Advanced Hydroxide Conducting Membranes

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Project ID: FC123

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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)

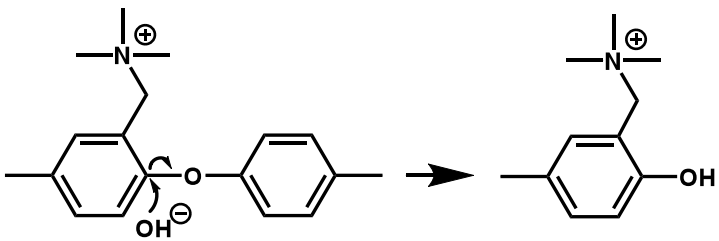
[a] *Y.S. Kim, Resonance-Stabilized Anion Exchange Polymer Electrolytes, US DOE 2014 Annual Merit Review, June, 16-20, 2014*
[b] *The interim project target was set for general fuel cell applications*
[c] *as of April 10, 2015*

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

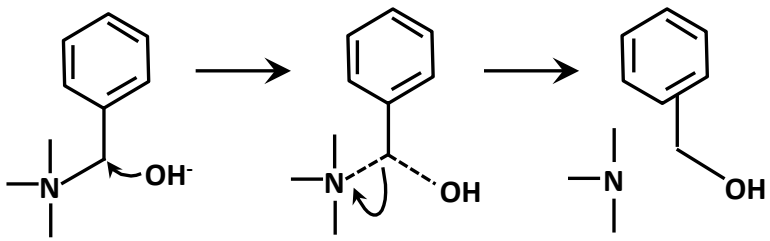
✓ Ether-free poly(phenylene) (SNL)

✓ 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]



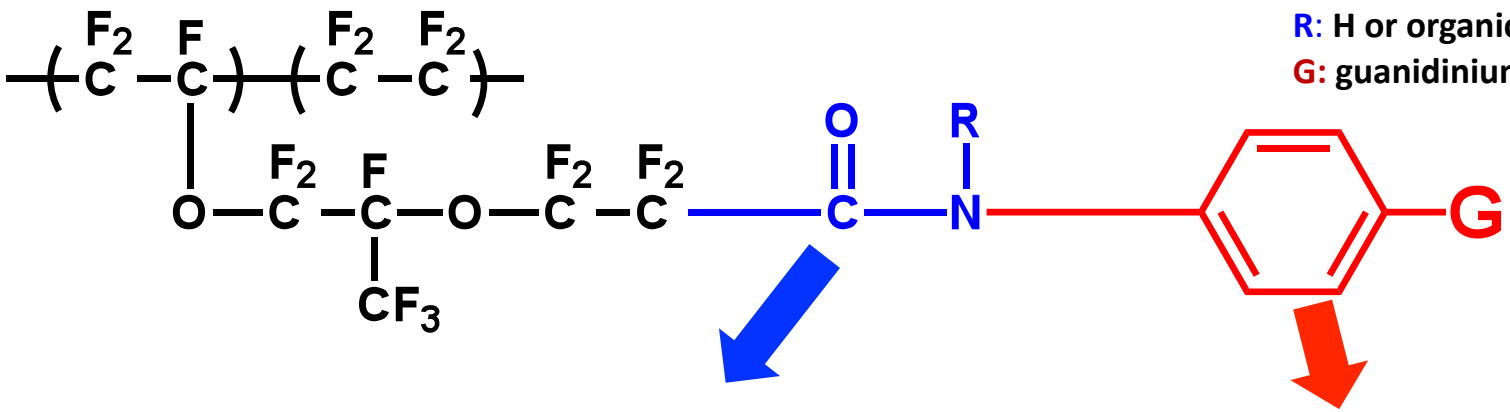
Our approach

✓ Hexamethyl ammonium (SNL, RPI)

✓ Phenyl guanidinium (LANL, SNL)

Approach: Anion exchange polymer dispersion

FY14 LANL Perfluorinated Ionomer*



Amide linkage

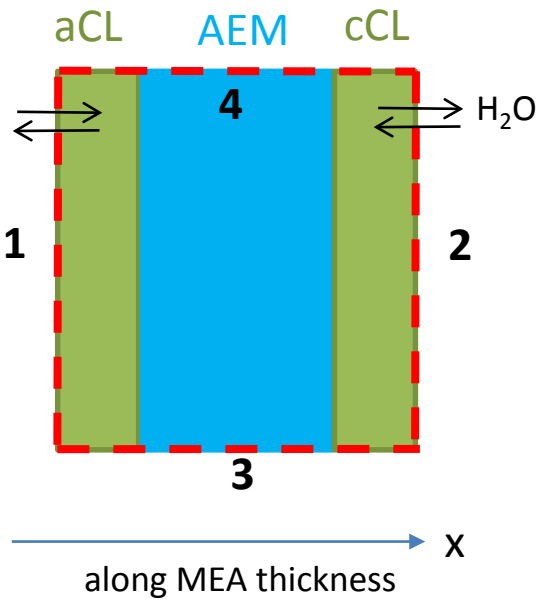
- Chemical stability of amide group: 8% loss after 72 h 0.5M NaOH at 80°C
- **Our approach**
  - ✓ Alkyl amide (LANL)

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:**

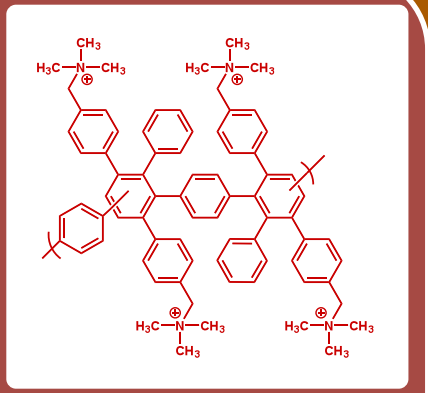
@ anode $$i_a = a_{Pt} i_{0,a} \left(\frac{C_{H_2}}{C_{H_2}^{ref}}\right)^{0.5} y_{OH^-} \exp\left(\frac{\alpha_a \eta_a F}{RT}\right) \qquad \eta_a = -\Phi_e - V_a^{eq} \qquad V_a^{eq} = \frac{RT}{nF} \ln(y_{OH}{}^2)$$

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

$a_{Pt} = 10^5\ \text{cm}^{-1}$ $\quad i_{0,HOR} = i_{0,ORR} = 3\ \text{mA/cm}^2$ $\quad C_{H_2} = C_{O_2} = 10\ \text{mol/m}^3$ (0.25 atm) $\quad C_{H_2}^{ref} = 16\ \text{mol/m}^3$

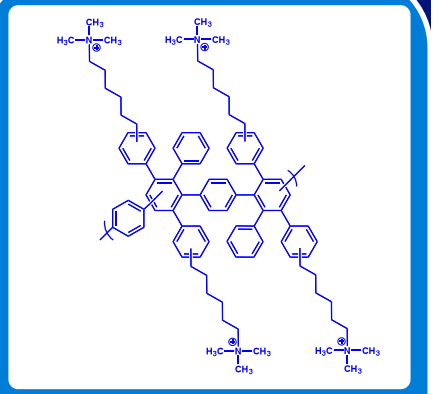
Accomplishments: Synthesized rigid polymers

ATM-PP Series



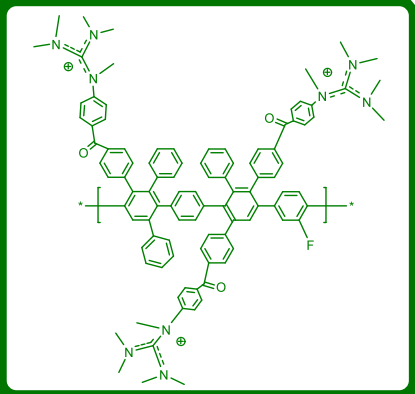
- **Control AEM (SNL)**
- **Progress**
  Polymer synthesis: 100%
  Characterizations: 100%
- **Demonstrated good polymer backbone stability in AMFC and AEM based water electrolysis**
- **Strength**
  Proven polymer stability
- **Weakness**
  Mechanical properties
  Cation stability

MRH Series



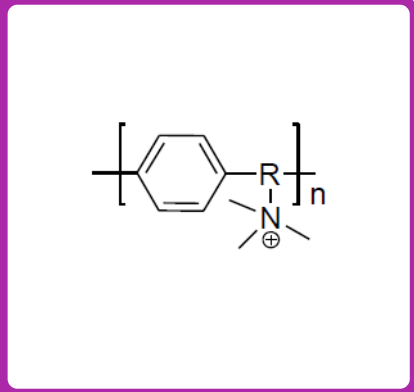
- **Hexamethyl ammonium functionalized poly(phenylene) AEM (SNL)**
- **Progress**
  Polymer synthesis: 100%
  Characterizations: 80%
- **Designed for enhanced cation stability**
- **Strength**
  Improved cation stability
  Better gas permeability
- **Weakness**
  Ionomer processibility

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

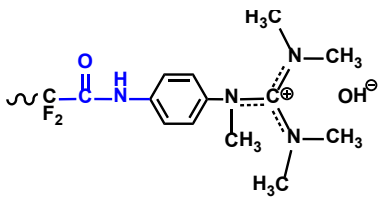


- **Hexamethyl ammonium functionalized poly(biphenylene) AEM (RPI)**
- **Progress**
  Polymer synthesis: 100%
  Characterizations: 60%
- **Introducing flexible alkyl group into the polymer backbone**
- **Strength (expected)**
  Improved mechanical properties
- **Weakness**
  ?

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

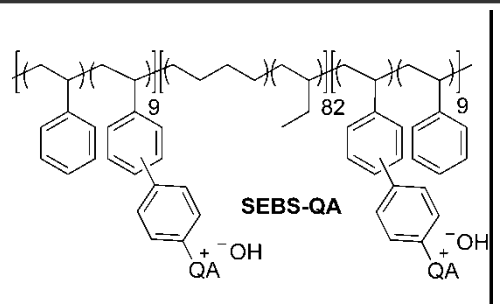
Accomplishments: Synthesized flexible polymers

Nafion®-FA-TMG Series



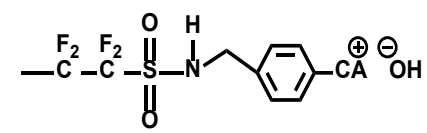
- **Perfluorinated (PF) control AEM (LANL & SNL)**
- **Progress**
  Polymer synthesis: 100%
  Characterizations: 100%
- **Guanidinium functionalized stable PF anion exchange polymer**
- **Strength**
  Low water uptake
  Excellent hydrophobicity ideal for ionomeric binder
- **Weakness**
  Processibility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

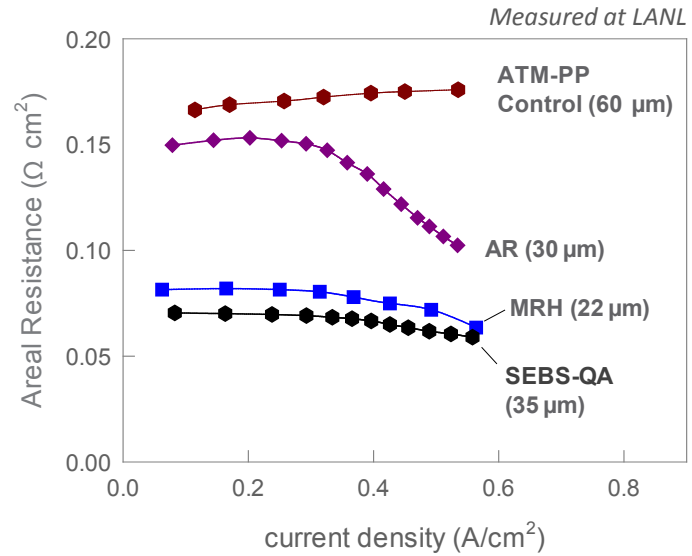
For AEM and dispersion appearance: see back-up slides 21, 22

Accomplishments: Membrane conductivity/resistance

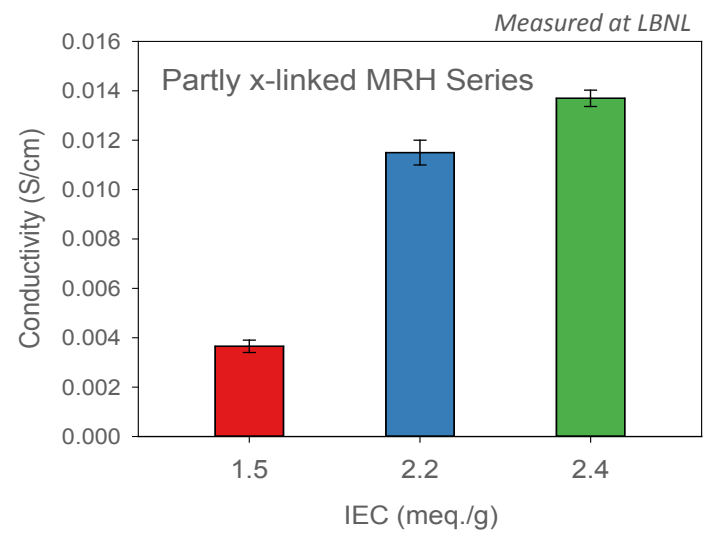
Conductivity Summary

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 cm²) for MRH and SEBS-QA AEMs**



Accomplishments: Membrane mechanical properties

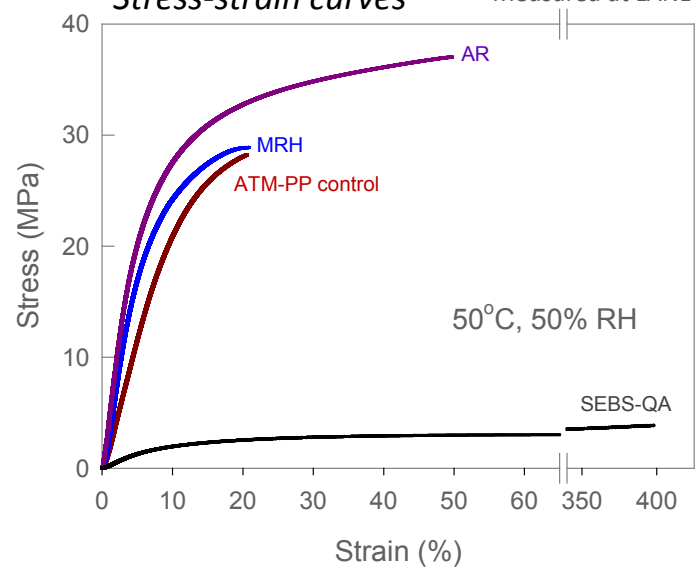
Summary of Mechanical Properties

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

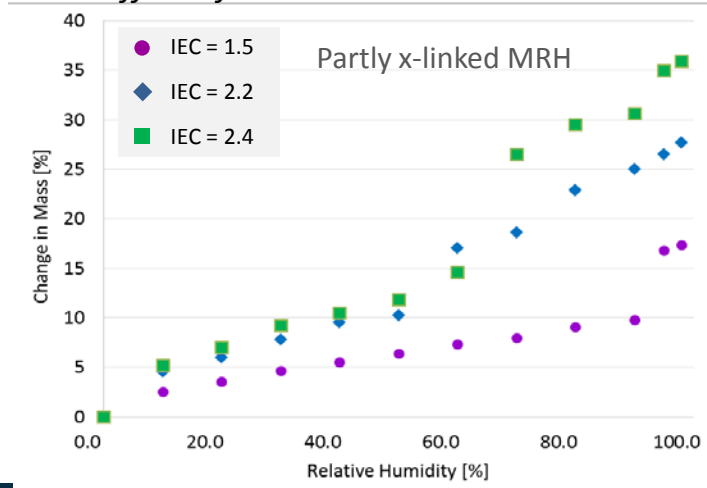
[a] measured at 30°C; [b] Hydroxide form AEMs measured at 50°C, 50% RH

- 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*

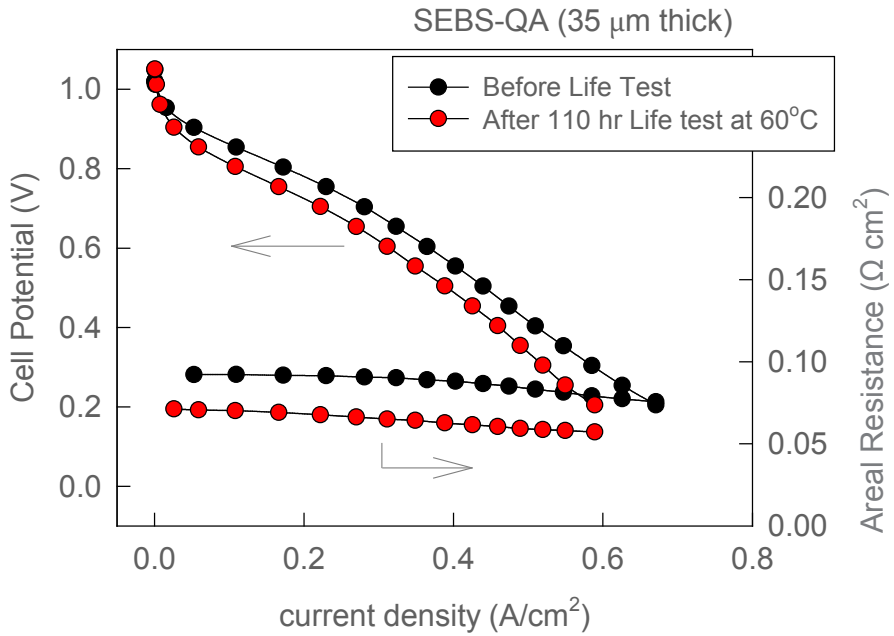


Accomplishments: Membrane stability

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

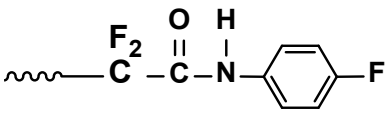
[a] Ref. M. R. Hibbs, J. Polym. Sci. Part B. 51, 1736, 2013



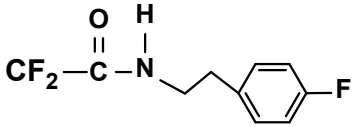
- Improved alkaline stability of FY15 AEMs compared with ATM-PP control from ex-situ test.
- Confirmed alkaline stability of SEBS-QA AEMs under AMFC operating conditions
- **Highlight: Achieved FY 15 stability milestone for AR and SEBS-QA: < 10% loss after 500 h, 0.5M NaOH at 80°C AEMs (May 30, 2015)**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

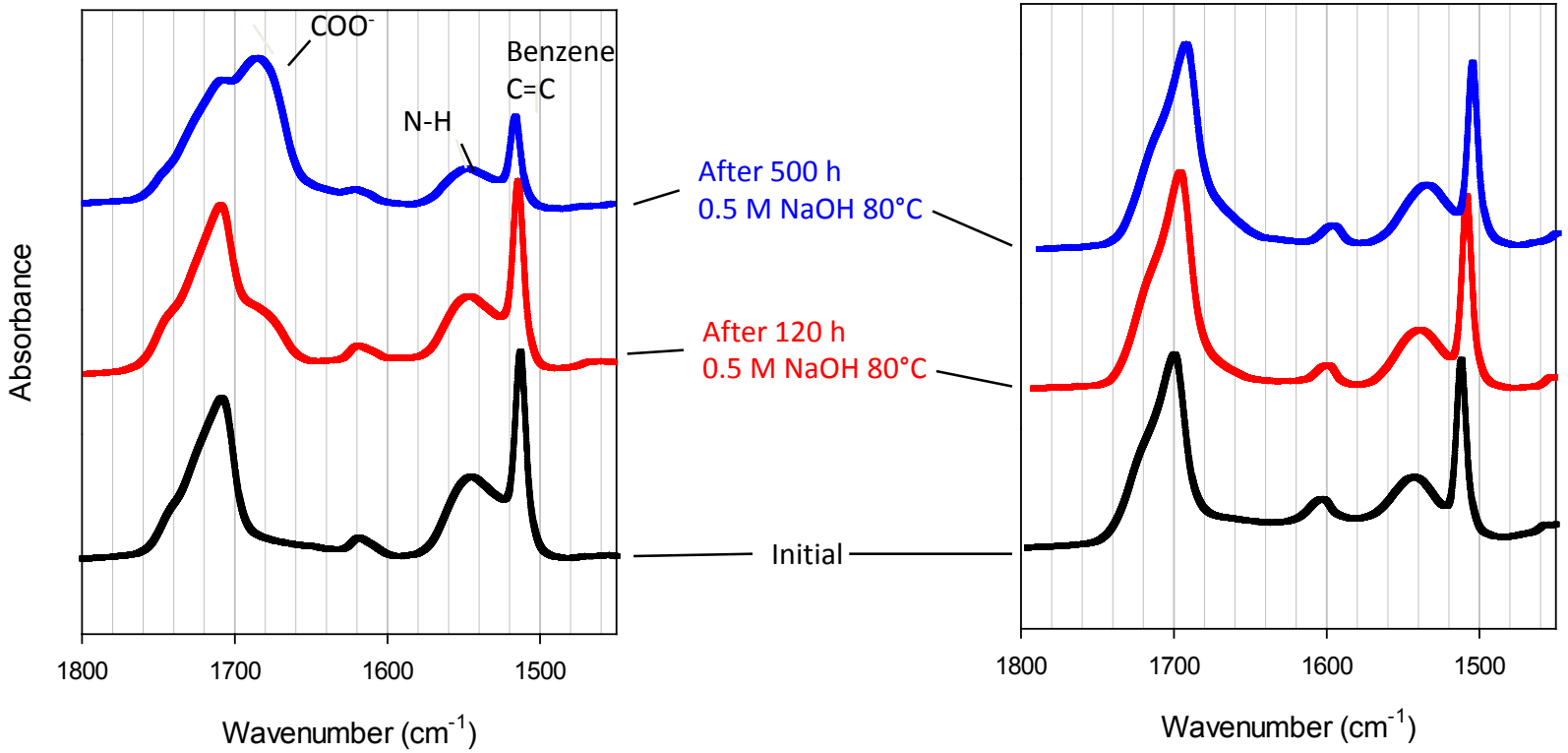
Accomplishments: Amide group stability of PF polymers

Phenyl Amide

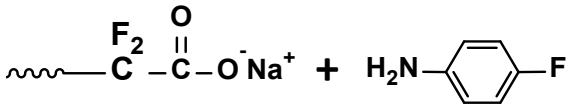


Phenyl Alkyl Amide





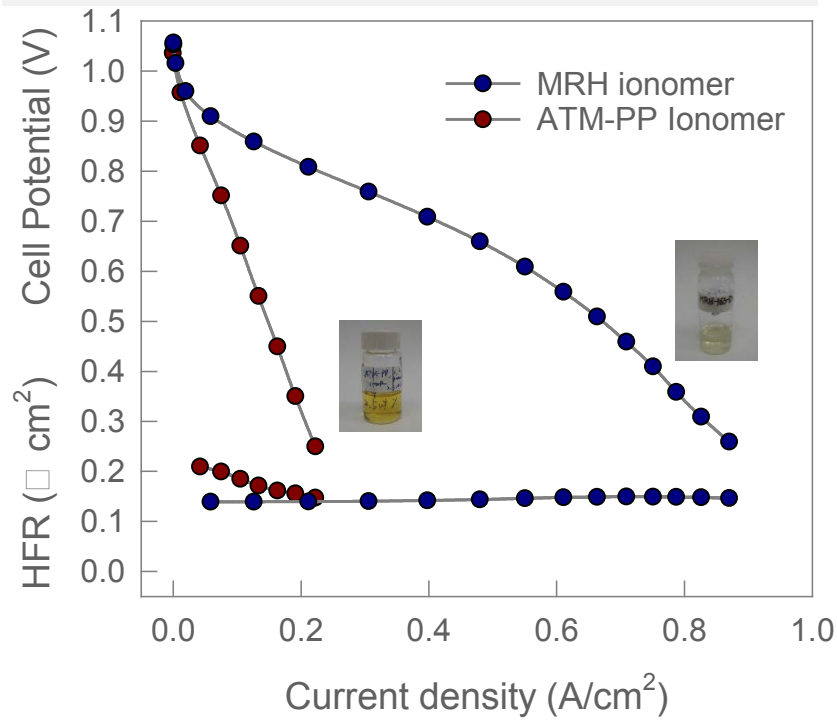
Degradation →



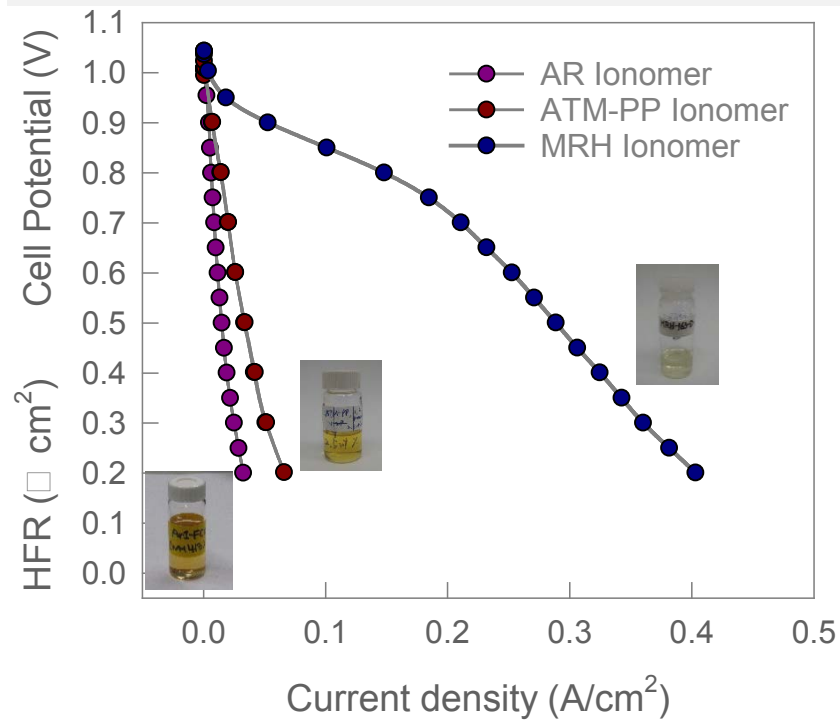
- Poor stability of phenyl amide group under high pH conditions
- No FTIR peak loss of phenyl alkyl amide group under high pH conditions

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



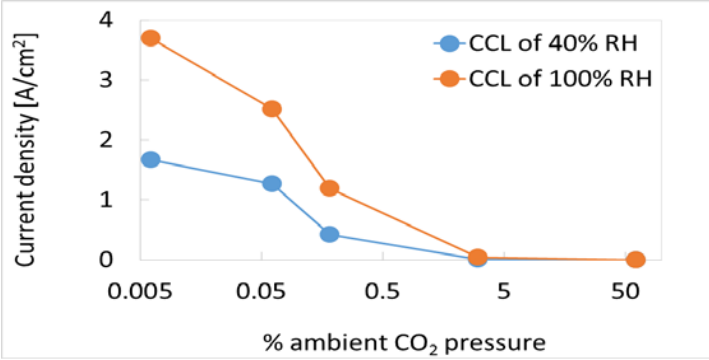
AEM: AR series (IEC = 1.9 meq./g)
AEM thickness: 25 - 30 μm
Catalyst: BASF 20% Pt/C, 0.2 mg_{Pt}/cm^2 for each electrode
Test conditions: H_2/O_2 feed, 80°C fully humidified conditions, 15 psig backpressure



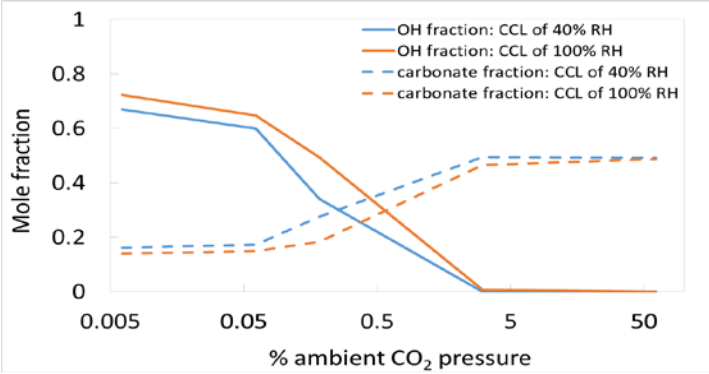
- Significant AMFC performance depending on ionomer structure; Best performance using MRH ionomers among other hydrocarbon ionomers
- **Next step:** Fuel cell performance optimization using PF ionomers

Accomplishments: CO_2 effect modeling

Current density @ 0.8 V versus [CO_2]

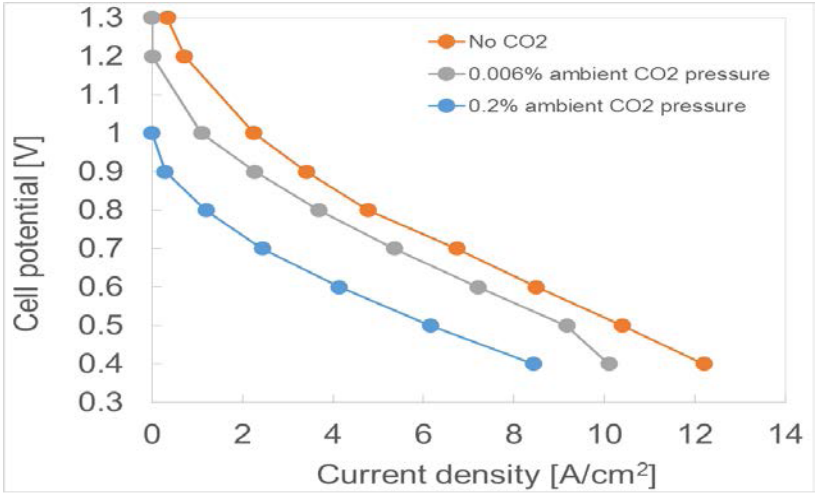


(OH^- & CO_3^{-2}) mole fraction versus [CO_2]

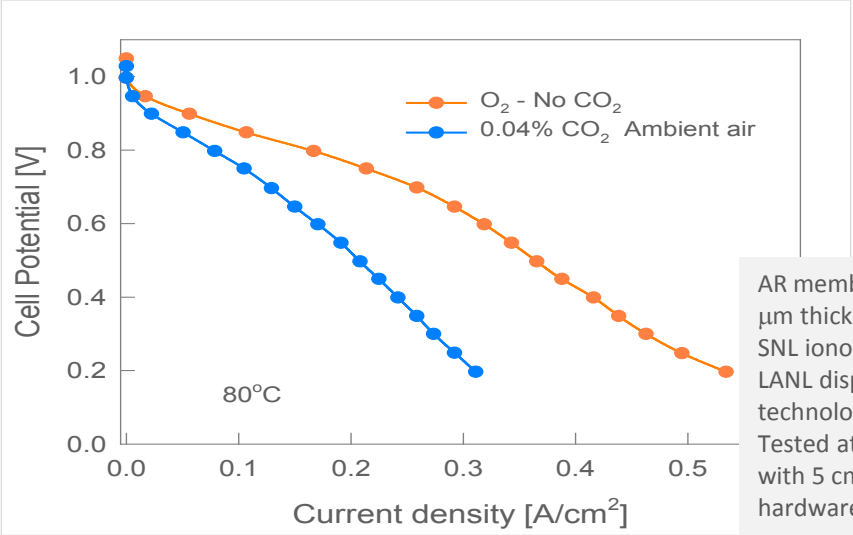


- Even the small amount of 50% of atmospheric CO_2 concentration (~ 0.02% CO_2) can significantly reduce the current density and deplete the OH^- species by CO_3^{-2} in the MEA.

Modeling results on CO_2 effect



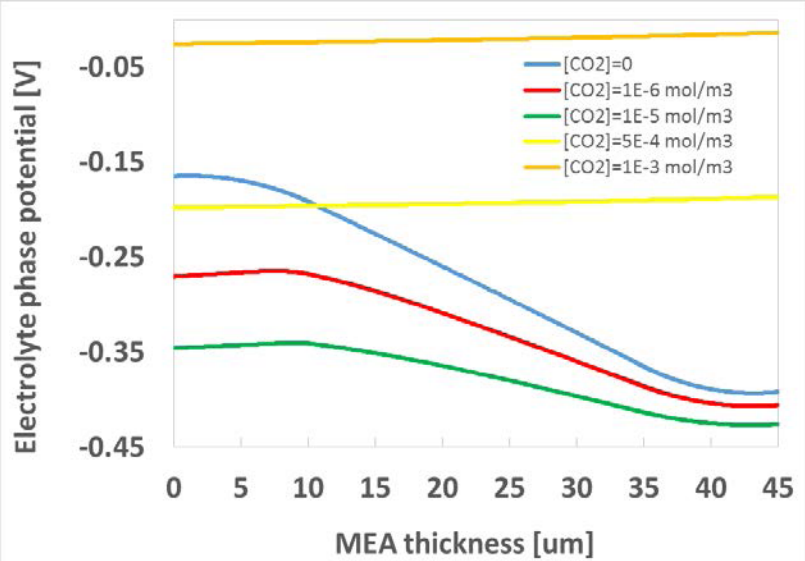
Experimental results on CO_2 effect



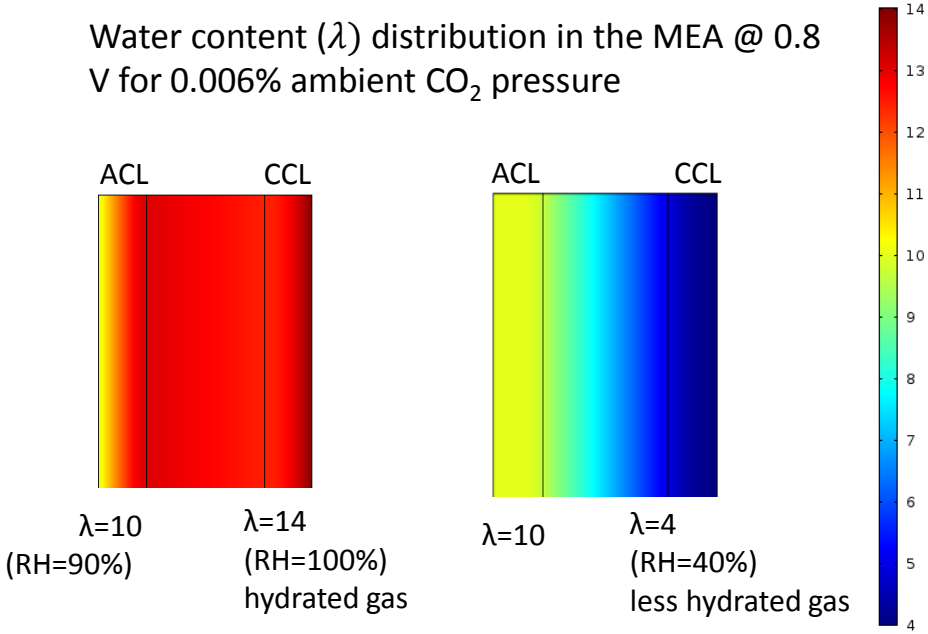
AR membrane (24 µm thick)
SNL ionomer
LANL dispersion technology
Tested at LANL with 5 cm² hardware

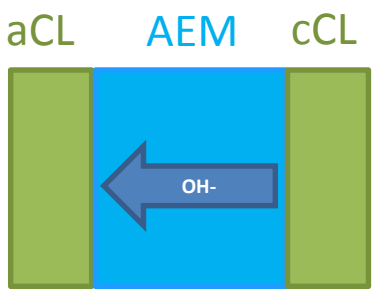
Accomplishments: Potential & water distribution modeling

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

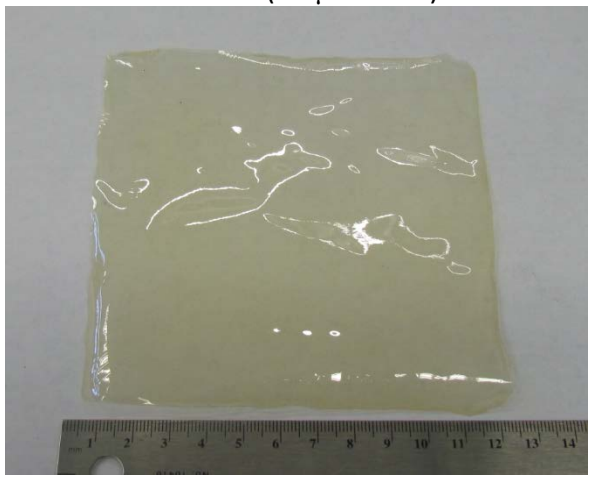
- FY15 MRH, AR and SEBS-QA series AEMs showed excellent conductivity, mechanical properties and alkaline stability compared with ATM-PP control.
  - Areal resistance < 0.1 Ω cm^2 was achieved for MRH and SEBS-QA series AEMs
  - Less than 5% degradation under > 1M KOH at 80°C was achieved for MRH, AR 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

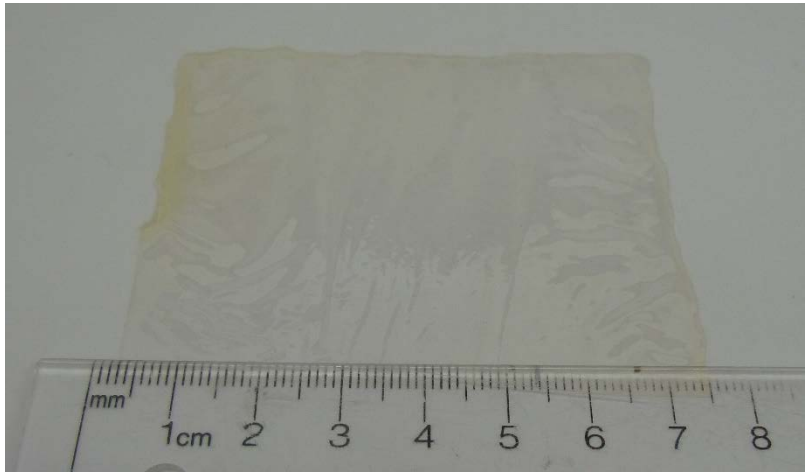
Solution Cast AEMs

ATM-PP (60 μm thick)

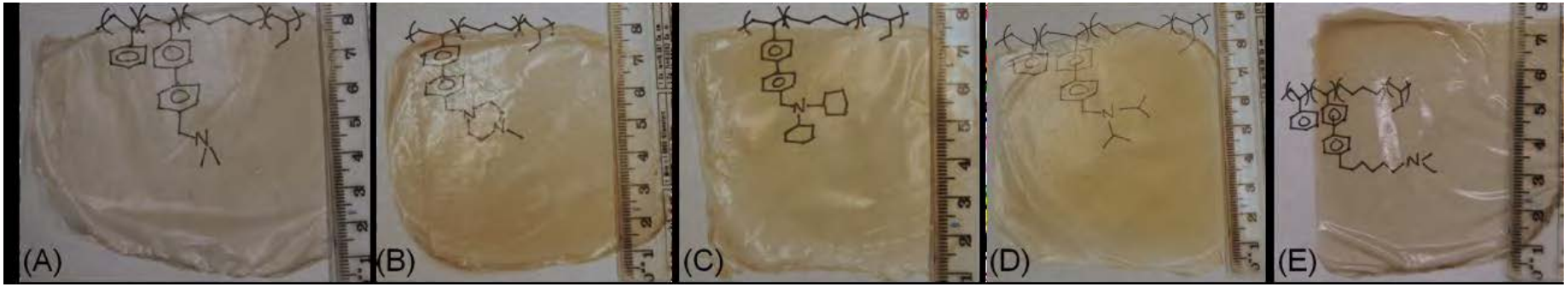
MRH (40 μm thick)



AR (20 μm thick)



SEBS-QA Series (30 - 50 μm thick)



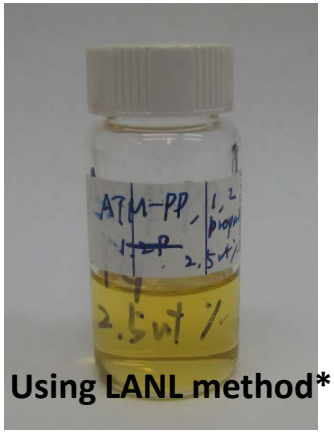
- Obtained thin, tough and uniform thickness membranes from solution cast techniques.

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)

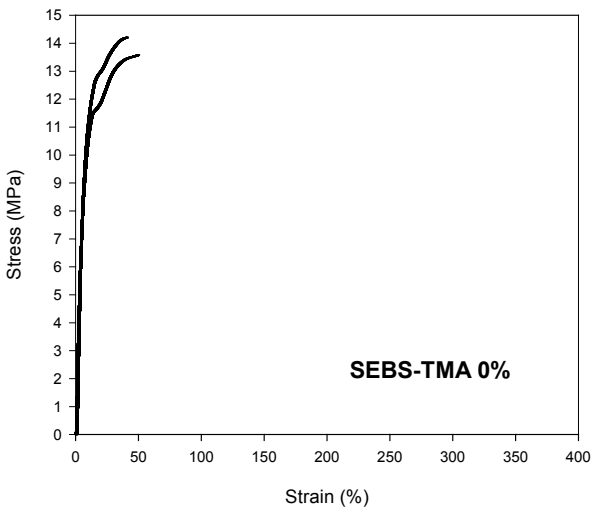
Fine dispersion
Particle size < 0.1 μm

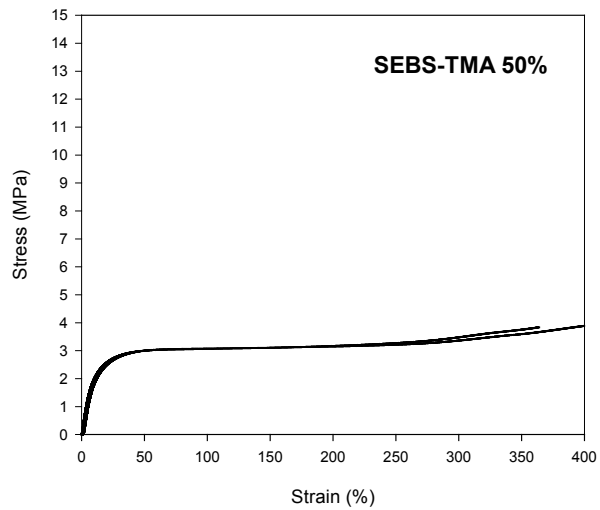
- 1 to 2.5 wt.% anion exchange ionomer dispersions were prepared.
- High quality dispersion using patent pending technology*

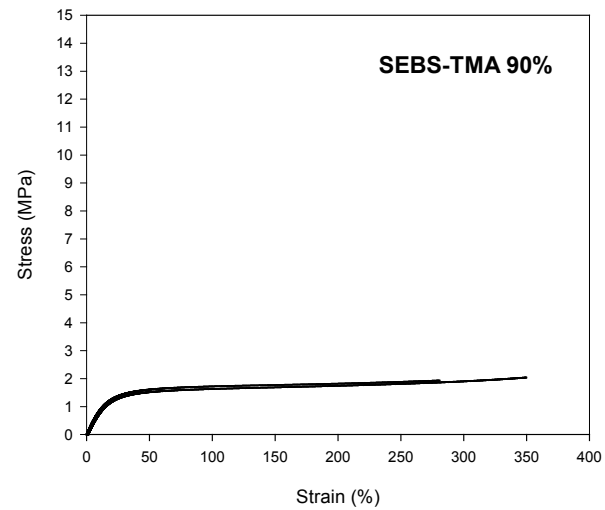
*Y.S. Kim, LANL Idea 15-00037

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

$$N_A = \underbrace{-D_A C_t \nabla y_A}_{\text{Diffusion}} + \underbrace{\frac{FD_A C_t}{RT} y_A \nabla\Phi}_{\text{Migration}} - \underbrace{\frac{D_A C_t}{RT} y_A \xi_A \nabla\mu_w}_{\text{Streaming-current}}$$

CO_3^{-2} flux

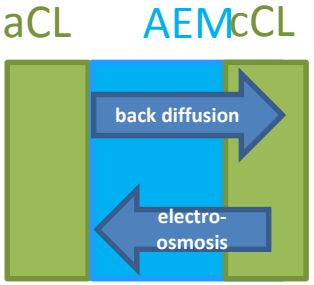
$$N_B = -D_B C_t \nabla y_B + \frac{2FD_B C_t}{RT} y_B \nabla\Phi - \frac{D_B C_t}{RT} y_B \xi_B \nabla\mu_w$$

HCO_3^- flux

$$N_C = -D_C C_t \nabla(1 - y_A - 2y_B) + \frac{FD_C C_t}{RT}(1 - y_A - 2y_B)\nabla\Phi - \frac{D_C C_t}{RT}(1 - y_A - 2y_B)\xi_C \nabla\mu_w$$

water flux

$$N_w = \underbrace{\left(\sum_{i=A,B,C} \xi_i N_i\right)}_{\text{Electro-osmotic drag}} - \underbrace{D_w C_t \nabla\lambda}_{\text{Back diffusion}} = \xi_A N_A + \xi_B N_B + \xi_C N_C - D_w C_t \nabla\lambda$$



$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$ $\quad$ $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$