Reinforced sulfonated poly(phenylene sulfone) membranes

Torben Saatkamp[1*], Giorgi Titvinidze[1,2*], Klaus-Dieter Kreuer[1]

[1] *Max Planck Institute for Solid State Research, Stuttgart, Germany*

[2] *Agricultural University of Georgia, Tbilisi, Georgia*

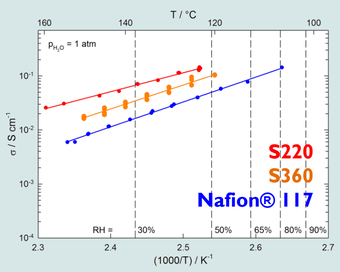
Email: t.saatkamp@fkf.mpg.de, g.titvinidze@agruni.edu.ge, kreuer@fkf.mpg.de

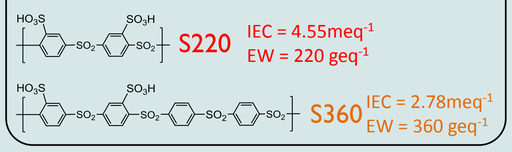
Introduction

Sulfonated poly(phenylene sulfone)s as membrane materials for PEM applications:

- Higher proton conductivities compared to PFSA membranes
- High thermal, oxidative, and hydrolytic stability in comparison with other poly(arylene sulfones)
- Increased acidity through electron-withdrawing sulfones
- High density of very narrow well ordered hydrated domains (~0.5 nm compared to ~2 nm for Nafion®)
- Unique microstructure controlled by strong electrostatic interactions

Conductivity [1,2]





Mechanical Properties

Unsatisfactory mechanical properties in the dry state (low RH) and at very high RH

Relative humidity (RH):

0% 20% 100%

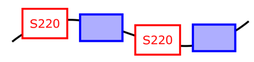
brittleness

soluble or strong swelling

Reinforcing Approaches

Goal: while preserving the very high conductivity; reduced swelling, elasticity

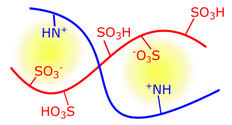
- **Hydrophilic-hydrophobic Multiblock Copolymers [3]**



Previous study utilizing polysulfones

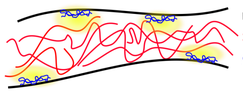
- **Acid-Base Blending**

Compatibilized blend of sulfonated polysulfones and hydrophobic polymers

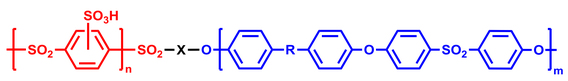


- **Fiber Composites**

Interaction with matrix induced by grafting



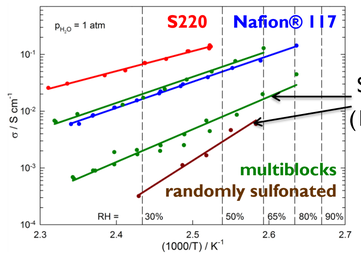
Previously: Multiblocks [3]

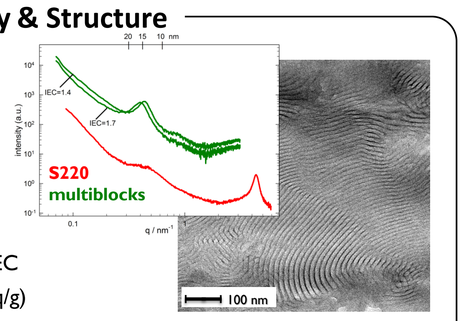


- Multiple sequential coupling of:
  - Hydrophilic fully sulfonated poly(phenylene sulfone) blocks
  - Hydrophobic poly(arylene ether sulfone) blocks

Conductivity & Structure

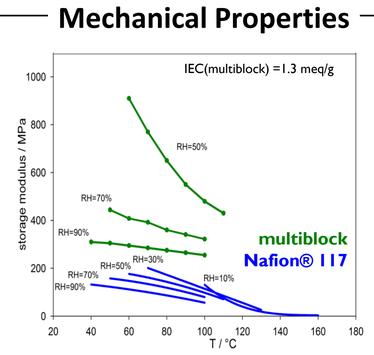
- IEC(multiblocks) =1.2-1.7 meq/g
- Higher conductivity than randomly sulfonated materials (same IEC)
- Locally: Behavior of pure S220





- Nano-phase separated bicontinuous morphology (d~15 nm)
- Preserved S220 microstructure

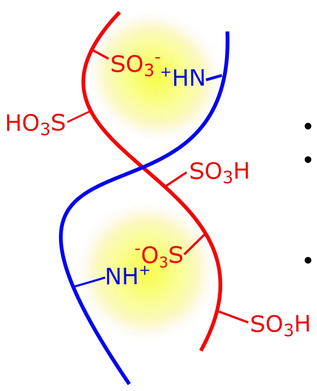
Mechanical Properties



- 1-5 times higher storage moduli than Nafion®, T > 100°C possible

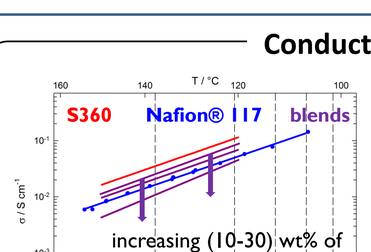
✓ **Preserved high conductivity**
✓ **Reduced swelling at high RH**
– Complex preparation
– Brittle when dry

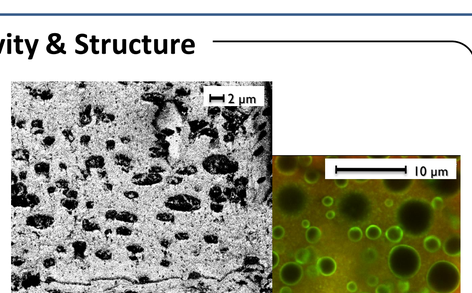
Acid-Base Blending



- Mixing of two polymers in solution:
  - S360
  - Basic (modified), mechanically stabilizing component
- Compatibilization via ionic interaction
- Variation of ionic interaction strength (via basicity) and amount of interaction (via modification degree)
- Investigation of several membrane depositioning techniques (vacuum oven, coater, printer)

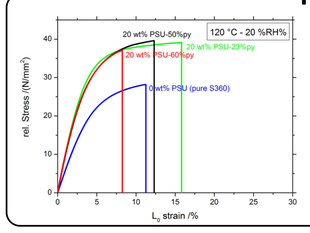
Conductivity & Structure





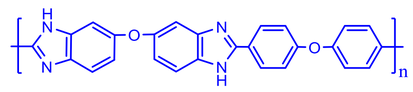
- Conductivity loss mainly due to volume effect
- Micro-phase separated basic component (~2-10 µm)

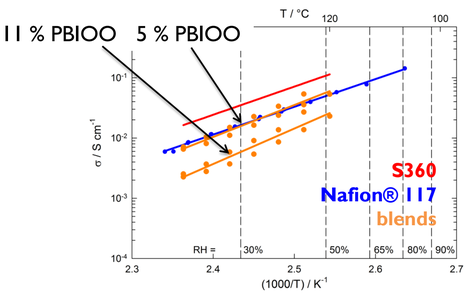
Mechanical Properties



- Stress-strain behavior impacted by composition and modification degree
  - Not systematic at high T, low RH
- Molecular weight of both components have critical impact on stress-strain behavior

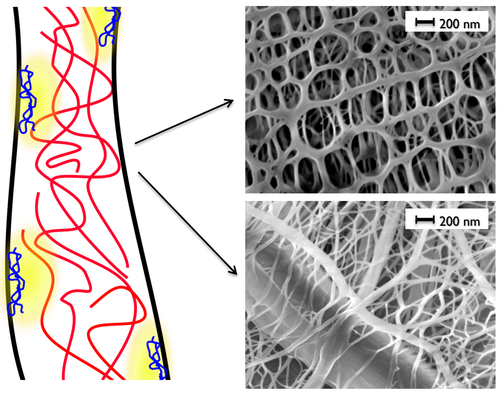
Homogeneous blend systems, e.g. S360 & PBIOO





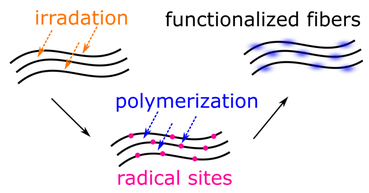
✓ **Simple preparation process**
✓ **Preserved high conductivity**
✓ **Improved mechanical behavior**
– Phase separation gives only small mechanical improvement
– Homogeneity accompanied by significant conductiviy loss

Fiber Composites



- Porous (~50-70%) Polyethylene/Polypropylene matrices impregnated with solutions of
  - S360
  - Acid-base blends (S360 + PSU-py)
- Homogeneous thicknesses even for thin (~20um) membranes

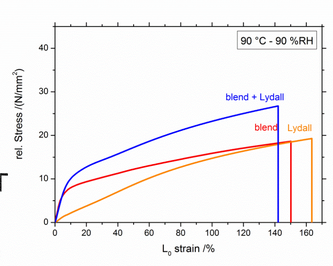
Graft Polymerization



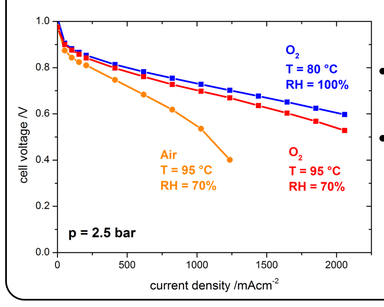
- Control of grafting degree via temperature, time and monomer concentration

Mechanical Properties

- Improved mechanical properties (T<100°C)
- Softening of matrix at high T leads to material failure



Fuel Cell Test



- Performance similar to Nafion® 112
- FC-test conducted on non-grafted composite (matrix + S360)

✓ **Viable method for thin membrane preparation**
✓ **Ungrafted composites show good performance in FC-test**
– Reinforcement effect small, therefore significant swelling (at high RH)

References

[1] Schuster, M.; Kreuer, K.D.; Andersen, H.T.; Maier, J. Macromolecules 2007, 40, 598.

[2] Schuster, M.; De Araujo, C.C.; Atanasov, V.; Andersen, H.T.; Kreuer, K.D.; Maier, J. Macromolecules 2009, 42, 3129.

[3] Titvinidze, G.; Kreuer, K.D.; Schuster, M.; De Araujo, C.C.; Melchior, J.P.; Meyer, W.H. Adv. Funct. Mater. 2012, 22, 4456.

Acknowledgements

- Prof. Dr. Joachim Maier
- Annette Fuchs
- Dr. Michael Marino
- Department Maier
- Dr. Anke Kaltbeitzel
- Dr. Michael Schuster
- Dr. Lorenz Gubler