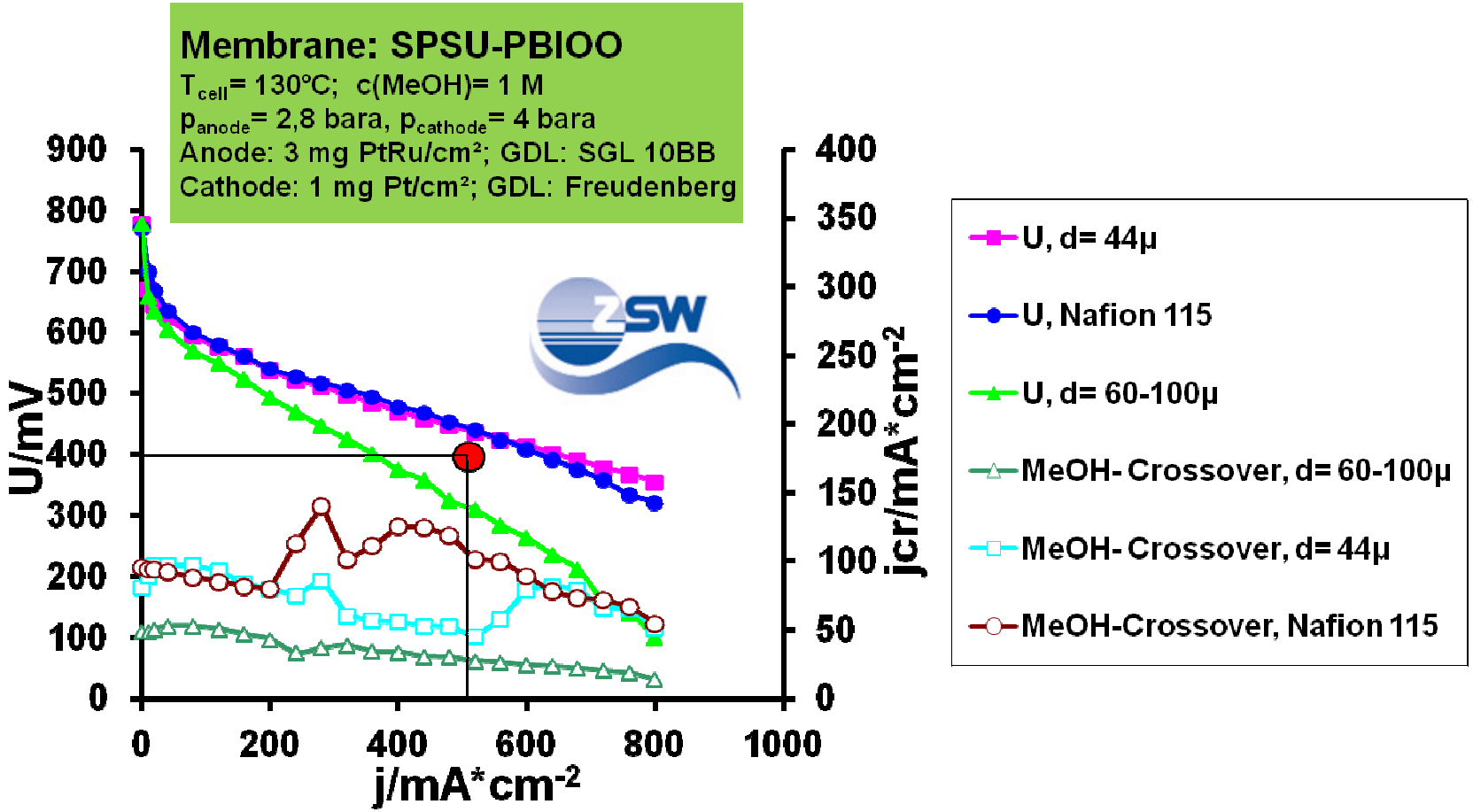
Ionical (or covalent) cross-linking:

☺ Limitation water uptake/swelling

☺ improved mechanical , thermal and chemical stability

- Development of Ionomer Membranes for Fuel Cells. Jochen A. Kerres, J. Memb. Sci. 2001, 185, 3-27
- Blend concepts for fuel cell membranes. Jochen Kerres, in: Polymer Membranes for Fuel Cells, Ed.: S. M. Javaid Zaidi, Takeshi Matsuura, 1st Ed., Springer US (**ISBN-10:** 0387735313, **ISBN-13:** 978-0387735313), p. 185 – 222, 2008

DMFC of sPSU-PBIOO Acid-Base Blends (130°C)

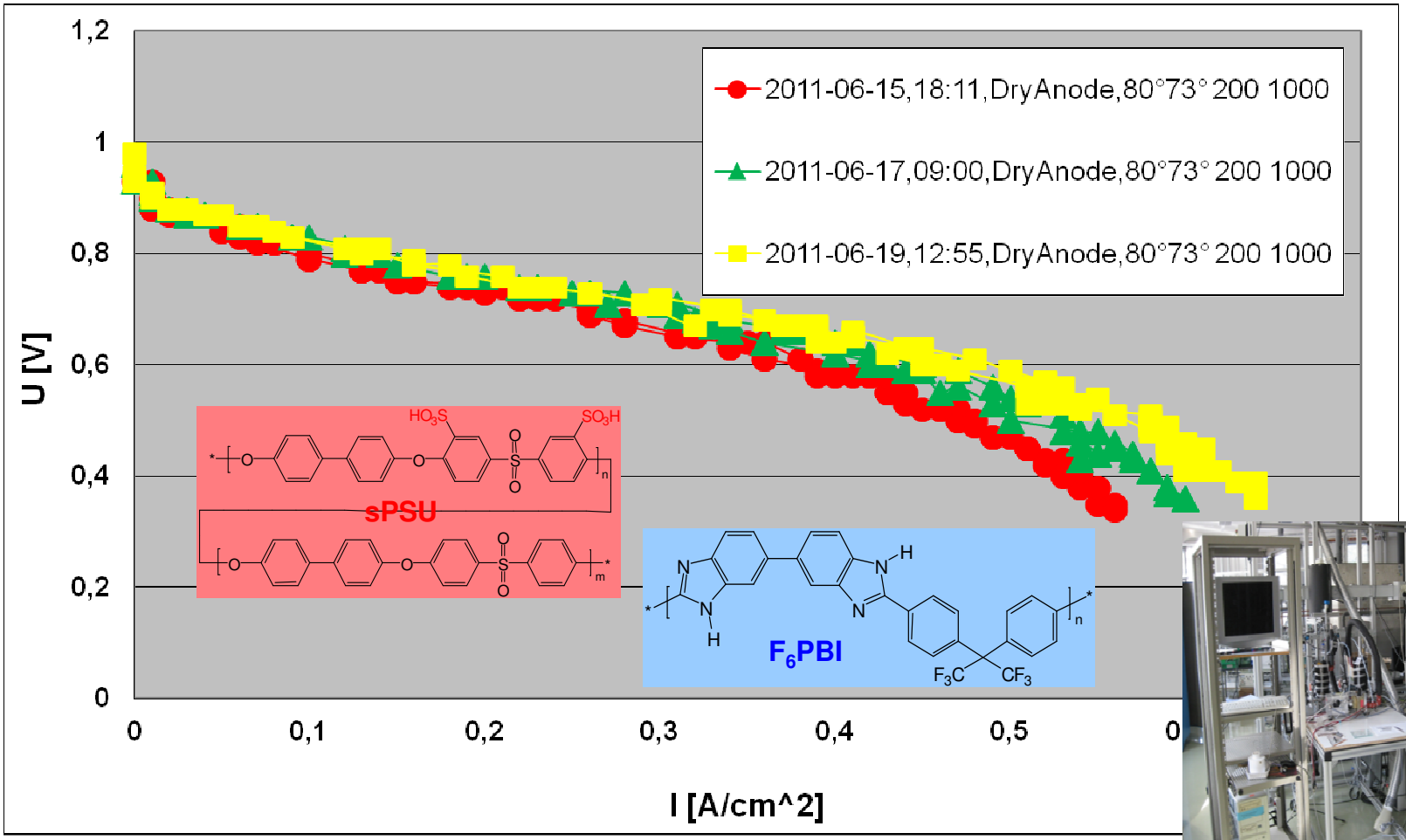


☺ Performance of sPSU-PBIOO similar to Nafion

☹ No sufficient contact between membrane and electrode

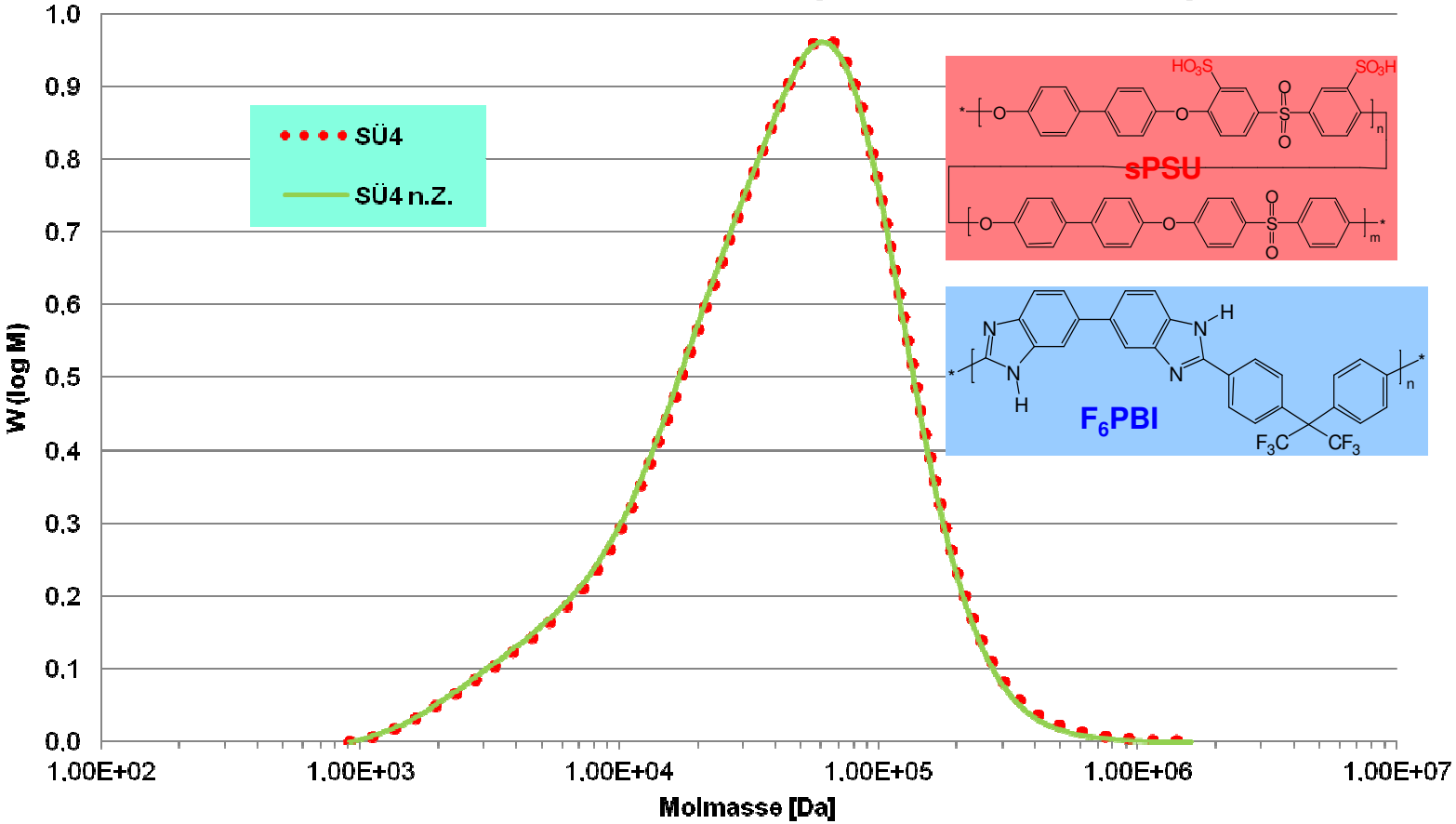
☹ Arylene ionomers in electrodes do not work properly

PEMFC of a SPSU-F_6PBI Blend Membrane Within 5 Days



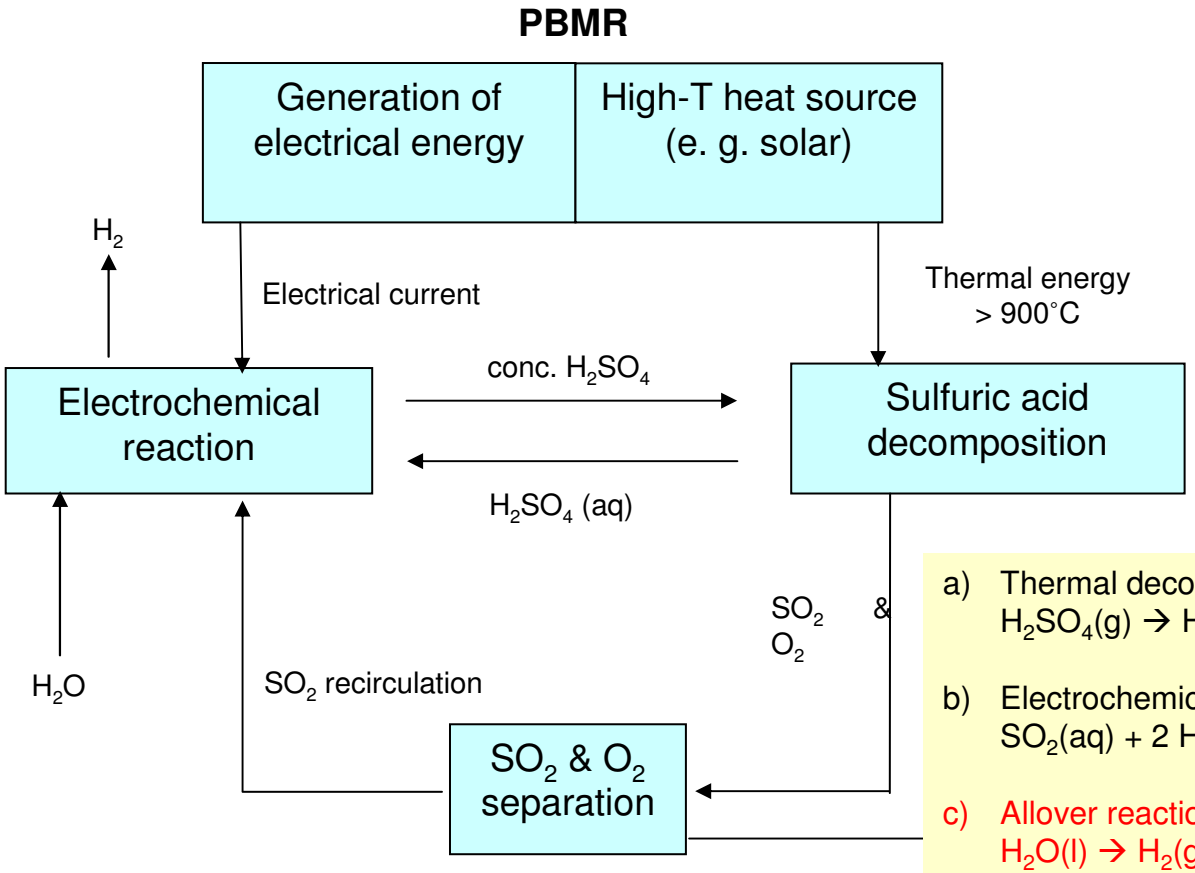
☺ Improvement of the polarisation curve within the operation time

GPC of a SPSU-F_6PBI Blend Membrane Before and After Fuel Cell Test (After 1 Week)



☺ No molecular weight degradation within the operation time

Principle HyS-Process



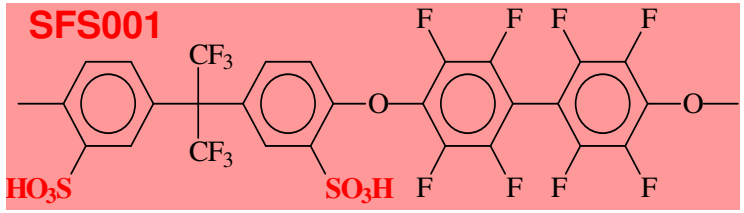
a) Thermal decomposition at ±900 °C:
$H_2SO_4(g) \rightarrow H_2O(g) + SO_3(g)\ (SO_2 + 0{,}5\ O_2)$ (1)

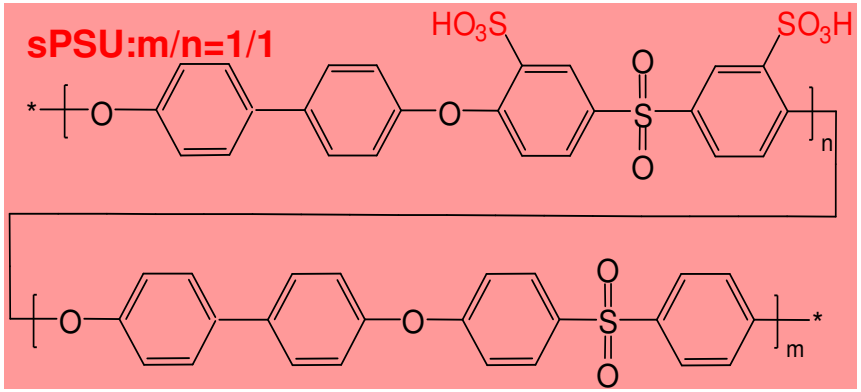
b) Electrochemical reaction at 80 – 120 °C:
$SO_2(aq) + 2\ H_2O(l) \rightarrow H_2SO_4(aq) + H_2(g)$ (2)

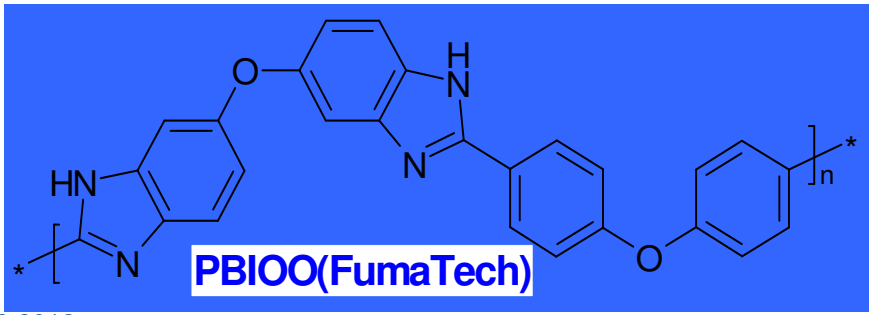
c) Allover reaction HyS process:
$H_2O(l) \rightarrow H_2(g) + 0{,}5\ O_2(g)$ (3)

HyS-Process: Investigated Membranes I: Acid-Excess

Membrane	Composition	Acidic Polymer	$IEC_{direct, calc.}$ ($IEC_{direct,exp.}$): Blend membrane [meq/g]
SFS-L	SFS001/PBIOO	SFS001	1.35 (1.0)
sPSU-L	SAC031/PBIOO	sPSU	1.35 (1.0)

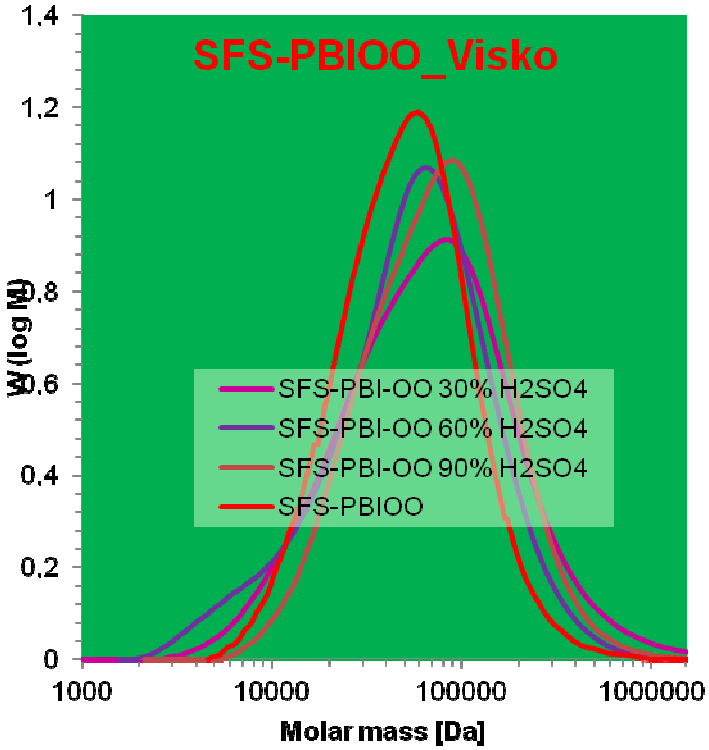


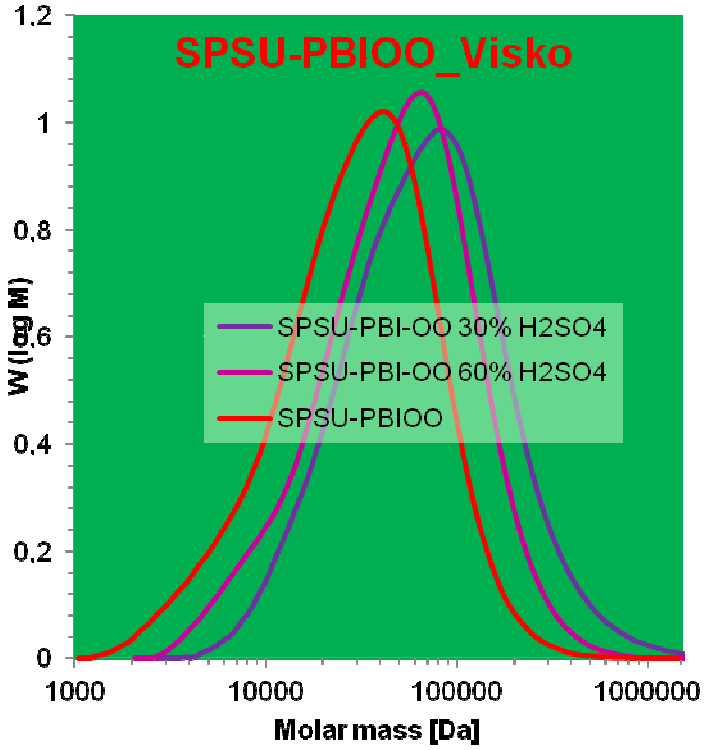


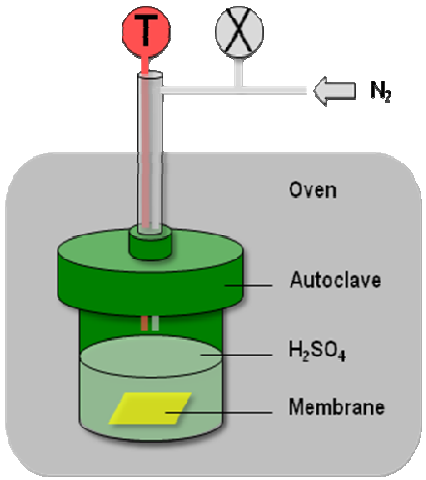


Treatment of PBIOO_L Blend Membranes in 30/60/90% H_2SO_4 at 80 °C

Molecular Weight Distribution before and after H_2SO_4 Test







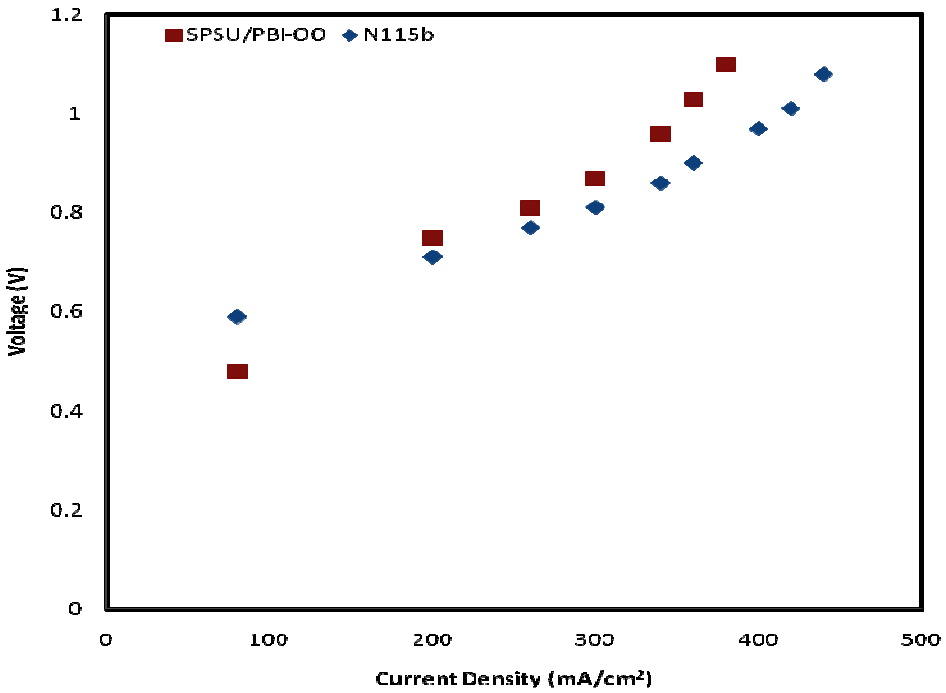
Conditions: H_2SO_4 30/60/90 wt% at 1bar and 80 °C for 120 hours

☺ PBIOO_L blend membrane stable in 30/60% H_2SO_4

☹ sPSU_L dissolves in 90% H_2SO_4 → further sulfonation

HyS-Elektrolysis of sPSU_L

Polarization Curve (Comparison with Nafion®)



☺ Slightly worse HyS-Performance of sPSU_L, compared to Nafion, despite non-optimized electrodes

H_2SO_4 stability of PBI-blend membranes for SO_2 electrolysis
Hannes Schoeman; Henning Manfred Krieg; Andries J Kruger; Andreas Chromik; Katica Krajinovic; Jochen Kerres
International Journal of Hydrogen Energy, 2012, 37, 603-614

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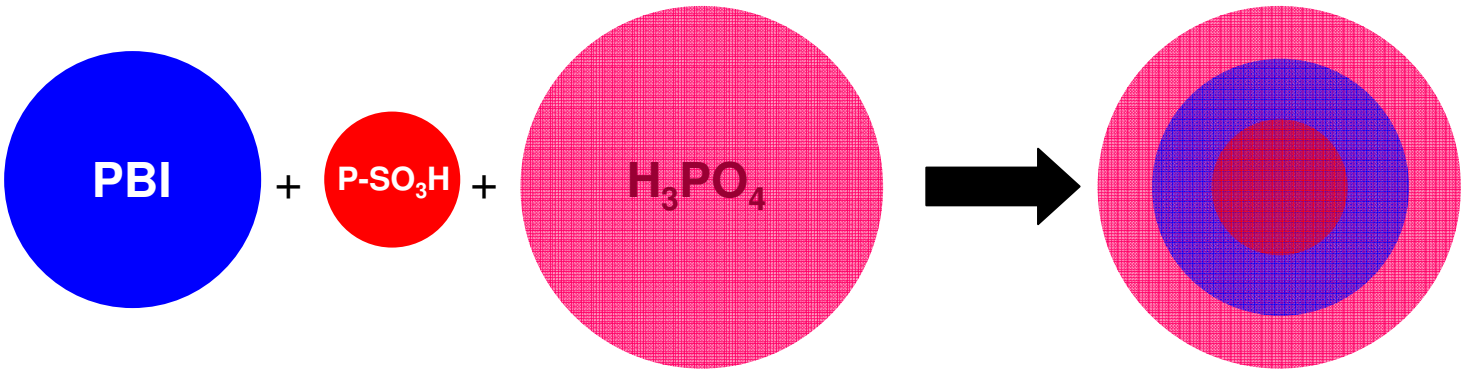
Desired Membrane Properties

- high H^+-conductivity between100-150(200)°C (humidification <50%)
- insolubility in H_3PO_4
- good long-term stability
- low price

Approaches for Intermediate T Fuel Cell Membranes

- Phosphonated Polymer (Blends)

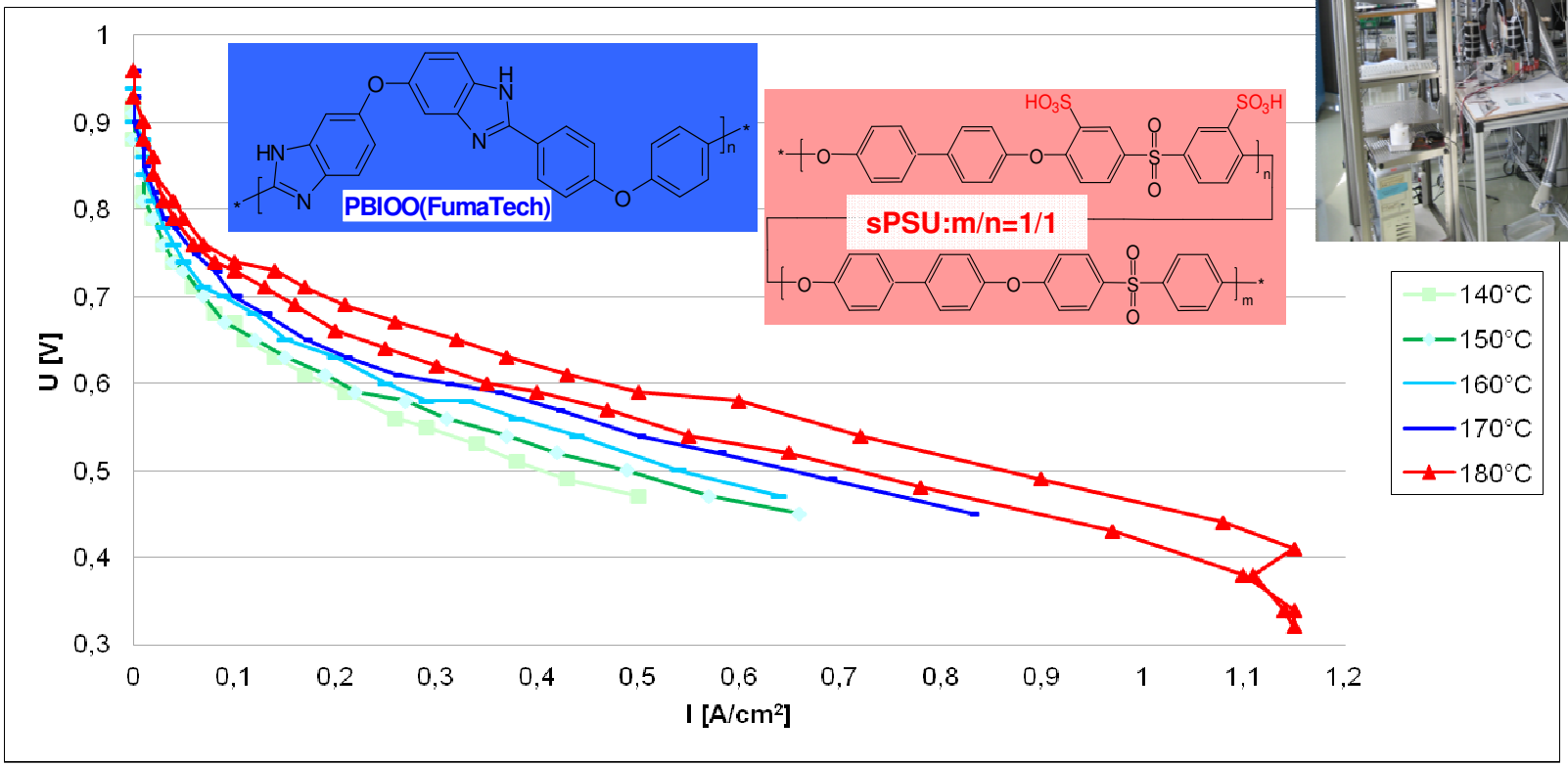
- Ternary blend membranes: PBI/sulfonated polymer/H_3PO_4



→ Attachment of H_3PO_4 to free PBI-imidazole groups (acid-base-interaction)
→ Sulfonated (or phosphonated) polymer as the acidic polymeric cross-linker

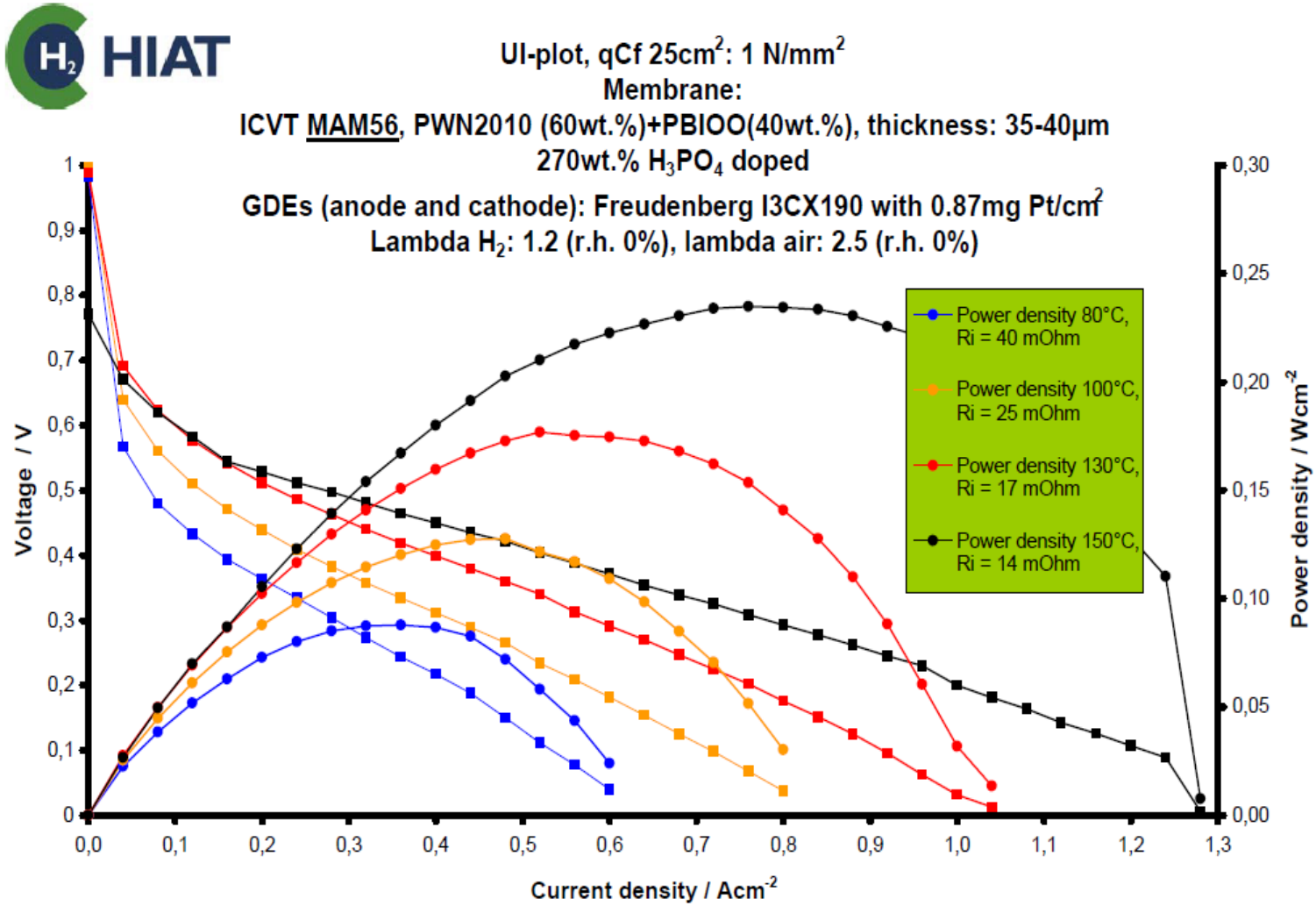
Polarization Curve of a H_3PO_4-Doped sPSU-PBIOO Acid-Base Blend

HT-PEM 140 - 180°C Hydrogen/Air



H_3PO_4-doping degree: 200%
active area 25 cm², H_2 flow 200 sccm, Air flow 1000sccm

H_2-PEMFC of H_3PO_4-Doped PWN 2010 (60%)/PBIOO (40%) Blends



Summary

➢ Polymer Development

- New sulfonated homoionomers using new perfluorinated monomers
- New block-co-ionomers showing high IEC and low meOH permeability
- New phosphonated polymer with high H^+ conductivities

➢ Membrane Development

- Development of ionically cross-linked acid-base blend membranes
  →improvement of thermal/mechanical stability
  →decrease of swelling/water uptake

➢ Fuel Cell and Electrolysis Tests

- Excellent DMFC and PEMFC performance of the acid-excess blend membranes
- Good PEMFC performance of the doped base-excess blend membranes
- Good HyS electrolysis performance of the sPSU and the SFS blend membranes

Acknowledgement

➢ R&D Projects $$:

- EU-Commission: Integrated Project „FURIM“
- DFG (German Research Foundation): Joint Project „Layer Structures for Fuel Cells“
- Joint Chinese-German Center for Science Promotion: Sino-German Project “Preparation and characterization of highly stable ionomers and ionomer membranes for medium temperature fuel cells”
- State Foundation Baden-Württemberg: Joint Project „DMFC Micro Fuel Cell Stack with Novel MEAs“
- German Department for Education and Research: Joint Project „BATTEXT“
- AiF: Joint Project „Membrane Development for PEM Fuel Cells by Means of a Novel Accelerated Degradation Test Based onto Fuel Cell Product Water Analytics“
- AiF: Joint Project „Novel stable anion-exchange membranes and MEAs for alkaline fuel cells“
- AiF: Joint Project „Electrolyzer Based onto High-T PEM Technology“
- DFG: Cluster Project „Fuel Cells with Intermediate T Membranes“
- DFG: Joint Project with NWU „Membranes for HyS Electrolysis“

➢ Cooperation Partners:

- North-West University (NWU), HySA, Chemical Resource Beneficiation: Andries Kruger, Hannes Schoeman, Henning Krieg
- ZSW group: V. Gogel, L. Jörissen
- DLR-ITT group: J. Schirmer, R. Reissner, T. Kaz, A. Friedrich
- NTNU Trondheim, Chemical Engineering Department (Norway)
- Between GmbH: T. Häring
- ZBT Duisburg: A. Heinzel, V. Peinecke, B. Oberschachtsiek et al.
- HIAT: B. Ruffmann et al.

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☺ **My group:**

K. Aniol, V. Atanasov, A. Chromik, I. Hajdok, A. Katzfuss, T. Kaz , K. Krajinovic, I. Kharitonova, G.Schumsky, C. Seyb