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Moléculaires et
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Inorganiques

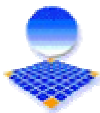
Composite membranes

or

how to get the most from proton conducting ionomers
for fuel cell application

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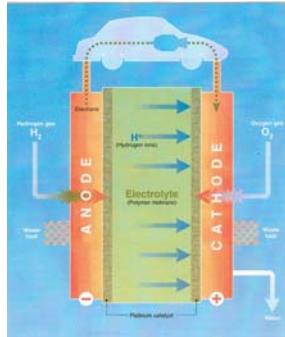


Introduction

- Proton transport in ionomeric membranes is involved in many different electromembrane processes
- Research in recent years in fuel cells (PEMFC) has raised interest in development of new materials
- In a PEMFC, the polymer membrane is responsible for separating anode and cathode reactant gases as well as transferring protons produced at the anode across the membrane to the cathode
- PEMFC operation imposes requirements on the membrane: chemical, electrochemical, mechanical stability...



FC membrane requirements



■ *conductivity*

- high proton conduction ($>10^{-2} \text{ Scm}^{-1}$ at the operating temperature)
- for temperature operation $>100^\circ\text{C}$
→ thermally stable polymer and conservation of proton conduction properties, even under non water saturated conditions

■ *lifetime*

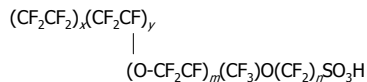
- 5000 - 10 000 h for mobile applications, 10 000 - 40 000 h stationary applications

- good mechanical strength
- low reactant crossover



Proton exchange membranes *perfluorosulfonic acid polymers*

Nafion® - DuPont - perfluorinated polymer with perfluorosulfonic acid side groups



Nafion: $m \geq 1$; $n = 2$; $x = 5 - 13.5$; $y = 1000$

Flemion: $m = 0$; $n = 1 - 5$

(Asahi Glass)

Aciplex: $m = 0.3$; $n = 2 - 5$; $x = 1.5 - 14$

(Asahi Chemical)

Dow: $m = 0$; $n = 2$; $x = 3.6 - 10$

Solvay membrane

- excellent chemical and mechanical stability

- high proton conductivity :

- $10^{-2} - 10^{-1} \text{ S/cm}$

depending on temperature, degree of membrane hydration...

- lifetime in FC operation $> 60,000 \text{ h}$

but

- high cost
- high methanol crossover
- instability at high temperature - current membrane technology appropriate for functioning at $\leq 80^\circ\text{C}$

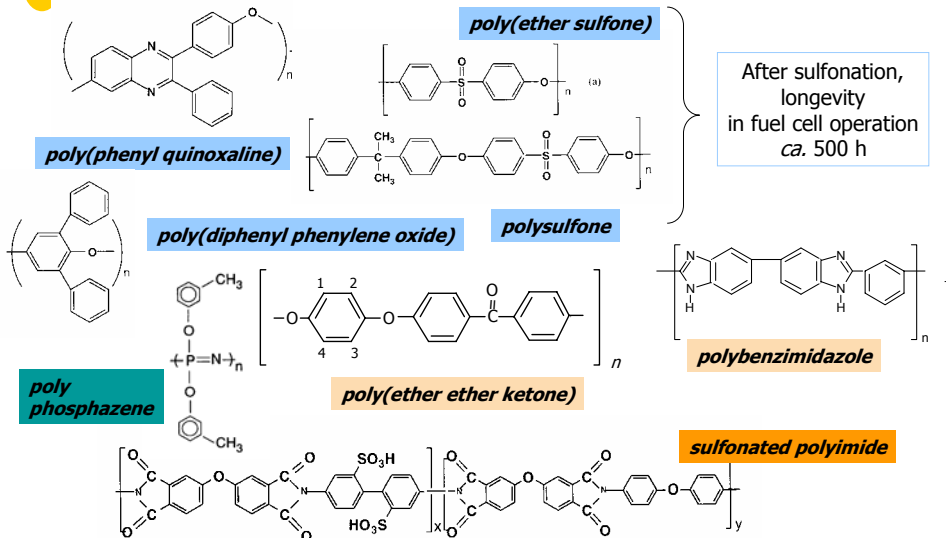


Increase of operation temperature >100°C

- ◆ fuel cell operation in 110 - 180°C range
 - ◆ simplifies the thermal and humidification sub-systems in automotive application
 - ◆ standard noble metal electrode technology becomes increasingly tolerant to CO levels. Important in the context of use of reformat (otherwise purification unit required)
 - ◆ stationary applications - cogenerated heat
- ◆ for use in this temperature range need thermostable polymers



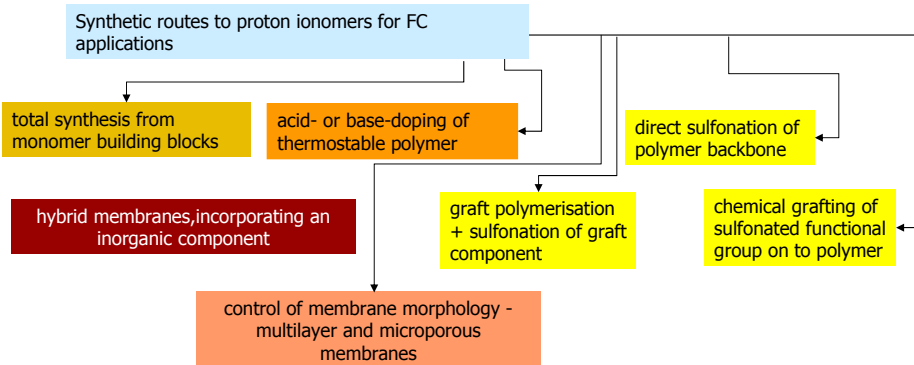
"advanced" thermostable polymers: polyaromatic hydrocarbons and heterocyclic polymers





Approaches to ionomer preparation

- Direct sulfonation of polymer backbone
- Chemical grafting to polymer backbone
- New polymer synthesis from monomers
- Radiation grafting to polymer backbone
- ...



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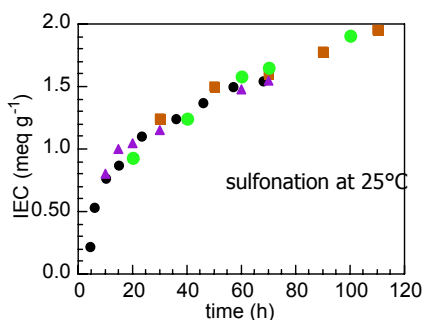
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Direct sulfonation of polyaromatic polymers

- ❖ direct sulfonation of an aromatic polymer backbone by electrophilic substitution is easily carried out – can be performed at large scale in an industrial process
- ❖ sulfonation of polyaromatics can be carried out directly in concentrated sulfuric acid
- ❖ extent of sulfonation controlled by the concentration of SO_3 , reaction time and temperature

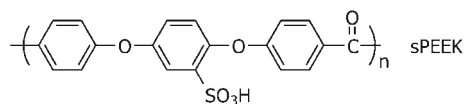


Different colour points represent reported data of other authors and own work

→ sulfonation is highly reproducible under defined conditions

Degree of sulfonation affects

- conductivity
- water uptake and swelling



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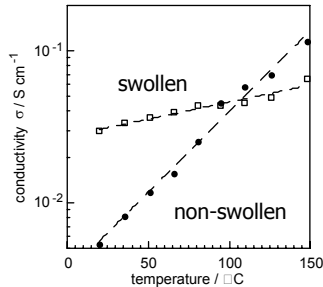
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Many factors influence conductivity of sPEEK

Membrane pre-treatment conditions



Bauer, Jones, Tchicaya, Rozière, Casciola, Alberti *et al.* J. New Mater. Electrochem. Syst. 3 (2000) 93

Conductivity at 100 - 150 °C
is $4 - 10 \cdot 10^{-2} \text{ S cm}^{-1}$
100% RH



Influence of casting solvent on membrane properties

- Solution casting can easily be performed at small and large (industrial level) scale
- it allows for many different process variables, as well as inclusion of e.g. membrane reinforcements
- the choice of solvent is important – solvent is not an inactive "bystander"

Solvent used for membrane casting	authors	Conductivity, $\overline{S/cm}$ (at 100°C, 100 % RH)	
N-methylpyrrolidone	Rozière <i>et al.</i>	$5 \cdot 10^{-2}$	sPEEK 50% sulfonation
N-methylpyrrolidone	Kreuer <i>et al.</i>	$6 \cdot 10^{-2}$	
Dimethylacetamide	Zaidi <i>et al.</i>	$3 \cdot 10^{-4}$	
Dimethylformamide	Rikukawa <i>et al.</i>	$4 \cdot 10^{-5}$	

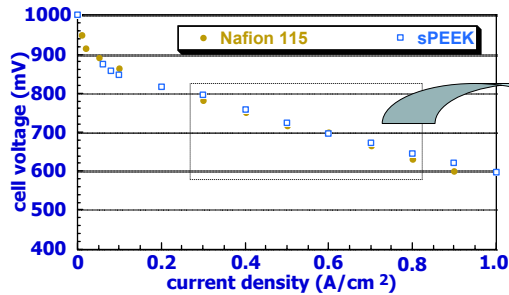
sPEEK membranes cast from DMAC and DMF have lower conductivity than those cast from NMP

- hydrogen bond interactions and chemical reaction between polymer and solvent



Conductivity of SPEEK

- ❖ Conductivity measurement is an essential parameter for membrane selection
- ❖ Difference in conductivity measurements could be attributed (rightly or wrongly) to a different measurement method (impedance spectroscopy..., measurement cell...)
- ❖ For membranes destined for FC application, *in situ* measurement in a working fuel cell is the most relevant
- ❖ Determination of membrane resistance from "linear region" of polarisation curve:



$5 \cdot 10^{-2} \text{ S cm}^{-1}$
i.e. in agreement with that from impedance spectroscopy

Membrane 70 μm operated at 85°C on H₂ - O₂



Approaches to reduce swelling of polyaromatic polymer membranes and dependence of conductivity on water content

Chemical composition and polymer structure

Mesoscopic level organisation of polymer backbone into hydrophobic and hydrophilic regions

"Physical" modification of membrane morphology

- **Polymer composition**
 - **Crosslinking of polymer chains** to reduce membrane swelling
 - **Introduction of segments** to introduce flexibility without affecting chemical stability
 - **Block co-polymer** increase nanophase separation, to improve proton transport
- Control **membrane morphology**: incorporation of inorganic component, modification of process conditions during membrane preparation



Preparation of composite membranes by ion-exchange: intra-membrane growth

- hydrophilic regions of sulfonated polymers such as sPEEK are "nanoreaction chambers" - preferential regions for particle growth *i.e.* inorganic sub-lattice is formed locally
- proton-exchange properties of sulfonated polymer membranes used to insert metal ions that are precipitated as a solid state proton conductor such as an acid phosphate (or phosphonate...) in a second step after casting



- non-trivial choice of precipitation reaction conditions – favour particle growth and avoid reverse exchange
- method lends itself to following the kinetics of formation of ZrP
- amount of inorganic phase that can be formed is limited by the IEC of the sulfonated polymer



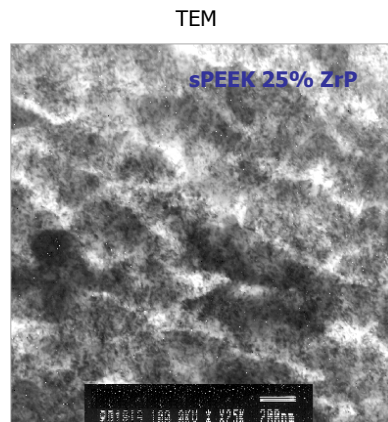
sPEEK - zirconium phosphate hybrid membranes



Optical microscope

homogeneous distribution of particles
size ca. 15 -30 nm x 5 - 10 nm

Optically homogeneous, transparent membranes



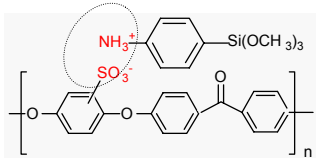


Inorganic-organic composite membranes

A more general method
Polymer matrix - sulfonated PEEK, PBI

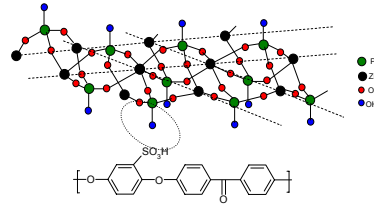
in situ condensation in solution

inorganic precursor – tetraethoxysilane
crosslinking agent
– aminophenyltrimethoxysilane
ionic interaction



Formation of a silica network

inorganic precursor – zirconyl propionate
precipitation/crosslinking reagent
– phosphoric acid
hydrogen bonding

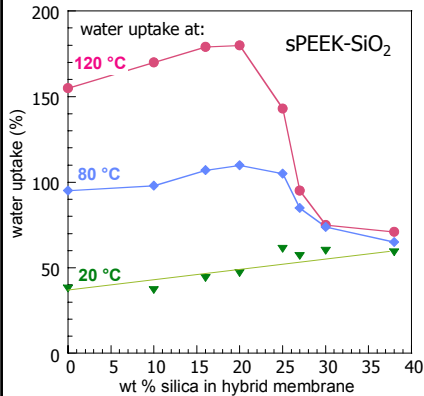


Formation of a zirconium phosphate network

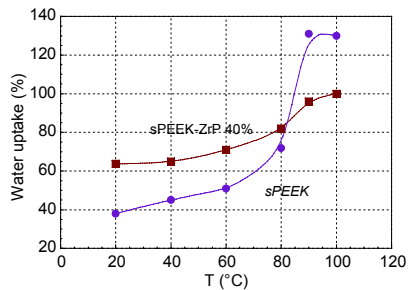
composite inorganic-organic membranes with up to 50 wt% inorganic component



Influence of inorganic material on membrane swelling



• swelling is reduced above ca. 25 wt% SiO₂
content effect is most marked at high temperature



• swelling of sPEEK-ZrP40 is lower than sPEEK >80 °C

sPEEK "confined" in an inorganic network
Important for mechanical stability



Approaches to reduce swelling of polyaromatic polymer membranes - "Physical" modifications to the membrane structure

Microporous membranes

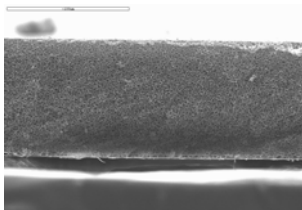
- Application of microporous membranes in separation processes is well known and commercialised, but their use as fuel cell membranes is much less well developed
 - In "Gore-type" membranes, a microporous support is impregnated with a sulfonated polymer. In other work, inorganic proton conductors are used as fillers for porous supports.
- The approach developed here uses a specific membrane preparation process (one-step procedure). Proton transport is assured by the porous polymer matrix, and the pore filling component mainly contributes mechanical strength



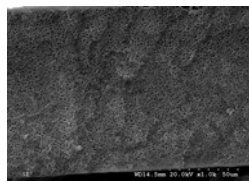
Microporous sulfonated PEEK membranes

- The concentration of polymer, co-solvent ratio, water tolerance of the system all influence the type of porosity:

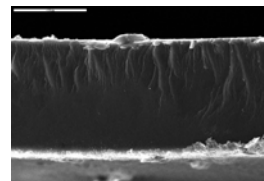
preparation conditions →



spherical pores of diameter 1 – 2 μm



spherical pores of diameter 0.4 – 0.8 μm

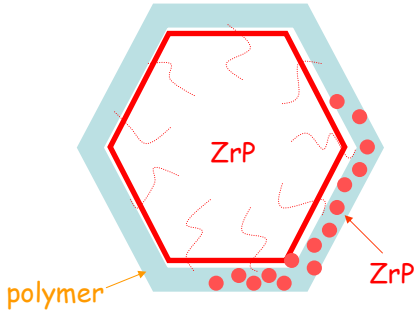
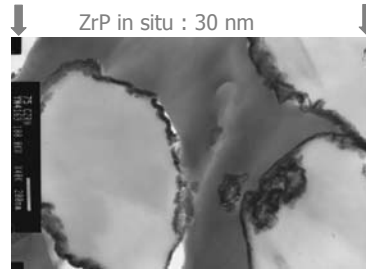
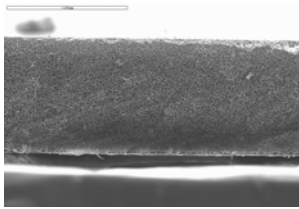


dense membrane

- The membranes are gas tight since the porosity is closed at the membrane surfaces
- To avoid microstructural collapse under such pressure (e.g. in an assembled fuel cell) – must fill the internal porosity



Microporous sPEEK composite membranes with sPEEK



mesoporous ZrP formed

- in the pore walls, by ion exchange with protons of $-\text{SO}_3\text{H}$ (pore size 4 - 10 nm)
- in the pores, in an egg-shell type arrangement, by impregnation (pore size 400 - 500 nm). Thickness of eggshell: 30 - 40 nm.

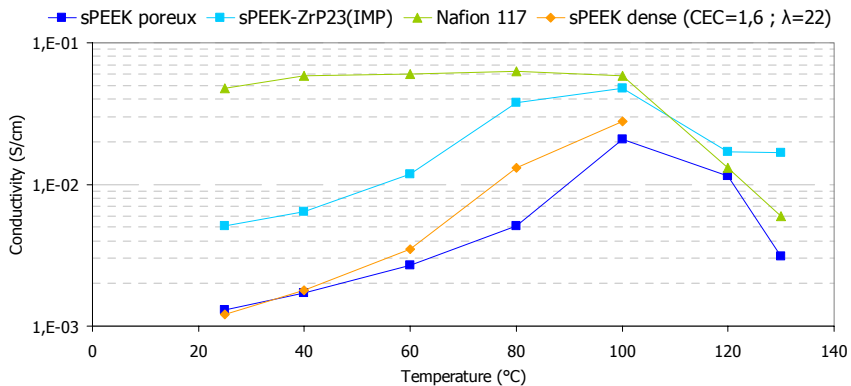
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Conductivity of microporous sPEEK-ZrP



at 100 % RH

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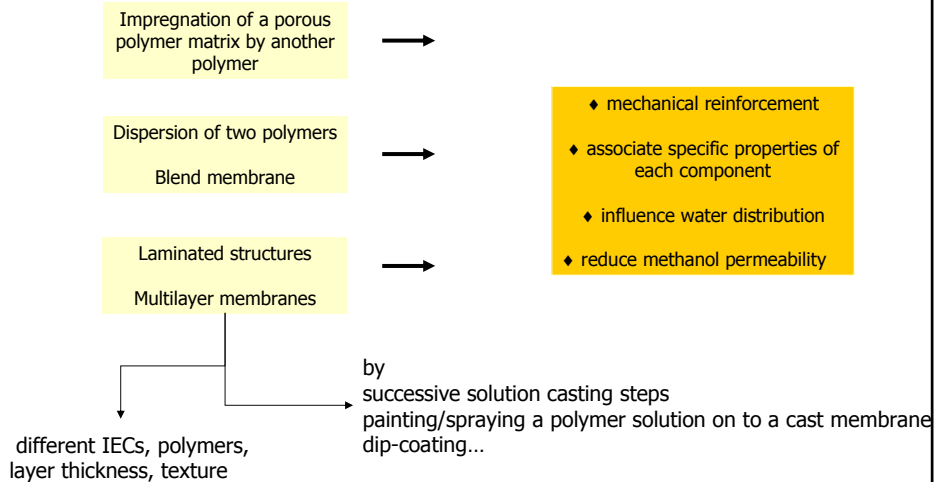
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Approaches to reduce swelling of polyaromatic membranes by "physical" modifications to the membrane structure

Composite (organic-organic) membranes



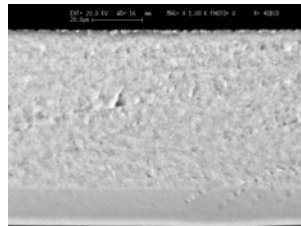
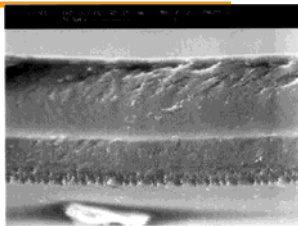
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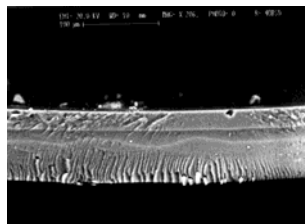
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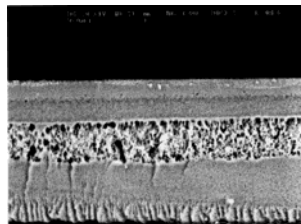
Influence of preparation conditions on interface and morphology



sPEEK bilayers: porosity difference
influence of preparation conditions on porosity and interface



sPEEK trilayer



sPEEK-PBI-sPEEK trilayer
(dense - porous - dense)

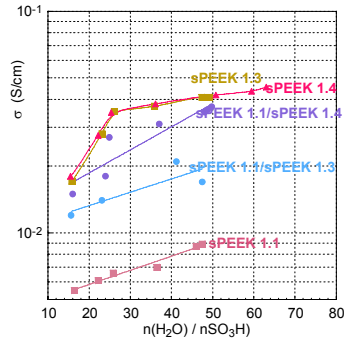
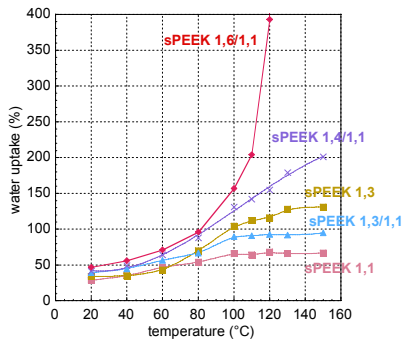
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Swelling and conduction properties of bilayer membranes



- water uptake depends on the component polymer IEC
- overall water uptake lies between that of the separate component polymers

- conductivity > 5.10^{-3} S/cm (25°C) above $\lambda = 15$ for all membranes
- conductivity increases with hydration number

- Each layer contributes its own swelling properties, reducing overall water uptake of the system
- High adhesion at the interlayer interface gives low interlayer resistance, maintains high conductivity

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Influence of IEC and water uptake properties: sPEEK bilayers

- FC operation using bilayer membranes without gas humidification
- water production at anode and cathode was determined under various operation conditions
 - orientation of bilayer with respect to anode/cathode



- ❖ reversal of the direction of water production at anode/cathode
- ❖ The relative swelling properties of the component polymers under the given temperature conditions influence the direction of water production at anode/cathode
- influence of bilayer membranes of different IECs, temperature, current density – see poster J. Péron

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Conclusion

- Possible application of new polymer membranes of polyaromatic, polyheterocyclic types for high temperature FC operation ($>100\text{ }^{\circ}\text{C}$)
- Solutions must be found to their principal drawbacks – membrane swelling and the hydration requirement for proton transport
- Textural control by physical modification – inorganic-organic, microporous and multilayer membranes (and their combinations) all contribute to limiting the effect of hydration
 - dimensional change limited
 - hydration profile
 - retention of conductivity

and contribute to extending membrane lifetime and temperature of application