Polymer-ceramic composite membranes for intermediate temperature PEM fuel cells

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SMN
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Centre for Materials Science
and Nanotechnology (SMN)

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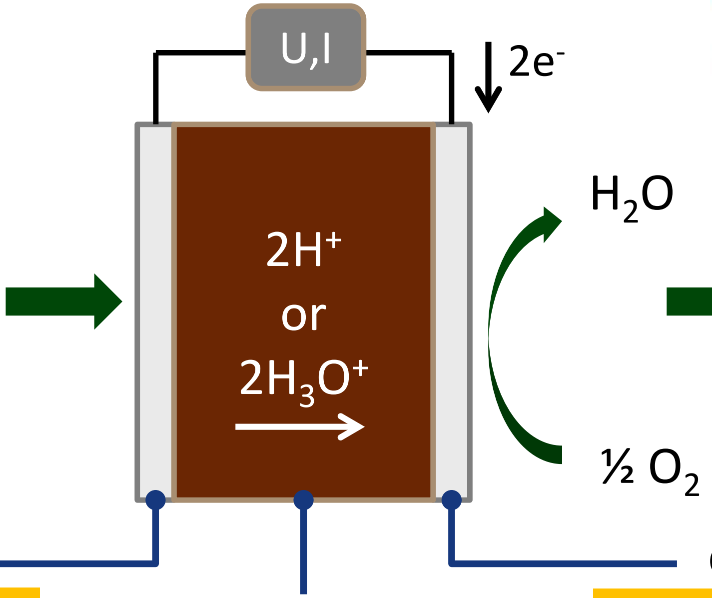
MoZEES
Mobility Zero Emission Energy Systems

FME

Polymer Electrolyte Membrane Fuel Cell (PEMFC)

Membrane Electrode Assembly (MEA)



U,I

$\downarrow 2e^-$

H_2 (+ $2H_2O$)

$2H^+$
or
$2H_3O^+$

H_2O

$½\ O_2$

+ Heat

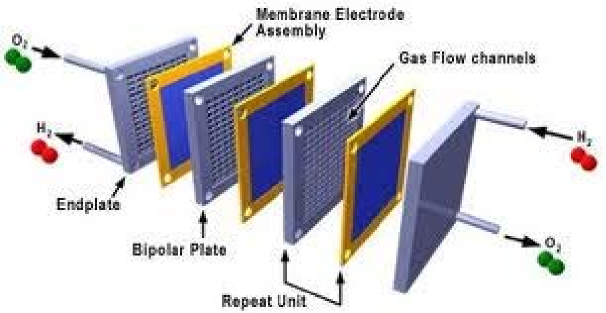
Anode

$H_2 \rightarrow 2H^+ + 2e^-$

Polymer Electrolyte Membrane (PEM)

Cathode

$2H^+ + 2e^- + ½O_2 \rightarrow H_2O$



Net total reaction: H_2 + ½ O_2 → H_2O

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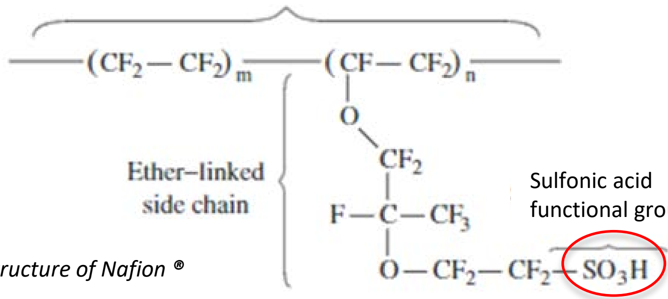
Water containing membranes: Nafion®

- Nafion®: PFSA-type membranes

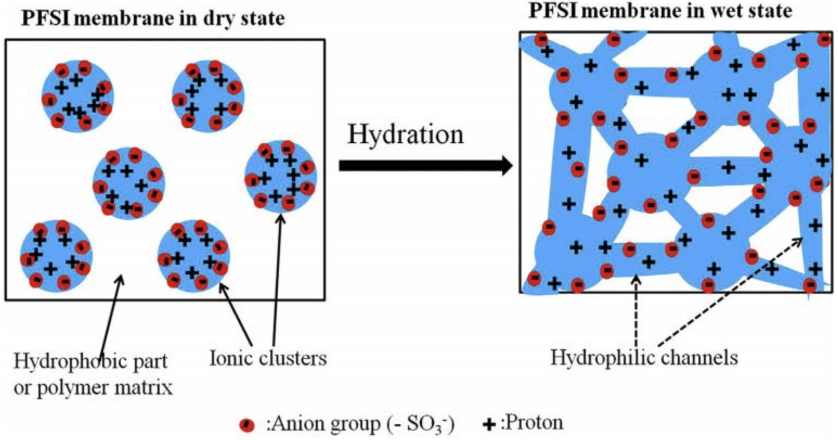
Perfluorinated backbone (hydro*phobic* framework)



Sulfonic acid functional groups

Structure of Nafion ®

A. A. Shah. et al. / Journal of The Electrochemical Society 156, (2009) 465-484



E. Bakangura. et al. / Progress in Polymer Science 57 (2016) 103 - 152

- High RH required: fluorinated membranes, sulfonated aromatic hydrocarbons (e.g. SPEEK)
- Operating temperature: < 80˚C (LT-PEM material)

LT- PEMFC (< 80˚C): Challenges

- **Electrode kinetics**

ORR: slowest kinetics

Cathode overpotential responsible for main part of cell voltage losses

- **CO poisoning of the anode**

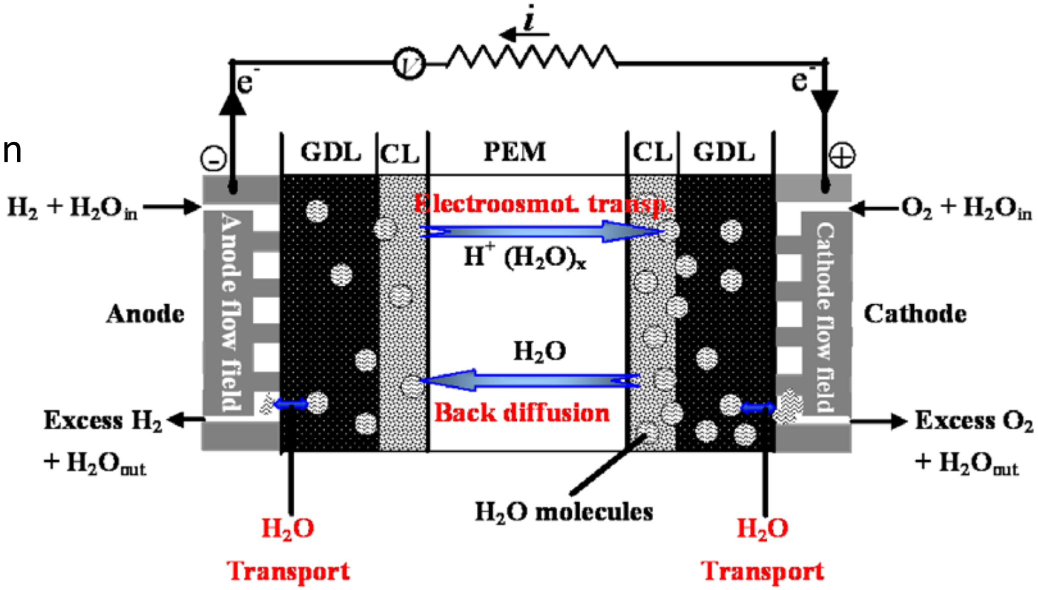
99.999% pure H_2 required

- **Heat management**

Advanced cooling technology required

- **Water management**

Water flooding (GDL & CL)



Ji M. and Wei Z., Energies, 2, 2009, 1057

Advantages and challenges at elevated temperature (> 80˚C)

Advantages

- Improve kinetics
- Increased CO tolerance of the electrocatalyst
- Better usage of waste heat
- Reduce cathode flooding

Challenges

- Membrane dehydration, decreased proton conductivity
- Faster chemical degradation
- Reduced mechanical stability

Characteristic	**2015 US DOE targets for PEM for transport application**
Maximum operating temperature	120˚C
Unassisted start up from temperature	- 40˚C
Conductivity	0.1 S cm^{-1} (120˚C) 0.07 S cm^{-1} (ambient temperature)
Area specific resistance	0.02 Ω cm^2
Relative humidity/inlet water vapour partial pressure	50%/1.5 kPa
Hydrogen/oxygen crossover at 1 atm	2 mA cm^{-2}
Cost	20 US$/$m^2$
Durability with cycling	5000 h

DOE Technical Targets for Polymer Electrolyte Membrane Fuel Cell Components

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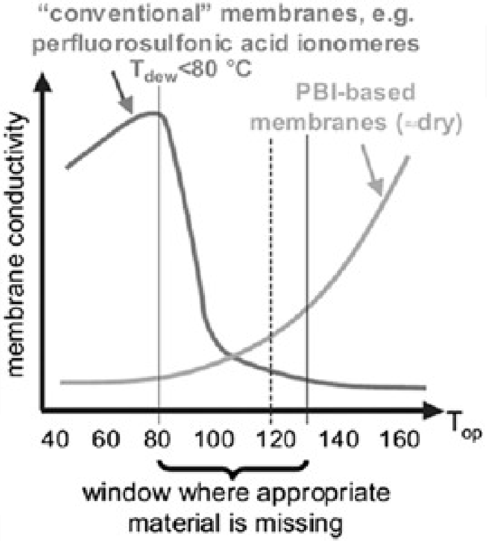
Common approaches to higher temperature PEMs

- **Ceramic fillers** in water-based polymers such as Nafion®
- **Acid-doped polymers** such as PBI, PEEK
- **Ceramic fillers** in **acid-doped polymers**, e.g. PBI, PEEK



A.Chandan et al., Journal of power source, 231, 2013, 264-278

Our approaches:

- **Critical** to intended and claimed effects of fillers: Critical review and own measurements
- **Reduce or eliminate heavy acid doping**
- Via fundamentals to new directions: **High risk & gain** to make a difference
- Apply principles of **nano-ionics**, including novel surface and interface **protonics**

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Nafion®-based composite membranes

Filler particles proposed to improve water uptake and retention

I. "Hygroscopic" oxides (SiO_2, TiO_2, ZrO_2)

II. "Solid acids" (sulfonated ZrO_2)

III. "Proton conducting" heteropolyacids ($H_3PW_{12}O_{40}$)

IV. Other polymers (Polyaniline – PANI)

V. Functionalized carbon nanomaterials (e.g. sulfonated carbon nanotubes)

VI. Metal organic frameworks – MOFs (ZIF-8)

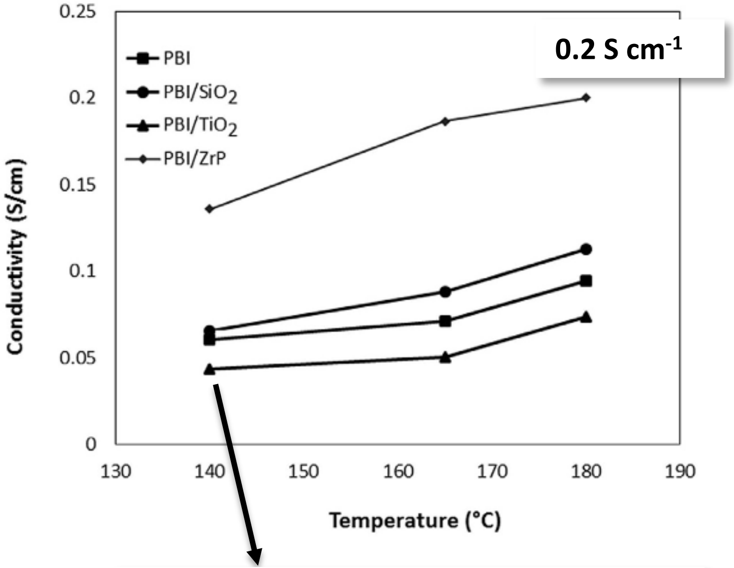
Methodology:

- Challenge these approaches, own experiments
- *in-situ* (EB, UV) formation of sub-channel-sized nanoparticles in Nafion® membranes

PBI based composite membranes

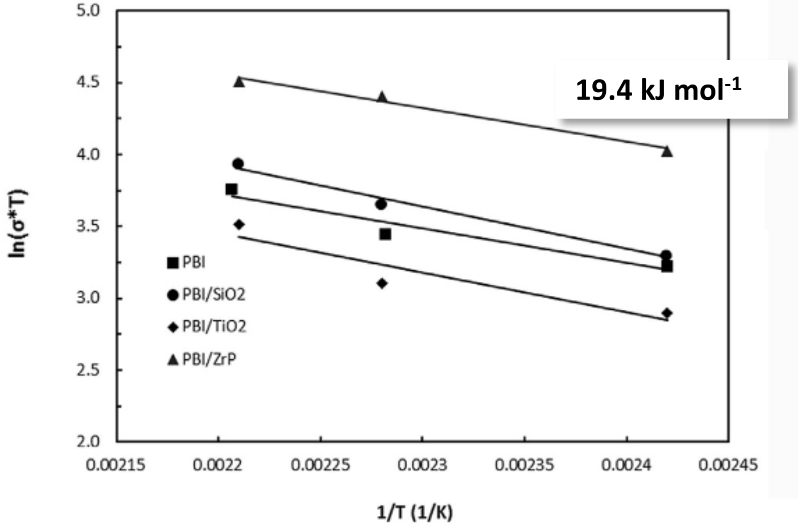
Inorganic fillers: maintain mechanical strength, improve acid retention capability and protonic conductivity

But does it work? And how?



0.2 S cm^{-1}

Non-uniform structure of membrane



19.4 kJ mol^{-1}

Ozdemir, Y., et al., International journal of hydrogen energy, Vol. 42, Issue 4, 2017

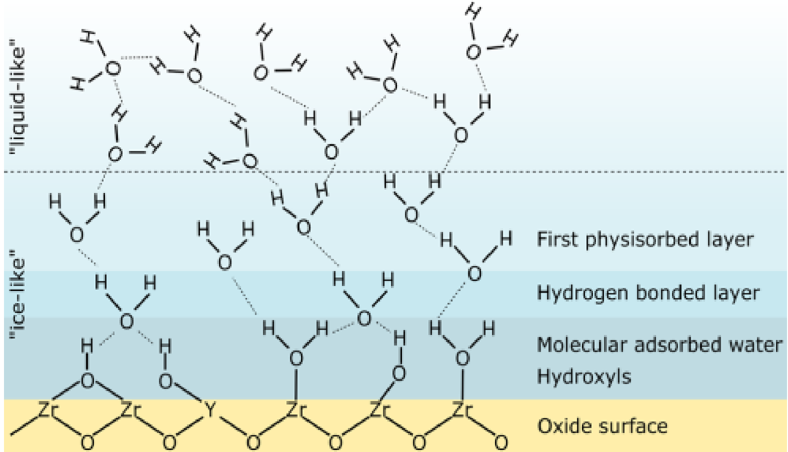
Surface and interface protonics

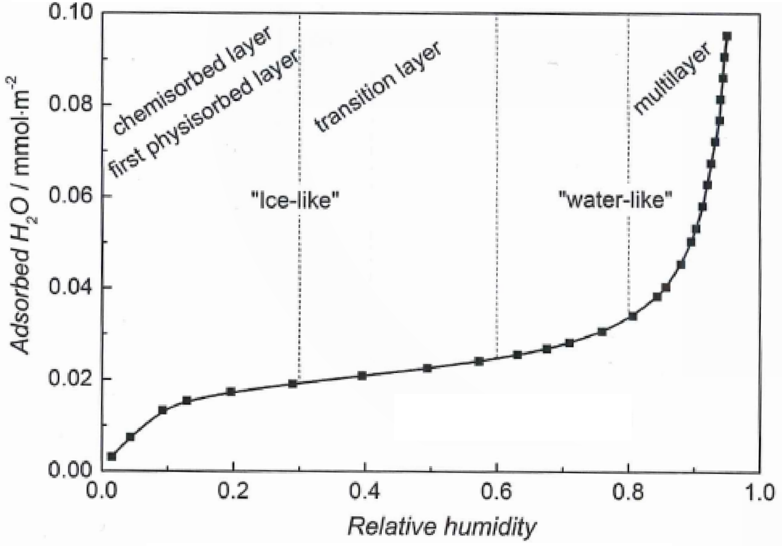
- Liquid-like physisorbed water at high RH
- Protonic surface conduction
- Enhanced by acidic or basic doping

- Filler particles open polymer nanostructure:
  - Ceramic and polymer internal surfaces
  - Ceramic-polymer interface

- Charge separation and space-charge effects
- «Job-sharing» principle

- Evaluate surface and interface protonic transport for ceramic-PBI composite membranes





Stub S., et al., J. Phys. Chem C, 121, 2017, 12817

Outlook

Catalysts **2018**, *8*(12), 657; https://doi.org/10.3390/catal8120657 Open Access Review

Earth-Abundant Electrocatalysts in Proton Exchange Membrane Electrolyzers

Xinwei Sun [1], Kaiqi Xu [1], Christian Fleischer [1], Xin Liu [1], Mathieu Grandcolas [2], Ragnar Strandbakke [1], Tor S. Bjørheim [1], Truls Norby [1] and Athanasios Chatzitakis [1,*]

- Medio 2019 – second review: «Composite membranes for PEM fuel cells at temperatures above 100 °C: a critical review», X. Sun *et al.*

- Develop method for *in-situ* formation of nanoparticles in Nafion® membranes

- Challenge established approaches on water retention etc.
    - Composite Nafion-ceramic membranes vs T, RH

- Surface/interface protonic conduction model for PBI-based composite membranes