PFAS-free electrolysis and fuel cells

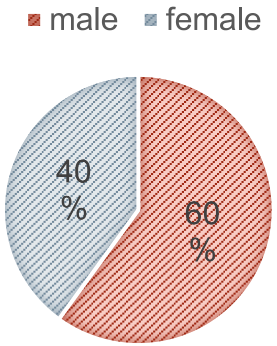
Carolin Klose, Andreas Münchinger, Severin Vierrath

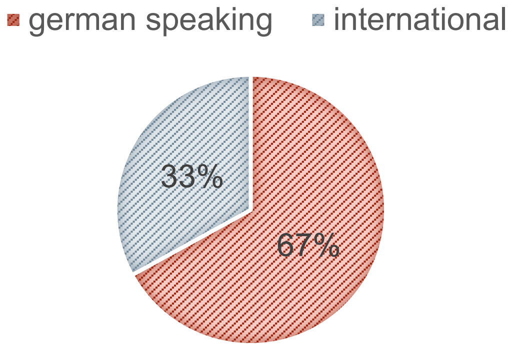
Electrochemical energy systems (EES) group

Host institutions:

- Hahn-Schickard (State-funded research institute in Baden-Württemberg)
- University of Freiburg

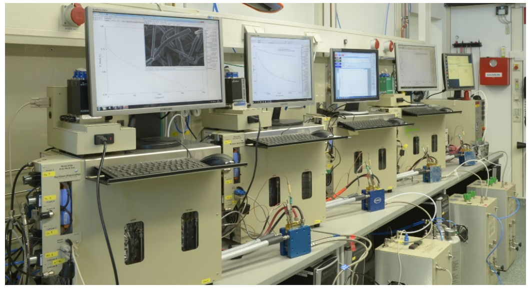
35 students with various backgrounds





https://www.ees-lab.org/

EES development circle



Novel Materials

- Polyme
- Catalys
- Electros
  Nanofib

Characterization

- Electrochemical characterization
- Electron microscopy + tomography
- Raman, XRD, BET, DLS, ...

MEAs

- Polymer elec
  (PEM/AEM)
- Fuel cells, electrolysis, (
  reduction
- Spray coating to roll-to-roll

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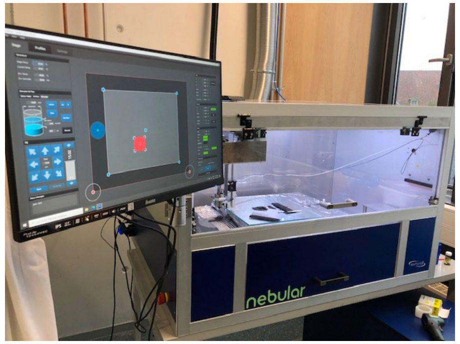

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Motivation to substitue PFSAs…

Hydrocarbon

- Potentially lower cost
- Potentially less environmental hazard
  - Synthesis
  - ~~Recycling of ionomer and catalyst~~
- **Suitable as membrane:**
  - Thermo-mechanically stable at high operating temperatures
  - Lower gas crossover
- Freedom in molecular design

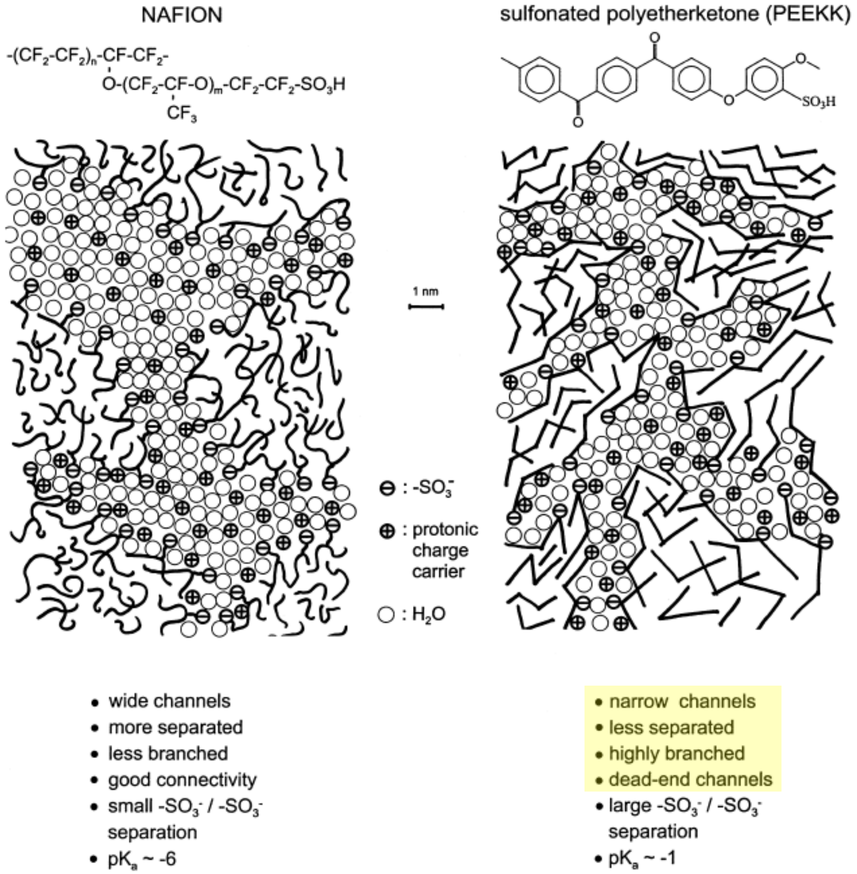
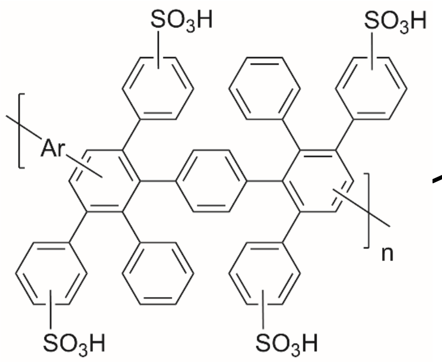


Fig. 2. Schematic representation of the microstructures of NAFION and a sulfonated polyetherketone (derived from SAXS experiments [19]) illustrating the less pronounced hydrophobic/hydrophilic separation of the latter compared to the first.

https://doi.org/10.1016/S0376-7388(00)00632-3

Hydrocarbon ionomers (fluorine free)



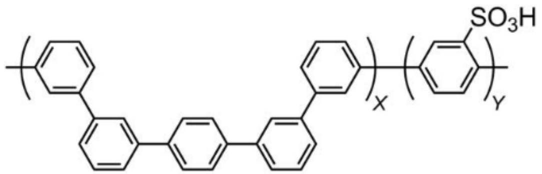
sulfonated phenylated polyphenylene

Prof. Holdcroft, Simon Fraser University (sPPB)
&
Ionomr (Pemion®)

Adamski, M.; Skalski, T. J. G.; Britton, B.; Peckham, T. J.; Metzler, L.; Holdcroft, S. Highly Stable, Low Gas Crossover, Proton-Conducting Phenylated Polyphenylenes. Angewandte Chemie (International ed. in English) **2017**, *56*, 9058–9061.

Balogun, E.; Adamski, M.; Holdcroft, S. Communication—Non-Fluorous, Hydrocarbon PEMFCs, Generating > 1 W cm −2 Power. *J. Electrochem. Soc.* **2020**, *167*, 84502.

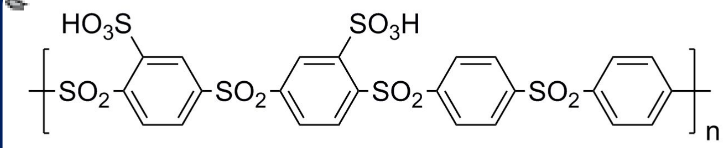
Fuel cell



sulfonated polyphenylene

Prof. Miyatake, Yamanashi University

Miyake, Junpei, et al. "Design of flexible polyphenylene proton-conducting membrane for next-generation fuel cells." *Science Advances* 3.10 (2017): eaao0476.



sulfonated polysulfone

K.D. Kreuer, MPI Stuttgart & Fumatech

Taken from: Schuster, M., et al., (2007). *Macromolecules*, *40*(3), 598-607.

Klose, C.; Saatkamp, T.; Münchinger, A.; Bohn, L.; Titvinidze, G.; Breitwieser, M.; Kreuer, K.-D.; Vierrath, S. All-Hydrocarbon MEA for PEM Water Electrolysis Combining Low Hydrogen Crossover and High Efficiency. Adv. Energy Mater. **2020**, *10*, 1903995.

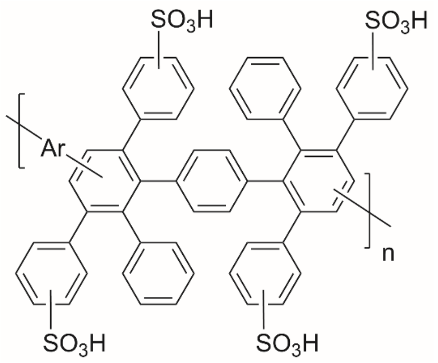
Water electrolysis

HC ionomers in catalyst layer – protonic conductivity

Bird, Ashley

&

Liepold, Hannes



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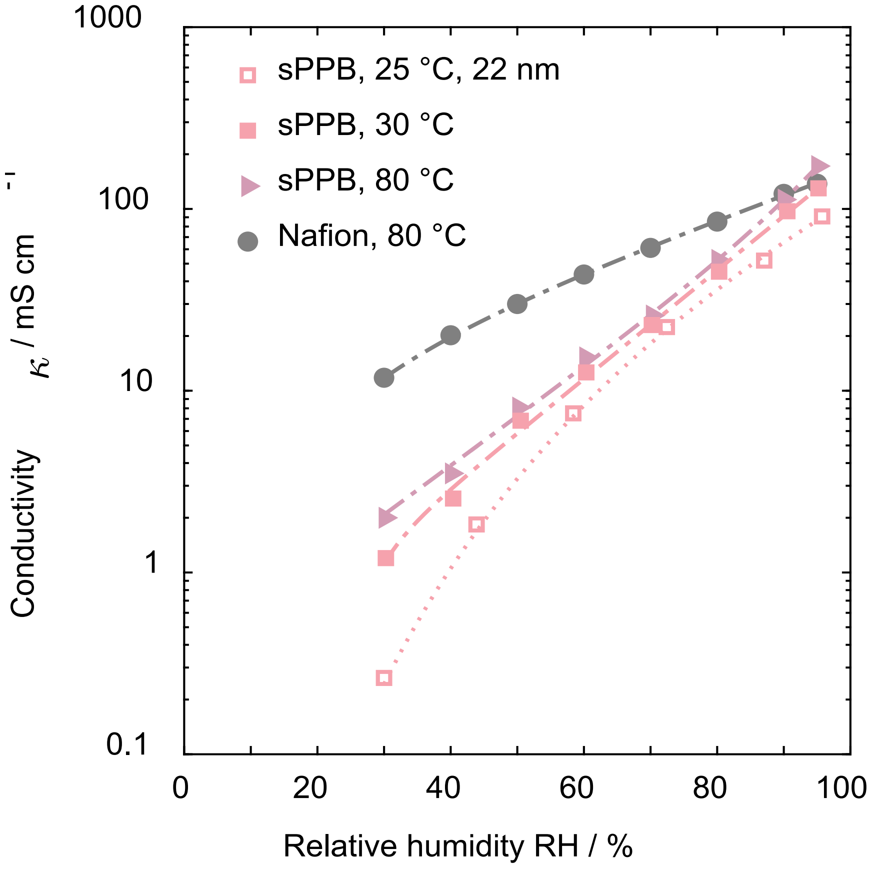


Proton conductivity

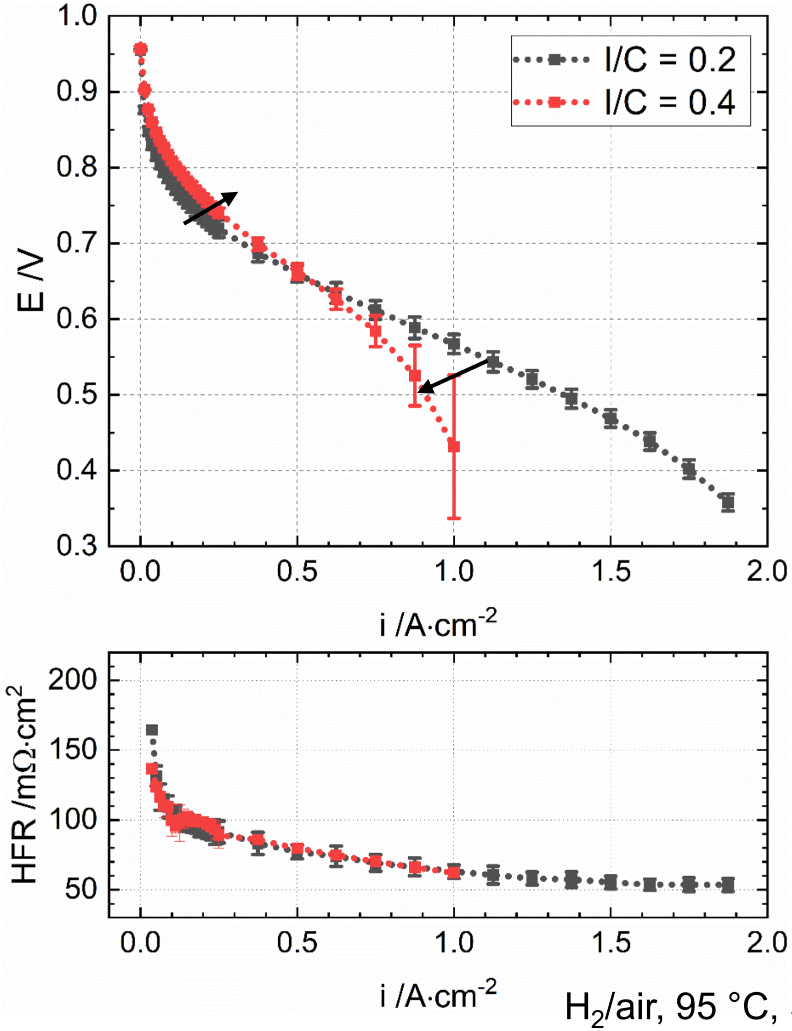
- Comparable proton conductivity for HC and PFSA at high RH
- Significant drop of proton conductivity for HC at low RH
- HC thin films are particularly affected

How to improve

- Increasing the I/C
- Gradient ionomer CL
- Thinner CL

HC ionomers in catalyst layer – increasing I/C ratio

Nguyen, H. et al. *Mater. Adv* 2022, 3, 8460-8468.



H_2/air, 95 °C, 50 % RH, 250 kPa_{abs}

Higher ionomer to carbon ratio of HC electrodes

- Improves proton conductivity
  → Improved performance at low-current density
- Limits mass transport
  → Lower performance at high-current density

HC ionomers in catalyst layer – thinner catalyst layer

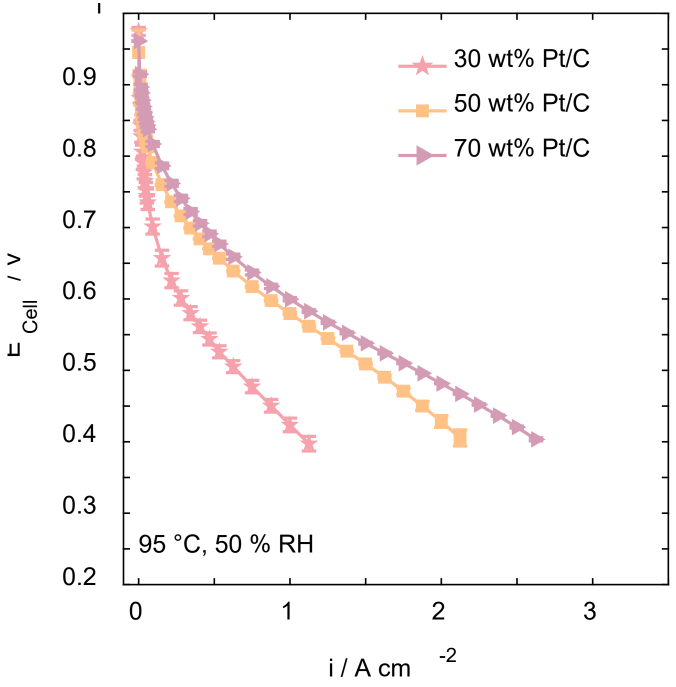
Liepold, Hannes

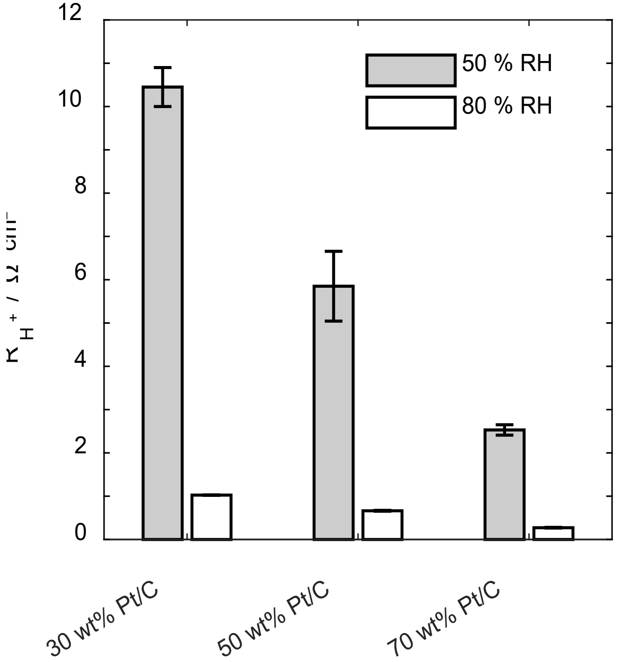
Hahn Schickard

- Catalysts with different Pt/C ratios were investigated
- 70 wt% Pt/C yields much thinner electrodes as 30 wt% Pt/C at similar Pt loading
- ECSA lower for higher Pt/C wt% due to less dispersed Pt particles
- Low H+ resistance outweighs low ECSA

→ Thin electrodes beneficial for HC electrodes

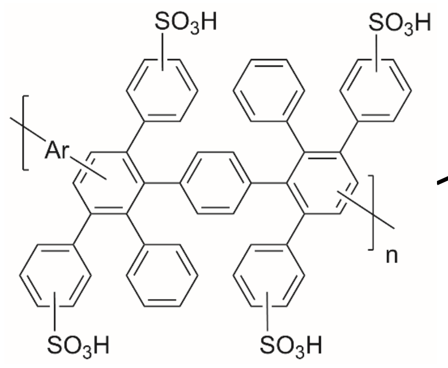
- No effect on mass transport





Pt/C ratio constant total laoding: 0.4 mg_{Pt}/cm^2	ECSA ($m^2\ g^{-1}$)	δ_{CL} (μm)	i at 0.75 V ($A\ cm^{-2}$)	
			50 % RH	80 % RH
30 wt% Pt/C	**82** ± 2	15.9 ± 0.5	50 ± 7	106 ± 5
50 wt% Pt/C	**66** ± 3	9.3 ± 0.5	180 ± 3	315 ± 15
70 wt% Pt/C	**48** ± 1	3.7 ± 0.6	251 ± 11	346 ± 12

hydrocarbon ionomers - water electroysis



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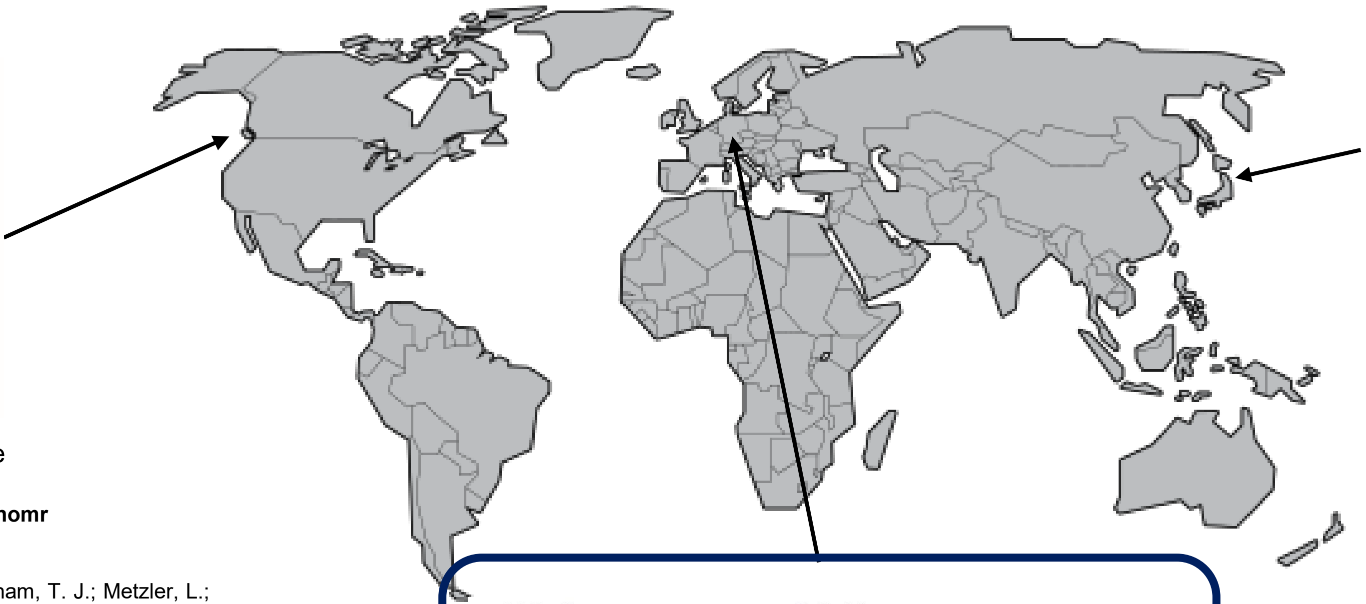

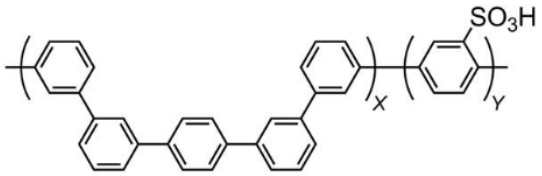

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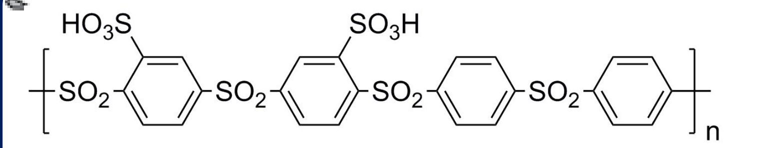

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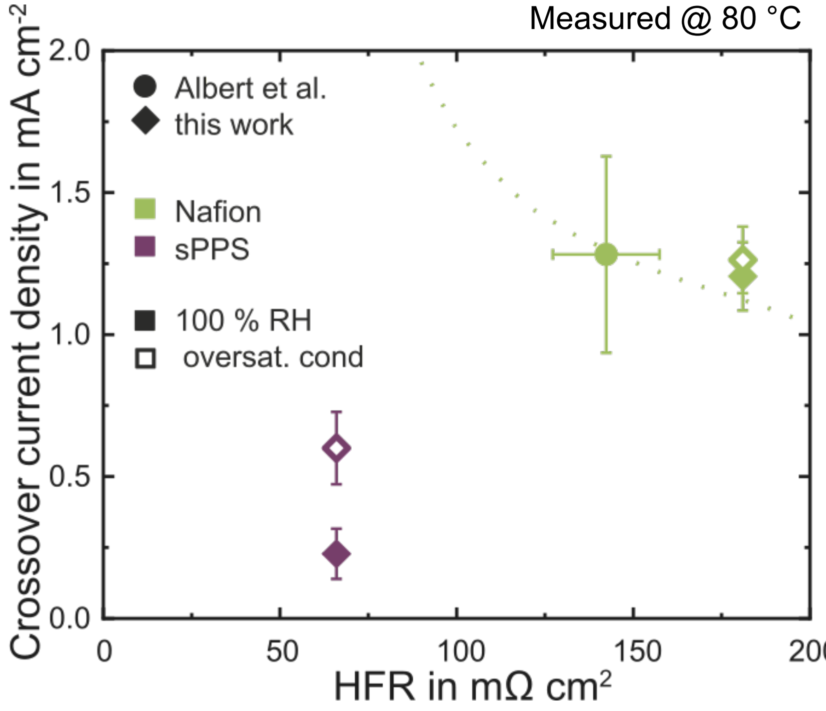
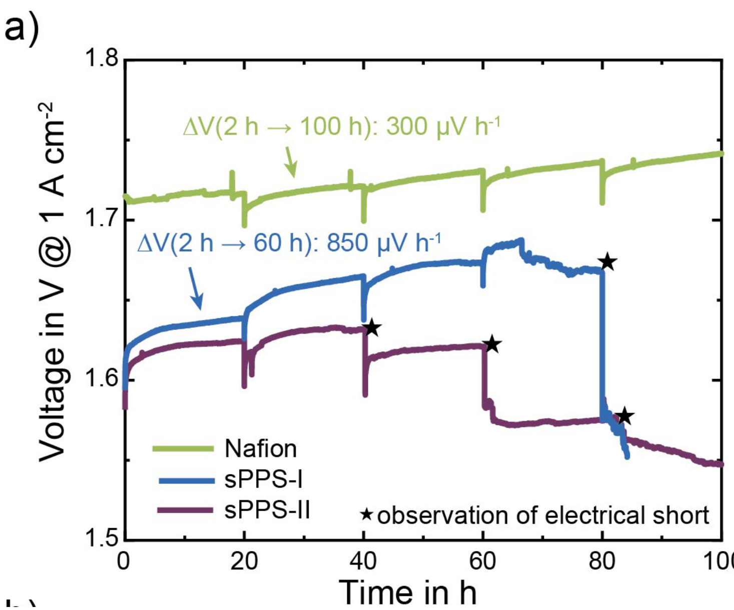
Sulfonated poly-phenylene-sulfones (sPPS) in PEMWEs

- Crossover measurement in PEMFC setup @ 2.5 bar (humidification by water vapour)
- 3 times lower crossover for sPPS membranes @ 100 % RH
- 2 times lower crossover for sPPS membranes at oversaturated conditions





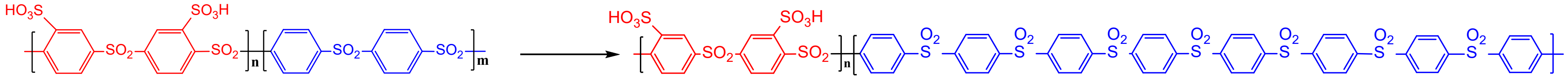
A. Albert, A.O. Barnett, M.S. Thomassen, T.J. Schmidt, L. Gubler, ACS applied materials & interfaces 7 (2015) 22203–22212.

Klose, C. Saatkamp, T., Münchinger A., Bohn L., Titvinidze G., Breitwieser M., Kreuer Klaus-Dieter, and Vierrath S., (2020). **Advanced Energy Materials**

Tailoring the polymer structure

sPPS with „blocky“ structure

- Increase length of unsulfonated fragments, while keeping total amount of unsulfonated phenyl rings same
- sPPS-400 → SPPS-400-XXL, IEC = 2.5 meq g^{-1}



- Lower swelling of „blocky“ membrane
- Casting of PE-reinforced membrane on pilot line
- Reduced water uptake enables CCM fabrication by direct coating of electrodes with solvent based ink

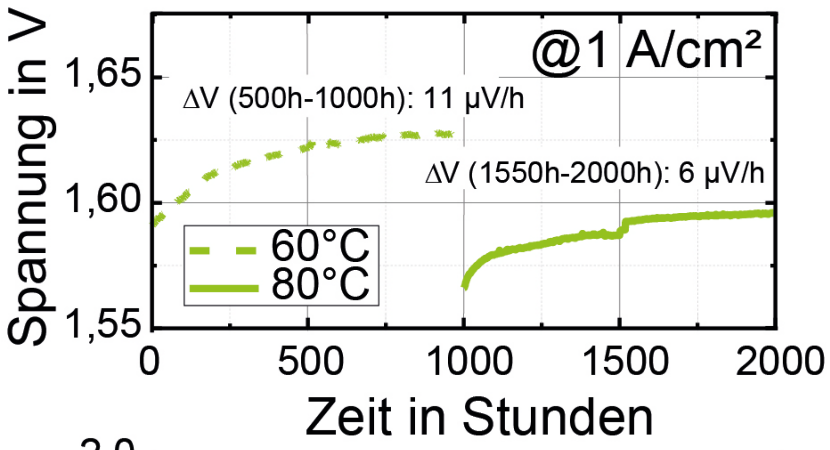
Giorgi Titvinidze
Nodar Dumbadze

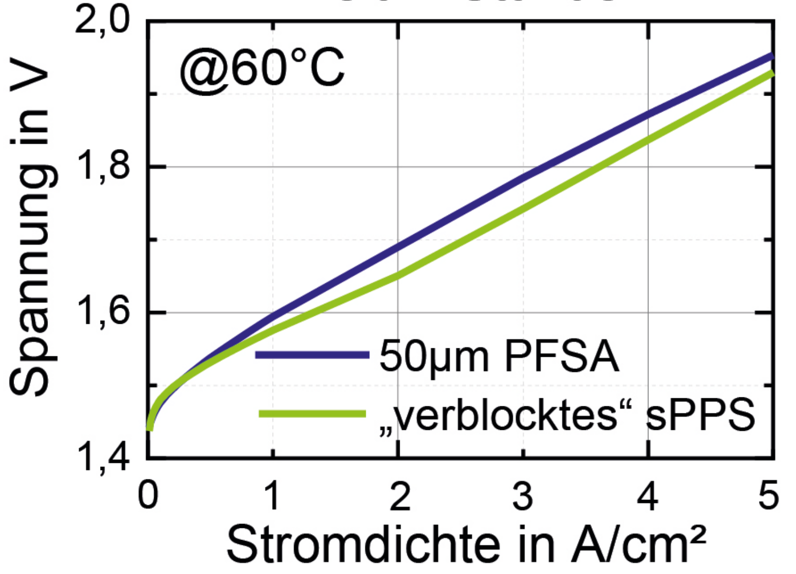
Clara Schare
Andreas Münchinger

Long-term stability: S400-XXL

Clara Schare

- Hydrocarbon CCM:
  - Membrane: 20 µm S400-XXL with 5 µm PE reinforcement
  - Anode: IrO_2, 1 mg_{Ir}/cm^2, 10 w% Nafion in solids
  - Cathode: GDEs, 0.5 mg_{Pt}/cm^2, 27 w% I/C
- Stability test: Constant current @ 1 A/cm^2
  - 1000 h @60 °C followed by 1000 h @80°C
  - Degradation rate: < 15 µV/h (500 h → 1000 h & 1550 → 2000 h)





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Summary: PFAS-free / hydrocarbon based ..

PEM fuel cells

- Potential advantages: higher temperature
- Current challenge: dry operation

PEM electrolyzers

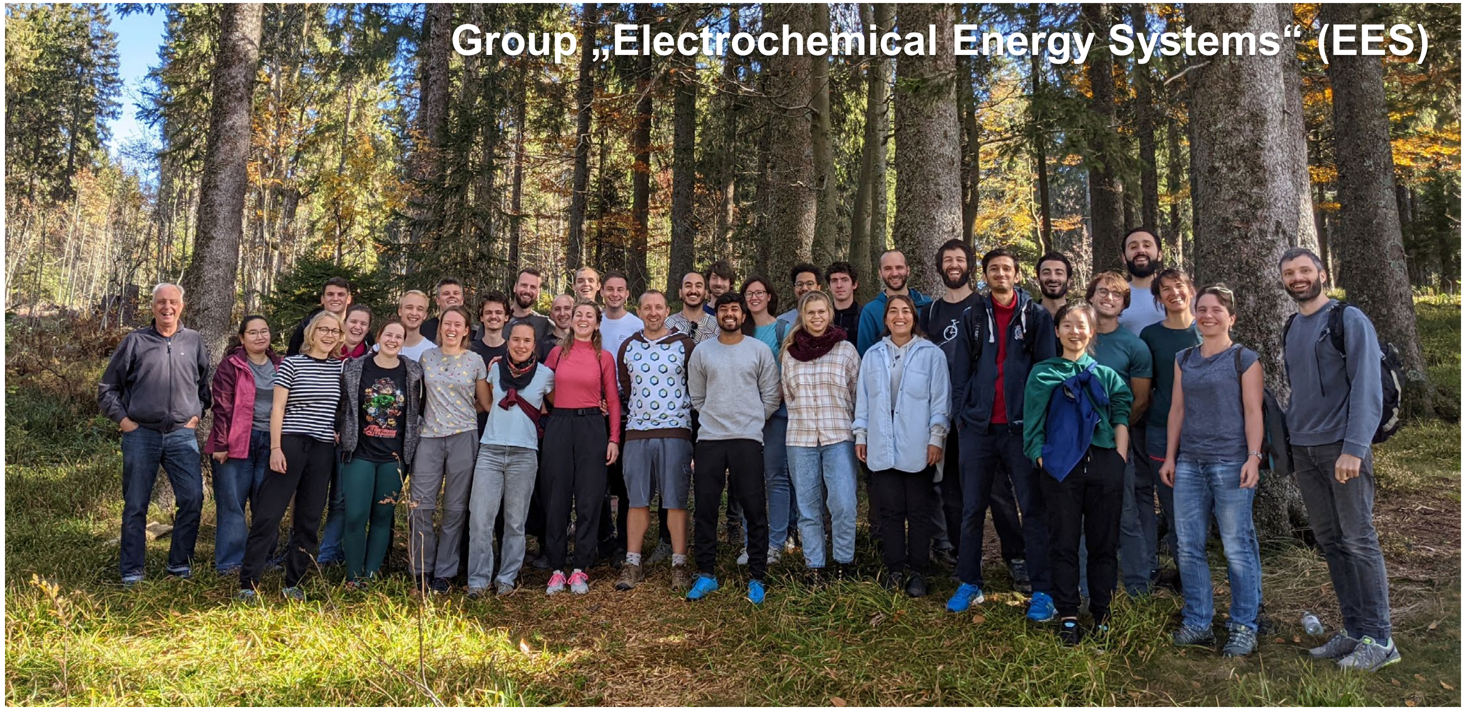
- Potential advantages: thinner membranes
- Current challenge: long-term stability

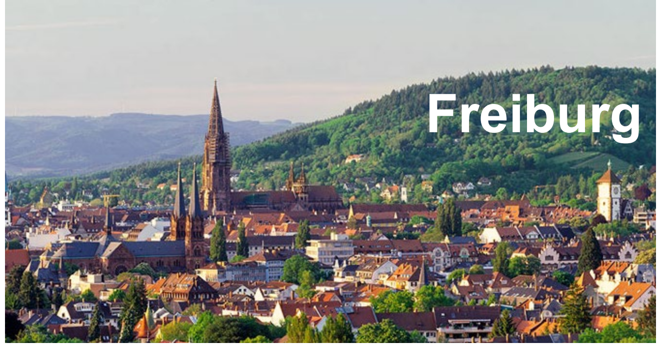
AEM electrolyzers

- Are also PFAS-free!
- (and iridium-free)

Thank you for your attention!

FIT IMTEK Hahn Schickard





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