Sulfonated Poly(phenylene sulfone) Polymers as Hydrolytically and Thermo-oxidatively Stable Proton Conducting Ionomers for PEM Fuel Cell Applications

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Introduction

The electrolyte material used in current PEM fuel cells is commonly a hydrated sulfonic acid functionalized polymer. Because of the harsh conditions in operating fuel cells (high temperatures, high water activities and the appearance of highly reactive oxidizing radicals), hydrolytic, thermo-oxidative and (electro-)chemical stabilities are key issues in the choice of the ionomer. Today's membranes are perfluorosulfonic acid (PFSA) polymers such as Nafion® (DuPont), featuring superior stability compared to most hydrocarbon based membranes. But their high water and methanol "cross-over", their low proton conductivity as well as their poor mechanical stability at elevated temperatures (T > 80 °C) and low degrees of humidification are still severe disadvantages of these state of the art membrane materials. According to recent reports, the transport properties of sulfonated poly(arylene) membranes seem to be advantageous over these of perfluorosulfonic acid ionomers, which renders them promising alternatives, provided that their stability problems are solved.
On this poster we present a new class of sulfonic acid functionalized poly(arylene) ionomers combining high stability and high proton conductivity. The materials are the first outcome of our attempts to form an extremely electron-deficient poly(arylene) with high ion exchange capacity.

Approach

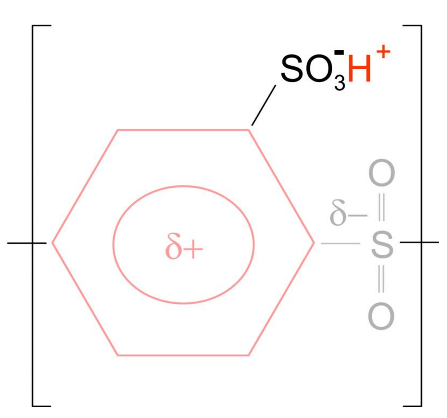
DMFC

- **reduce hydrophobic / hydrophilic separation and swelling**
  reduction of hydrodynamic transport (electroosmotic drag and permeation)
- **increase polar character (charge separation)**
  increase methanol rejection

HT-PEM-FC

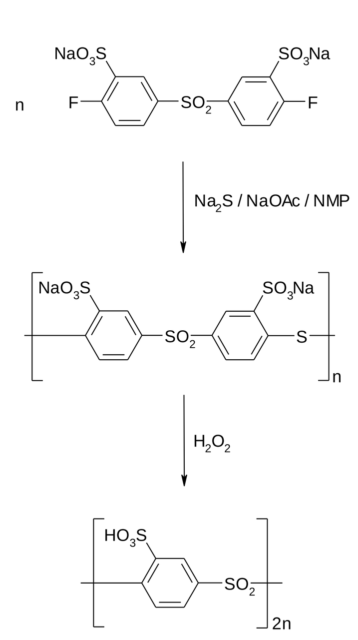
- **increase concentration of protonic charge carriers (increase [-SO_3H] and acidity) without increasing swelling**
  increases conductivity especially at low humidification
- **avoid any chemical group susceptible to oxidation and hydrolysis**
  stability

Electron poor sulfonated poly(phenylene sulfone)s

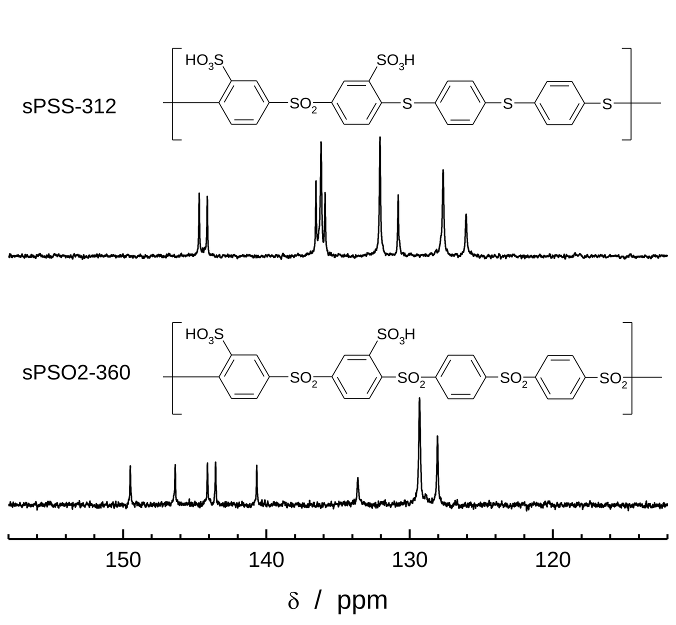


- stability
- acidity
- polarity
- no phase separation

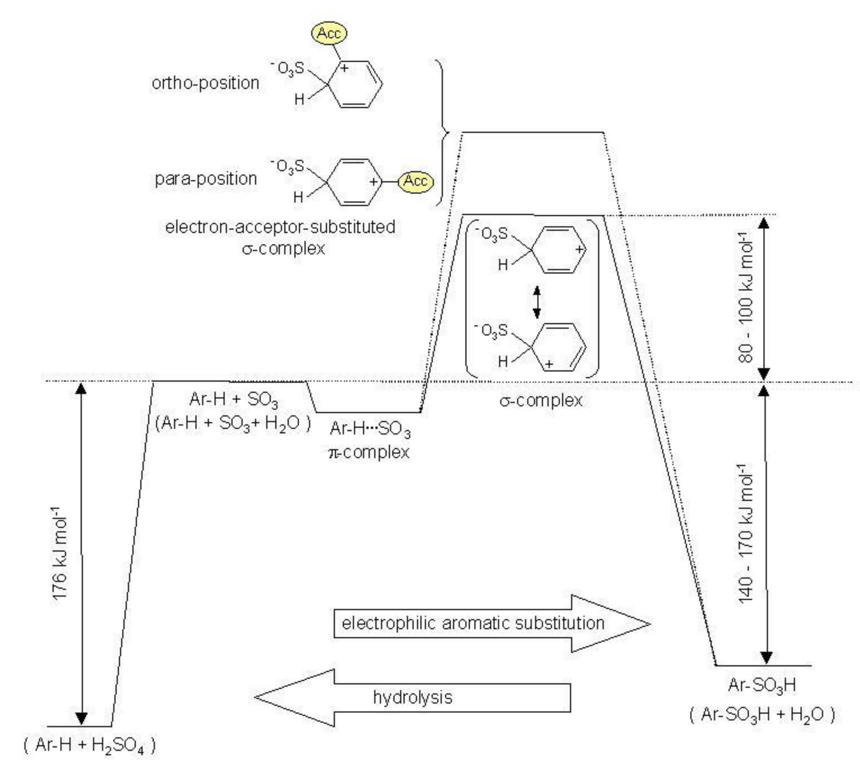
preparation



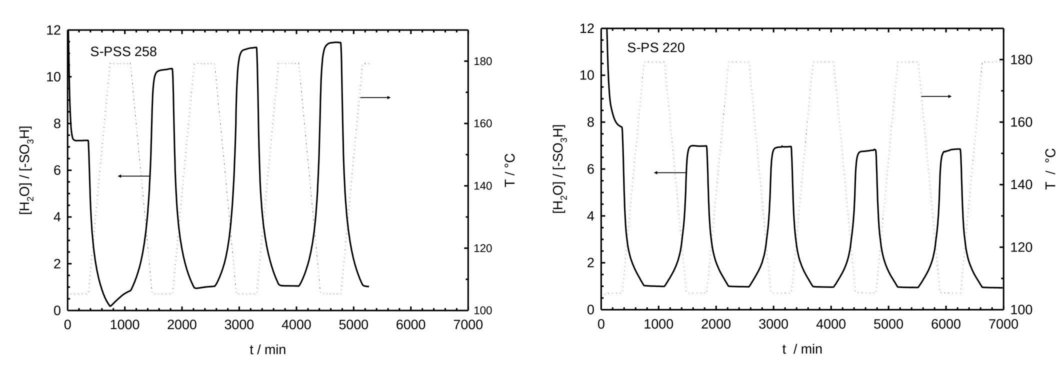
NMR

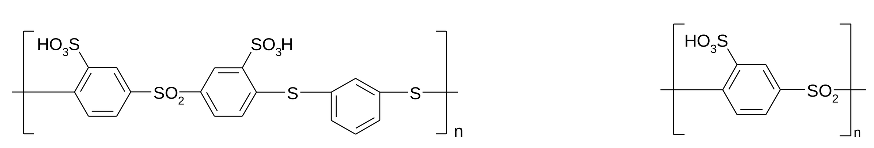


Stability



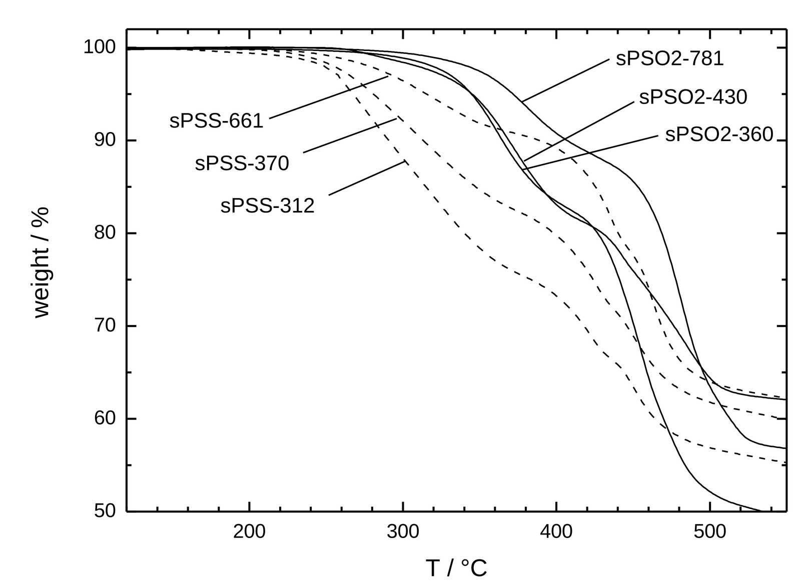
TGA under water atmosphere
p(H_2O) = 1 atm (10^5 Pa)





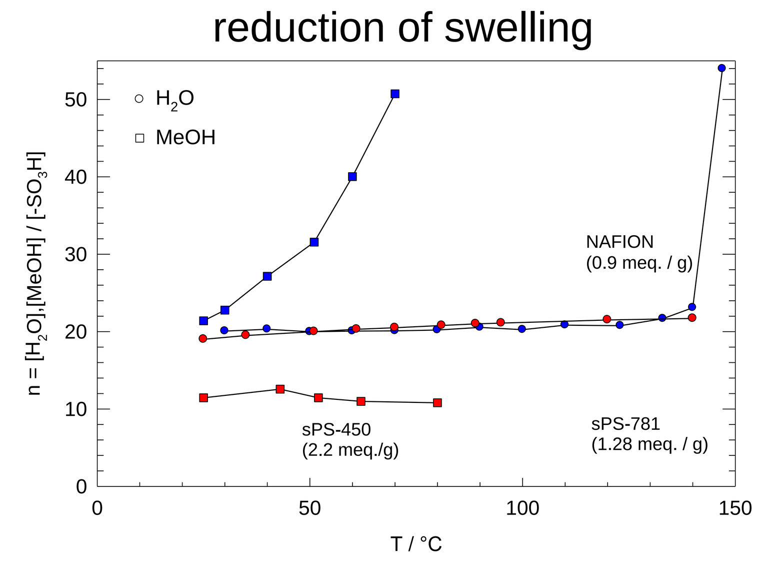
→ hydrolytically stable

TGA in nitrogen atmosphere
heating rate 2 K / min

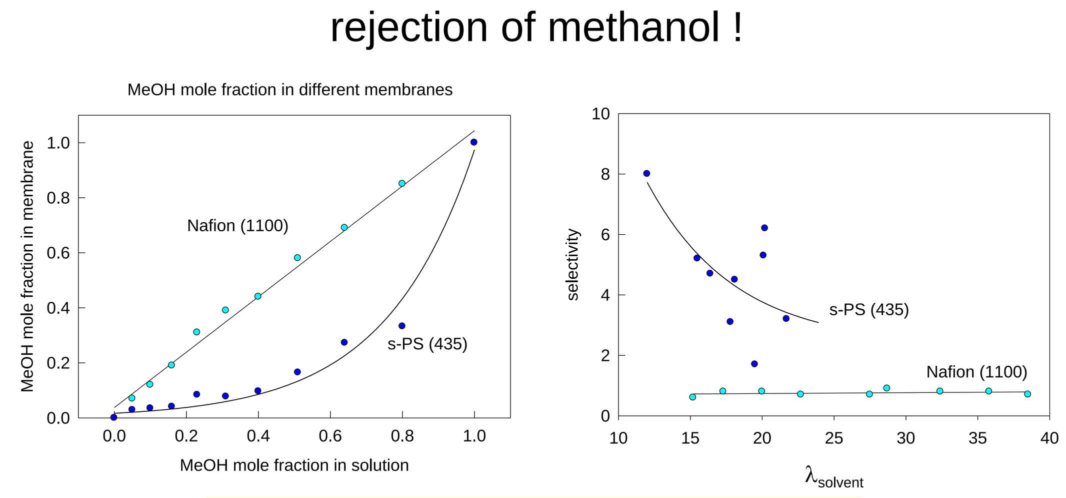


Swelling in water and methanol

reduction of swelling



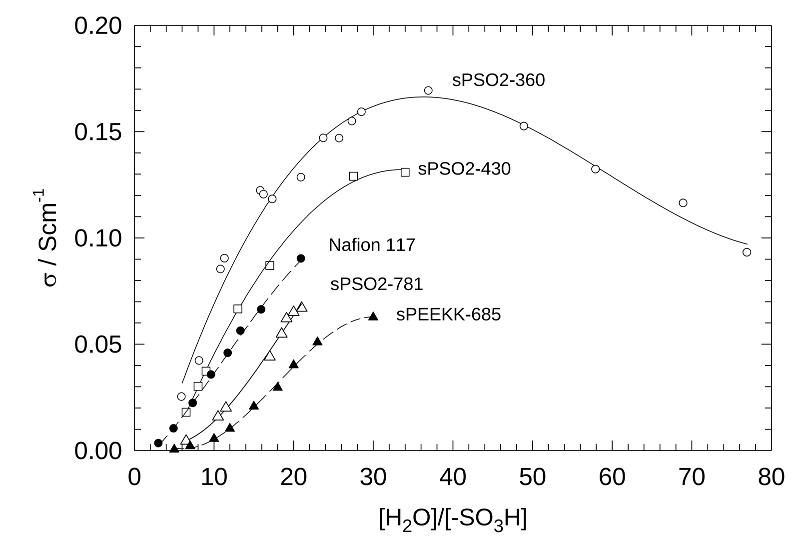
rejection of methanol !



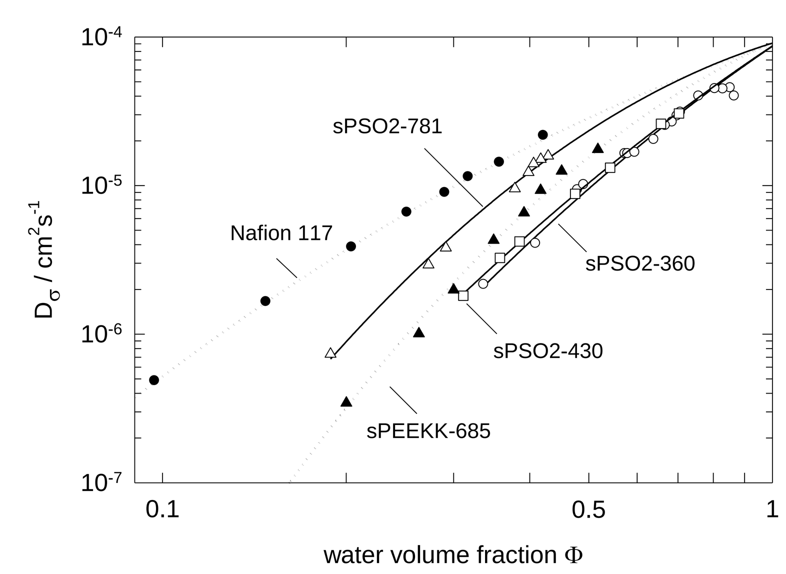
→ reduction of methanol cross-over (~12 times)!

Transport

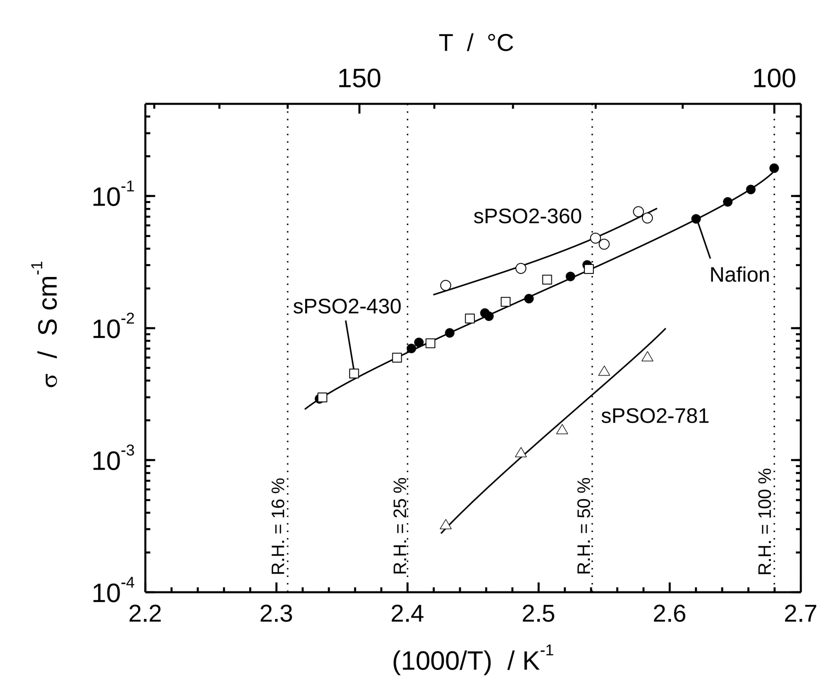
proton conductivity



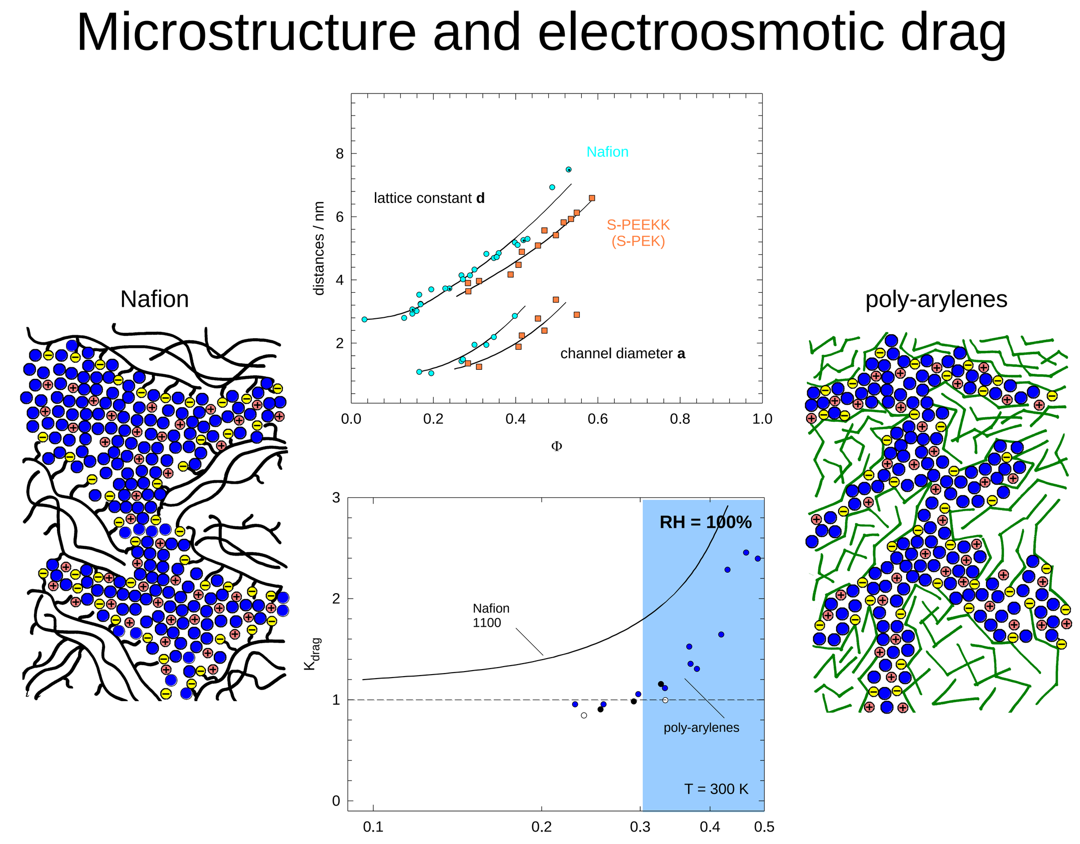
proton mobility D_σ as a function of water volume fraction



conductivity at high temperature
p(H_2O) = 1 atm (10^5 Pa)



Microstructure and electroosmotic drag



Conclusions

poly (arylene-sulfone)s have the potential to push the limits for the application of polymer electrolyte membranes (Nafion) in fuel cells

DMFC

- water / methanol cross over reduced (~1.5-2)
- selective water uptake (methanol rejection) (selectivity ~8)
  → methanol cross-over may be reduced by one order of magnitude

HT-PEM-FC

- operation temperature may be increased by about 20 K (90°C - 110°C)!
- high hydrolytic stability

but

- brittle in the dry state
- soft (solubility in the wet state) → further work in progress
  (especially for high IEC)

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