Towards Robust Membranes Based On Poly-Electrolytes

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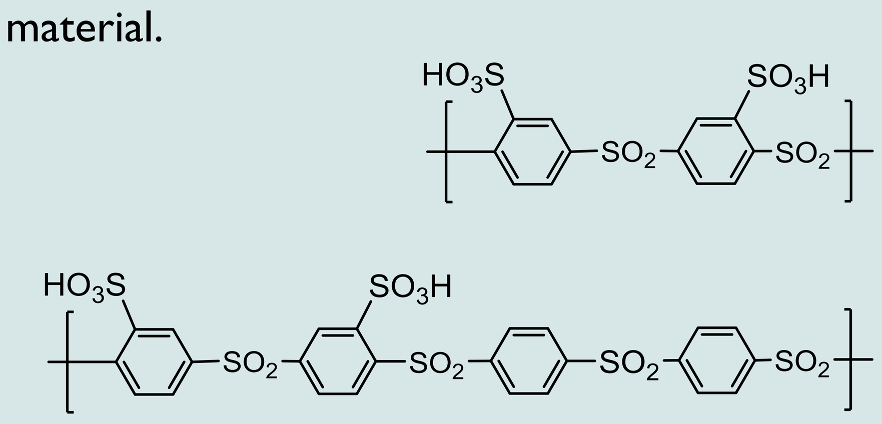
Introduction

Proton-exchange membranes (PEMs) are used in fuel cells. Commercial PEM materials are primarily perfluorosulfonic acid-based ionomers (PFSAs, e.g. Nafion®). Under fuel cell operating conditions at high temperature (>90°C) and low relative humidity (RH), PFSAs show a significant drop in conductivity, limiting the overall performance. Sulfonated poly(phenylene sulfone)s ($sPSO_2s$) with their exceptionally high conductivities could overcome these limitations, if their mechanical weakness at low and high RH can be reduced.

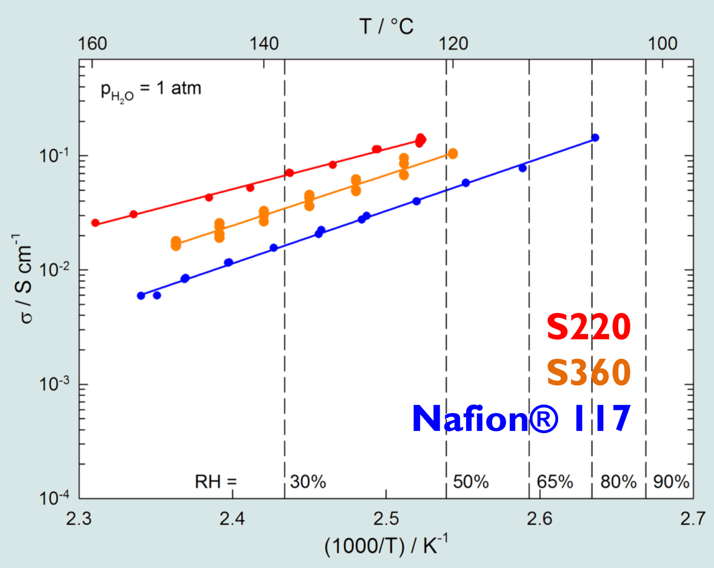
Sulfonated poly(phenylene sulfone)s[1][2][3]

Sulfonated poly(phenylene sulfone)s can be obtained in various very high ion exchange capacities (IEC) which give rise to their favorable transport properties. Their extreme backbone polarity results in high chemical stability and the electron-withdrawing sulfones increase the acidity of the material.



S220 IEC = 4.55meq^{-1}, EW = 220 geq^{-1}

S360 IEC = 2.78meq^{-1}, EW = 360 geq^{-1}



Conductivities at high temperatures in comparison to Nafion®117

Advantages

- High IECs and proton conductivities compared to fluorinated ionomers (PFSAs)
- High thermal, oxidative, and hydrolytic stabilities compared to other poly(arylene sulfone)s
- Low water transport and low gas permeability

Disadvantages

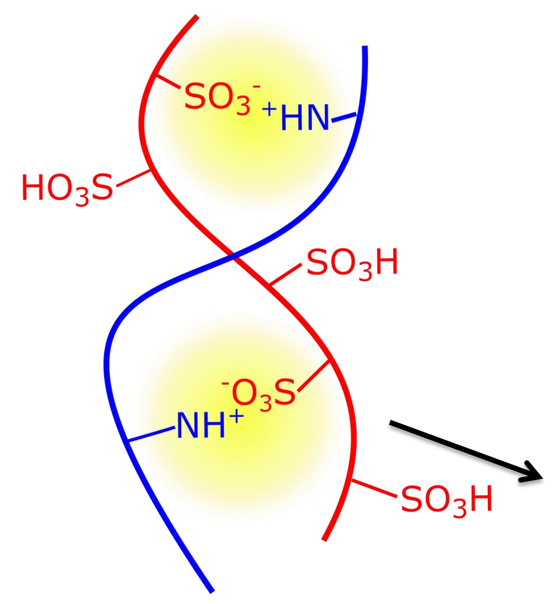
- Unsatisfactory mechanical properties at low & high RH

0% 20% RH 100%

brittleness — solubility **(S220)** or strong swelling **(S360)**

Approaches for improving mechanical properties of $sPSO_2s$

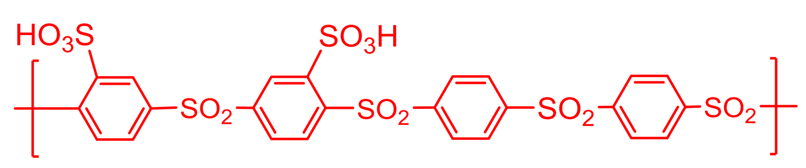
1. Acid-Base Blending



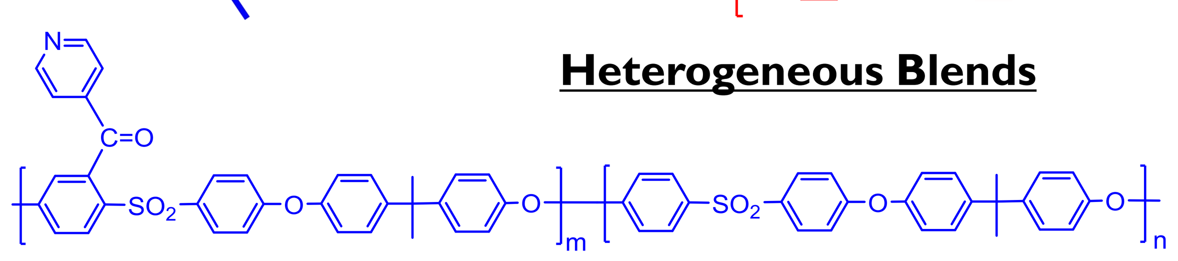
Goal: elimination of brittleness in the dry state, reduction of swelling at high RH

Concept:
- mixing of two polymers in solution
- Use of commercial materials
- Compatibilization via ionic interaction

S360

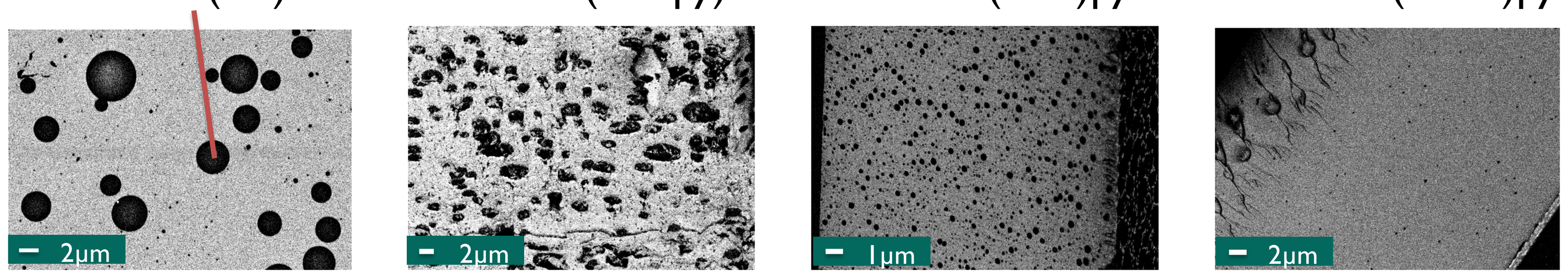


Heterogeneous Blends



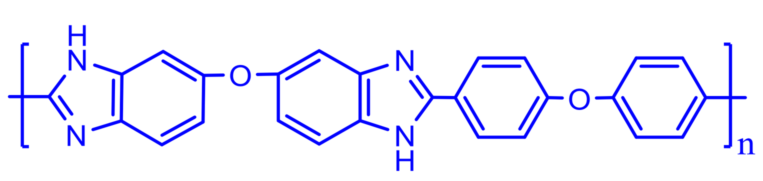
Modified polysulfone (PSU-py)

20% PSU(0%) | 20% PSU(23%py) | 20% PSU(61%)py | 20% PSU(125%)py



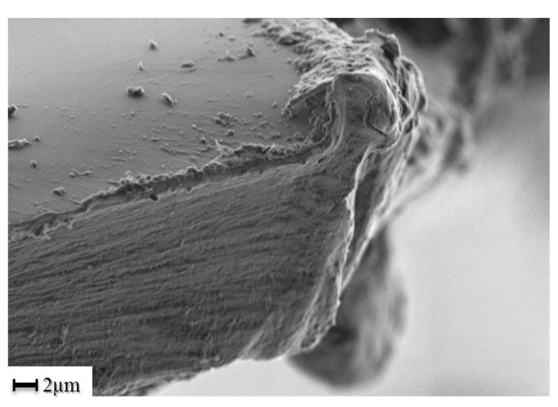
- Loss of conductivity mainly due to volume effect of PSU-py
- High pyridine-modification results in more even distribution of PSU-phase
- High modification changes micro-phase separation to nano-phase separation
- Trade-off between
  - improved blending behavior
  - decreased mechanical stability of PSU (PSU-125%py itself is brittle)

Homogeneous Blends



Polybenzimidazole (PBIOO)

11% PBIOO

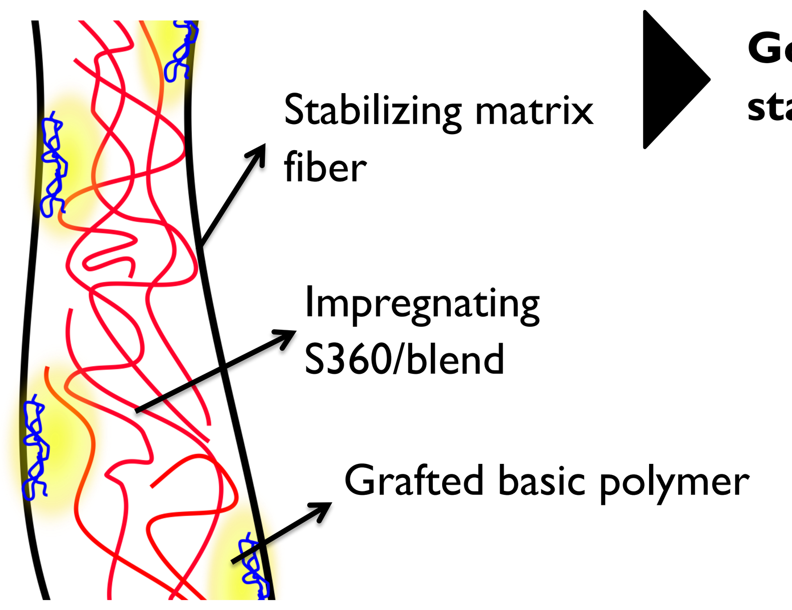


- High loss of conductivity due to ionic cross-linking (reduced IEC)
- Benzimidazole is stronger base than pyridine
- Small EW of PBIOO → low amounts (wt%) possible
- Neutralization of S360 necessary for blending

Mechanical Analysis - First Results

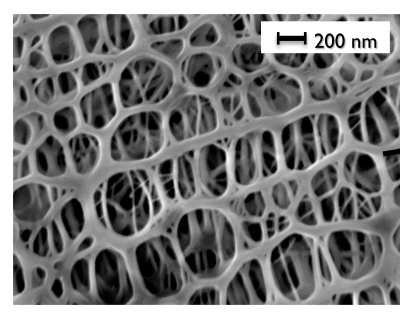
- Micro-phase separated blends provide only small, insystematic stabilization
- Homogeneous blends provide stabilization at the cost of reduced conductivity

2. Fiber Composites



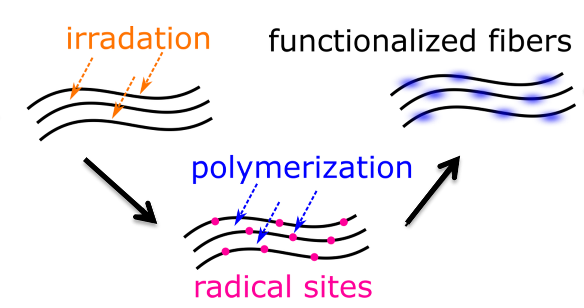
Goal: elimination of brittleness in the dry state, reduction of swelling at high RH

Concept:
- Impregnation of porous matrix (PE/PP, porosity ~70%, thickness ~15 µm
- Use of commercial materials
- Grafting of basic polymer onto matrix fibers for compatibilization



Structure of porous matrix

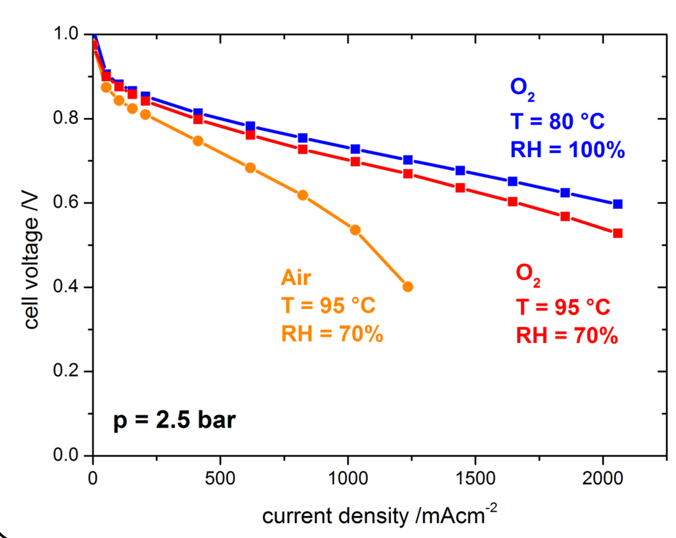
Graft Polymerization



- Control of grafting degree via temp., time and monomer concentration

Various monomers for grafting, e.g.:
- Vinylpyridine
- Vinylimidazole

S360-composite Fuel Cell Test



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

First Results

- Easy thin membrane preparation
- Stabilizing effect at low temp. (limit of PE)
- Significant swelling (at high RH)
- Impregnation control crucial

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] Wohlfarth, A., Dissertation, Universität Stuttgart, 2015.

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