Fuel cell membranes based on polyelectrolytes

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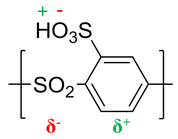
Introduction

Seperator membranes in PEMFCs generally are perfluorosulfonic acid-based ionomers (PFSAs, e.g. Nafion®). Here, we present alternative membranes which utilize the striking properties of sulfonated poly(phenylene sulfone)s ($sPSO_2s$), a family of fluorine-free, hydrocarbon polyelectrolytes.
Their unique electronic structure and high ion density give rise to high chemical stability[1,2] compared to PFSAs, superior proton conductivity[2-4] compared to other poly(arylene sulfone)s, and low electroosmotic water drag[3] (especially at high temperature). To compensate for the salt-like brittleness in the dry state and exaggerated swelling (or even dissolution) in water we use the polyelectrolytes as constituents in polymer blends to form robust membranes. The combination of stabilizing $sPSO_2s$ by **blending** and then directly **spray-coating** thin blend membrane layers onto electrodes (electrode-supported MEAs) allow for first very promising fuel cell performances.

Polyelectrolyte

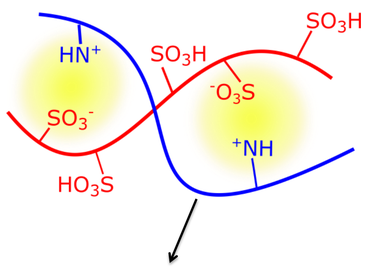
sulfonated
poly(phenylene sulfone)s
$sPSO_2s$



- ✓ high conductivity
- ✓ high (thermal, chemical, morphological) stability
- ✓ fluorine-free
- × strong swelling when wet
- × brittle when dry

Polymer blend

membrane formation
via
acid-base blending

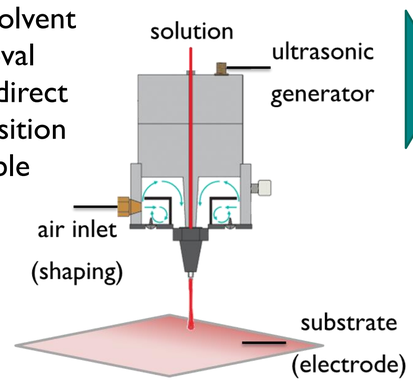


- mechanically strong
- commercial material

Processing

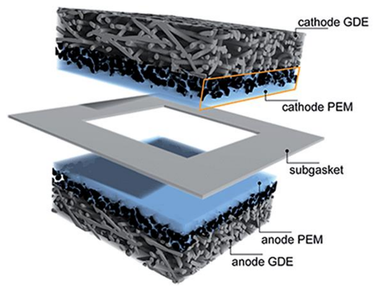
thin membrane preparation
via
ultrasonic spray-coating

- fast solvent removal
- thin, direct deposition
- scalable



Application

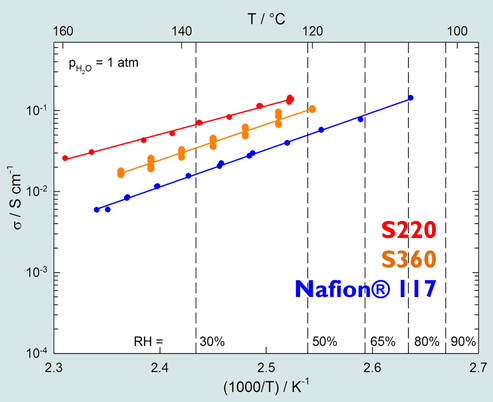
directly deposited
hydrocarbon membranes
in
electrode-supported MEAs



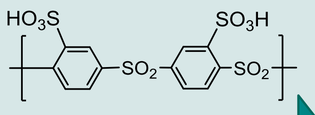
from: M. Klingele, M. Breitwieser, R. Zengerle, S. Thiele, *J. Mater. Chem. A.*, **3**, 11239-11245, **2015**.

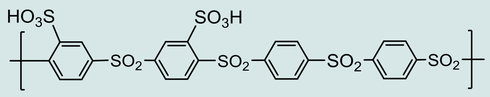
Polyelectrolyte: sulfonated poly(phenylene sulfone)s[1-4]

Conductivity at high temperatures
in comparison to Nafion®117



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





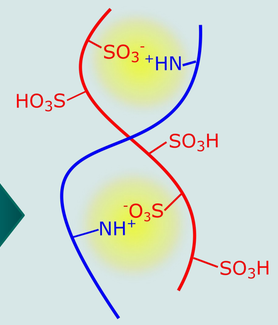
S360 IEC = 2.78 meq^{-1}, EW = 360 geq^{-1}

unfavorable mechanical properties

0% 20% 100% RH

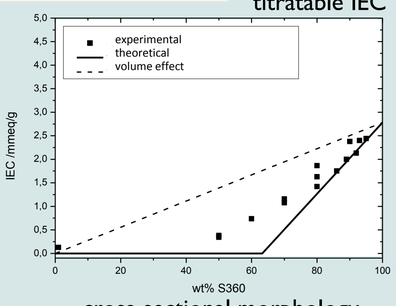
brittleness — solubility **(S220)** or strong swelling **(S360)**

Polymer blend: acid-base concept[5-6]

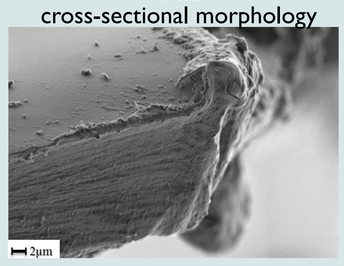


- compatibilization via acid-base interaction
- neutralization of S360 necessary for blending
- reduction of ion exchange capacity (and conductivity) through acid-base crosslinks
- homogeneous morphology

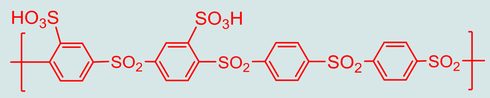
titratable IEC

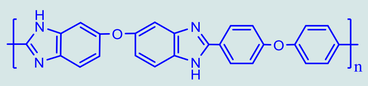


cross-sectional morphology



S360



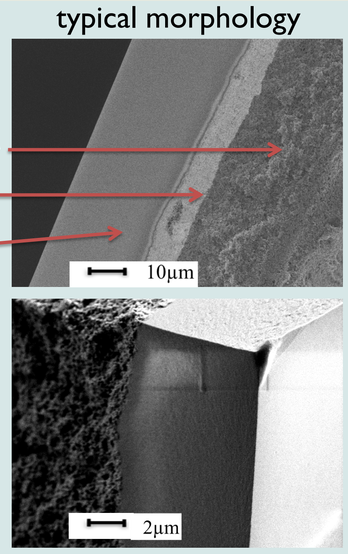


Polybenzimidazole
(PBIOO, EW = 208 geq^{-1})

Processing: MEA formation via ultrasonic spray-coating

- controlled ultrasonic dispersion
- thin depositioning onto electrode
- thickness and morphology control
- scalable

typical morphology



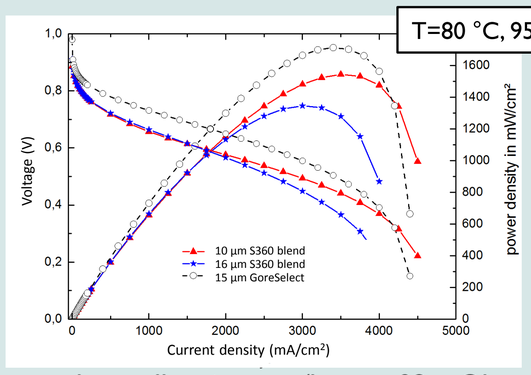
advantages of spray-coating for $SPSO_2s$ blends

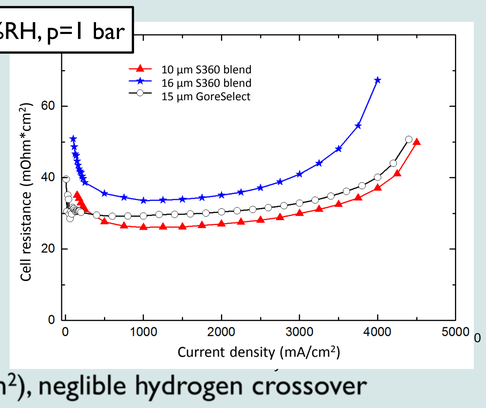
low hydrogen permittivity and improved chemical stability compared to Nafion-type membranes, (which undergo chemical degradation (thinning) during operation) allows for ultra-thin membrane layers

Application: first fuel cell test

measured by M. Breitwieser; references taken from Breitwieser, M.; Klose, C., et al., *Journal of Power Sources* **2016**, 337, 137.

T=80 °C, 95 %RH, p=1 bar





- very low cell resistance (lowest: 23 mOhm·cm^2), neglible hydrogen crossover
- max. performance = 2.7 W/cm^2 at 80 °C, 200 kPa backpressure
- further investigation: performance under atmospheric pressure does not match resistance
- next step: thinner membrane layers, development of $sPSO_2$-based electrode

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fumatech functional membranes for fuel cells

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