Advanced Hydroxide Conducting Membranes

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Los Alamos National Laboratory

Project ID: FC123

Overview

Timeline

- **Project Start:** August 1 **2014**
- **Project End:** July 31 **2015**
- **Percent Complete:** **70**

Budget

- **Total Project Budget (K):** **500**
- **Funding Received in FY 15 (K):** **500**
- **Total DOE Funds Spent (K):** **340**

No cost share *68% spent as of April 10, 2015*

Barriers

- **B. Cost**
- **C. Electrode performance**
- **A. Durability**

Project lead

- **Los Alamos Nat. Lab.**

  (Project Management, Ionomer Synthesis, MEA Fabrication and Fuel Cell Testing)

  Yu Seung Kim (PI)

  Kwan-Soo Lee

Collaborators/Interactions

Subcontractors

Sandia Nat. Lab. (Membrane Synthesis)	Cy Fujimoto Michael Hibbs
Lawrence Berkeley Nat. Lab. (Property & Modeling)	Adam Weber Huai-Suen Shiau Shouwen Shi Ahmet Kusoglu

Collaborators/Interactions

Rensselaer Polytech. Institute (Membrane Synthesis)	Chulsung Bae Angela Mohanty
Solvay (Material Supply)	Dan Ireland
Ion Power (Material Supply)	Steve Grot
IRD Fuel Cell (Fuel Cell Testing)	Madeleine Odgaard
National Institute of Advanced Industrial Science and Technology (Stability Modeling)	Yoong-Kee Choe

Relevance

Objectives

Develop (1) ***chemically stable hydroxide-conducting anion exchange membranes*** *and (2)* ***solvent processable perfluorinated ionomers*** and (3) ***modeling approaches (HOR, ORR and polarization behaviors)*** to demonstrate high performance/durable alkaline membrane fuel cells.

Technical Barriers

- ☐ Low hydroxide conductivity
- ☐ Poor cationic functional group & polymer backbone stability
- ☐ Mechanical-instability to make thin films
- ☐ Low quality perfluorinated ionomer dispersions

Targets and Current Status

Characteristics	Units	*2014 status* [a]	*Target* [b]	*Current status* [c]
Areal resistance	**$\Omega \cdot cm^2$**	**0.17**	**≤ 0.10**	**0.06 – 0.08**
IEC loss after >100 h 0.5 M NaOH at 80°	**%**	**10**	**No decrease**	**No decrease**
Peak power density of AEMFC	**W/cm^2**	**580** (14 mg_{Pt}/cm^2)	**>600** (0.4 mg_{Pt}/cm^2)	**330** (0.4 mg_{Pt}/cm^2)

[a] *Y.S. Kim, Resonance-Stabilized Anion Exchange Polymer Electrolytes, US DOE 2014 Annual Merit Review, June, 16-20, 2014*

[b] *The interim project target was set for general fuel cell applications*

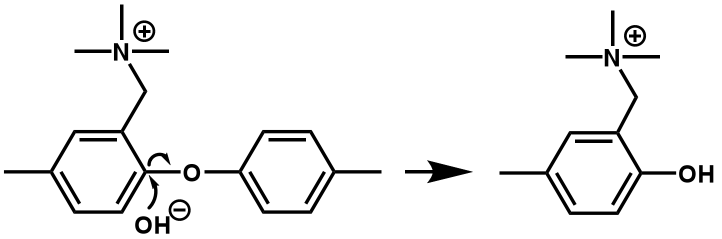
[c] *as of April 10, 2015*

Approach: Anion exchange membranes

- **Polymer Backbone**

✓ Developing polymers without ether or electron-withdrawing groups in the polymer backbone

Aryl-ether cleavage reaction[a]



- **Our approach**

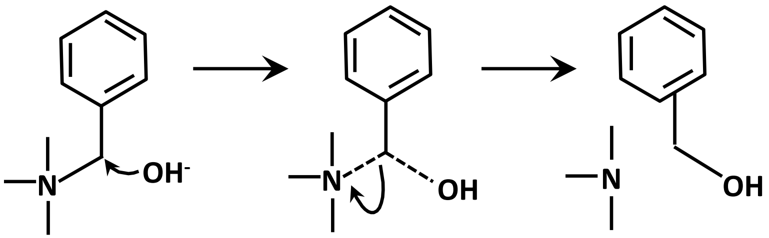
✓ Ether-free poly(phenylene) (SNL)

✓ Ether-free polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene (RPI)

- **Cationic Functional Group**

✓ Replacing benzyl trimethyl ammonium (BTMA) with more alkaline stable cations

S_N2 degradation of BTMA[b]



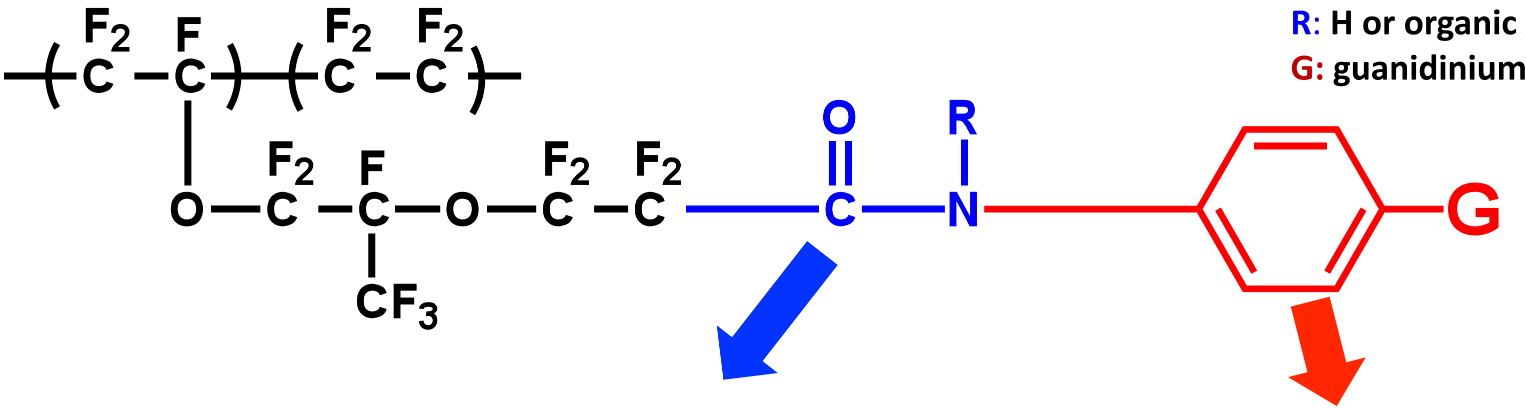
- **Our approach**

✓ Hexamethyl ammonium (SNL, RPI)

✓ Phenyl guanidinium (LANL, SNL)

Approach: Anion exchange polymer dispersion

FY14 LANL Perfluorinated Ionomer*



Amide linkage

- Chemical stability of amide group: 8% loss after 72 h 0.5M NaOH at 80°C
- **Our approach**

✓ Alkyl amide (LANL)

Cationic functional group

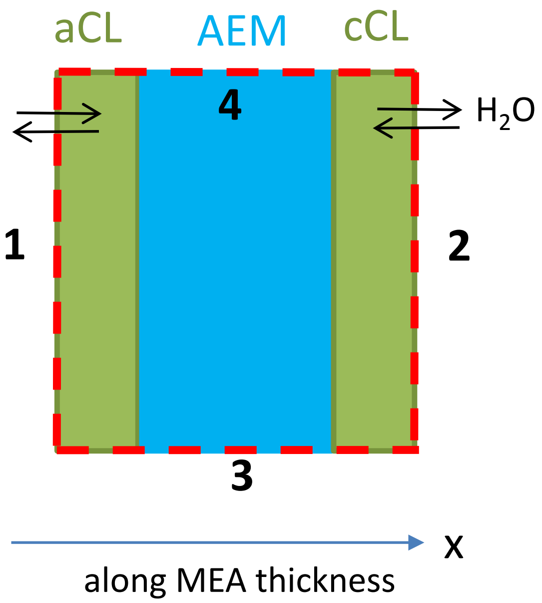
- Sulfone and benzyl guanidinium is not stable under high pH conditions
- **Our approach**

✓ Phenyl guanidinium (LANL)

✓ Other cations (LANL)

* D.S. Kim et al. *Macromolecules*, 46, 19, 7826-7833 (2013)

Approach: Performance modeling



- **Boundary conditions:**
  1. 1 - 4 no flux for OH^-, CO_3^{-2} and HCO_3^- except for H_2O at boundaries 1 and 2.
  2. At the boundary 1 (aCL/GDL interface), the water content is fixed at $\lambda = 10$
     At the boundary 2 (cCL/GDL interface), $\lambda = 10$ (RH = 100%) or $\lambda = 4$ (RH 40%)

- **Properties:**
  1. Thickness of aCL and cCL = 10 µm and that of AEM = 25 µm.
  2. Cell potential = 0.8 V and T = 80 °C
  3. $[CO_2]$ in the aCL and cCL are the same (0.005% to 50% ambient $[CO_2]$)
     $[CO_2]$ in the AEM is set to be zero (assuming AEM has low CO_2 tolerance).
     Note: ambient CO_2 pressure = 0.0004 atm (ambient $[CO_2]$ = $1.6*10^{-5}$ mol/L).
  4. OH^- conductivity = 0.08 S/cm for 100% hydrated AEM.

- **Electrode kinetics:**

@ anode
$$i_a = a_{Pt} i_{0,a} \left(\frac{C_{H_2}}{C_{H_2}^{ref}}\right)^{0.5} y_{OH^-} \exp\left(\frac{\alpha_a \eta_a F}{RT}\right) \qquad \eta_a = -\Phi_e - V_a^{eq} \qquad V_a^{eq} = \frac{RT}{nF}\ln(y_{OH}{}^2)$$

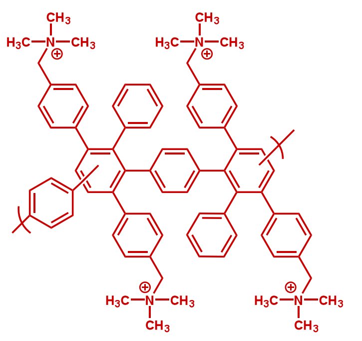
@ cathode
$$i_c = a_{Pt} i_{0,c} \left(\frac{C_{O_2}}{C_{O_2}^{ref}}\right)\lambda \exp\left(\frac{-\alpha_c \eta_c F}{RT}\right) \qquad \eta_c = \Phi_{cell} - \Phi_e - V_c^{eq} \qquad V_c^{eq} = 1.23 + \frac{RT}{nF}\ln(y_{OH}{}^2)$$

$$a_{Pt} = 10^5\ \text{cm}^{-1} \qquad i_{0,HOR} = i_{0,ORR} = 3\ \text{mA/cm}^2 \qquad C_{H_2} = C_{O_2} = 10\ \text{mol/m}^3 \qquad C_{H_2}^{ref} = 16\ \text{mol/m}^3$$

(0.25 atm)

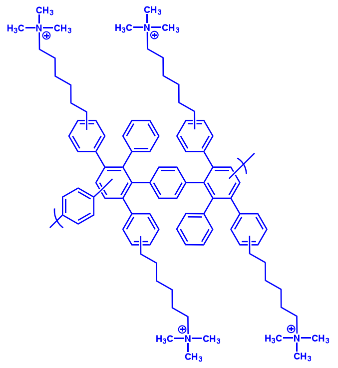
Accomplishments: Synthesized rigid polymers

ATM-PP Series



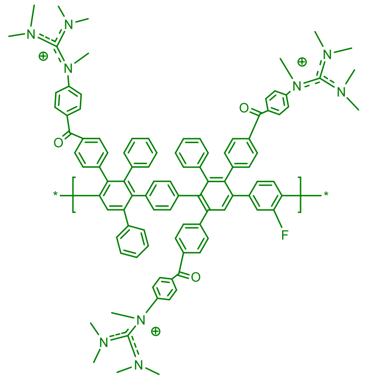
- **Control AEM (SNL)**
- **Progress**
  Polymer synthesis: 100%
  Characterizations: 100%
- **Demonstrated good polymer backbone stability in AMFC and AEM based water electrolysis**
- **Strength**
  Proven polymer stability
- **Weakness**
  Mechanical properties
  Cation stability

MRH Series



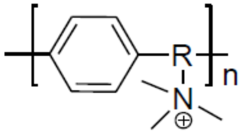
- **Hexamethyl ammonium functionalized poly(phenylene) AEM (SNL)**
- **Progress**
  Polymer synthesis: 100%
  Characterizations: 80%
- **Designed for enhanced cation stability**
- **Strength**
  Improved cation stability
  Better gas permeability
- **Weakness**
  Ionomer processibility

SPG Series



- **Phenyl guanidinium functionalized AEM (SNL & LANL)**
- **Progress**
  Polymer synthesis: 80%
  Characterizations: 20%
- **Introducing stable super base**
- **Strength (expected)**
  Improved cation stability
  Better dimensional stability *via* lower water uptake
- **Weakness**
  ?

AR Series

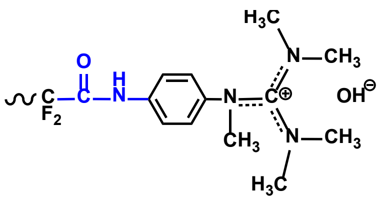


- **Hexamethyl ammonium functionalized poly(biphenylene) AEM (RPI)**
- **Progress**
  Polymer synthesis: 100%
  Characterizations: 60%
- **Introducing flexible alkyl group into the polymer backbone**
- **Strength (expected)**
  Improved mechanical properties
- **Weakness**
  ?

For AEM and dispersion appearance: see back-up slides 21, 22

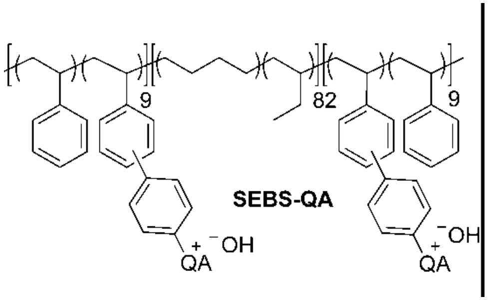
Accomplishments: Synthesized flexible polymers

Nafion®-FA-TMG Series



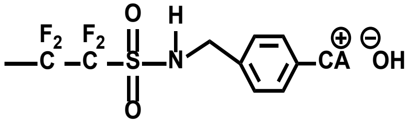
- **Perfluorinated (PF) control AEM (LANL & SNL)**
- **Progress**
  Polymer synthesis: 100%
  Characterizations: 100%
- **Guanidinium functionalized stable PF anion exchange polymer**
- **Strength**
  Low water uptake
  Excellent hydrophobicity ideal for ionomeric binder
- **Weakness**
  Processibility for ionomer dispersion
  Instability of amide group

SEBS-QA Series



- **SEBS based AEM (RPI)**
- **Progress**
  Polymer synthesis: 100%
  Characterizations: 80%
- **Highly conductive and stable polymers prepared from C-H borylation and coupling reactions**
- **Strength**
  High conductivity
  Good polymer stability
  Mechanical toughness
- **Weakness**
  Processibility for ionomer dispersion
  Relatively high water uptake

PF Alkyl Amide Series



- **PF polymers having alkyl amide group (LANL)**
- **Progress**
  Polymer synthesis: 80%
  Characterizations: 0%
- **PF polymers prepared from new chemistry**
- **Strength (expected)**
  Better conductivity
  Good amide stability
  Improved processibility for ionomer dispersion
- **Weakness**
  ?

For AEM and dispersion appearance: see back-up slides 21, 22

Accomplishments: Membrane conductivity/resistance

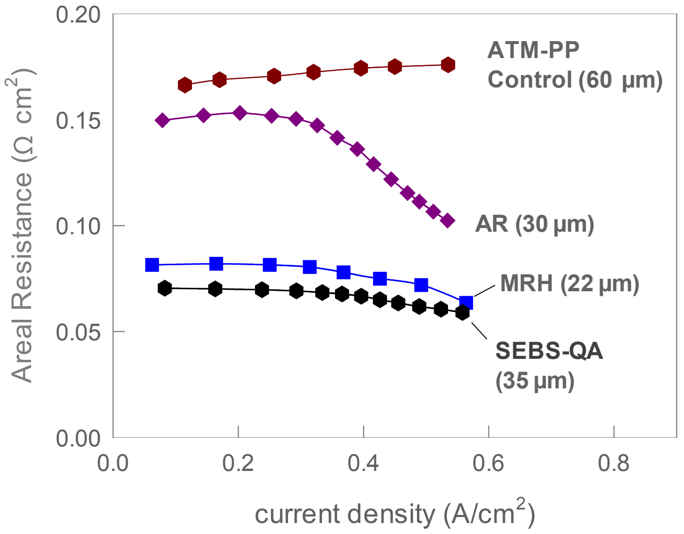
Conductivity Summary

Membrane code	IEC[a]	OH^- cond.[b]	Areal Resistance[c] (film thickness)
	meq./g	mS/cm	$\Omega \cdot cm^2$ (μm)
ATM-PP	1.7	40	0.17 (60)
MRH	2.0 – 2.4	40 – 60	0.06-0.08 (30)
AR	1.9 – 2.1	41 – 54	0.10-0.15 (22)
SEBS-QA	1.0 – 1.9	29 – 45	0.06-0.07 (35)

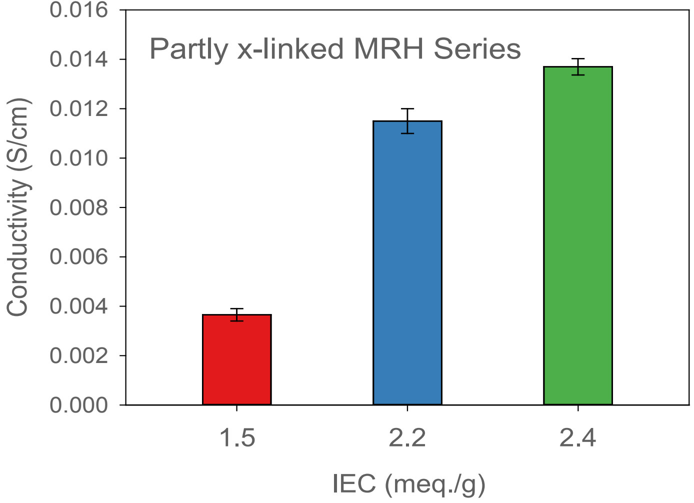
[a] by titration; [b] measured at 30°C; [c] measured at 80°C

- Reduced areal resistance of FY 15 AEMs compared with that of ATM-PP control.
- Less resistance variation with current density for MRH and SEBS-QA AEMs, indicating better water management
- Highlight: **Achieved FY15 areal resistance milestone (< 0.1 Ω cm^2) for MRH and SEBS-QA AEMs**

Measured at LANL



Measured at LBNL



Accomplishments: Membrane mechanical properties

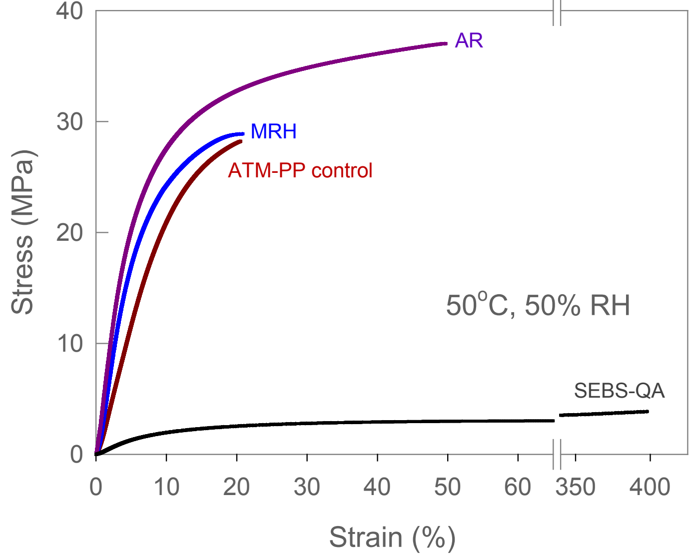
Summary of Mechanical Properties

Membrane code	**Water uptake**[a]	**Stress**[b]	**Strain**[b]
	(wt. %)	(MPa)	(%)
ATM-PP	83	28	20
MRH	126	28	23
AR	120	36	50
SEBS-QA	220	4	>300

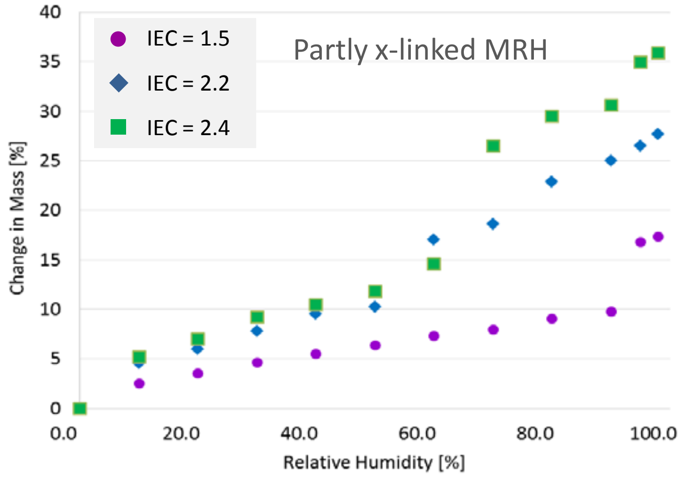
[a] measured at 30°C; [b] Hydroxide form AEMs measured at 50°C, 50% RH

- Improved mechanical properties of AR series AEMs compared with ATM-PP control
- More than 300% strain for SEBS-QA AEMs at 50°C, 50% RH; > 20% strain at 0% RH (Back-up slide 23)
- Durable MEAs could be fabricated from all FY15 AEMs

Stress-strain curves *Measured at LANL*



Effect of IEC on WU *Measured at LBNL*

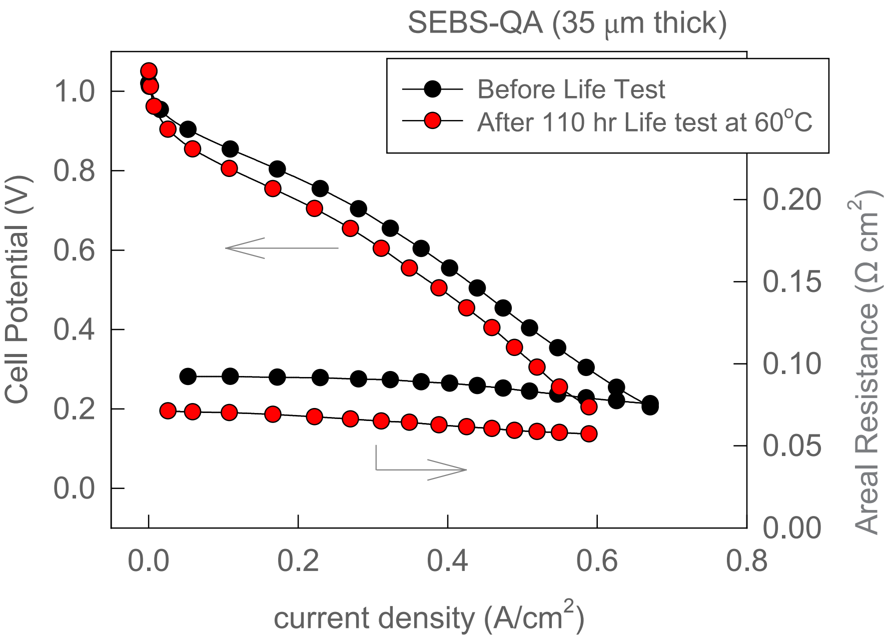


Accomplishments: Membrane stability

Summary of Stability

Membrane code	**Test conditions**	**IEC loss (%)**
ATM-PP[a]	4M KOH, 90°C, 14 days	14
MRH[a]	4M KOH, 90°C, 14 days	0
AR	1M NaOH, 80°C, 30 days	0
SEBS-QA	1M NaOH, 80°C, 28 days	3

[a] Ref. M. R. Hibbs, J. Polym. Sci. Part B. 51, 1736, 2013

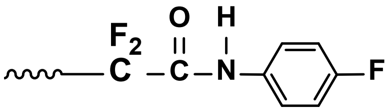


SEBS-QA (35 μm thick)

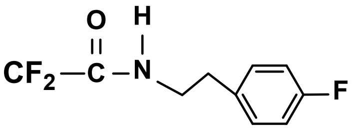
- Improved alkaline stability of FY15 AEMs compared with ATM-PP control from ex-situ test.
- Confirmed alkaline stability of SEBS-QA AEMs under AMFC operating conditions
- Highlight: **Achieved FY 15 stability milestone for AR and SEBS-QA: < 10% loss after 500 h, 0.5M NaOH at 80°C AEMs (May 30, 2015)**
- **Next step:** Complete In-situ and ex-situ life test for MRH, SPG, and AR series AEMs

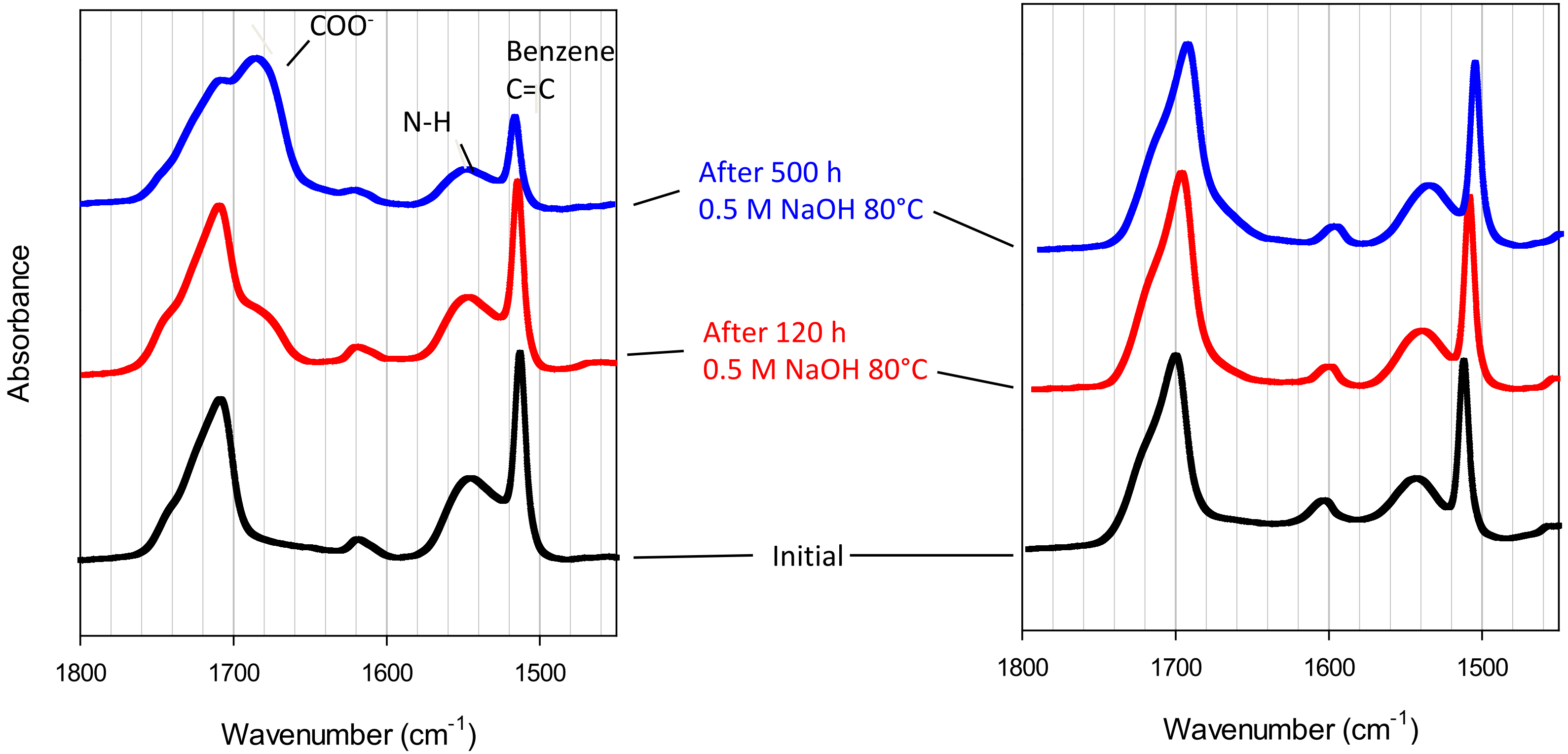
Accomplishments: Amide group stability of PF polymers

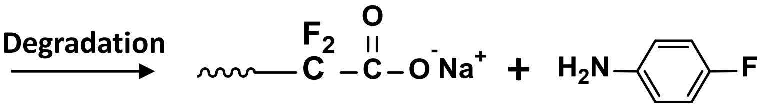
Phenyl Amide



Phenyl Alkyl Amide



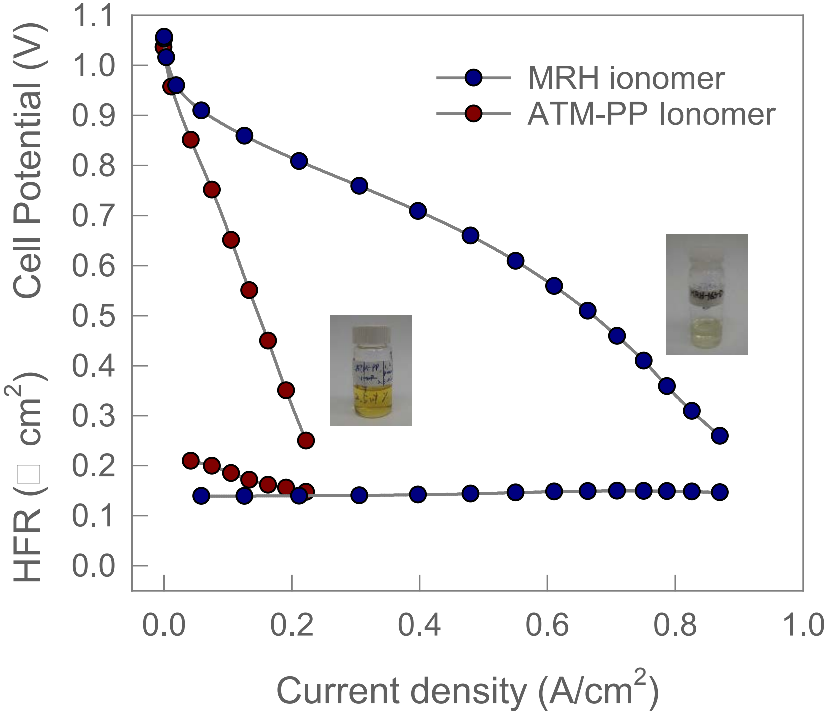




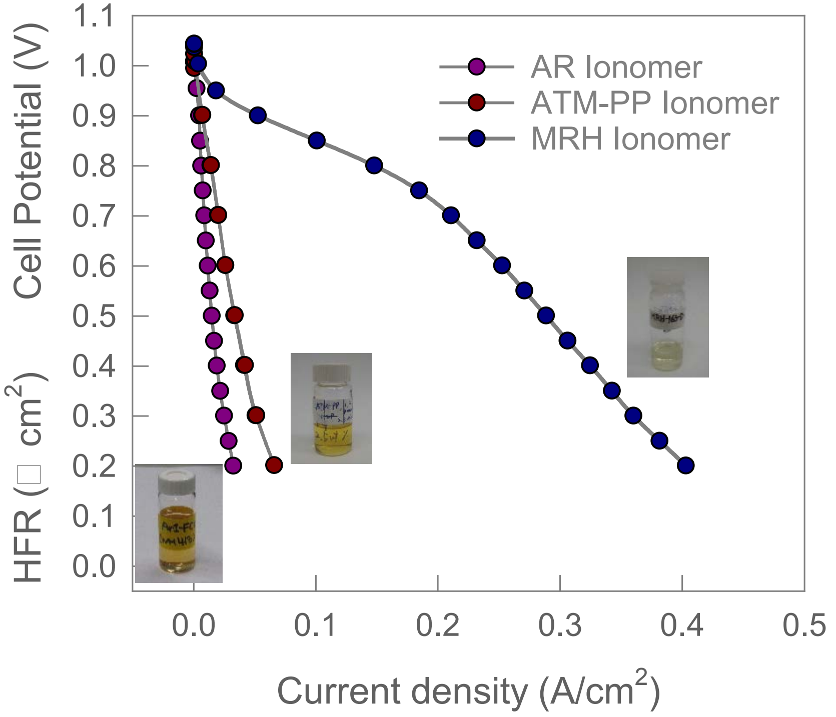
- Poor stability of phenyl amide group under high pH conditions
- No FTIR peak loss of phenyl alkyl amide group under high pH conditions

Accomplishments: On-going fuel cell performance test

AEM:	SEBS-QA series (IEC = 1.4 meq./g)
AEM thickness:	40 μm for MRH, 30 μm for ATM-PP ionomer
Catalyst:	TKK 46% Pt/C, 0.4 mg_{Pt}/cm^2 for each electrode
Test conditions:	H_2/O_2 feed, 60°C fully humidified conditions, 15 psig backpressure



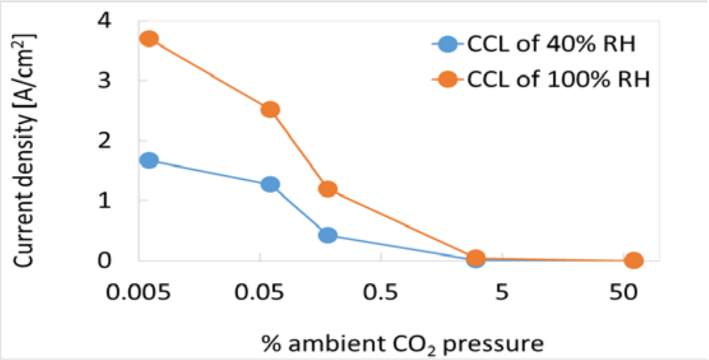
AEM:	AR series (IEC = 1.9 meq./g)
AEM thickness:	25 - 30 μm
Catalyst:	BASF 20% Pt/C, 0.2 mg_{Pt}/cm^2 for each electrode
Test conditions:	H_2/O_2 feed, 80°C fully humidified conditions, 15 psig backpressure



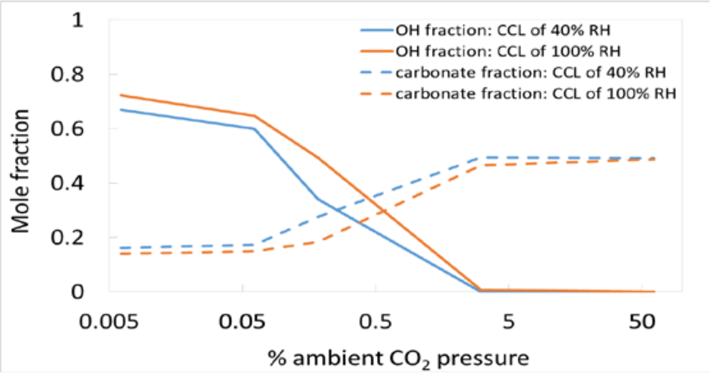
- Significant AMFC performance depending on ionomer structure; Best performance using MRH ionomers among other hydrocarbon ionomers
- **Next step:** Fuel cell performance optimization using PF ionomers

Accomplishments: CO_2 effect modeling

Current density @ 0.8 V versus [CO_2]

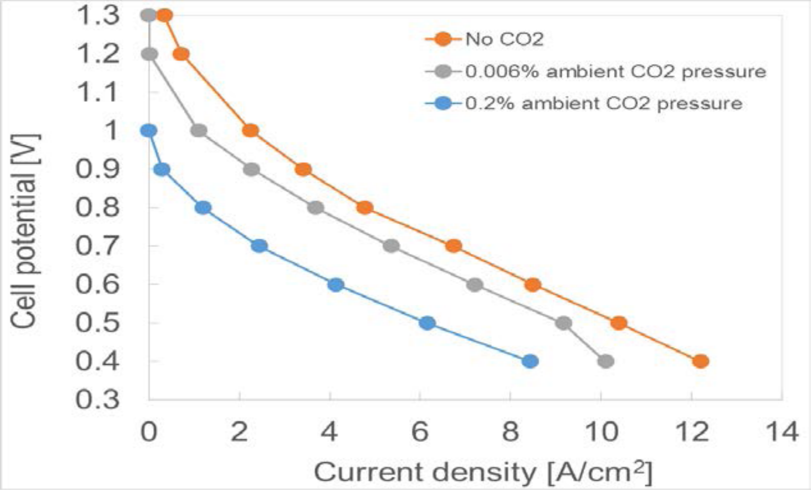


(OH^- & CO_3^{-2}) mole fraction versus [CO_2]

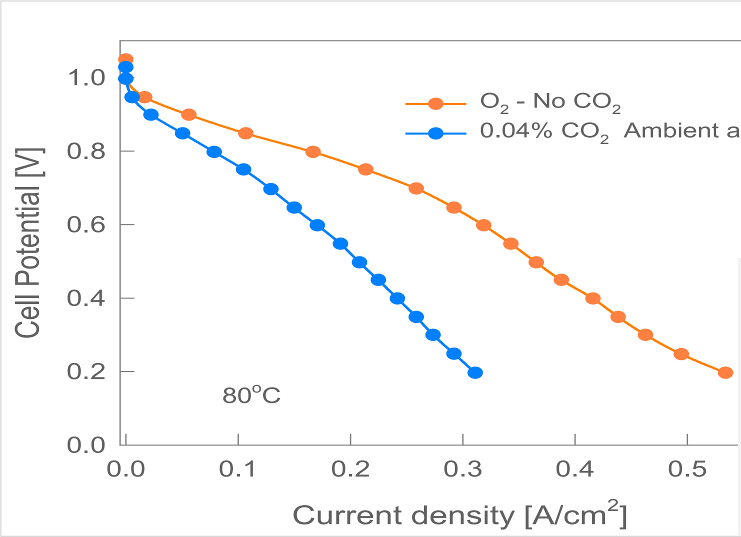


- Even the small amount of 50% of atmospheric CO_2 concentration (~ 0.02% CO_2) can significantly reduce the current density and deplete the OH^- species by CO_3^{-2} in the MEA.

Modeling results on CO_2 effect



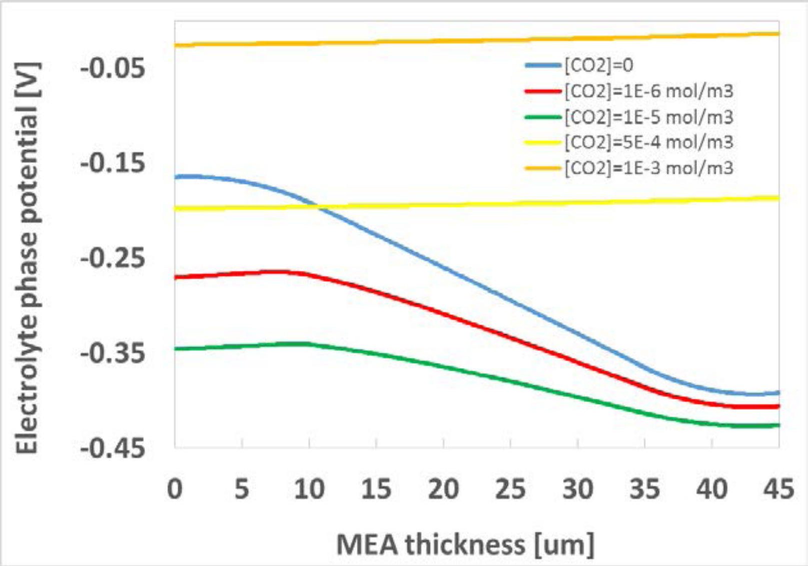
Experimental results on CO_2 effect



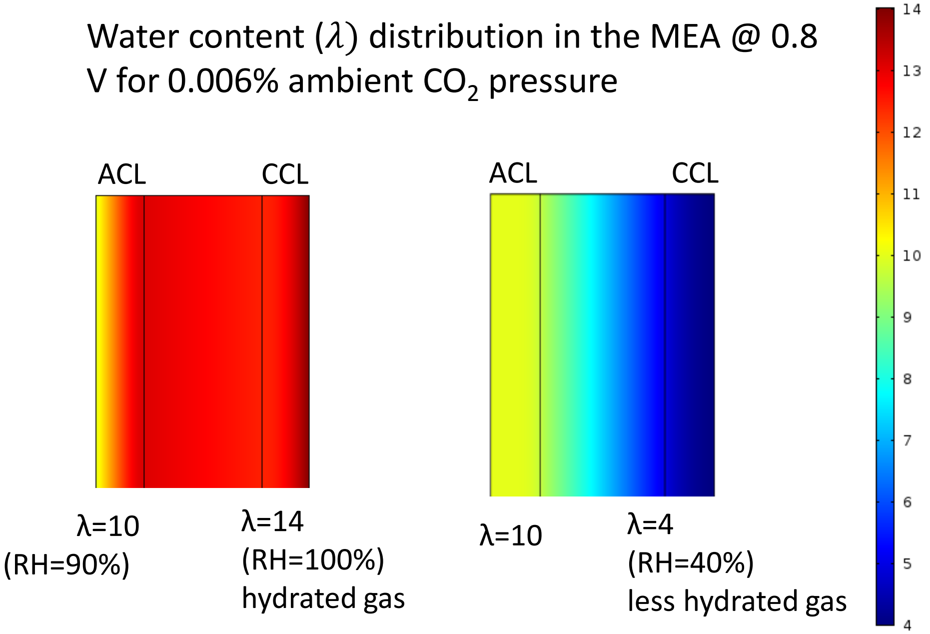
AR membrane (24 μm thick)
SNL ionomer
LANL dispersion technology
Tested at LANL with 5 cm^2 hardware

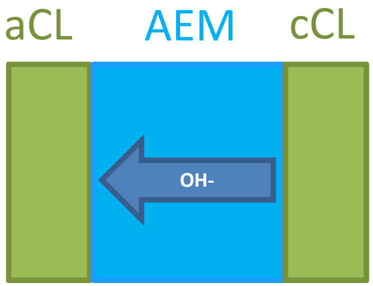
Accomplishments: Potential & water distribution modeling

Electrolyte phase potential distribution along the MEA thickness



Water content (λ) distribution in the MEA @ 0.8 V for 0.006% ambient CO_2 pressure





$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

- OH^- transport is governed mainly by migration due to potential gradient. However, there is less variation in the ionic potential across MEA with higher $[CO_2]$, reducing OH^- flux.

For modeling details: see the back-up slides 24

Collaborations/Interactions

Institutions	Type	Extent	Role and Importance
Los Alamos National Laboratory	Federal Laboratory	Major	- *DOE Hydrogen and Fuel Cell Program (Prime)* - Synthesis and characterization of AEMs and ionomer dispersion - Membrane, electrode and fuel cell performance test
Sandia National Laboratories	Federal Laboratory	Major	- *DOE Hydrogen and Fuel Cell Program (Sub)* - Synthesis and characterization of poly(phenylene) AEMs - Access to the state-of-the-art poly(phenylene) AEMs
Lawrence Berkeley National Laboratory	Federal Laboratory	Major	- *DOE Hydrogen and Fuel Cell Program (Sub)* - Characterization and modeling of AEMs
Rensselaer Polytechnic Institute	Academia	Major	- *RPI Internal Funding (Outside DOE program)* - Synthesis and characterization of SEBS and poly(biphenylene) AEMs
Solvay/Ion Power	Industry	Medium	- Supply of non-standard PFSA precursors
IRD	Industry	Minor	- *DOE Incubator Program* - 50 cm^2 MEA testing
National Institute of Advanced Industrial Sci. and Technol.	Foreign National Laboratory	Medium	- *LANL Cooperative Research and Development Agreements* - DFT modeling

Remaining Challenges and Barriers

- Membrane
  - **Alkaline stability:** Long term fuel cell performance loss associated with AEMs and possible mitigation strategy should be investigated.
- Ionomeric binder
  - **Quality of ionomer dispersion:** Ionomer particle size in liquid dispersion plays major role in interfacial reaction of electro-catalysts. Current ionomer dispersion does not provide best three-phase interface structure in the electrode layer.
- Membrane electrode assembly
  - **Interfacial compatibility:** Interfacial compatibility/adhesion between hydrocarbon membrane and PF ionomer-bonded electrode needs to be improved for high AMFC performance.
- AMFC performance
  - **(Bi) carbonate contamination:** Performance loss due to (bi) carbonate contamination may be problematic for end-use applications. Mitigation strategy needs to be developed.
  - **Catalyst HOR activity:** Cation adsorption to anode catalysts significantly lowers the overall performance. → leveraged research efforts with DOE Incubator project.
  - **Non-precious metal catalysts:** Extensive works with MEA fabrication and fuel cell testing are required. → leveraged research efforts with DOE Incubator project.
  - **Water management:** Flooding and water management issues may still remain.

Proposed Future Work

Task	Description	Expected completion day
1	Property optimization of AR series AEMs (RPI)	June 30, 2015
2	Synthesis and characterization of sulfone (or ketone) phenyl guanidinium functionalized poly(phenylene) AEM (SNL, LBNL and LANL)	June 30, 2015
3	Development of high quality PF alkyl amide polymer dispersion (LANL)	June 30, 2015
4	AMFC test under O_2 and air conditions (initial and long-term test) (LANL, IRD)	July 31, 2015
5	Incorporate the GDL and flow channels into the existing AMFC model (LBNL)	July 31, 2015
6	Manuscript submission and Patent filing (RPI, SNL, LBNL, LANL)	October 30, 2015

Summary

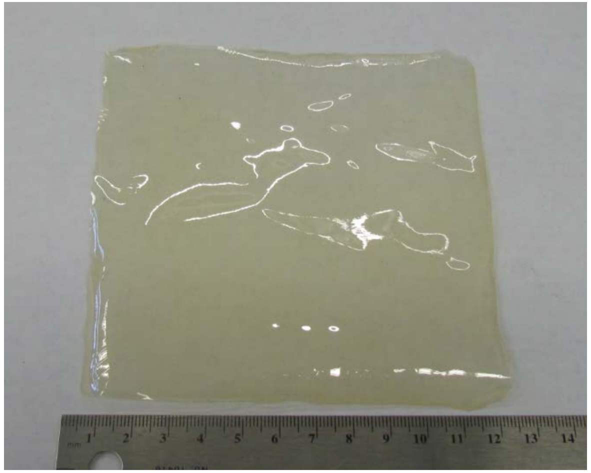
- FY15 MRH, AR and SEBS-QA series AEMs showed excellent conductivity, mechanical properties and alkaline stability compared with ATM-PP control.
  - Areal resistance < 0.1 Ω cm^2 was achieved for MRH and SEBS-QA series AEMs
  - Less than 5% degradation under > 1M KOH at 80°C was achieved for MRH, AR and SEBS-QA series
- FY15 PF ionomer with alkyl amide linkage was designed to increase amide stability under basic conditions; Fuel cell performance measurement using these ionomers is on-going.
- Developed a membrane+electrode model that takes into account the effect of CO_2 contamination on the AMFC performance; Combining with experimental data, benefits of higher temperature operation in the presence of CO_2 was demonstrated.

Technical Back-Up Slides

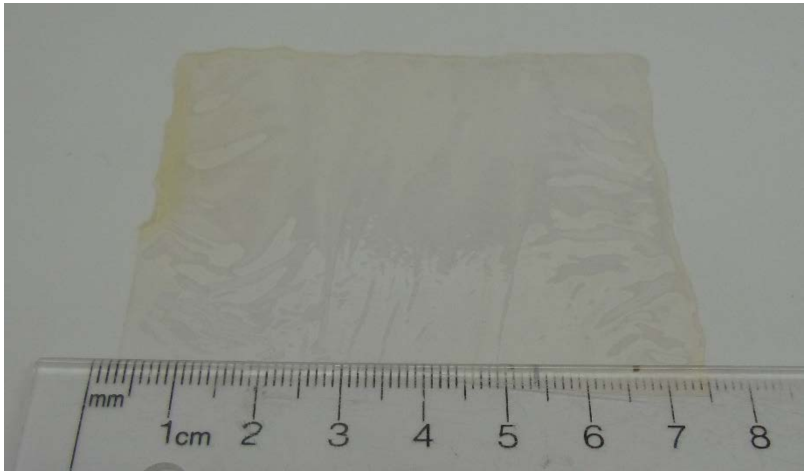
Solution Cast AEMs

ATM-PP (60 μm thick)

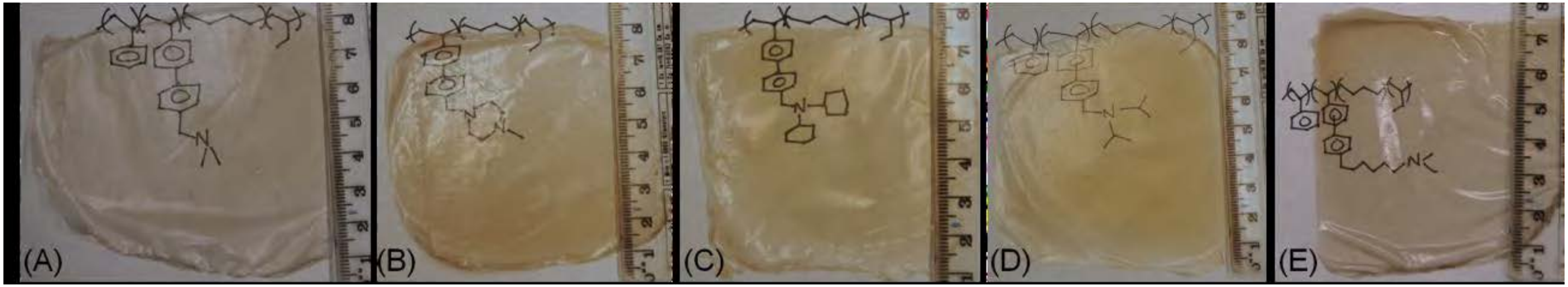
MRH (40 μm thick)



AR (20 μm thick)



SEBS-QA Series (30 - 50 μm thick)

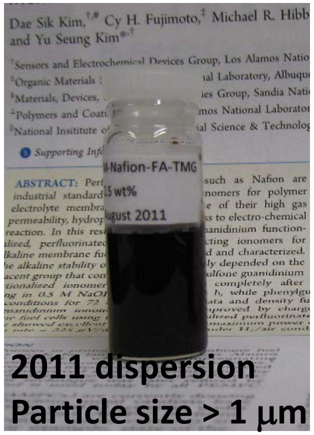


- Obtained thin, tough and uniform thickness membranes from solution cast techniques.

Ionomer Dispersions

Nafion®-FA-TMG

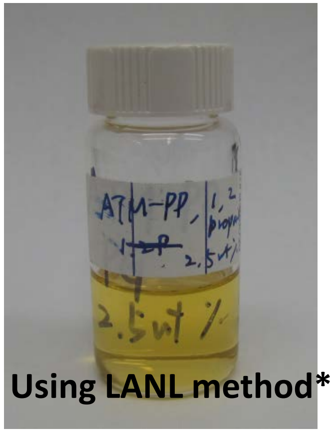
(2.5 wt.% dispersion)



2011 dispersion
Particle size > 1 µm

ATM-PP

(2.5 wt.% dispersion)



Using LANL method*

MRH

(1 wt.% dispersion)

Gel dispersion*

AR

(5 wt.% dispersion)

Nafion®-FA-TMG

(2.5 wt.% dispersion)

2014 dispersion
Particle size > 0.2 µm

PF Alkyl Amide

(1 wt.% dispersion)

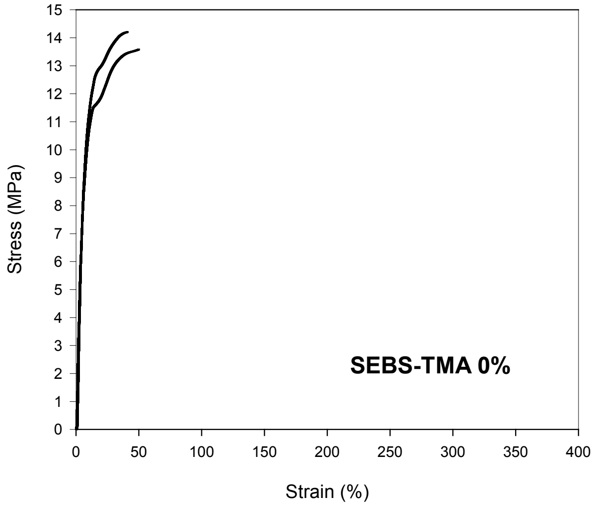
Fine dispersion
Particle size < 0.1 µm

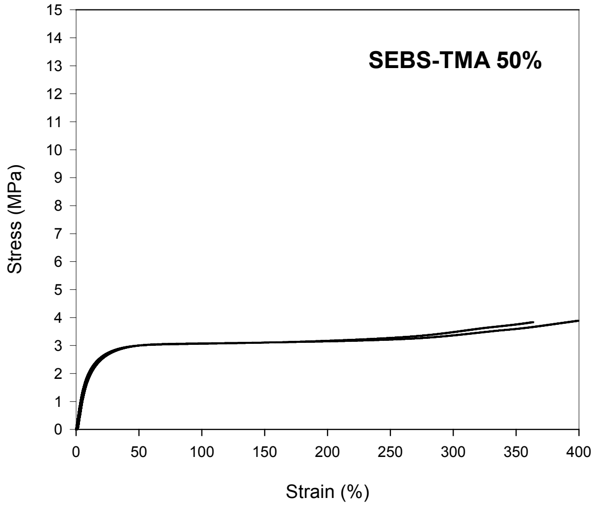
- 1 to 2.5 wt.% anion exchange ionomer dispersions were prepared.
- High quality dispersion using patent pending technology*

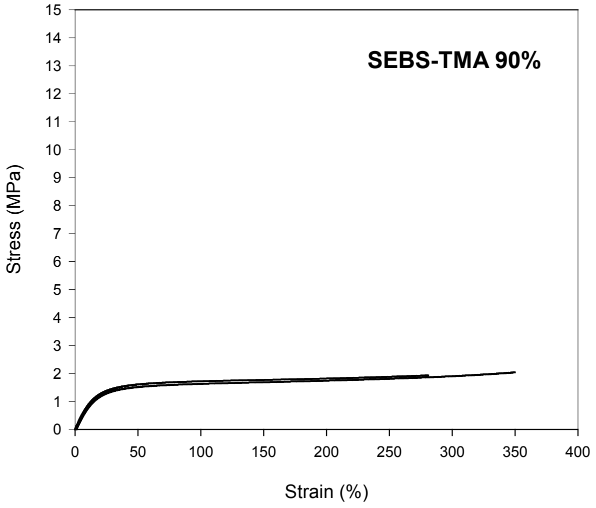
*Y.S. Kim, LANL Idea 15-00037

Effect of RH on Mechanical Properties of SEBS-QA AEMs

Cell temperature: 50°C; RH: 0, 50, 90%;
Number of samples: 2
Equilibrium time: 0% and 50% RH → 40 min; 90% RH → 60 min;
Load: 0.5 MPa/min; testing time: 2 to 5 hours / sample







- Like other ion exchange membranes, tensile strength increased and elongation at break of SEBS-QA AEMs decreased as RH increased.

Governing equations for ion and water fluxes

Electro-neutrality

$$C_{OH^-} + 2C_{CO_3^{-2}} + C_{HCO_3^-} = C_{ammonium^+} = C_t$$

OH$^-$ fraction

$$y_{OH^-} = \frac{C_{OH^-}}{C_t}$$

CO$_3^{-2}$ fraction

$$y_{CO_3^{-2}} = \frac{C_{CO_3^{-2}}}{C_t}$$

HCO$_3^-$ fraction

$$y_{HCO_3^-} = 1 - y_{OH^-} - 2y_{CO_3^{-2}}$$

$A \equiv OH^-$

$B \equiv CO_3^{-2}$

$C \equiv HCO_3^-$

$w \equiv water$

D_i : diffusion coefficient

ξ_i : electro-osmotic drag coefficient

OH$^-$ flux

$$\mathrm{N}_A = -\overbrace{D_A C_t \nabla y_A}^{\text{Diffusion}} + \overbrace{\frac{F D_A C_t}{RT} y_A \nabla \Phi}^{\text{Migration}} - \overbrace{\frac{D_A C_t}{RT} y_A \xi_A \nabla \mu_w}^{\text{Streaming-current}}$$

CO$_3^{-2}$ flux

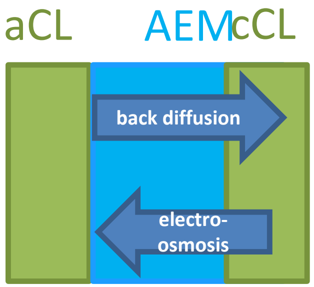
$$\mathrm{N}_B = -D_B C_t \nabla y_B + \frac{2F D_B C_t}{RT} y_B \nabla \Phi - \frac{D_B C_t}{RT} y_B \xi_B \nabla \mu_w$$

HCO$_3^-$ flux

$$\mathrm{N}_C = -D_C C_t \nabla (1 - y_A - 2y_B) + \frac{F D_C C_t}{RT}(1 - y_A - 2y_B)\nabla \Phi - \frac{D_C C_t}{RT}(1 - y_A - 2y_B)\xi_C \nabla \mu_w$$

water flux

$$\mathrm{N}_w = (\overbrace{\sum_{i=A,B,C} \xi_i N_i}^{\text{Electro-osmotic drag}}) - \overbrace{D_w C_t \nabla \lambda}^{\text{Back diffusion}} = \xi_A N_A + \xi_B N_B + \xi_C N_C - D_w C_t \nabla \lambda$$



$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$