CNRS.Montpellier

Laboratoire des
Agrégats
Moléculaires et
Matériaux
Inorganiques

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

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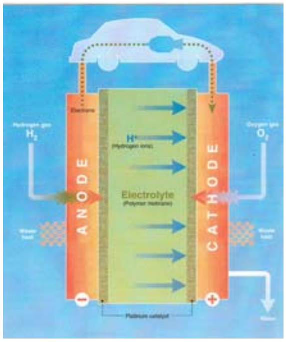
Introduction

- 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} Scm^{-1} at the operating temperature)
  - for temperature operation >100°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

$(CF_2CF_2)_x(CF_2CF)_y$
|
$(O\text{-}CF_2CF)_m(CF_3)O(CF_2)_nSO_3H$

Nafion: m ≥ 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} S/cm
  depending on temperature, degree of membrane hydration...
- lifetime in FC operation > 60,000 h

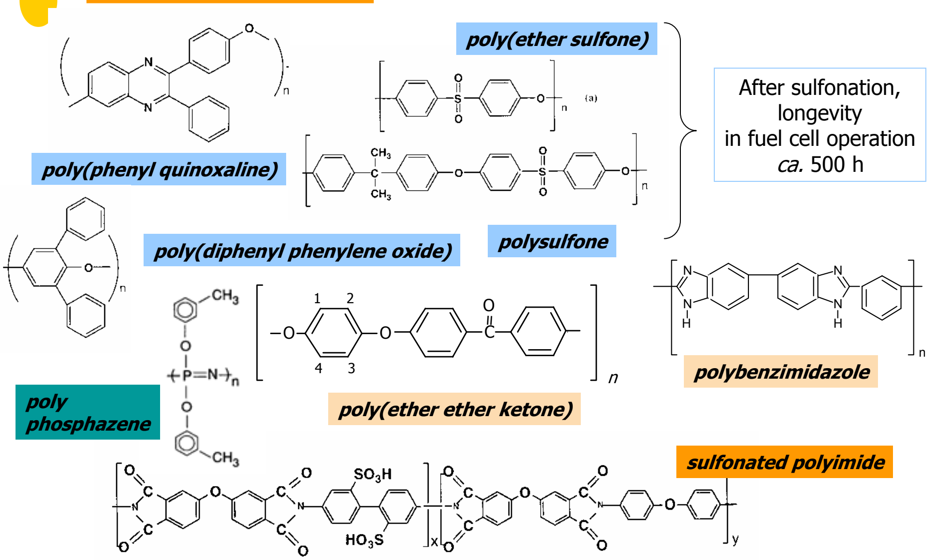
but

- high cost
- high methanol crossover
- instability at high temperature - current membrane technology appropriate for functioning at ≤80°C

Increase of operation temperature >100°C

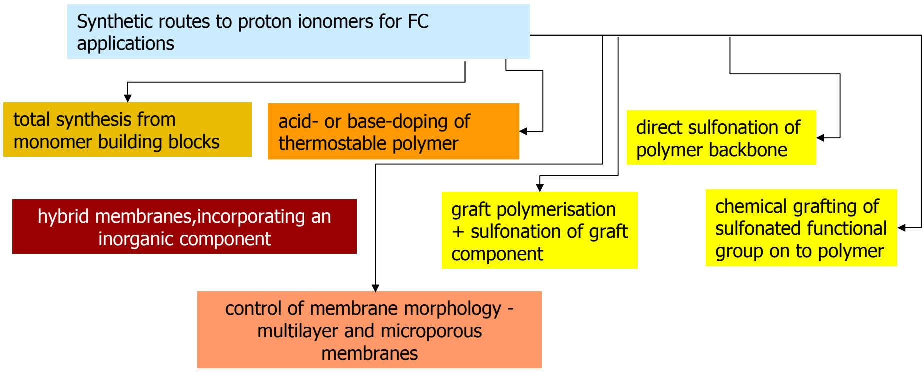
- fuel cell operation in 110 - 180°C range
  - simplifies the thermal and humidification sub-systems in automotive application
  - standard noble metal electrode technology becomes increasingly tolerant to CO levels. Important in the context of use of reformate (otherwise purification unit required)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

"advanced" thermostable polymers: polyaromatic hydrocarbons and heterocylic 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
- …

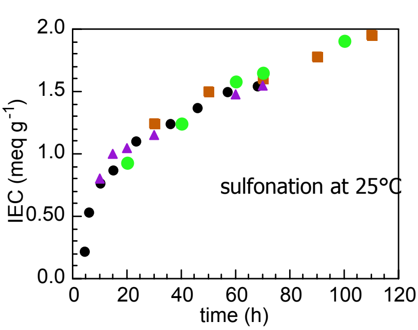


Direct sulfonation of polyaromatic polymers

❖ 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

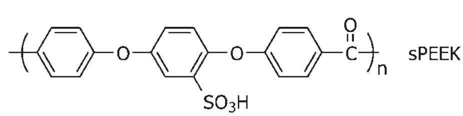


Different colour points represent reported data of other authors and own work

→ sulfonation is highly reproducible under defined conditions

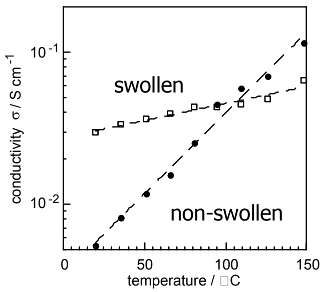
Degree of sulfonation affects

- conductivity
- water uptake and swelling



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•10^{-2} 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, S/cm (at 100°C, 100 % RH)	
N-methylpyrrolidone	Rozière *et al.*	5.10^{-2}	
N-methylpyrrolidone	Kreuer *et al.*	6.10^{-2}	
Dimethylacetamide	Zaidi *et al.*	3.10^{-4}	
Dimethylformamide	Rikukawa *et al.*	4.10^{-5}	sPEEK 50% sulfonation

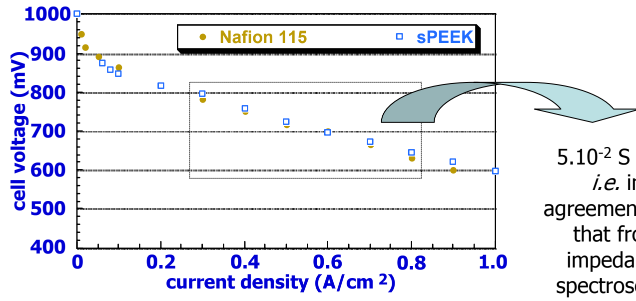
sPEEK membranes cast from DMAC and DMF have lower conductivity than those cast from NMP
- hydrogen bond interactions and chemical reaction between polymer and solvent

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...)

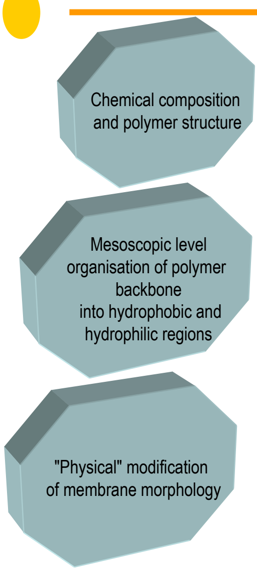
- ❖ For membranes destined for FC application, *in situ* measurement in a working fuel cell is the most relevant
- ❖ Determination of membrane resistance from "linear region" of polarisation curve:



5.10^{-2} S cm^{-1} *i.e.* in agreement with that from impedance spectroscopy

Membrane 70 µm operated at 85°C on H_2 - O_2

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



- **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

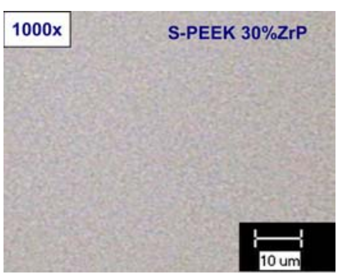
Preparation of composite membranes by ion-exchange: intra-membrane growth

- 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

$$\text{sPolymer (H+)} \xrightarrow{ZrOCl_2} \text{sPolymer (Zr)} \xrightarrow{H_3PO_4} \text{sPolymer (ZrP)}$$

- 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

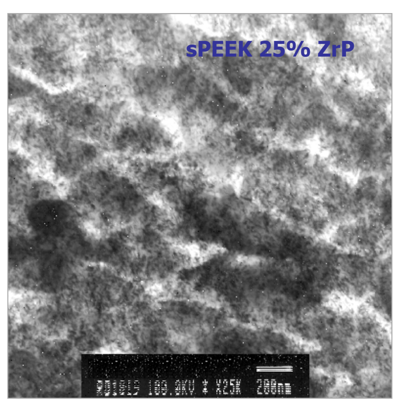
sPEEK - zirconium phosphate hybrid membranes



Optical microscope

Optically homogeneous, transparent membranes

TEM



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

Inorganic-organic composite membranes

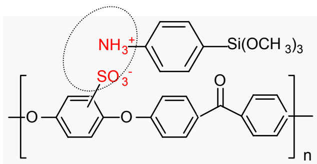
A more general method

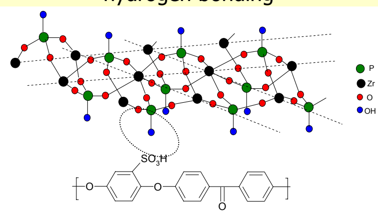
Polymer matrix - sulfonated PEEK, PBI

in situ condensation in solution

inorganic precursor – tetraethoxysilane
crosslinking agent
– aminophenyltrimethoxysilane
ionic interaction

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



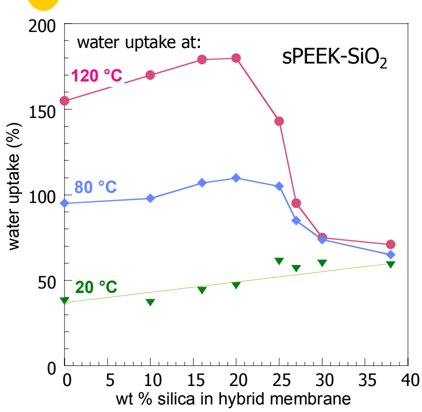


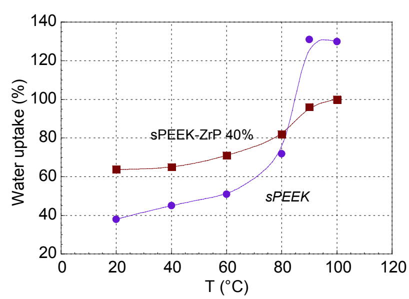
Formation of a silica network

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

- swelling is reduced above *ca.* 25 wt% SiO_2 content effect is most marked at high temperature

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

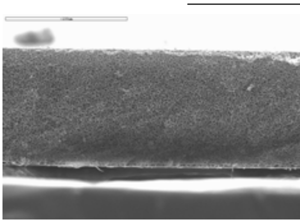
- Application of microporous membranes in separation processes is well known and commercialised, but their use as fuel cell membranes is much less well developed
  - In "Gore-type" membranes, a microporous support is impregnated with a sulfonated polymer. In other work, inorganic proton conductors are 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

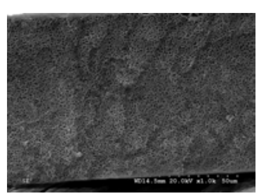
Microporous sulfonated PEEK membranes

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

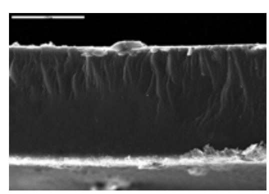
preparation conditions →



spherical pores of diameter 1 – 2 µm



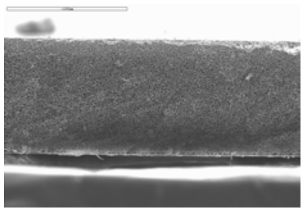
spherical pores of diameter 0.4 – 0.8 µm



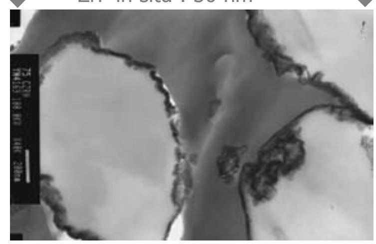
dense membrane

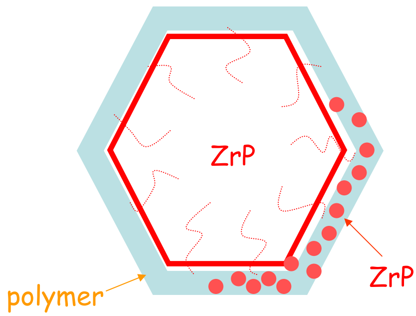
- The membranes are gas tight since the porosity is closed at the membrane surfaces
- To avoid microstructural collapse under such pressure (e.g. in an assembled fuel cell) – must fill the internal porosity

Microporous sPEEK composite membranes with sPEEK



ZrP in situ : 30 nm

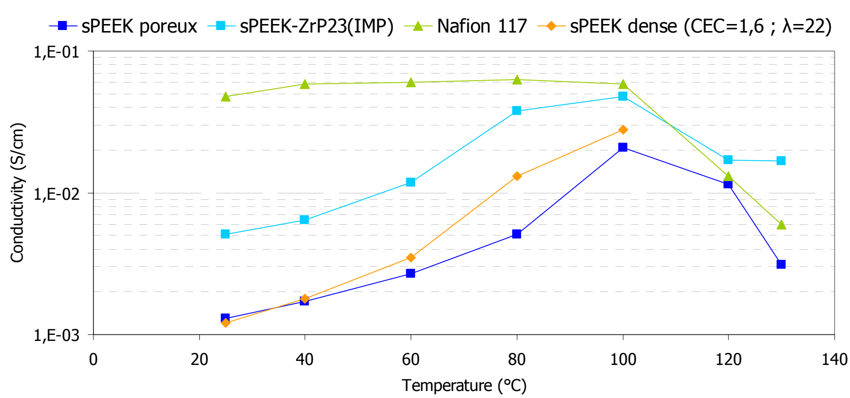




mesoporous ZrP formed
- in the pore walls, by ion exchange with protons of $-SO_3H$ (pore size 4 - 10 nm)

- in the pores, in an egg-shell type arrangement, by impregnation (pore size 400 – 500 nm). Thickness of eggshell: 30 – 40 nm.

Conductivity of microporous sPEEK-ZrP



at 100 % RH

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

Composite (organic-organic) membranes

Impregnation of a porous polymer matrix by another polymer →

Dispersion of two polymers

Blend membrane →

Laminated structures

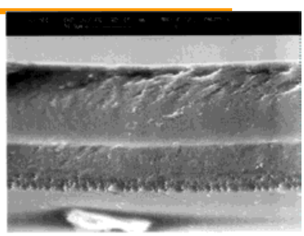
Multilayer membranes →

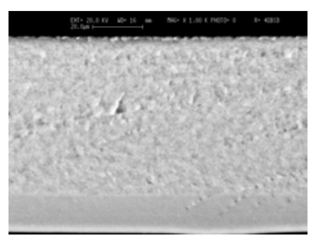
- mechanical reinforcement
- associate specific properties of each component
- influence water distribution
- reduce methanol permeability

different IECs, polymers, layer thickness, texture

by
successive solution casting steps
painting/spraying a polymer solution on to a cast membrane
dip-coating…

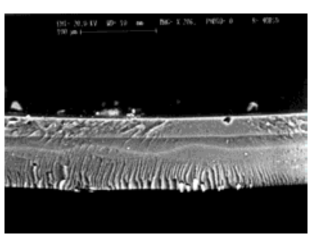
Influence of preparation conditions on interface and morphology



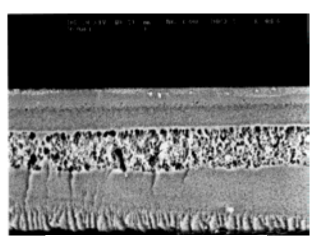


sPEEK bilayers: porosity difference

influence of preparation conditions on porosity and interface

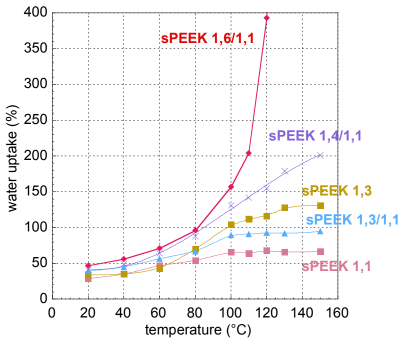


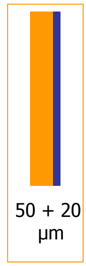
sPEEK trilayer

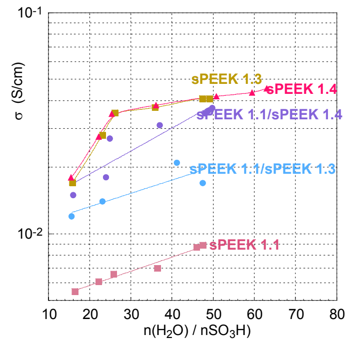


sPEEK-PBI-sPEEK trilayer
(dense - porous - dense)

Swelling and conduction properties of bilayer membranes







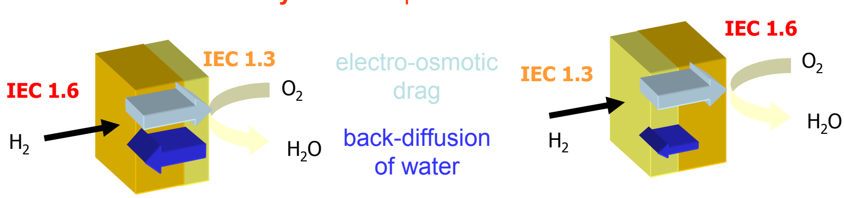
- water uptake depends on the component polymer IEC
- overall water uptake lies between that of the separate component polymers

- 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

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**

Conclusion

- Possible application of new polymer membranes of polyaromatic, polyheterocylic types for high temperature FC operation (>100 °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