Hydrocarbon electrolytes with nitrile groups for direct methanol fuel cells

Hürter, Stefan; Müller, Martin; Guiver, Michael D.; Scoles, Ludmila; Stolten, Detlef

For the publisher's version, please access the DOI link below./ Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

https://doi.org/10.4224/21085172

Mitglied der Helmholtz-Gemeinschaft

JÜLICH FORSCHUNGSZENTRUM

Hydrocarbon Electrolytes with Nitrile Groups for Direct Methanol Fuel Cells

Stefan Hürter

Martin Müller, Michael D. Guiver, Ludmilla Scoles, Detlef Stolten

19th World Hydrogen Conference 2012, Toronto, Ca

7th June 2012

Outline

- Characteristics of a DMFC system
- New membranes for DMFCs
  - Structure
  - Properties
- Application of membranes in DMFC applications
- Different MEA- preparation procedures
  - MEA- assembling by hot pressing
  - Sandwich-MEA

DMFC System: Introduction

Characteristics (DMFC V3.3)

Membrane material: Nafion 115

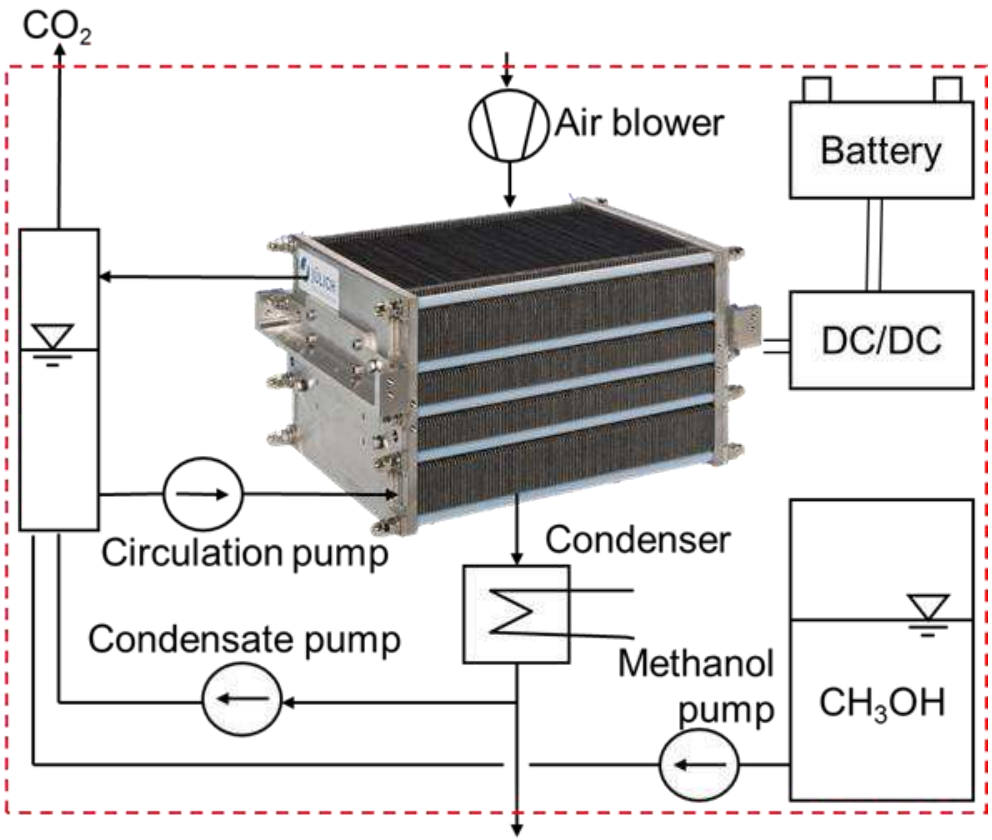
Stack temperature: 60 - 70 °C

Fuel: pure methanol

Fuel utilization: ~ 65 %

Efficiency FC: ~ 30 %

DMFC: Function and Characteristics

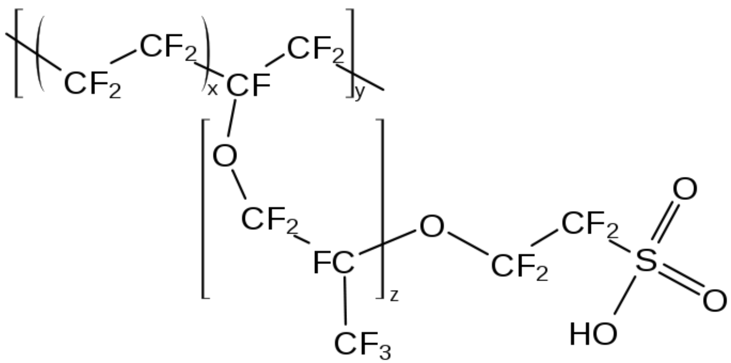


- ~ 30% Fuel loss during operation due to methanol permeation
  - → Reduction of fuel efficiency
- Water permeation during operation
  - → Large amount of water which has to be recycled within system (0.24 g/(h*cm^2) @ 70 °C)

Target:
Decrease of MeOH- and H_2O-Permeation through utilization of sulfonated Poly(Ether Ether Nitriles)

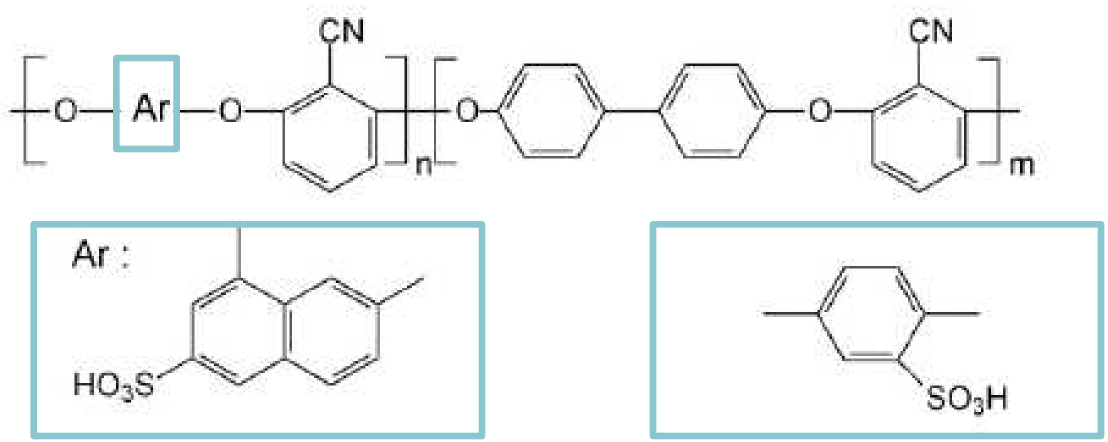
Alternative Membranematerial: Structure

Nafion



Journal of Membrane Science 326 (2009) 721–726

Sulfonated Poly(aryl ether ether nitrile)s-sPAEENs

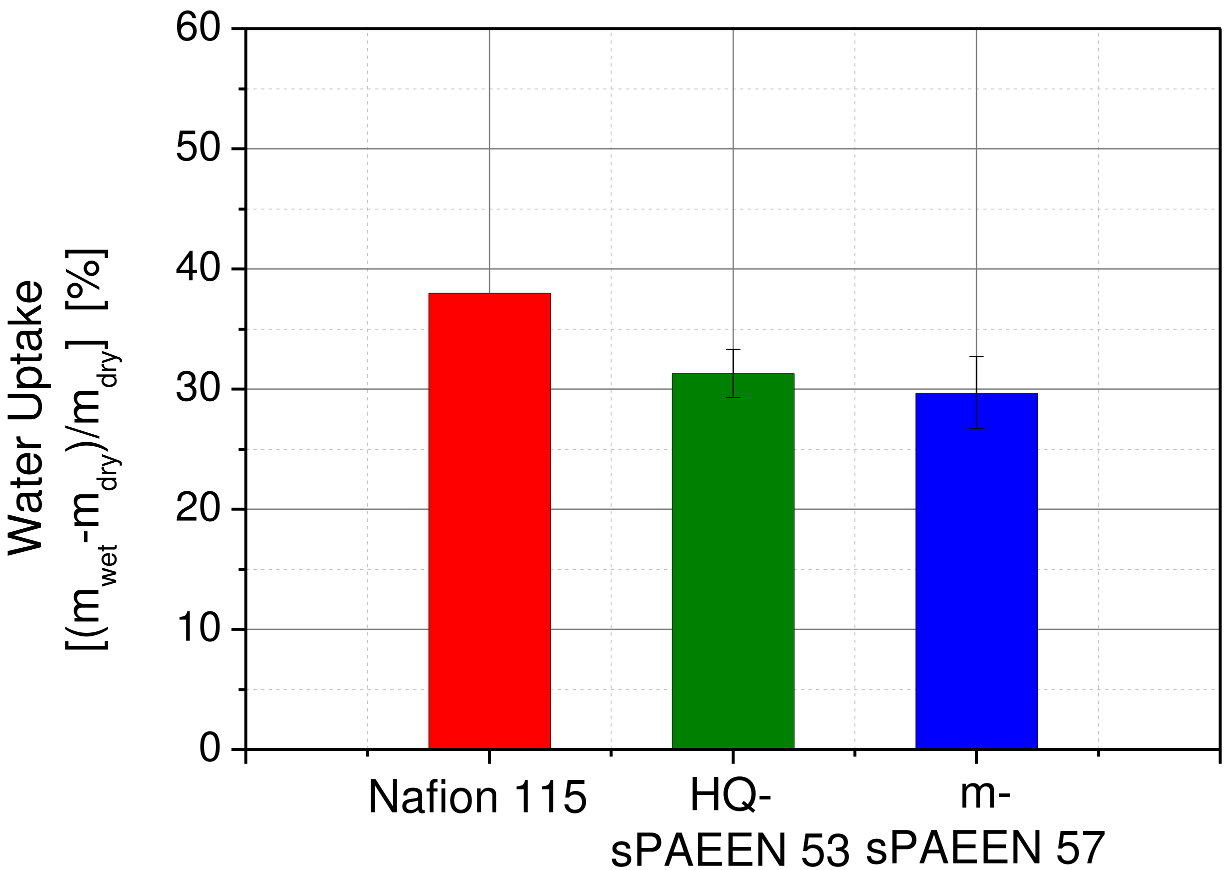


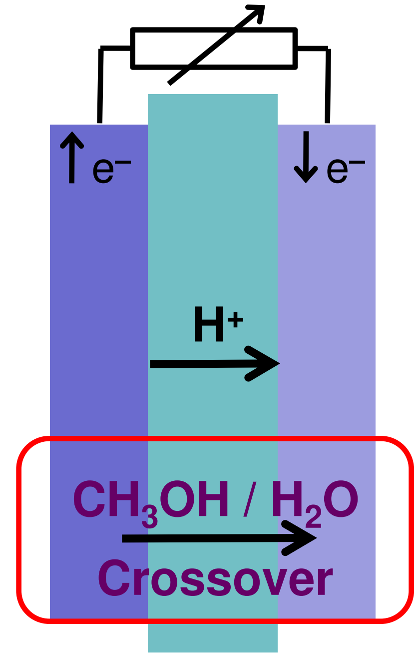
(*m*-SPAEEN) (*HQ*-SPAEEN)

Kim, Kim, Guiver, Pivovar, J. Membrane Sci. 321 (2008) 199

Target:
Low water uptake
→ Low MeOH- and H_2O permeation
High proton conductivities
→ Low cell resistance

Water Uptake: sPAEEN-membranes





Membrane- Electrode- Assembly (MEA)

Nafion 115: DuPont product information

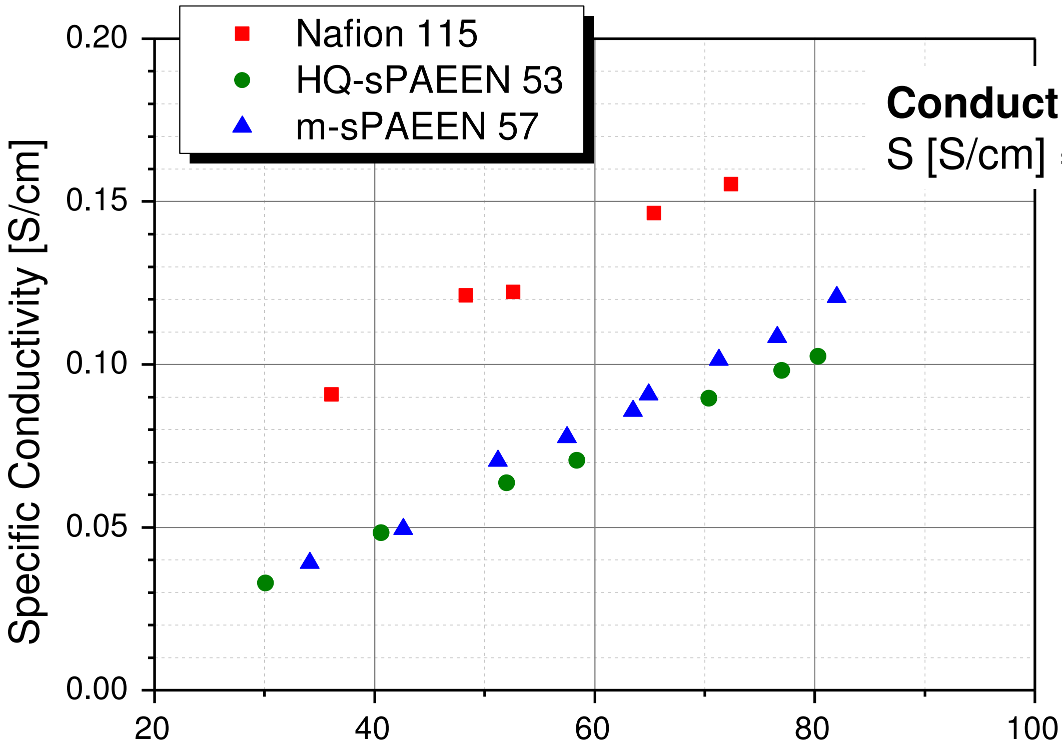
Testing conditions:

Drying of membrane: 6h at 60°C

Wetting of sample for 3h at 80°C, then for 24h at RT in deionized water

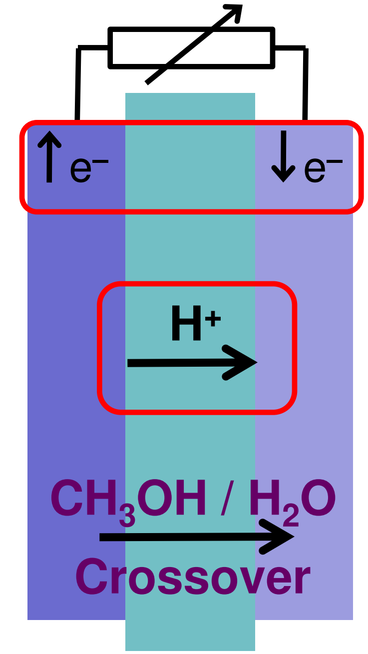
Calculation of WU by remeasuring the weight of the sample (dry and wet)

Conductivity sPAEEN-Membranes



Relative Humidity: φ= 100%

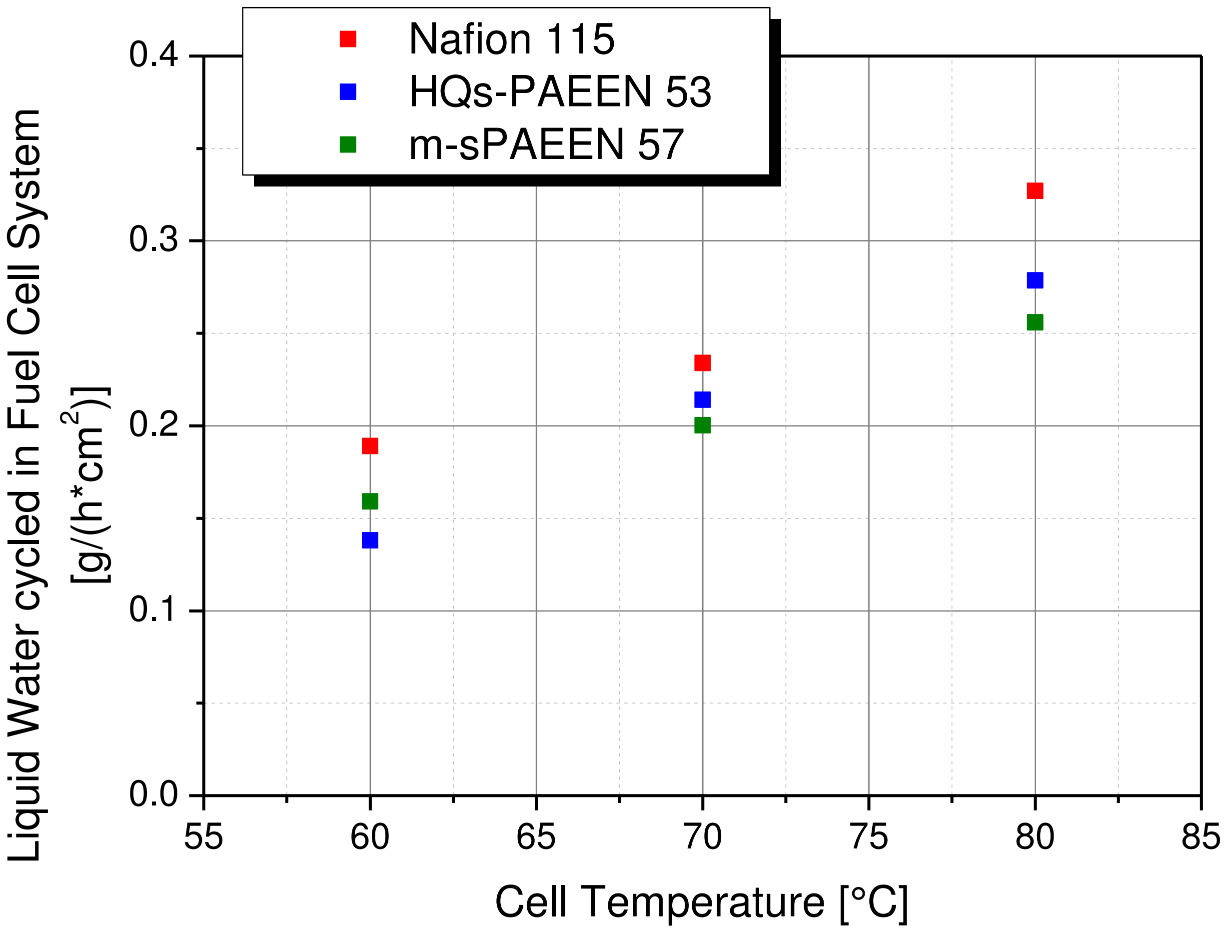
Conductivity
S [S/cm] = d / (R*A)



Membrane- Electrode- Assembly (MEA)

	Degree of sulfonation [n/(n+m)]	IEC calc. [meq/g]	Thickness [µm]	**Areic membrane resistance at 70°C [Ohm*cm²]**
Nafion 115	n.a.	0.89	127	**0.085**
HQ-sPAEEN	53	1.84	39	**0.043**
m-sPAEEN	57	1.80	40	**0.04**

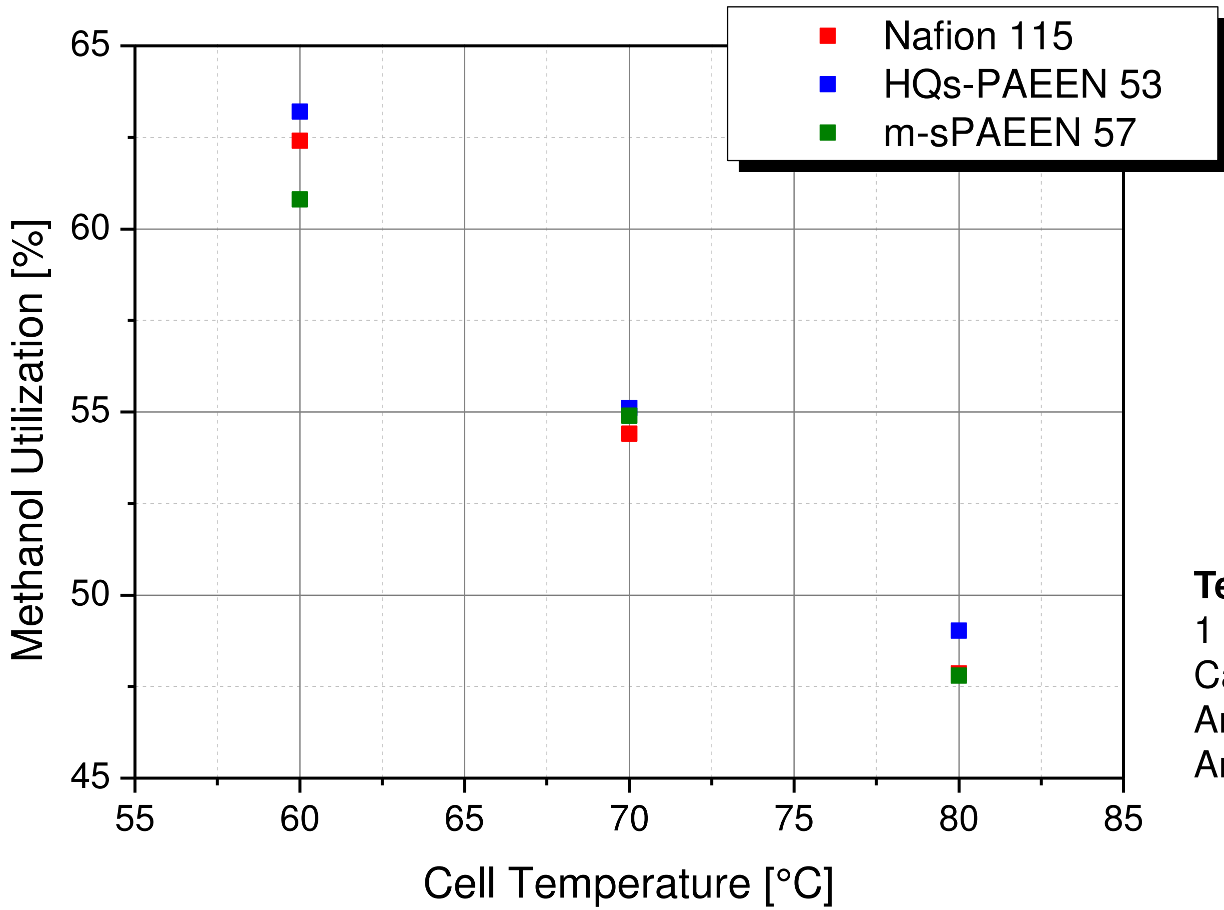
Water Management of FC System



Testing conditions: j= 0.1 A/cm²
1 M aq. MeOH / air
Cathodic Flow Rate: 20 ml / (min*cm²)
Anodic Flow Rate: 0.22 ml / (min*cm²)
Ambient Pressure

Lower amount of liquid water cycled in FC system lower when sPAEEN membranes are utilised

Methanol Utilization of HQ- and m-sPAEEN

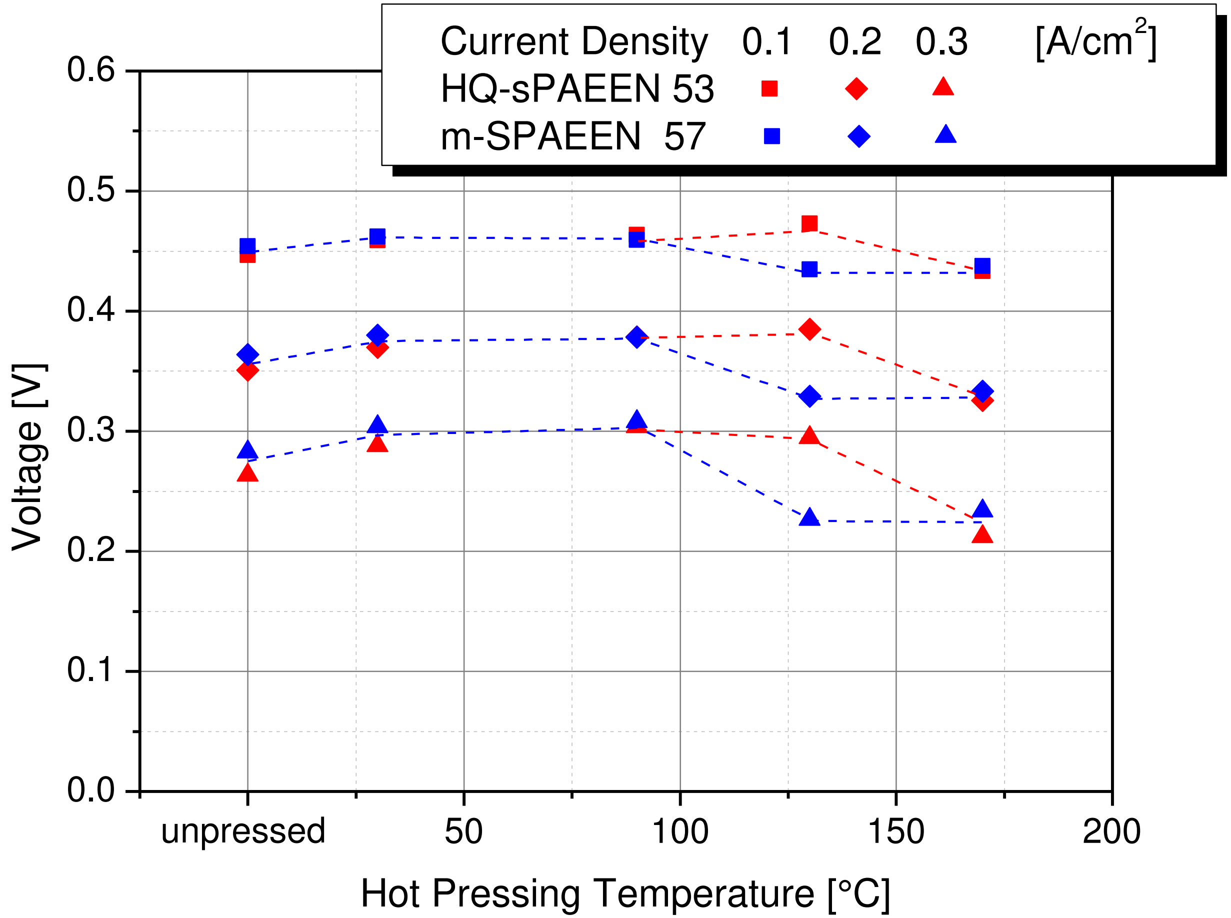


Testing conditions: j= 0.1 A/cm²
1 M aq. MeOH / air
Cathodic Flow Rate: 20 ml / (min*cm²)
Anodic Flow Rate: 0.22 ml / (min*cm²)
Ambient Pressure

HQ-sPAEEN MEAs with higher methanol utilization than MEAs with Nafion 115

m-sPAEEN MEAs show comparable or worse methanol utilization than MEAs with Nafion 115

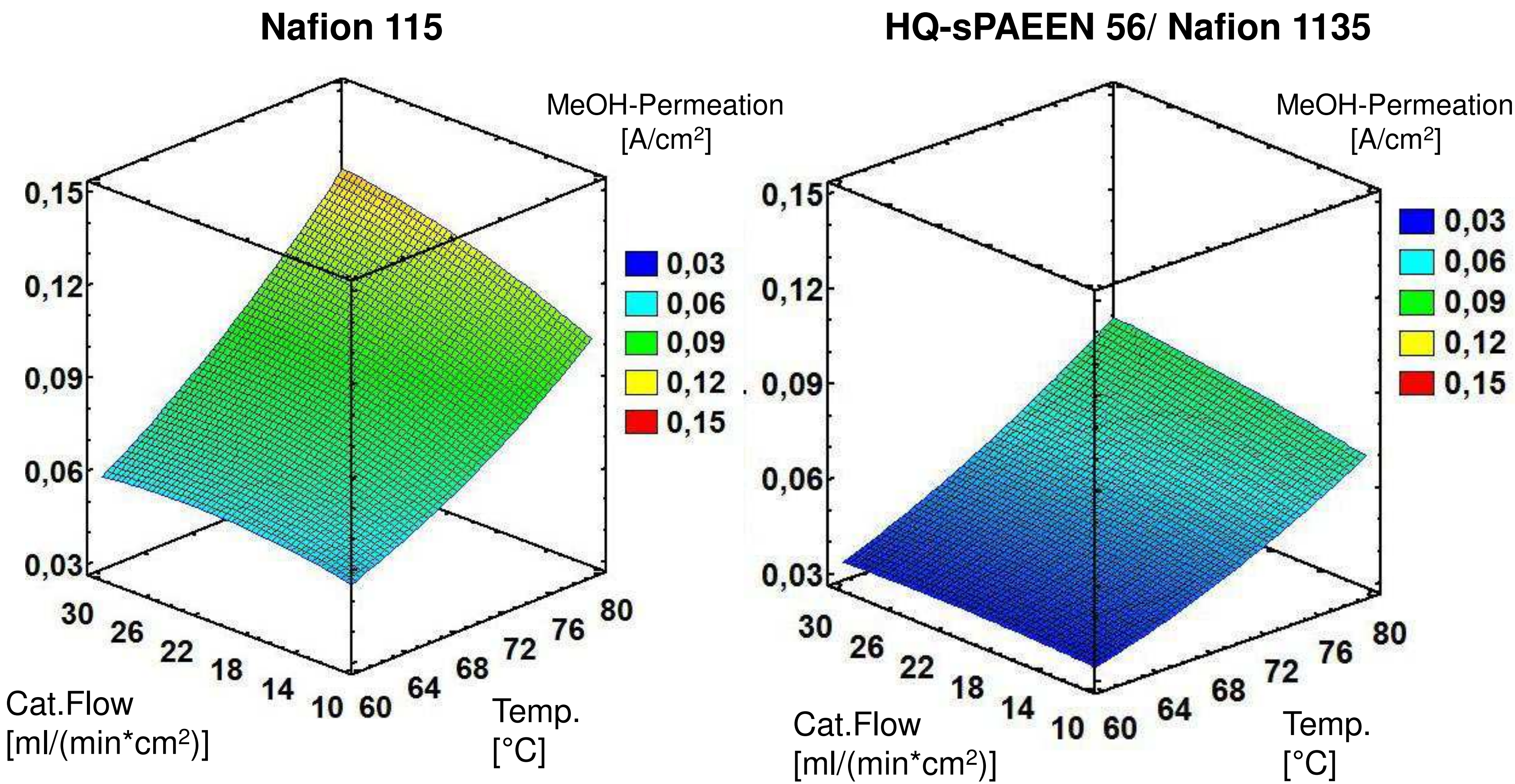
Influence Hot Pressing Temperature on sPAEEN- MEAs



Testing conditions: j= 0.1 A/cm²
1 M aq. MeOH / air
Cathodic Flow Rate: 36.5 ml / (min*cm²)
Anodic Flow Rate: 0.22 ml / (min*cm²)
Ambient Pressure
T= 70 °C

Decrease of MEA performance with increasing hot pressing temperatures
→ Increase of MEA resistance
→ Decrease of proton conductivity

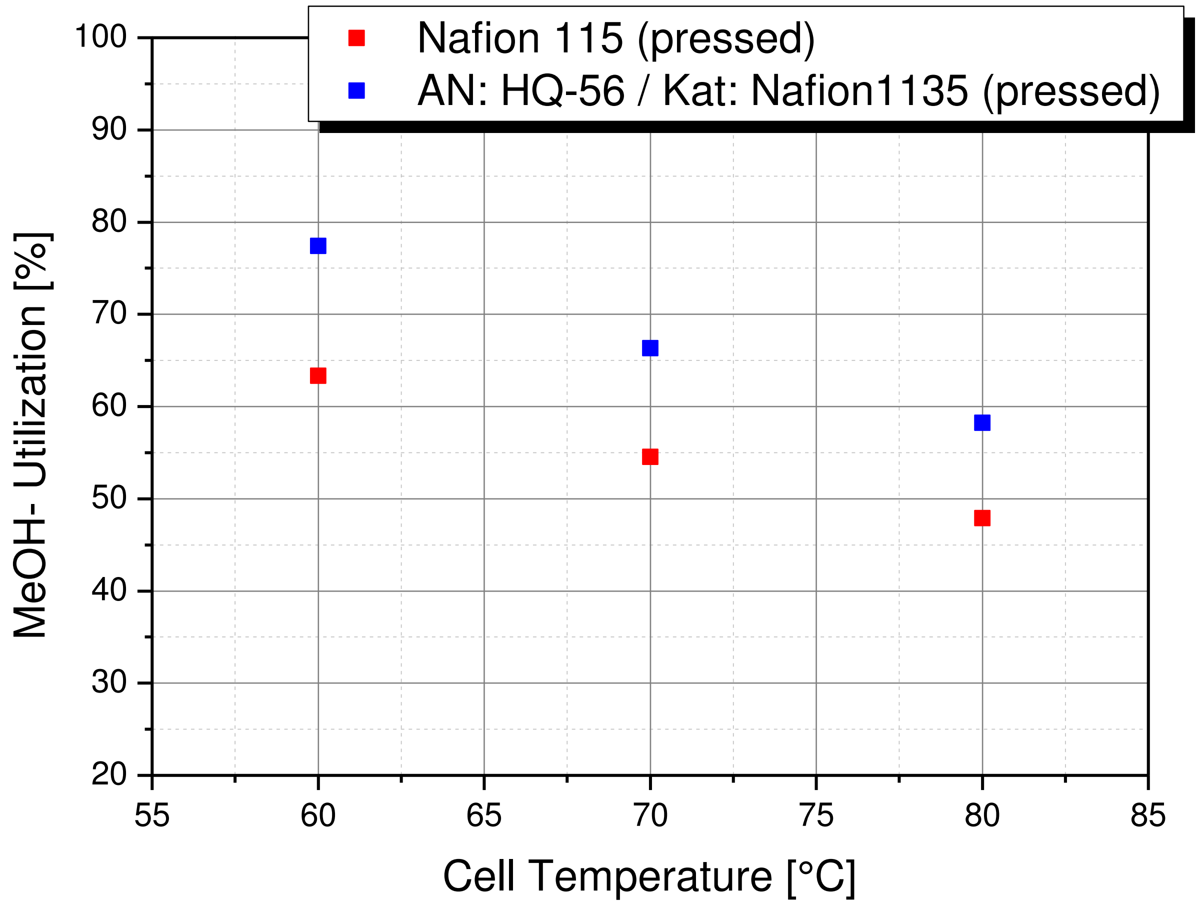
Sandwich MEA: Characteristic Methanol Permeation



Testing conditions: j= 0.1 A/cm^2

1 M aq. MeOH / air; Anodic Flow Rate: 0.22 ml / (min*cm^2); Ambient Pressure

Methanol Utilization Sandwich MEA



Testing conditions: j= 0.1 A/cm²

1 M aq. MeOH / air

Cathodic Flow Rate: 15.0 ml / (min*cm²)

Anodic Flow Rate: 0.22 ml / (min*cm²)

Ambient Pressure

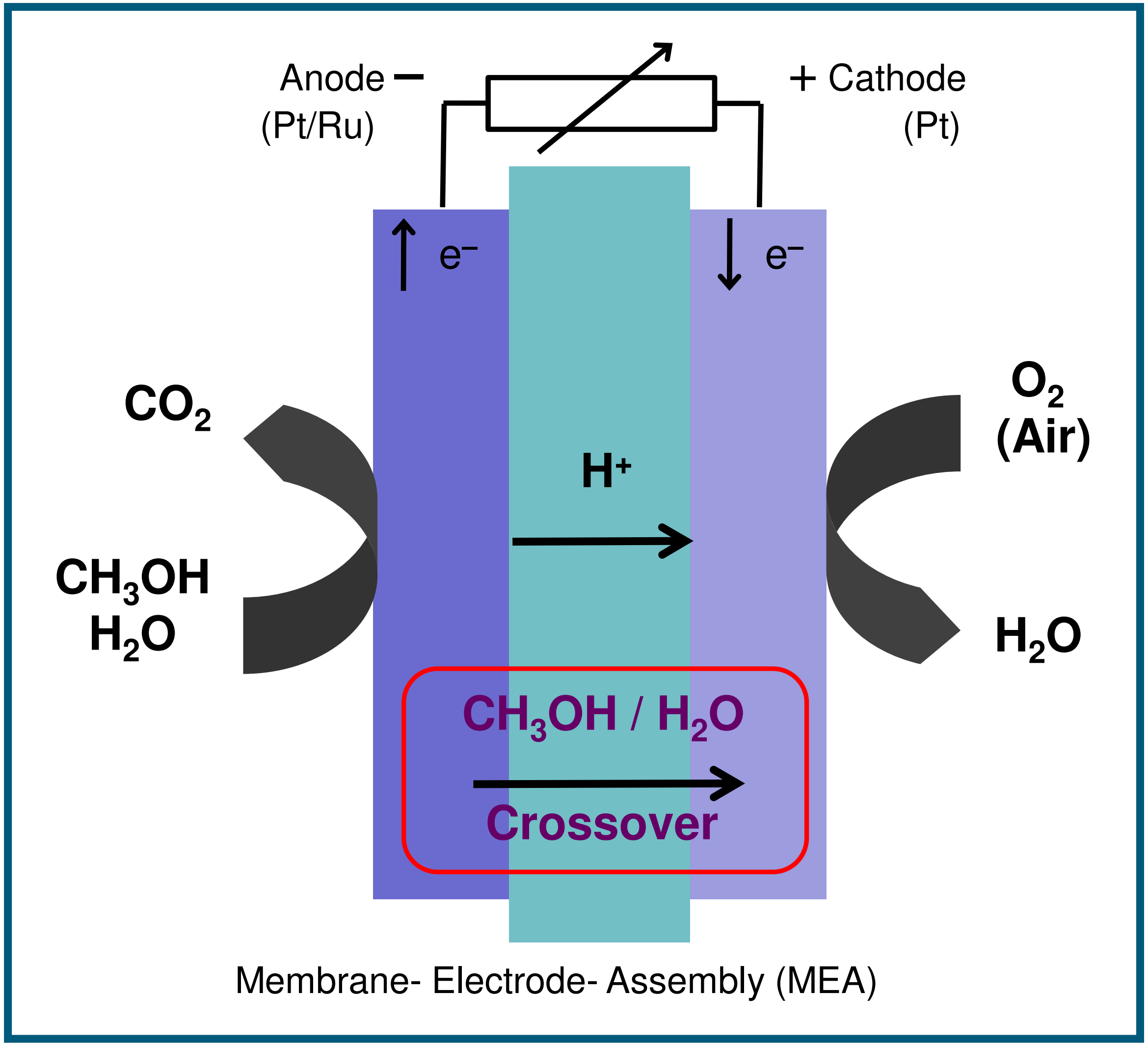
Summary sulfonated Poly(Aryl Ether Ether Nitriles)

- Lower methanol permeation of MEAs with sPAEEN-membranes leads to a higher methanol utilization (increase of ~3 %)
- Reduced water flux through sPAEEN membranes leads to lower amount of of cycled water in the DMFC system (reduction of ~25 %)
- MEA assembling at high temperatures leads to performance loss (~10 %)
- Sandwich MEA with HQ-sPAEEN 56 and Nafion 1135 leads to large decrease of methanol permeation (~35 %)
  - Increase of methanol utilization of ~15 %

Thank you for your attention!

Bundesministerium
für Wirtschaft
und Technologie

DMFC: Function and Characteristics



Anode Reaction:
$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode Reaction
$^3/_2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

Complete Reaction
$CH_3OH + ^3/_2O_2 \rightarrow CO_2 + 2H_2O$