AMFC Challenges – Membrane Electrode Assembly

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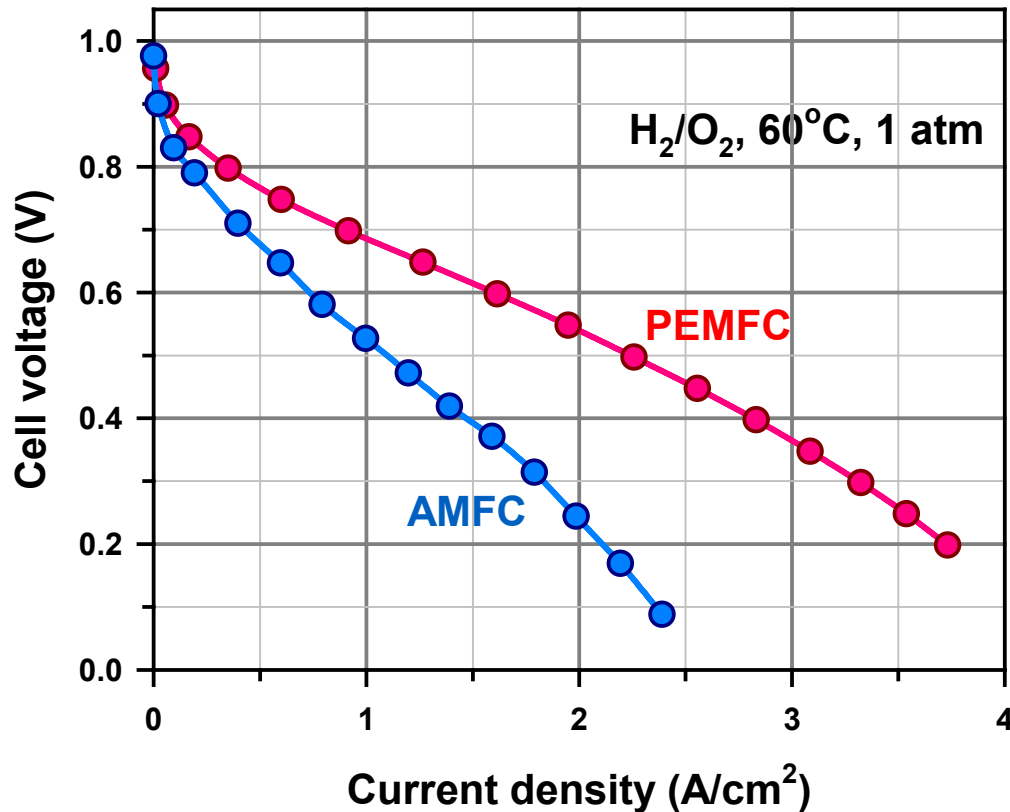
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Objective

Comparison of PEMFC and AMFC performance

Anode/cathode catalyst: Pt/C 0.4 mg_{Pt}/cm^2; AMFC membrane: 50 μm thick, aQAPS-S_8; PEMFC membrane: 50 μm thick, Nafion 212, fully humidified H_2/O_2

H_2/O_2, 60°C, 1 atm

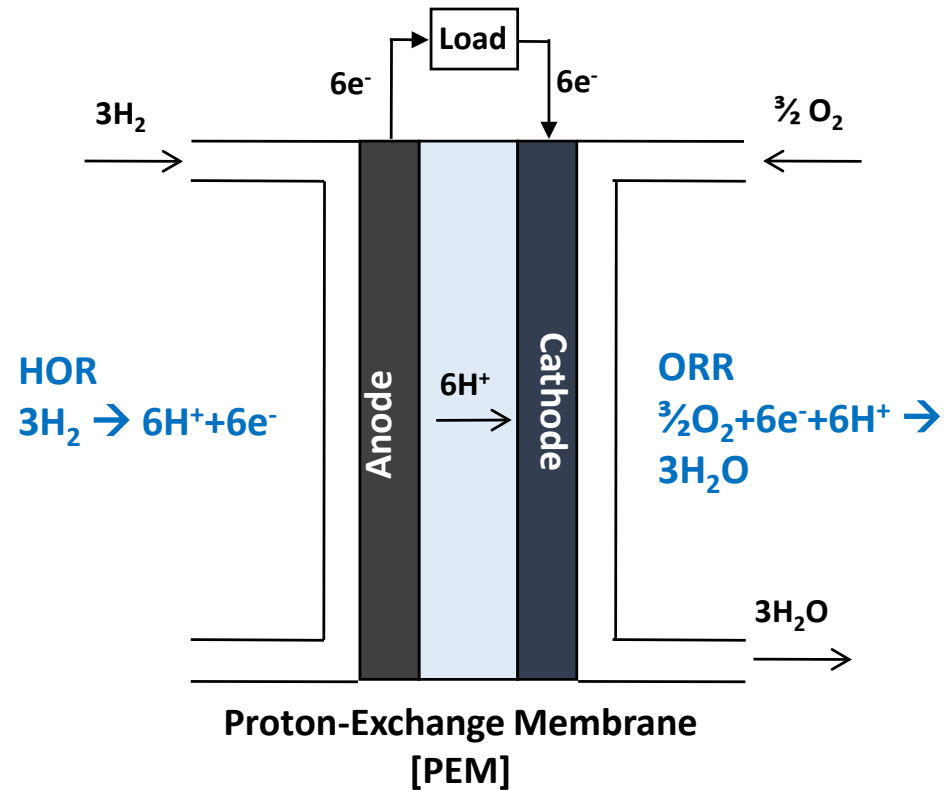PEMFC

AMFC

Cell voltage (V)

Current density (A/cm²)

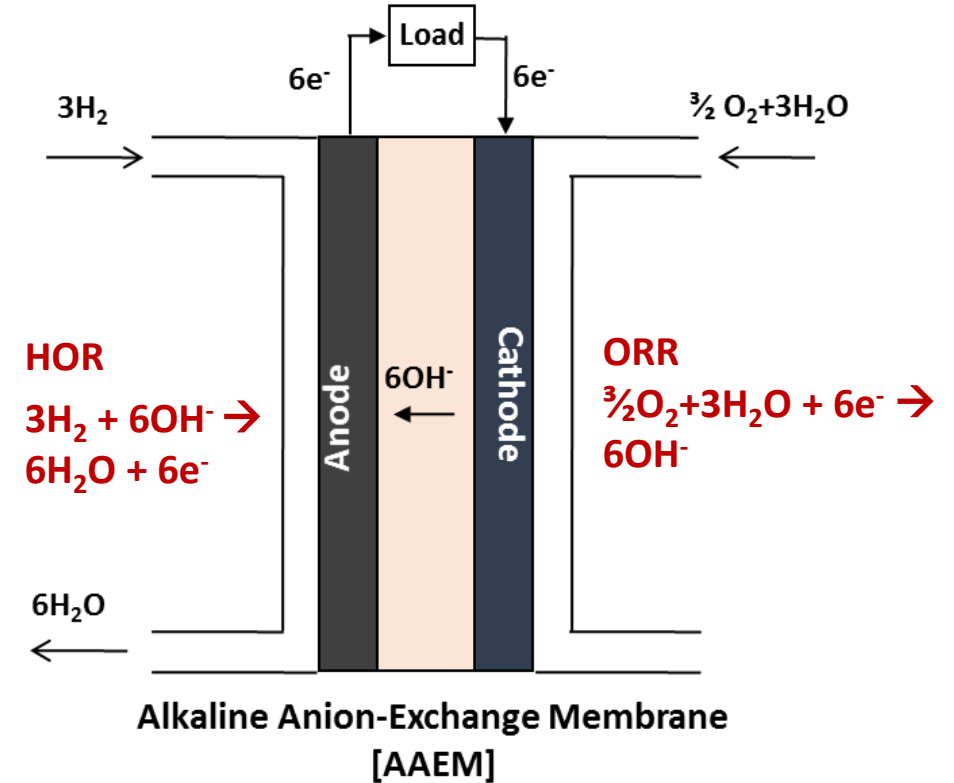**AMFC performance: Y. Wang et al.** *Energy & Environmental Sci.* 2015, 8, 177

- PEMFC performance is significantly better than AMFC when Pt/C catalyst used under same operating condition.

- The performance difference cannot be explained only by the difference of membrane resistance.

- The objective of this talk is to review the AMFC MEA issues that may result in such performance difference.

Comparison between PEMFC and AMFC
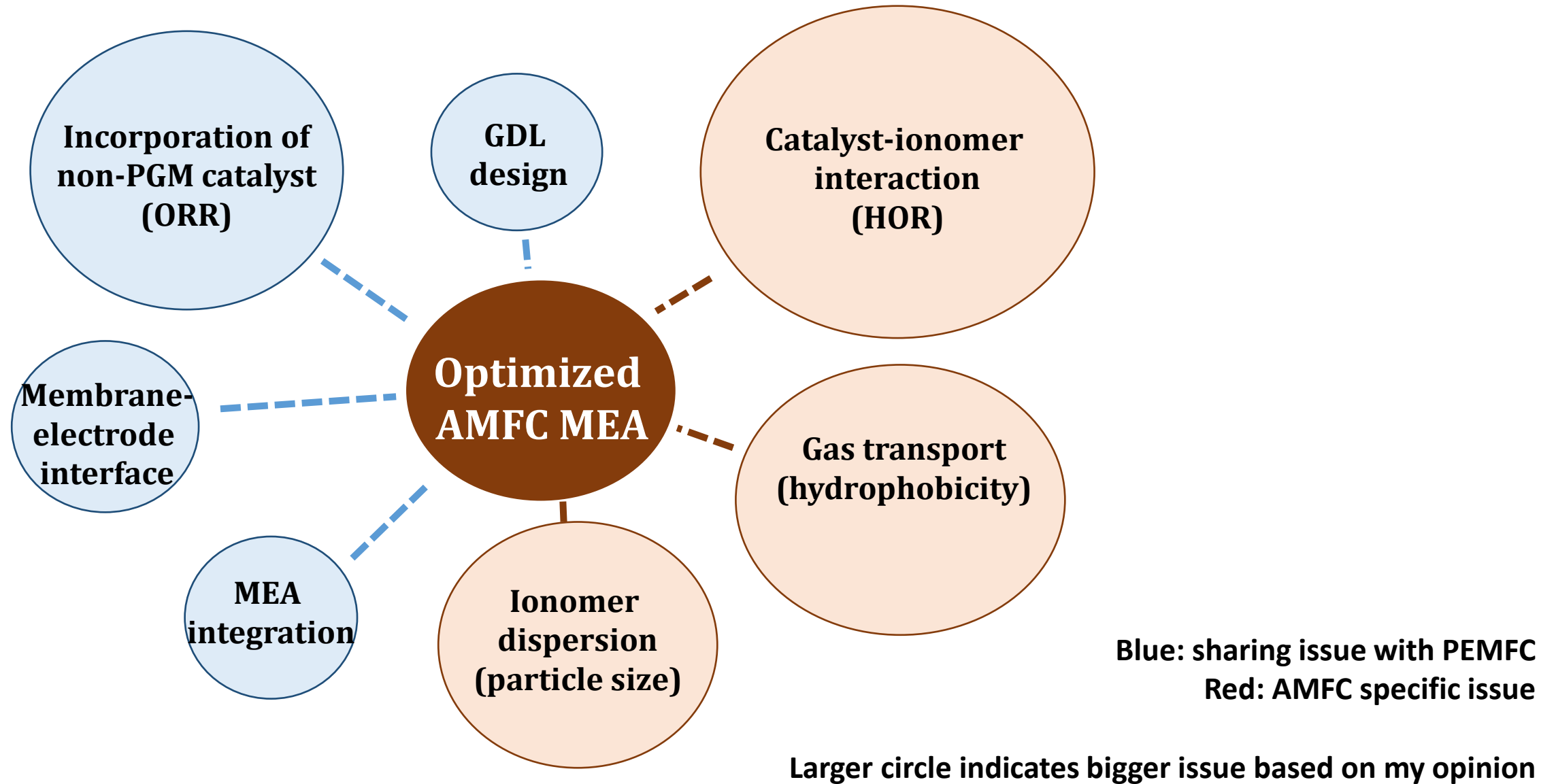
Proton exchange membrane fuel cell (PEMFC)

Alkaline membrane fuel cell (AMFC)

PEMFC (left diagram):

$3H_2$ | Load | $\frac{1}{2} O_2$

$6e^-$ ... $6e^-$

HOR
$3H_2 \rightarrow 6H^+ + 6e^-$

Anode | $6H^+$ | Cathode

ORR
$\frac{1}{2}O_2 + 6e^- + 6H^+ \rightarrow 3H_2O$

$3H_2O$

Proton-Exchange Membrane [PEM]

AMFC (right diagram):

$3H_2$ | Load | $\frac{1}{2} O_2 + 3H_2O$

$6e^-$ ... $6e^-$

HOR
$3H_2 + 6OH^- \rightarrow 6H_2O + 6e^-$

Anode | $6OH^-$ | Cathode

ORR
$\frac{1}{2}O_2 + 3H_2O + 6e^- \rightarrow 6OH^-$

$6H_2O$

Alkaline Anion-Exchange Membrane [AAEM]

- PEMFC and AMFC share most MEA issues. However, AMFC has its own MEA issues due to the different electrochemistry and water environment.

AMFC MEA Issues

Incorporation of non-PGM catalyst (ORR)

GDL design

Catalyst-ionomer interaction (HOR)

Membrane-electrode interface

Optimized AMFC MEA

Gas transport (hydrophobicity)

MEA integration

Ionomer dispersion (particle size)

Blue: sharing issue with PEMFC
Red: AMFC specific issue

Larger circle indicates bigger issue based on my opinion

Ionomer dispersion – particle size

# Dispersing agent for catalyst ink preparation

- General fact

    - Quaternized ionomers is less dispersible in solvents than sulfonated ionomers.

    - Dispersionability can be improved by avoiding hydroxide counter ions.

    - Quaternization reaction in the presence of electro-catalyst may be difficult.

    - Dispersionability of electrocatalyst needs to be considered.

- More critical issue associate with ionomer solubility

    - The control of dispersion morphology is a critical factor for AMFC performance.

Lesson from Nafion® ionomer

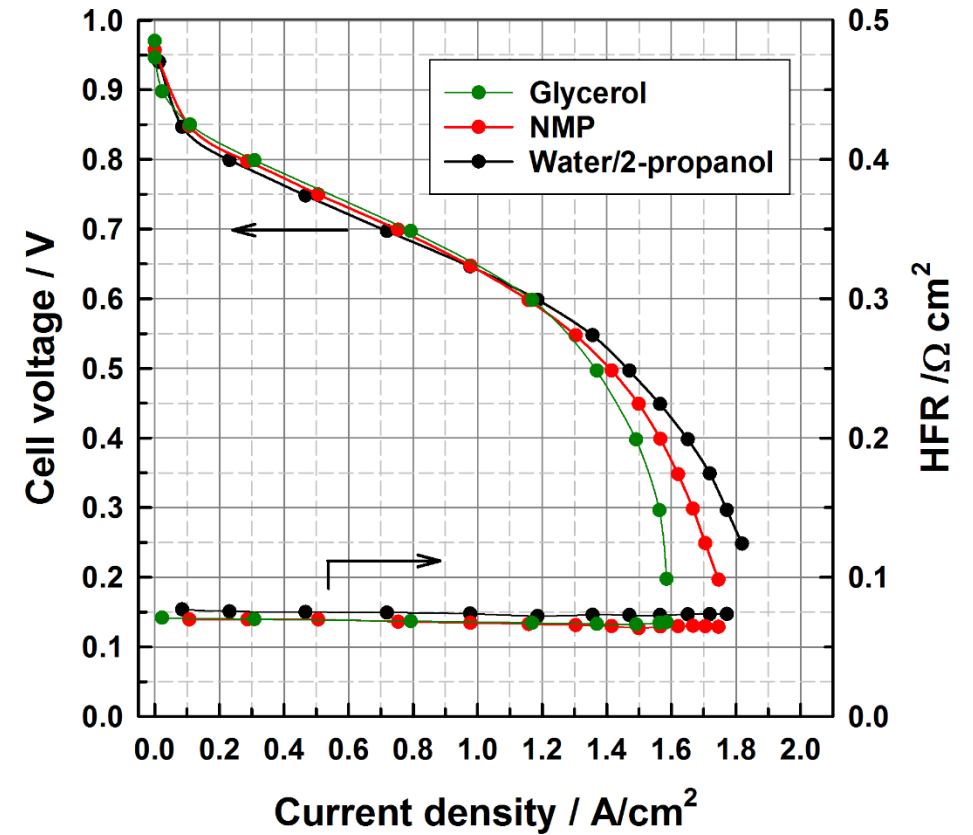Nafion particle morphology*
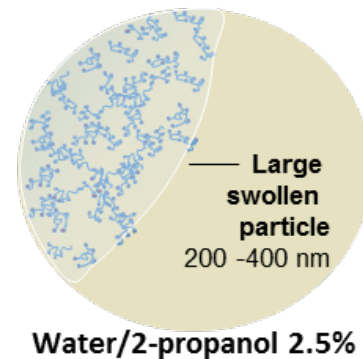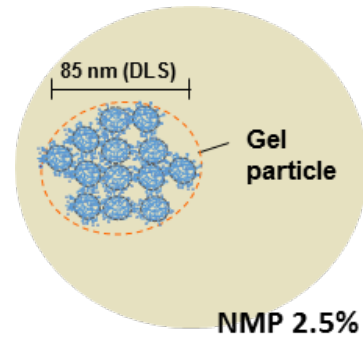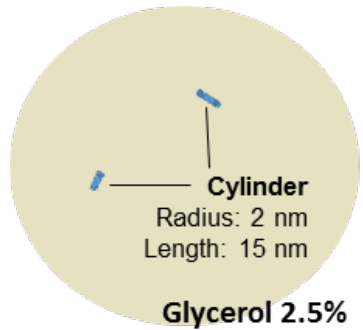
Electrode morphology
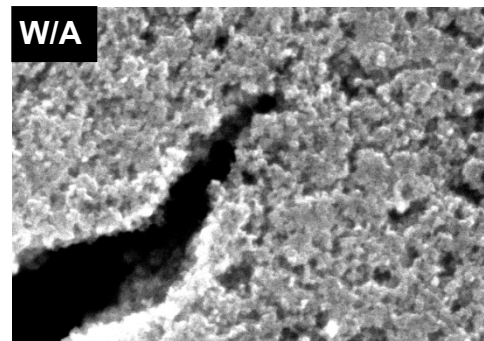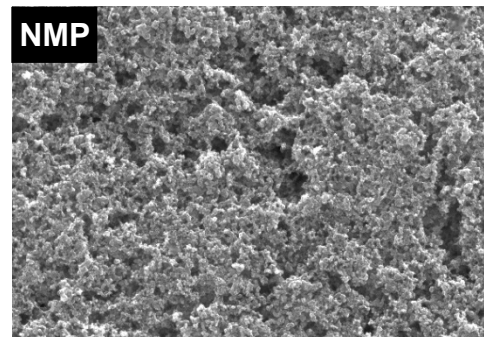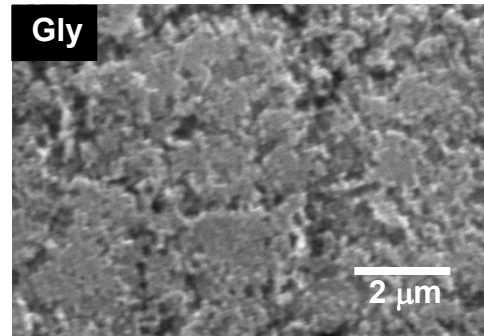
H$_2$/air PEMFC performance at 80°C

Catalyst: Pt/C 0.2 mg$_{Pt}$/cm^2; Membrane: Nafion 212
Cathode dispersing agent:
Glycerol, NMP and water/2-propanol

Y.S. Kim et al. *Macromolecules* 2015, 48, 2161

Y.S. Kim et al. *Phy. Chem. Chem. Phy.* 2014, 16, 5927
B. Choi et al. *J. Electrochem. Soc.* 2014, 161, F1154

H$_2$/O$_2$ AMFC performance at 60°C

**Catalyst: Pt/C 0.6 mg$_{Pt}$/cm², Membrane: QA-SEBS, Ionomer: Diels-Alder poly(phenylene)s**
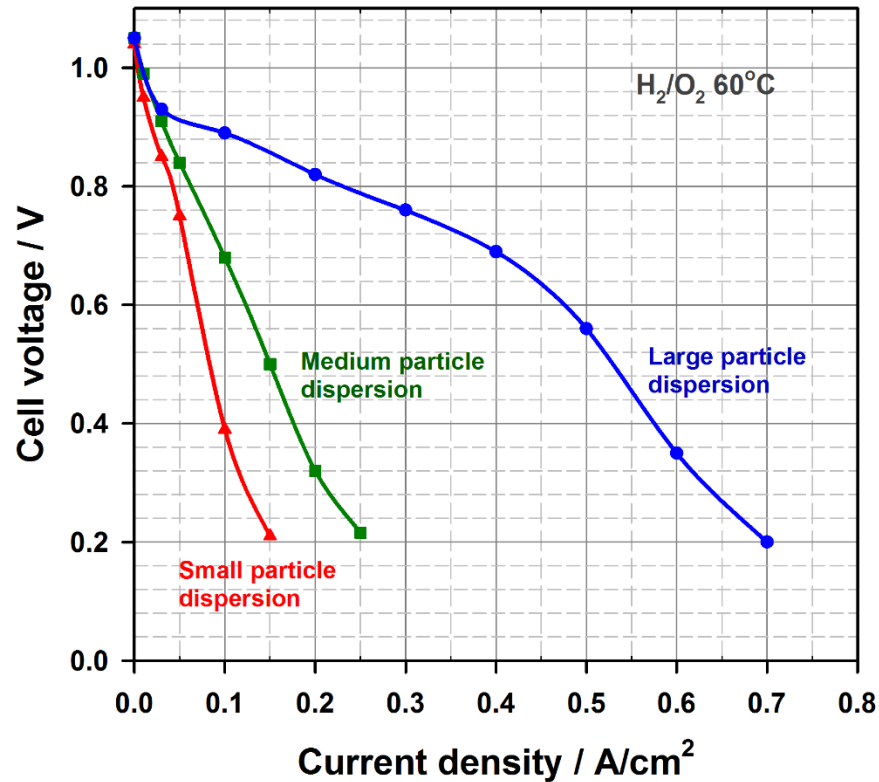
- Impact of ionomer particle size on fuel cell performance seems more significant in AMFCs.

- Understanding interaction between ionomer and dispersing agent and gelation behavior of concentrated ionomer dispersion are critical.

- Making relatively large (sub micrometer scale) and stable ionomer particle is the key for better gas transport.
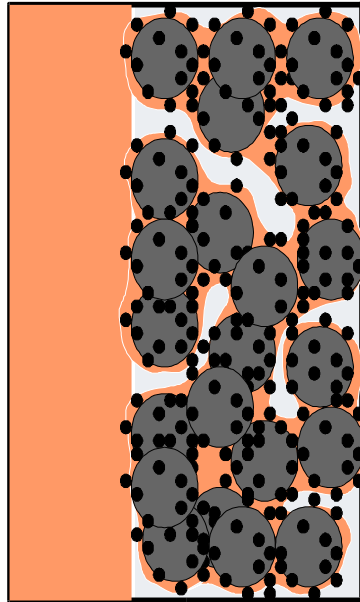
Gas transport- hydrophobicity
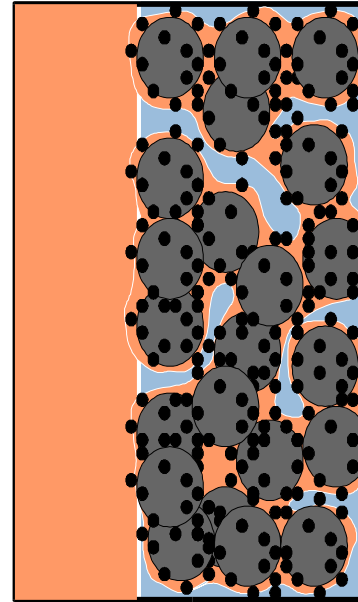
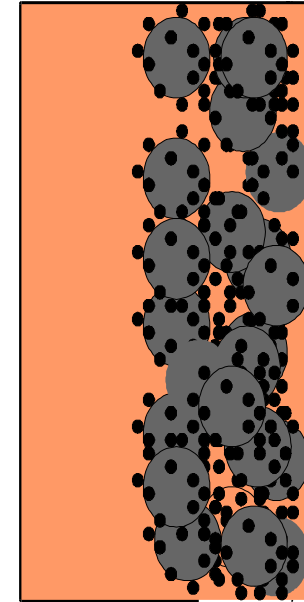# Reactant gas permeability at electrode and GDL

**Type I
(gas filled pore)**
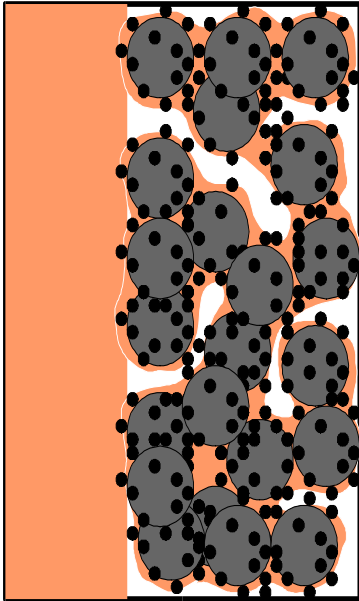
**Type II
(water vapor filled)**
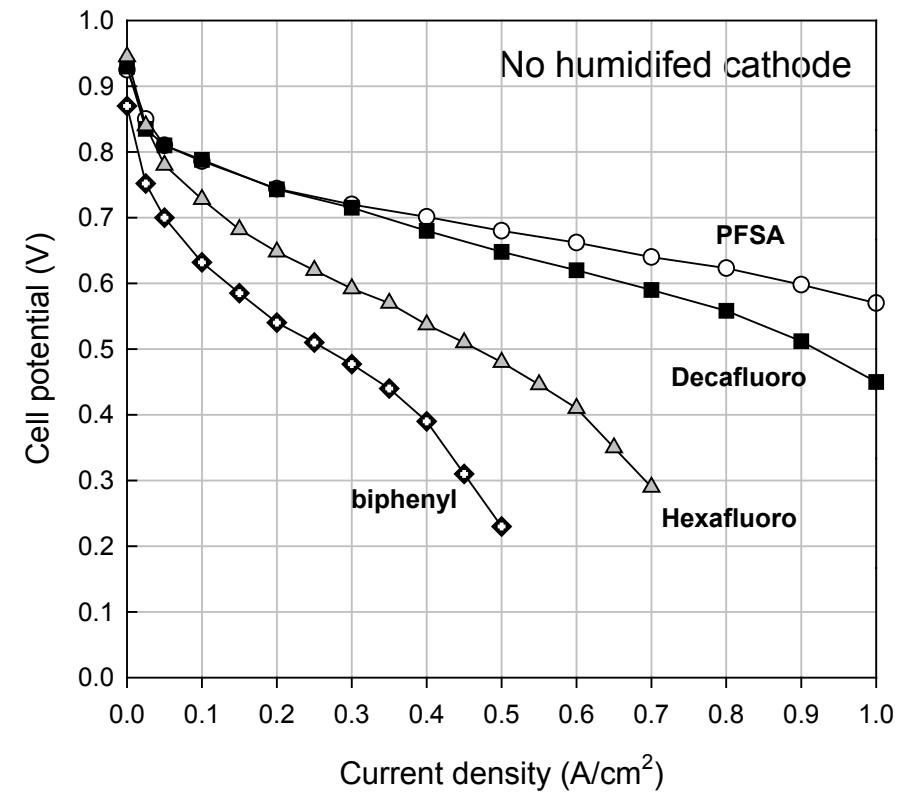
**Type III
(Liquid water filled)**

**Type IV
(ionomer filled)**

O_2 diffusion coefficient*

	PTL (g)	MPL (g)	Electrode (g) **Type I**	Electrode (w) **Type III**	Electrode (agg) **Type IV**
Transporting phase	Gas-filled	Gas filled	Gas filled	Water filled	Ionomer filled
D (m^2/s)	3×10^{-5}	3×10^{-5}	3×10^{-6}	2×10^{-9}	8×10^{-10}
D^{eff} (m^2/s)	1.26×10^{-6}	4.93×10^{-6}	**2.68×10^{-8}**	**2.00×10^{-9}**	**2.83×10^{-10}**

*Malevich et al. *J. Electrochem. Soc.* 156 (2) B216-B224 (2009)

Effect of hydrophobicity of ionomer on PEMFC performance

Cathode ionomer

PFSA   Decafluoro based Polyaromatic   Hexafluoro bisphenol based Polyaromatic   Biphenyl based Polyaromatic

Hydrophobicity

Fully humidified cathode

- PFSA
- Decafluoro
- biphenyl
- Hexafluoro

Cell potential (V)

Current density (A/cm^2)

No humidifed cathode

- PFSA
- Decafluoro
- biphenyl
- Hexafluoro

Cell potential (V)

Current density (A/cm^2)
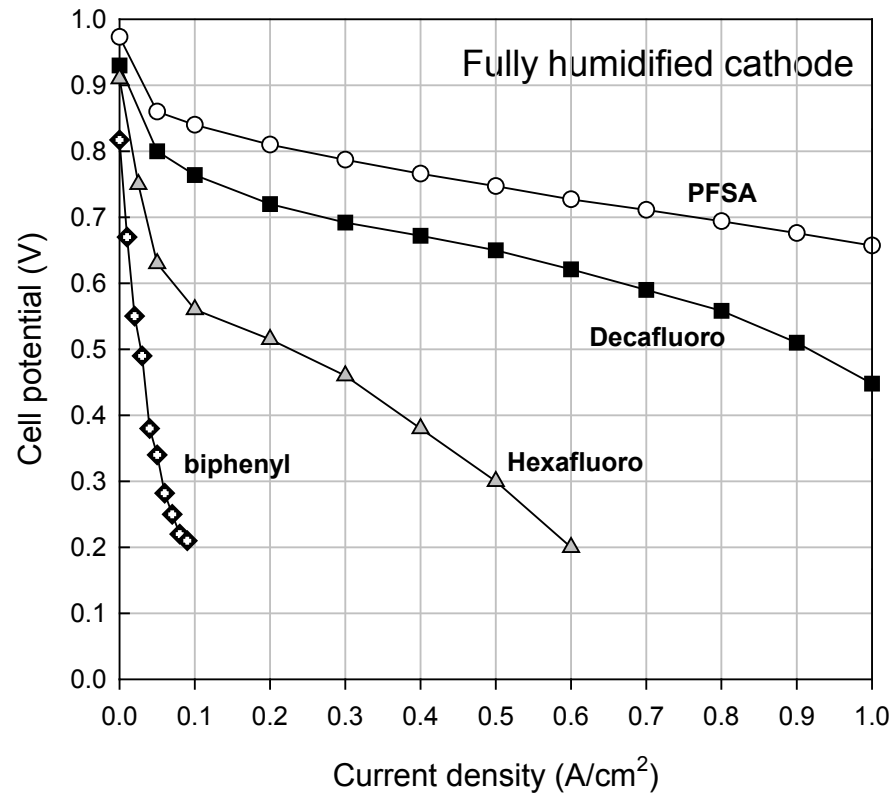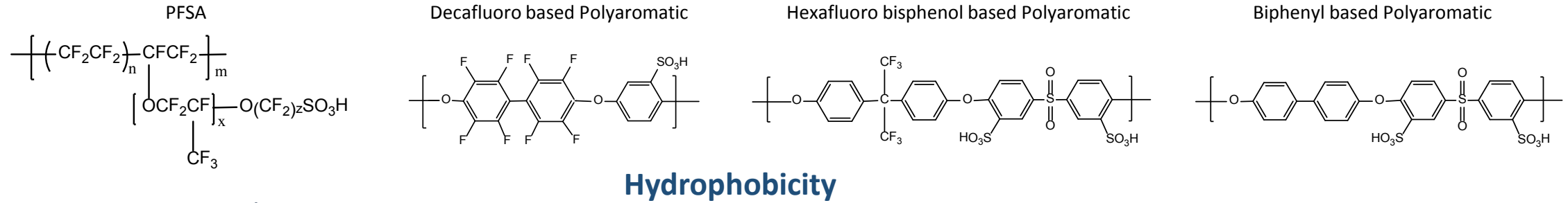
AMFC MEA challenge – Gas transport

- Preparing stable fluorinated anion exchange ionomers is difficult due to the instability of electron deficiency of the neighbor atoms. Effectiveness of partially fluorinated ionomers may not be high.

- Synthesis of perfluorinated anion exchange ionomer is challenging.

- Adding hydrophobic additives to the electrode may be possible* but not efficient due to the phase segregation.

- Reducing ion exchange capacity of ionomer can decrease the hydrophobicity of the ionomers. However, this also decreases hydroxide conductivity and gas diffusivity.

*Kaspar et al. *J. Electrochem. Soc.* 162 (6) F438-F448 (2015)
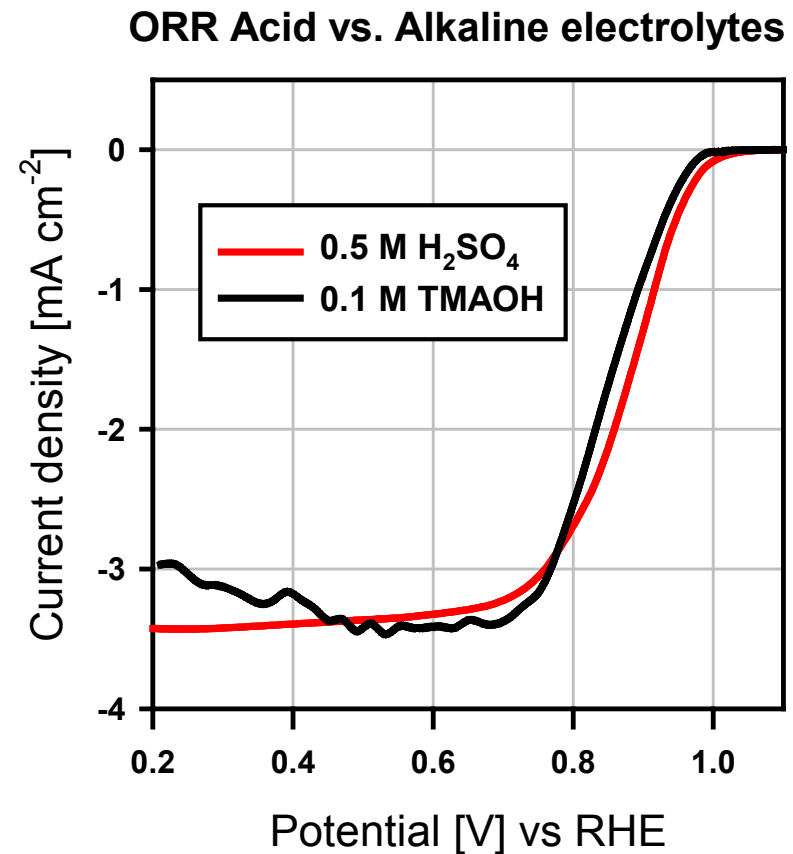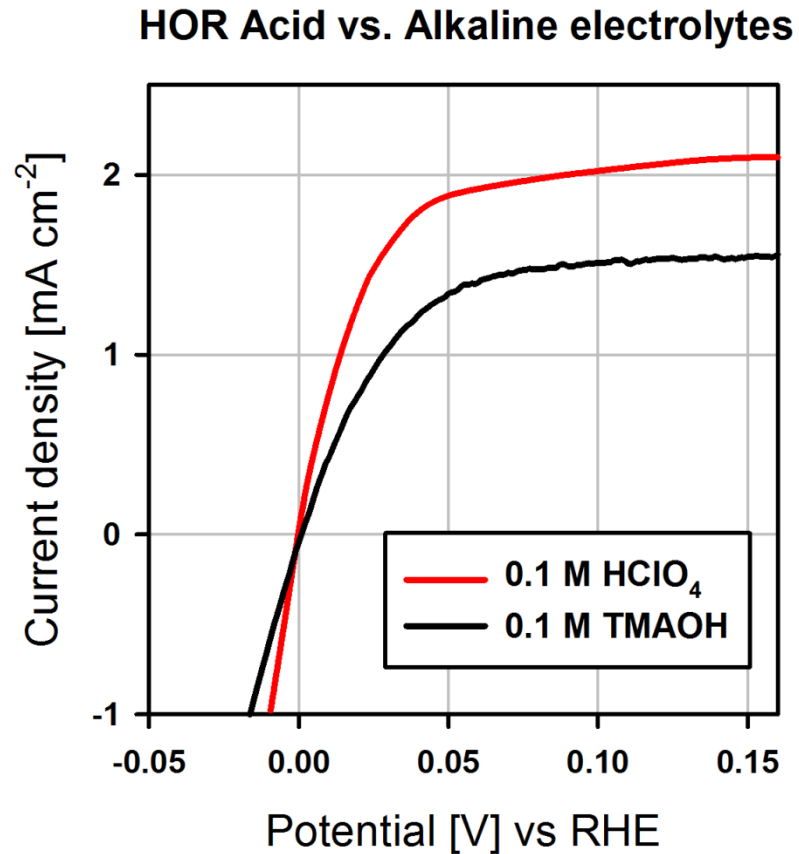
H_2/O_2 PEMFC performance at 80°C

Catalyst: Pt 6mg$_{Pt}$/cm^2; Membrane: QA-poly(phenylene) ionomer:
QA-poly(phenylene) or perfluorinated ionomer
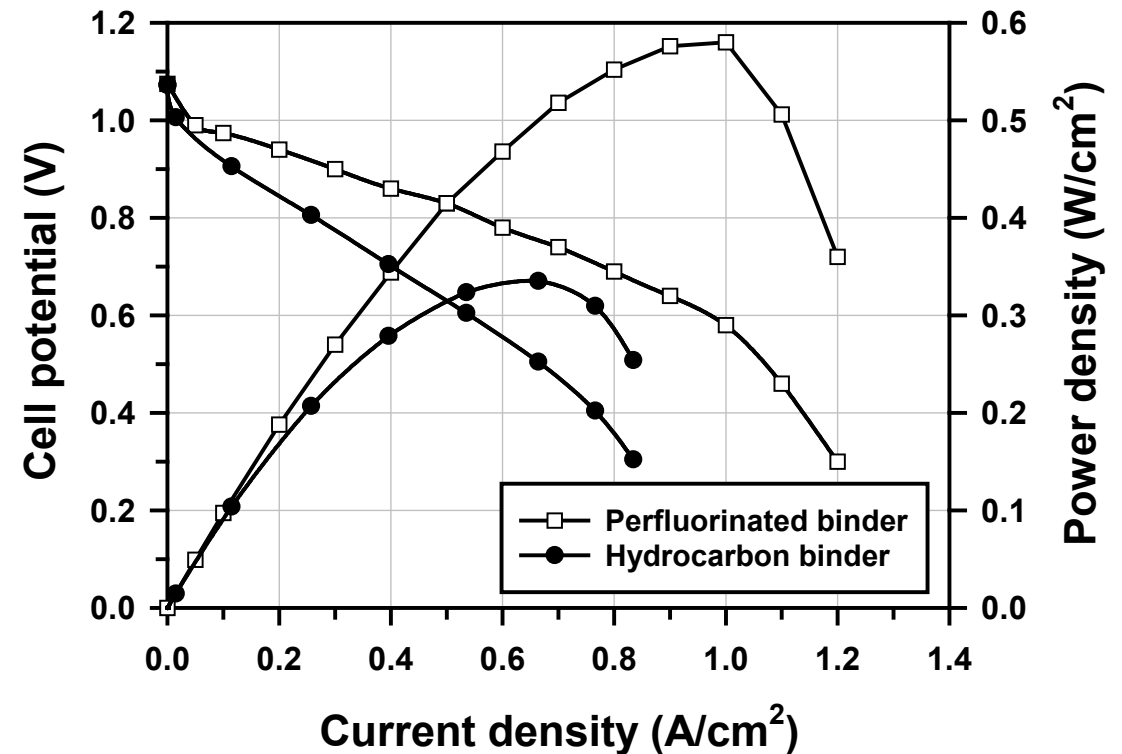
D.S. Kim et al. *Macromolecules* 2013, 46, 7826
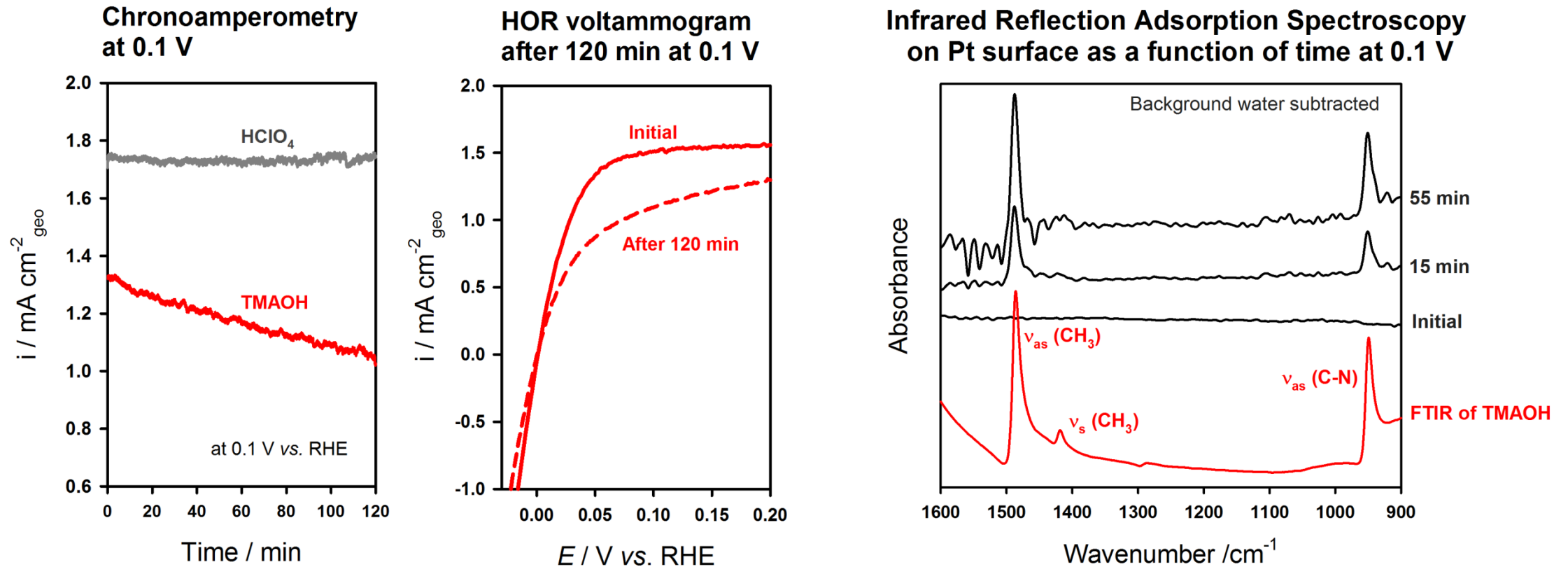
Catalyst-ionomer interaction (HOR)

Electrode performance comparison

HOR Acid vs. Alkaline electrolytes

Legend: 0.1 M HClO₄ (red), 0.1 M TMAOH (black)
X-axis: Potential [V] vs RHE
Y-axis: Current density [mA cm⁻²]

ORR Acid vs. Alkaline electrolytes

Legend: 0.5 M H₂SO₄ (red), 0.1 M TMAOH (black)
X-axis: Potential [V] vs RHE
Y-axis: Current density [mA cm⁻²]

Voltammograms of Pt/C in acid and alkaline electrolytes were performed at 25°C, rotating speed: 900 rpm, scan rate: 5 mVs⁻¹

- The HOR performance of AMFC is much inferior to the HOR performance of PEMFC.

Chemisorption of cationic functional group

Chronoamperometry at 0.1 V

HOR voltammogram after 120 min at 0.1 V

**Infrared Reflection Adsorption Spectroscopy on Pt surface as a function of time at 0.1 V**

Voltammograms of Pt/C in acid and alkaline electrolytes were performed at 25°C, rotating speed: 900 rpm, scan rate: 5 mVs^{-1}
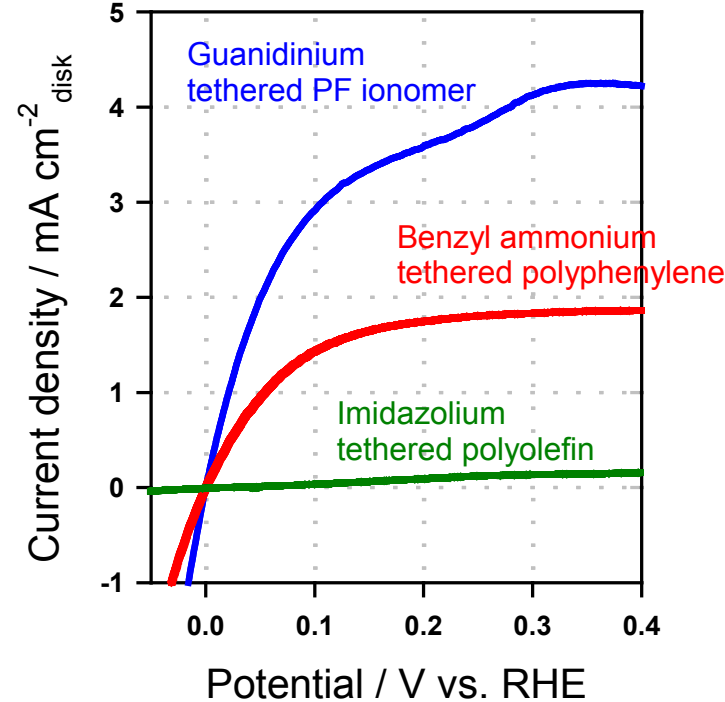
- Cationic group chemisorption reduces the HOR current of Pt electrode

Impact of cationic group and electrocatalysts

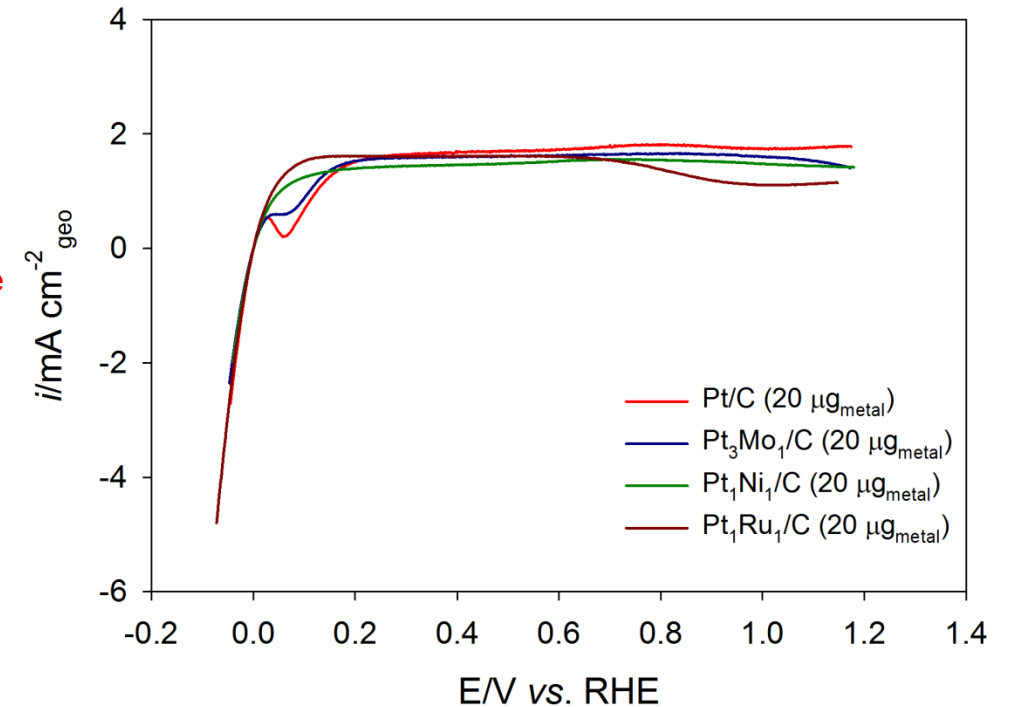
Liquid electrolyte
(electrocatalyst: Pt/C)
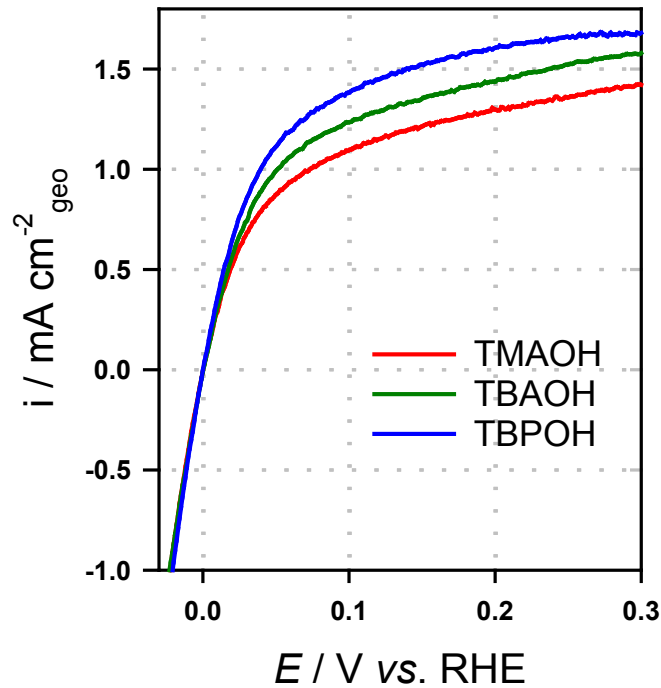
Polymer electrolyte
(electrocatalyst: Pt)

Electrocatalyst
(electrolyte:0.1M BTMAOH)

- Cationic group chemisorption depends on type of cationic group, polymer chain mobility, and electrocatalysts.

- Undesirable interaction between cationic functional group and catalyst adversely impact the HOR of AMFC.

- Chemisorption can be prevented by applying high potential, ca. 1.2 V (data not shown) but this may not easy to implement during AMFC operations.

- The chemisorption mostly impacts the hydrogen diffusion (data not shown), which creates significant transport issue when combined with anode flooding.

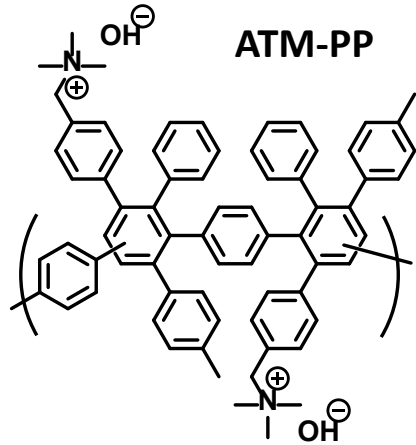- Catalyst-ionomer interaction also impact the ORR (right figure) but less problematic than in HOR.

ORR voltammogram of Pt/C RDE

Voltammograms of Pt/C in alkaline electrolytes were performed at 25°C, rotating speed: 900 rpm, scan rate: 5 mVs^{-1}
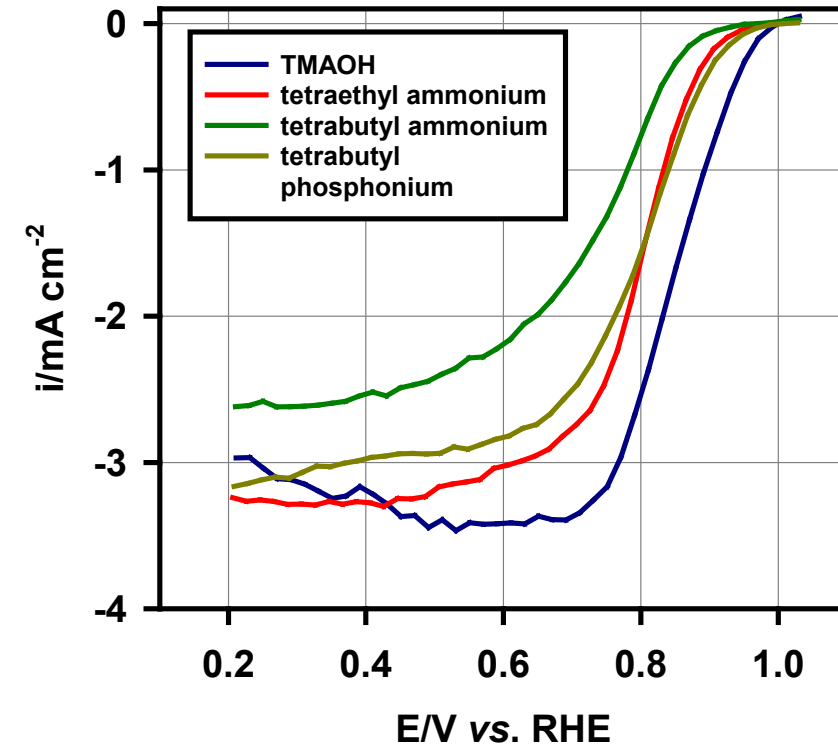
Other MEA issues
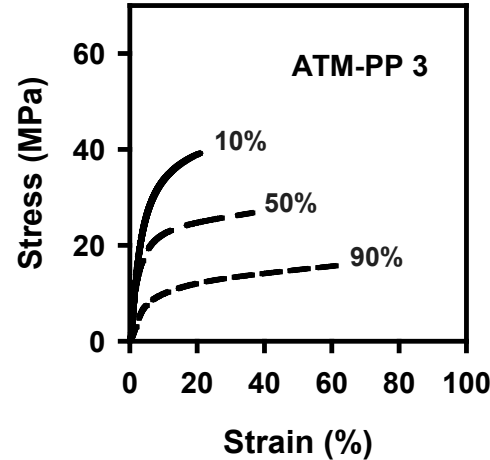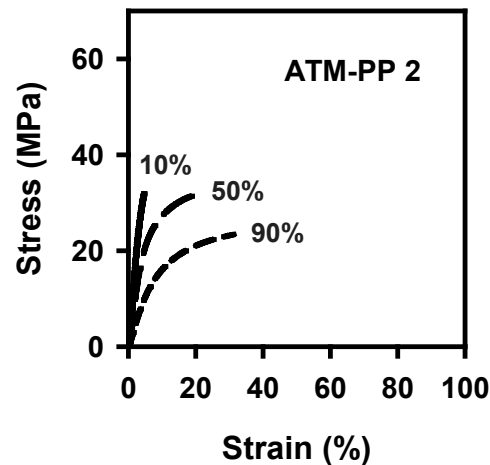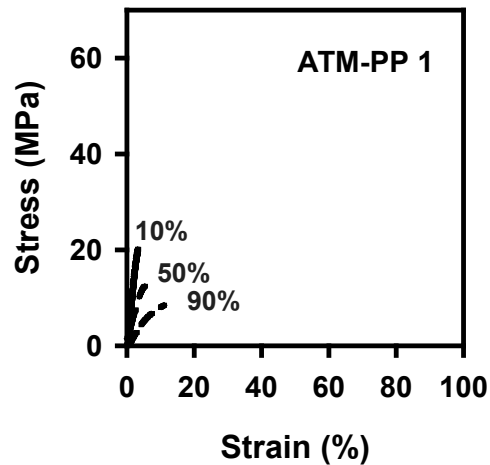
Membrane-electrode interfacial issue

ATM-PP

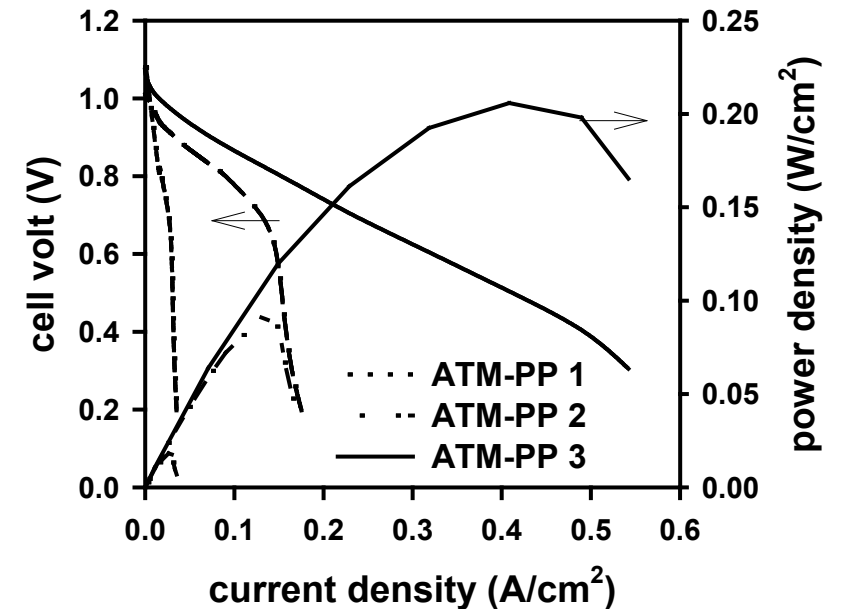| Sample	$M_w \times 10^3$ [a] (g/mol)	IEC (meq./g)	WU (wt.%)	σ [b] (mS/cm)	HFR (Ω cm^2)
ATM-PP1	61	1.7	72	30	1.67
ATM-PP 2	77	1.6	64	35	1.23
ATM-PP 3	196	1.7	70	37	0.21

[a] measured by GPC using the parent polymers
[b] measured at 80°C using salt form membranes

Stress-strain curves at 50°C

C. Fujimoto et al. *J. Memb. Sci.* 2012, 423, 438

For more information on interfacial issue and diagnostics, See Pivovar et al. J. Electrochem. Soc. 154, B739 (2007)

AMFC MEA degradation issue

- Cationic group adsorption
  - Mostly unrecoverable
  - Occurs first 0-20 h operation
  - Partly compensated with cell break-in

- Membrane backbone degradation
  - Unrecoverable
  - Catastrophic cell failure during a few hours
  - Accelerated by dry operation

- Carbonation/bicarbonation formation
  - Recoverable
  - Detected by constant cell resistance increase
  - Can occur over few hundred of hour operation

- Membrane cationic group degradation
  - Similar with carbonation/bicarbonation but this is unrecoverable

- Others: Membrane dissolution, Interfacial failure, MEA edge failure, Ru crossover*, etc

Extended-term AMFC test
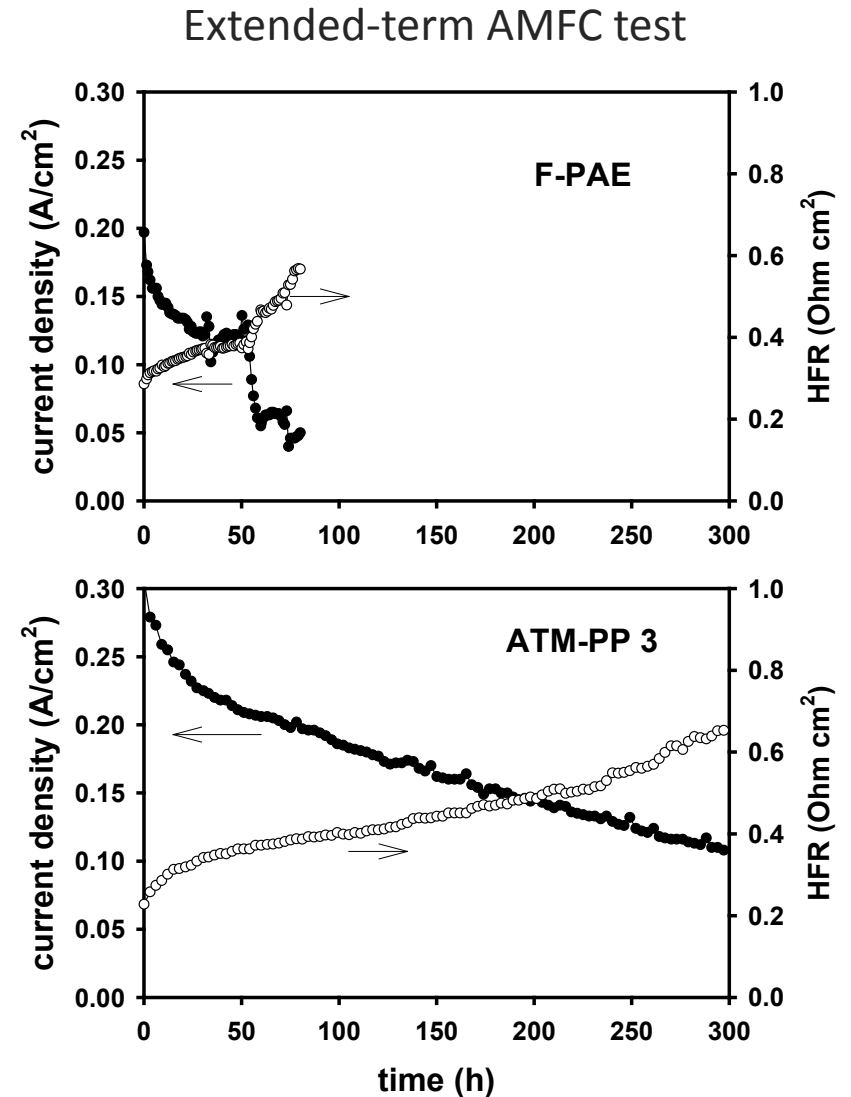
*Piela et al. *J. Electrochem. Soc.* 151 (12) A2053-A2059 (2004)

Summary

- Due to the absence of good working ionomers, identifying MEA issues is rather difficult.

- AMFC-specific MEA issues are ionomer dispersion, hydrophobicity of electrode and catalyst-ionomer interactions are

- With AMFC system issues (carbonate/bicarbonate, water transport), MEA issues directly impact the AMFC performance and operating conditions.

Acknowledgment