Channeling Engineering of Hydroxide Ion Exchange Polymers and Reinforced Membranes

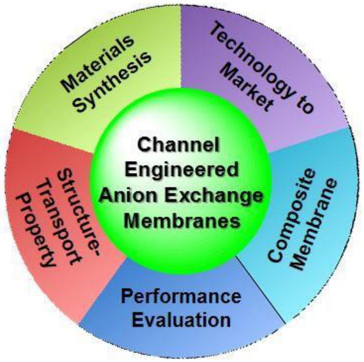
PI: CHULSUNG BAE

RENSSELAER POLYTECHNIC INSTITUTE

APRIL 30, 2019

Award No.: DE-AR0000769

Overview



Timeline

- Duration: 36 months
- Start: 01/20/17
- End: 01/19/20

Barriers

- Cost
- Performance
- Durability

Budget

- Total Project Budget: $ 2,497,726
- Total Cost Share: $ 252,399
- Total Federal Share: $ 2,245,327
- Total DOE Fund Spent: $ 1,315,476 (as of 02/19/2019)

Partners

- Georgia Institute of Technology
- Xergy
- Proton OnSite

Relevance

Objectives

- To develop ***highly ion conductive*** hydroxide anion exchange membranes (AEMs) by designing ***chemically stable bonds*** and improving ***mechanical stability*** by ***composite membrane approach***, which will meet or exceed the IONICS FOA metrics.
- The technology-to-market activities will prepare a pathway to ***the first commercial AEM products*** suitable for electrochemical energy conversion technology.

FOA Metrics	Current Year	Final Target
Chemical Stability 1M KOH aq., 80 °C	800 h, <2% drop	1000 h, <2% drop
Membrane Area 10x10 cm	≥90% uniformity	≥90% uniformity
Ionic ASR (Ohm-cm^2)	<0.06 80 °C	<0.04 80 °C
RH ASR (Ohm-cm^2)	<0.12 80 °C, ≤50% RH	<0.08 80 °C, ≤50% RH
Humidity Cycling	≥5,000 RH cycles ≥80% properties	≥20,000 RH cycles ≥50% properties
Humidity Stability	≥ 5	≥ 5
Swelling in water (OH^- form)	<30%, 25 °C <50%, 80 °C	<20%, 25 °C <25%, 80 °C
Pressure Differential	≥ 1 bar (14.5 psi)	≥ 1 bar (14.5 psi)
Cost	N/A	≤$20/m^2
Mechanical Strength 50 °C and 50% RH	stress: ≥24 MPa, strain: ≥80%	stress: ≥30 MPa, strain: ≥100%

Relevance

Impact (April 2018 - March 2019)

- A material that meets at least ***8 of the 9*** current FOA Metrics has been produced (Table, highlighted in green). This is a significant advancement in ***overcoming the barriers*** to commercialization.
- 3 downselected materials were reinforced by collaborator, Xergy, to form robust ***composite AEMs***. Optimizations are ongoing.
- Characterizations by RPI and by collaborator, Proton OnSite, are ongoing.

FOA Metrics	Current Year
Chemical Stability 1M KOH aq., 80 °C	800 h, <2% drop
Membrane Area 10x10 cm	≥90% uniformity
Ionic ASR (Ohm-cm^2)	<0.06 80 °C
RH ASR (Ohm-cm^2)	<0.12 80 °C, ≤50% RH
Humidity Cycling	≥5,000 RH cycles ≥80% properties
Humidity Stability	≥ 5
Swelling in water (OH^- form)	<30%, 25 °C <50%, 80 °C
Pressure Differential	≥ 1 bar (14.5 psi)
Mechanical Strength 50 °C and 50% RH	stress: ≥24 MPa, strain: ≥80%

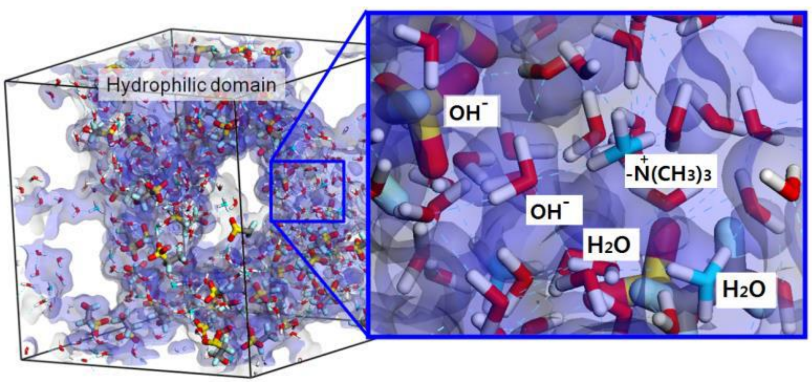
Meets Current Year Target (green)

Under Evaluation (blue: Humidity Cycling)

Approach

Innovation

- Polymers made of ***chemically stable*** C–C backbones and ionic side groups
- Creation of ***hydrophilic channels with high ion density*** via self-aggregation of ionic side groups of polymer
- Impregnation into dimensionally stable matrix for scalable ***composite membranes***



Task outline, technical objectives

1. All carbon-based aromatic random and block anionic polymers (RPI)
2. Norbornene-based random and block anionic polymers (Georgia Tech)
3. Reinforced composite membranes (Xergy)
4. Membrane performance evaluations (Proton Onsite)
5. Techno-economic analysis (Xergy)

Tech-to-Market Objectives

- **RPI** & **Georgia Tech**: scalable low-cost ionic polymer resins
- **Xergy**: membrane manufacturer exploring different markets
- **Proton OnSite**: membrane evaluator exploring electrolysis market
- **Xergy** will provide commercial AEMs to other customers within 12 mo. **(lead T2M)**

Approach

Anticipated challenges and approach:

- **Low area specific resistance (ASR)** ➡ *thin* membrane (10-15 μm)
- **Mechanical stability** ➡ ***high MW, crosslinking, composite*** membrane
- **Scalability** ➡ membrane manufacturing by ***roll-to-roll*** process
- **Cost** ➡ *convenient synthesis* using inexpensive chemicals

Statement of Work		Schedule (Quarter)
Task #	**Task Description**	
1	1.1 SEBS-based Anionic BCP	1-8
	1.2 Polynorbornene-based Anionic BCPs	1-10
	1.3 Biphenyl-based Anionic Copolymers	4-10
2	Reinforced Composite Membrane	4-11
3	Polymer Membrane Characterization	5-10
4	Membrane Performance Evaluation	6-12
5	Cost Analysis of Membranes	11-12

Accomplishments and Progress

RPI

- 3 downselected free-standing membranes have already met most of the 10 final targets (highlighted in green).
- Excellent performance and high chemical stability is demonstrated, with humidity cycling remaining as the major challenge to overcome.

FOA Metrics	Polymer A	Polymer B	Polymer C
Chemical Stability 1M KOH aq., 80 °C	IEC loss: <1%	IEC loss: 1.5%	IEC loss: <1.5%
Membrane Area	>90% uniform	>90%	>90%
Ionic ASR, 80 °C	0.023 Ohm-cm^2	0.031 Ohm-cm^2	0.023 Ohm-cm^2
RH ASR 80 °C, 70% RH	0.042 Ohm-cm^2	0.028 Ohm-cm^2	0.057 Ohm-cm^2
Humidity Cycling 20,000 Cycles	Under evaluation	Under evaluation	1,000 cycles stress: 52 MPa strain: 9%
Humidity Stability	12	4.33	3
Swelling in water (OH^- form)	22%, 25 °C 32%, 80 °C	32%, 25 °C 27%, 80 °C	9%, 25 °C 19%, 80 °C
Pressure Differential	Passed up to 250 psi	Passed up to 250 psi	Passed up to 250 psi
Mechanical: 50 °C and 50% RH	stress: 32 MPa strain: 234%	stress: 40 MPa strain: 140%	stress: 13 MPa strain: 105%

- Cost analysis are not yet available.

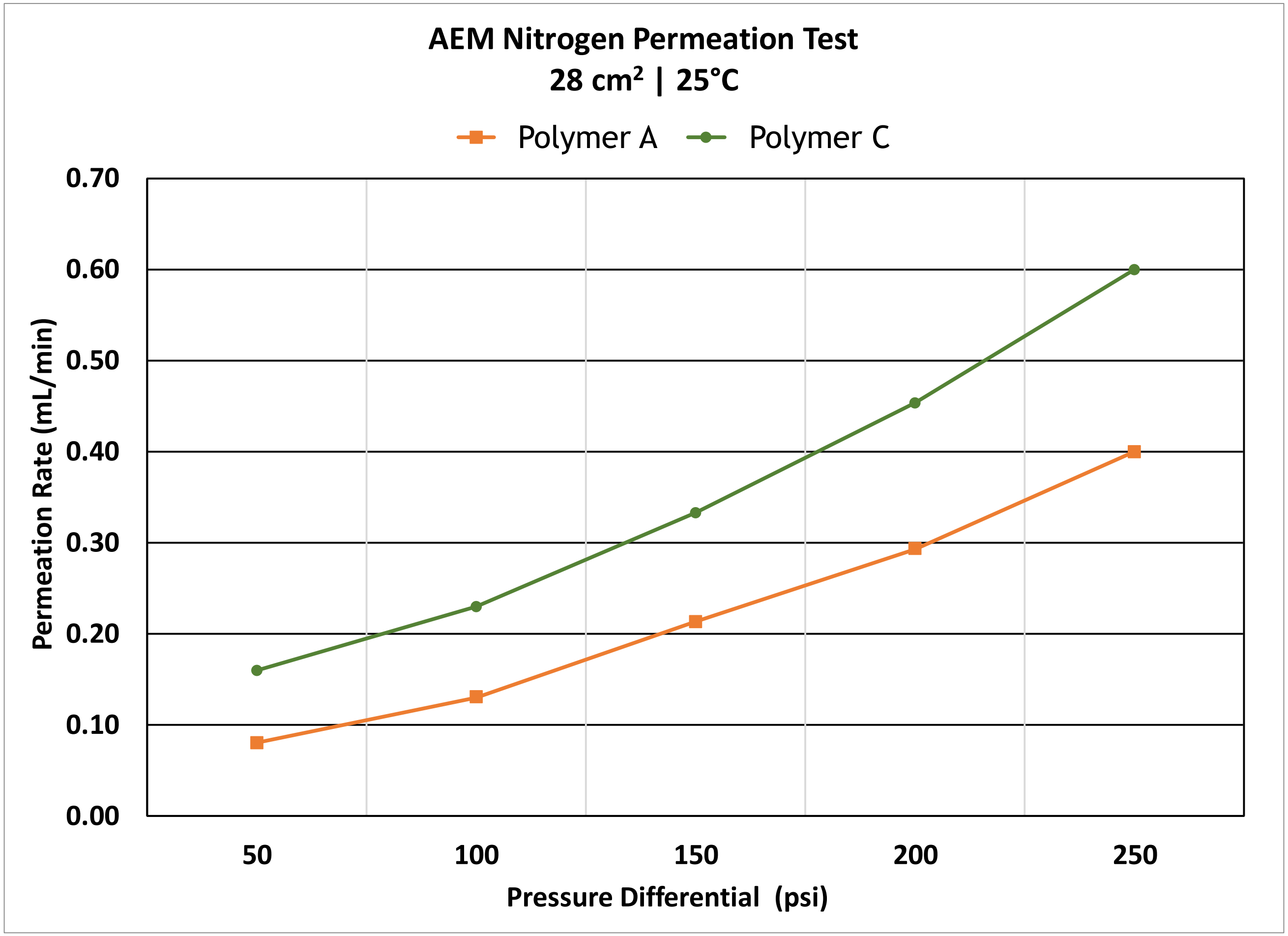
Meets Final Target (green)

Does Not Meet Final Target (blue)

Accomplishments and Progress

Proton OnSite

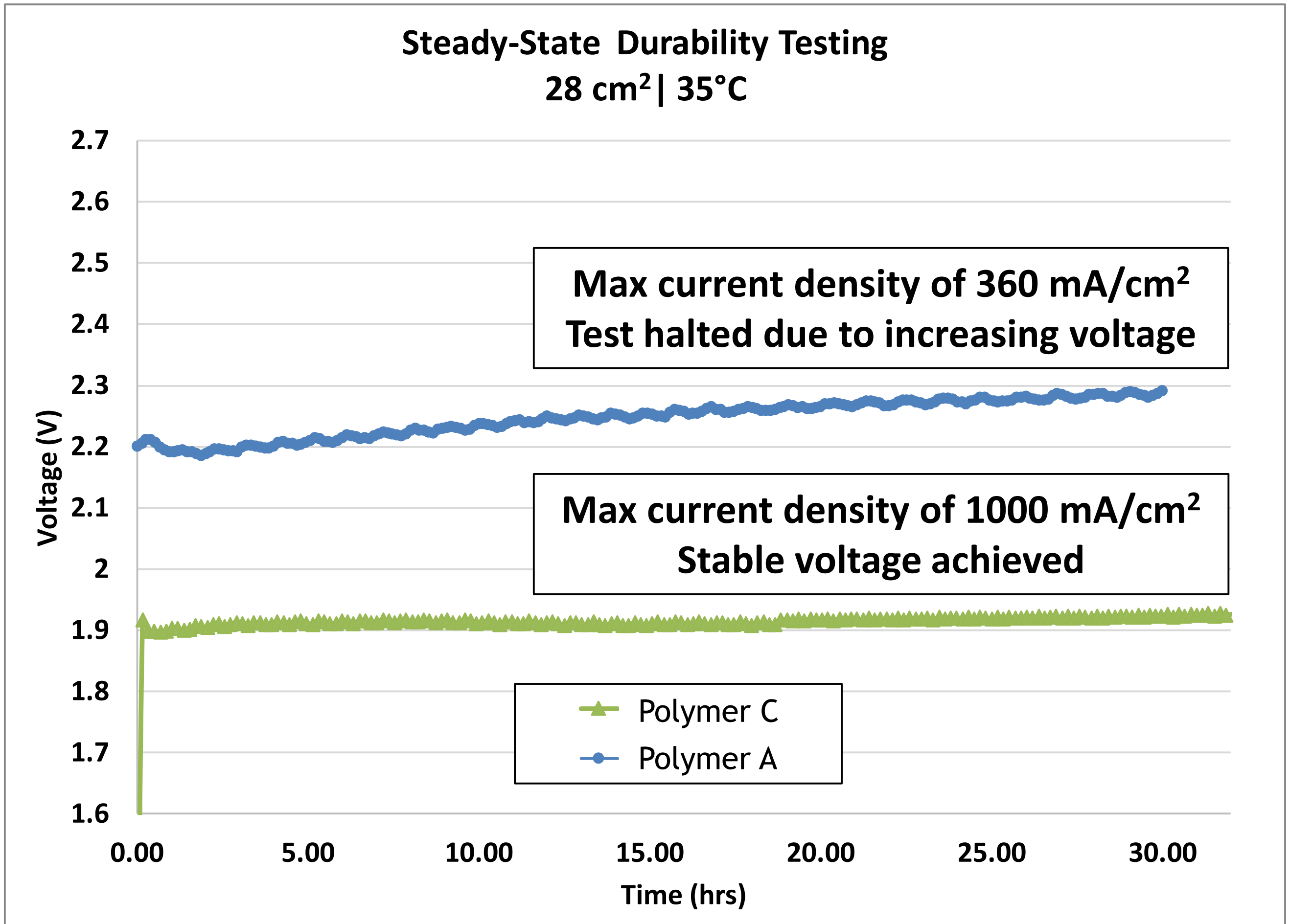
- Diffusion measurements were successful at nitrogen differential pressures up to 250 psi
- Proton's commercial 28cm^2 cell stack was used to simulate typical device sealing and active area forces

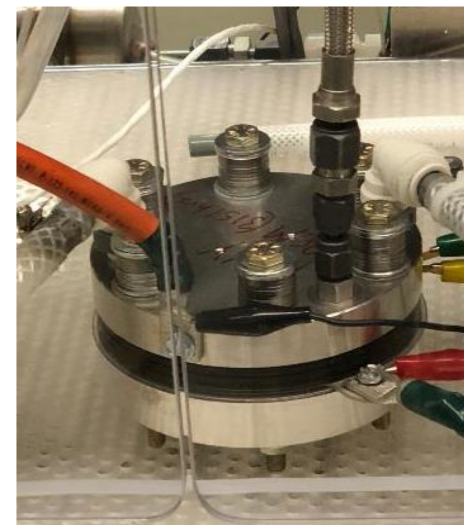


Accomplishments and Progress

Proton OnSite: RPI AEMs in Electrolyzer Test

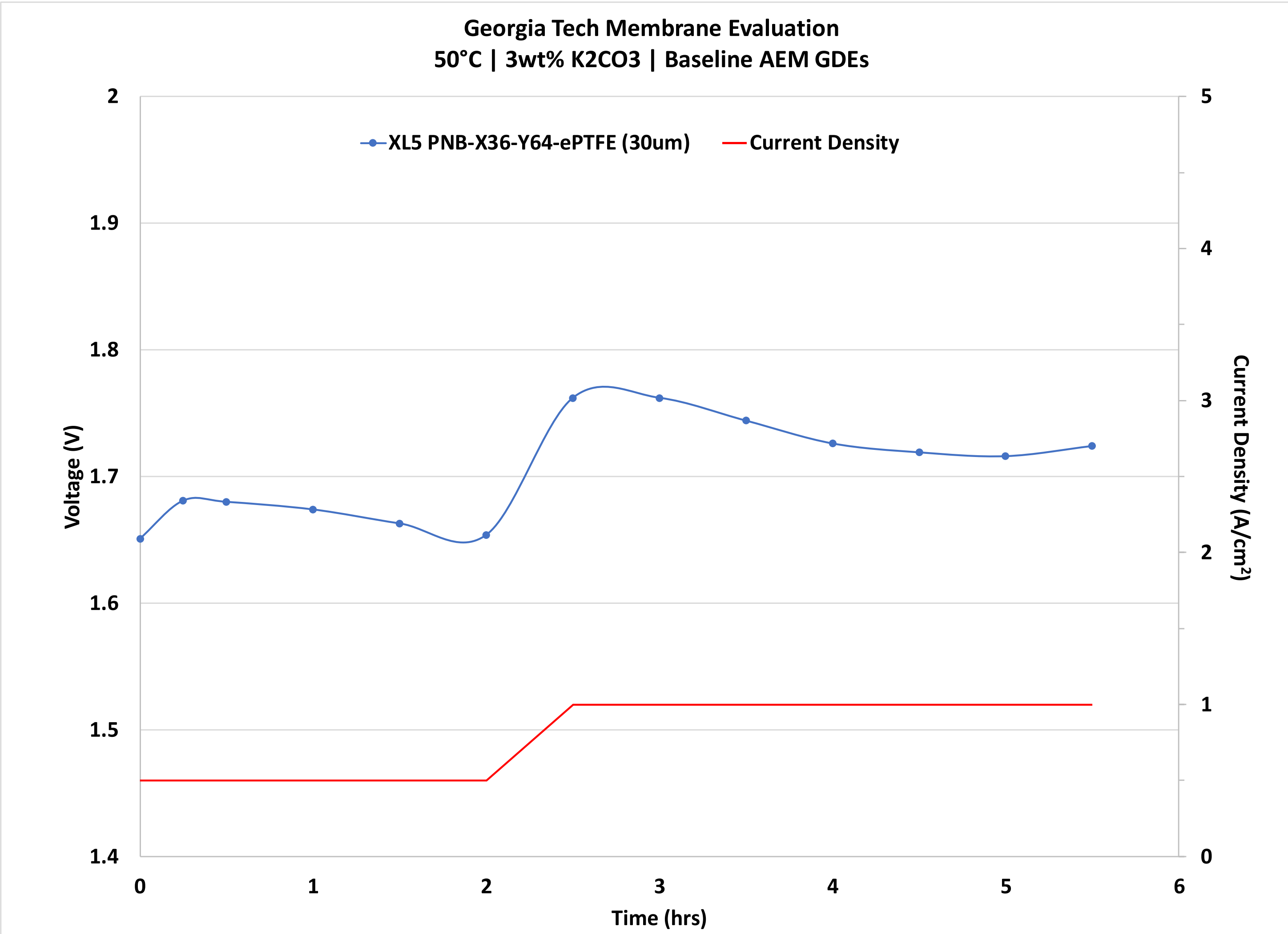
- Conducts durability tests.





Accomplishments and Progress

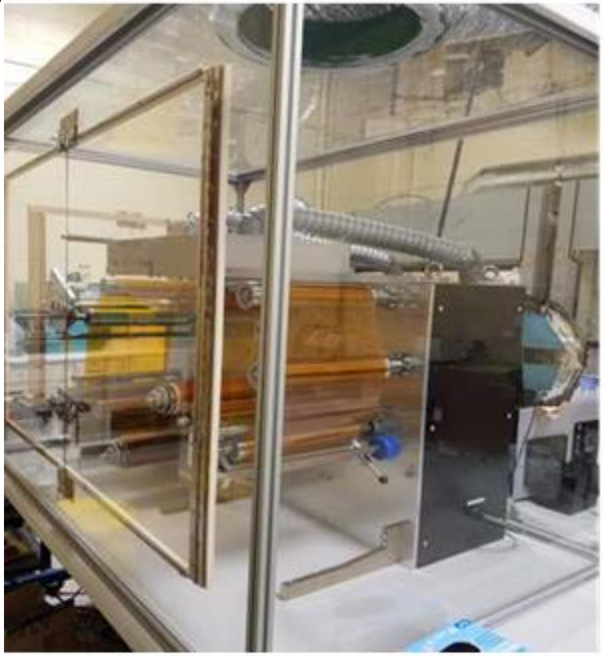
Proton OnSite: GT-Xergy AEM in Electrolyzer Test

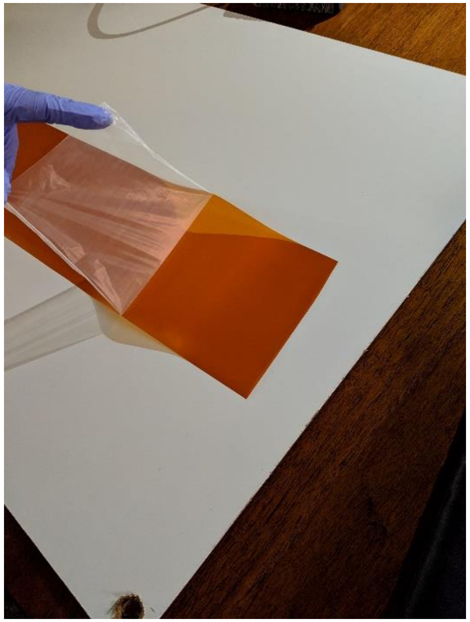


Accomplishments and Progress

Xergy

- To lower ionic resistance and swelling, Xergy impregnated the ionic copolymers of RPI and Georgia Tech into a low-cost, chemically-inert, mechanically-stable matrix and produced thin reinforced composite membranes.
- Fabricated composite AEMs with GT's PNB at lower concentrations and viscosities with new generation ePTFE support materials.
- To reduce the ASR, Xergy optimized fabrication of thinner (~8 μm) membranes and identified reinforcement materials with lower resistances.
- Xergy has demonstrated roll-to-roll production of composite membranes up to ~0.5 m^2 (Type A series)





Accomplishments and Progress

RPI-Xergy Reinforced AEMs

- Three reinforced membranes, in the table, have already achieved many of the 10 final targets (highlighted in green) or are under evaluation
- Excellent performance is demonstrated, with humidity cycling and area specific resistance (RH ASR) remaining as the major challenges

FOA Metrics	A-reinforced	B-reinforced	C-reinforced
Chemical Stability 1M KOH aq., 80 °C	Under evaluation	Under evaluation	Under evaluation
Membrane Area	>90% uniform	>90%	>90%
Ionic ASR, 80 °C	0.015 Ohm-cm^2	0.013 Ohm-cm^2	0.007 Ohm-cm^2
RH ASR 80 °C, 70% RH	0.110 Ohm-cm^2	0.091 Ohm-cm^2	Not yet
Humidity Cycling 20,000 Cycles	Under evaluation	5,000 cycles stress: 37 MPa strain: 16%	Under evaluation
Humidity Stability	3	3.8	5.6
Swelling in water (OH^- form)	7%, 25 °C	3%, 25 °C	7%, 25 °C
Pressure Differential	Under evaluation	Under evaluation	Under evaluation
Mechanical: 50 °C and 50% RH	stress: 52 MPa, strain: 25%	stress: 51 MPa, strain: 29%	stress: 31 MPa, strain: 69%

- Cost analysis are not available.

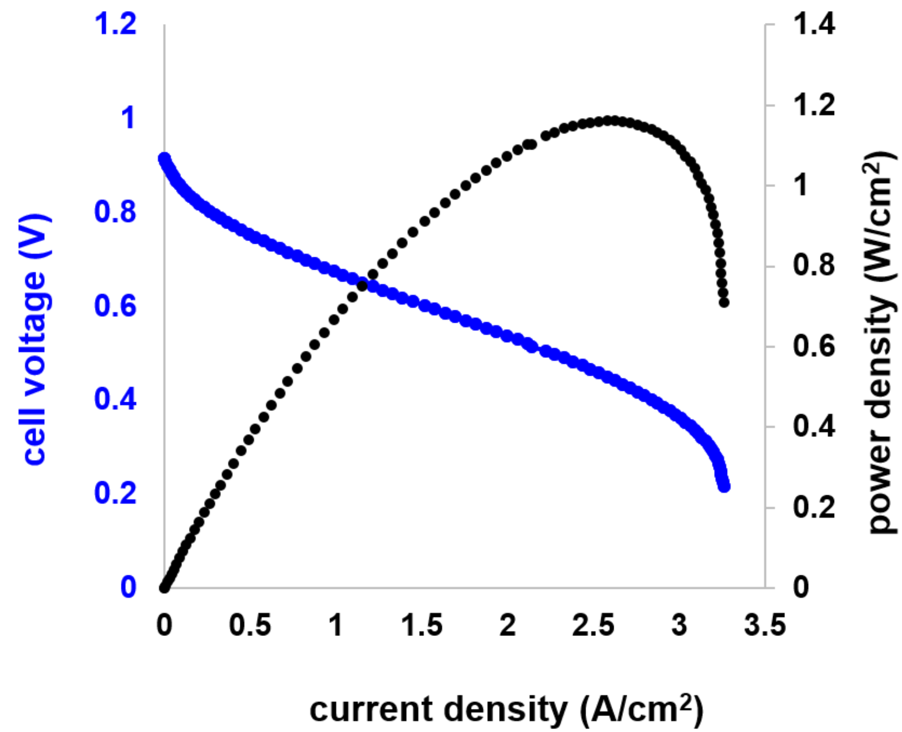
Meets Final Target

Does Not Meet Final Target

Accomplishments and Progress

RPI-Xergy Reinforced AEM in Fuel Cells

- Excellent fuel cell performance: **1.2 W/cm^2**
- Conditions: H_2/air (CO_2-free), 80 °C cell temperature, 1.5 bar cathode pressure, reinforced membrane (~20 mm thickness), a proprietary ionomer, low loading (<0.15 mg/cm^2) platinum group metal catalyst



Performance of a MEA by PO-CellTech Ltd.

Accomplishments and Progress

Georgia Tech-Xergy
Reinforced Poly(norbornene) AEMs

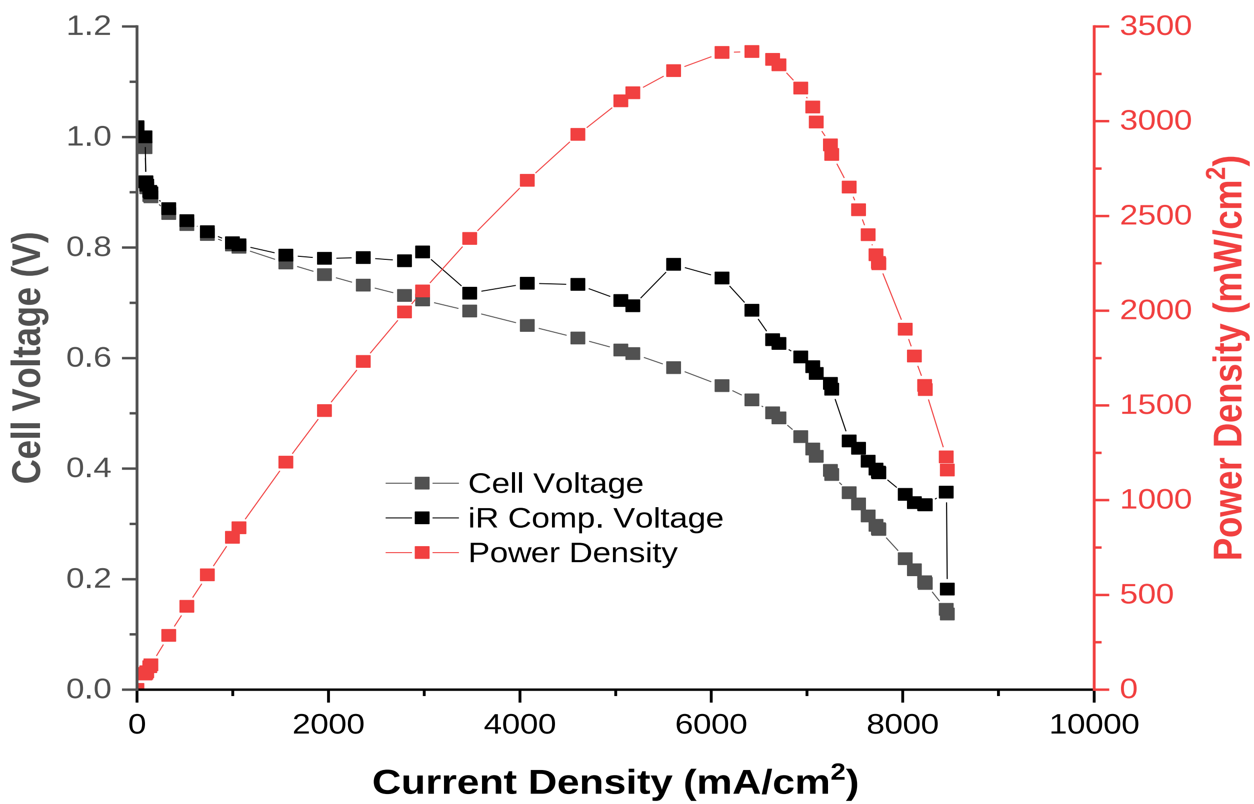
- These materials have excellent chemical stability (1% loss at 1,000 h in 1M KOH at 80 °C)
- Films are robust with adjustable modulus (60 to 550 MPa) and thin (10 to 30 μm), which promote low ASR (0.02 Ω cm^2)

	IEC, meq/g	ASR, Ω cm^2	Modulus, MPa	% Water Uptake, (non-reinforced)	Swelling Ratio
GT64-0	3.37	0.038	67	88	68
GT64-2.5	3.36	0.056	75	82	45
GT64-5	3.34	0.041	119	65 (90)	39
GT64-10	3.31	0.033	129	35 (61)	24
GT64-15	3.28	0.020	175	29	14
GT64-20	3.25	0.025	458	24	11
GT64-25	3.22	0.024	553	18	7

Accomplishments and Progress

Georgia Tech-Xergy Reinforced AEM in Fuel Cells

- Record fuel cell performance: **3.4 W/cm^2** (80°C, H_2/O_2) 70% higher than existing published record (2 W/cm^2) for AEM fuel cell.[1]
- Highest reported hydroxide conductivity: **212 mS/cm** (80°C)

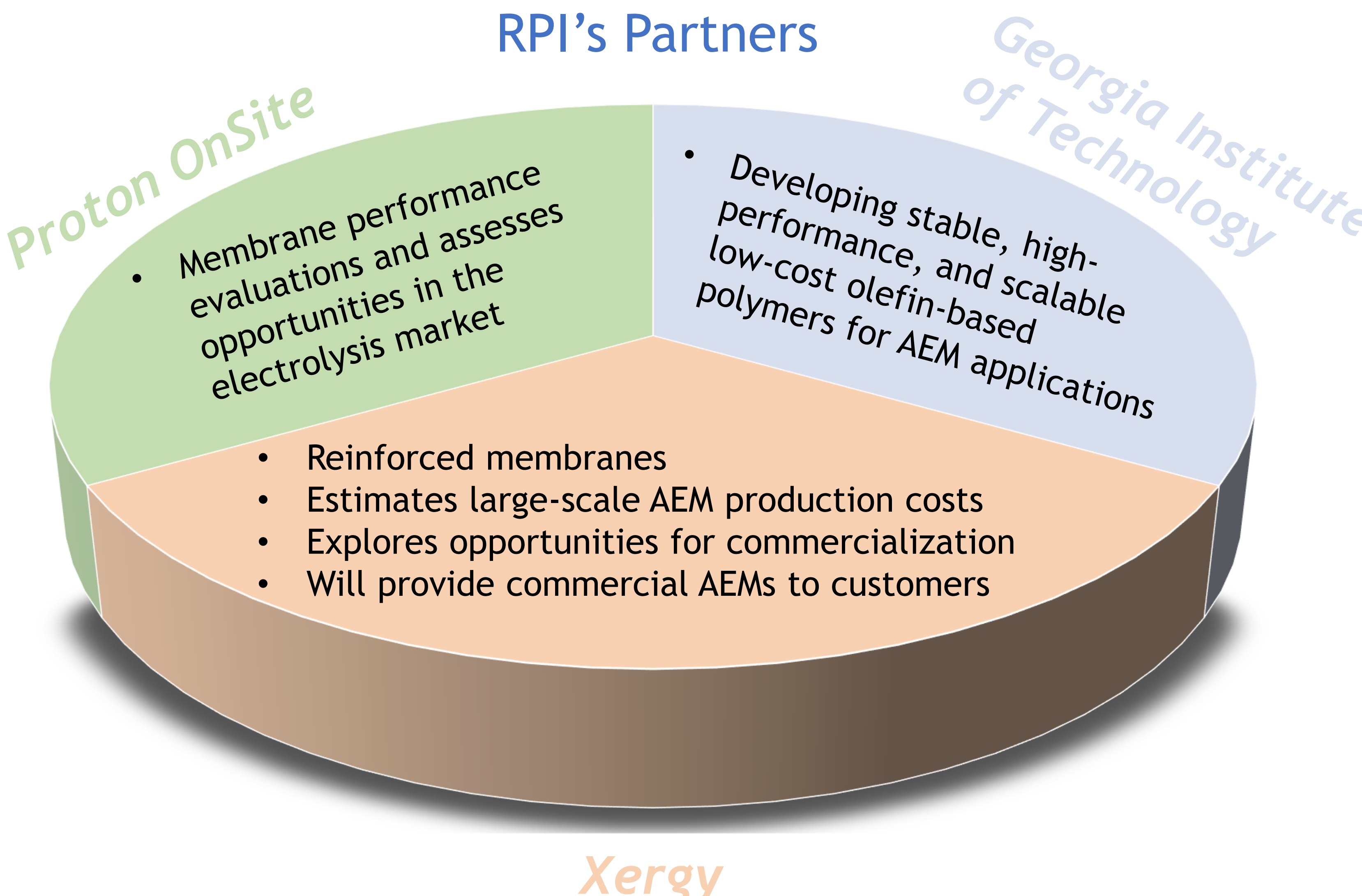


1. L. Wang, M. Bellini, H. A. Miller, J. R. Varcoe, J. Mater. Chem. A, 2018, 6, 15404–15412.

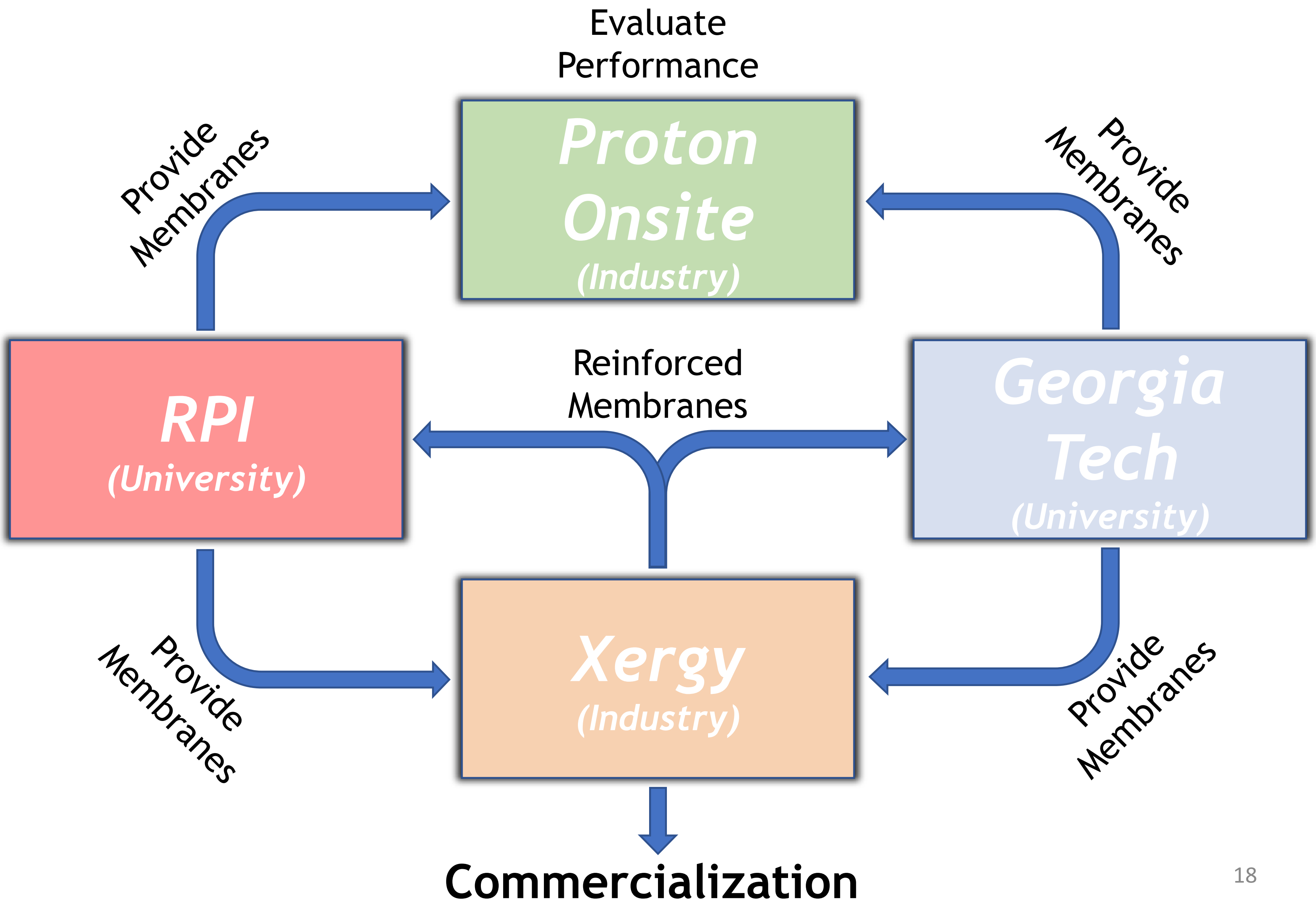
Response to Previous Year Reviewers' Comments

- This project was not reviewed last year.

Collaboration & Coordination



Collaboration & Coordination



Remaining Challenges and Barriers

- ***Gas crossover*** and ***costs to mass-produce*** are expected to be low, but data is needed.
- Poor elongation after 20,000 cycles of ***humidity cycling*** is a concern.
- Ensuring ***chemical and mechanical stability***, with ***high anionic conductivity*** will lead to rapid commercialization.

AEMs	Chemical Stability 1M KOH, 80 °C 1000 h, < 2% drop	Humidity Cycling ≥20,000 RH cycles ≥50% properties	RH ASR <0.08 Ohm-cm^2 80 °C, 70% RH
Polymer A	IEC loss: <1% σ (OH$^-$) drop: <1%	Georgia Tech	0.042
Polymer B	IEC loss: 1.5% σ(OH$^-$) drop: N/A	Georgia Tech	0.028
Polymer C	IEC loss: <1.5% σ(OH$^-$) drop: N/A	1,000 cycles stress: 52 MPa strain: 9%	0.057
A-reinforced	RPI	Georgia Tech	0.110
B-reinforced	RPI	5,000 cycles stress: 37 MPa strain: 16%	0.091
C-reinforced	RPI	Georgia Tech	N/A

Meets Final Target (green)
Does Not Meet Final Target (blue)
Under Evaluation (grey)

Proposed Future Work

- Overcome challenges and Barriers by:
  - Increase Ionic Conductivity
    - Increase content of BPN1 (above 50%) in the crosslinked blend membranes (*i.e.*, Type B and Type B reinforced)
    - Increase IEC by functionalizing Type B-based polymers with additional quaternized ammonium groups
      - Evaluate freestanding, blend, and crosslinked membranes
  - Improve mechanical stability with crosslinking and reinforcement
- Finish Performance Evaluations
  - Evaluation of performance & durability in electrochemical cells (fuel cells, electrolyzer, RFB, *etc*)
- Continue Commercialization Efforts
  - Process optimization for scale up

Any proposed future work is subject to change based on funding levels.

Technology Transfer Activities

- **Patents and IP**
  - Xergy has extensive ECC patent portfolio including high-pressure ECC (> 55 patents in process)
  - Our team has patent cases in process for these polymers and membranes. RPI have patents on poly(arylene) and SEBS-based AEMs. RPI and Xergy have joint IP on a poly(arylene)-based reinforced AEMs
  - Georgia Tech has filed a provisional patent on polynorbornene materials
- **Manufacturing scale-up**
  - Xergy has two composite membrane production lines which can produce large scale membrane production
- **Market Options**
  - Exploring applications for BPN/TPN, SEBS composite membranes in fuel cells, electrochemical compressors, flow battery, desalination, electrolysis and pervaporative applications.

Summary

Most of the 12 performance milestones have already been met

Record shattering fuel cell performance has been achieved

Successful roll-to-roll composite membrane manufacture, for scalability, has been demonstrated

Significant technology transfer activities have resulted and industrial partners are advancing the technology to market activities

Technical Backup Slides

Technical Backup

Membrane	Theoretical IEC	Titration IEC	OH^- form						CO_2H^- form
			WU (%) 25˚C	Swelling (%)	σ mS cm^{-1} 80˚C	ASR mΩ· cm^2 80˚C	σ mS cm^{-1} 80˚C, 70% RH	ASR mΩ· cm^2 80˚C, 70% RH	σ mS cm^{-1} 80˚C
Polymer A	2.19	2.18	45	22	127	23	73	42	43
Polymer B	2.38	2.19	96	32	131	31	108	28	-[a]
Polymer C	2.59	2.65	34	9	112	23	43	57	-[a]
A-reinforced	1.75	1.80	122 (±10)	7	65	15	9	110	54
B-reinforced	1.78	1.71	31 (±13)	3	89	13	11	91	-[a]
C-reinforced	1.94	1.83	78 (±10)	7	126	7	-[a]	-[a]	-[a]

[a]The membrane is under evaluation.

Technical Backup

Membrane	Stress (MPa)	Strain (%)	Stress (MPa)	Strain (%)	Linear Swelling	Humidity Stability Factor
	50˚C / 50 %RH		25˚C / 50 %RH		100˚C	
Polymer A	32	234	49	203	17	11.6
Polymer B	40	140	44	104	24	4.33
Polymer C	12	105	25	36	12	3
A-reinforced	52	25	61	28	9	3
B-reinforced	50	29	61	19	5	3.8
C-reinforced	31	69	34	50	9	5.6

Publications and Presentations

- “Rational design of polyaromatic ionomers for alkaline membrane fuel cells with >1 W cm^2 power density”, Sandip Maurya, Sangtaik Noh, Ivana Matanovic, Eun Joo Park, Claudia Narvaez Villarrubia, Junyoung Han, Chulsung Bae, and Yu Seung Kim, *Energy Environ. Sci.* **2018**, *11*, p.3283

- “Synthesis of Aromatic Anion Exchange Membranes by Friedel-Crafts Bromoalkylation and Cross-Linking of Polystyrene Block Copolymers”, Jong Yeob Jeon, Sungmin Park, Junyoung Han, Sandip Maurya, Angela D. Mohanty, Ding Tian, Nayan Saikia, Michael A. Hickner, Chang Y. Ryu, Mark E. Tuckerman, Stephen J. Paddison, Yu Seung Kim, and Chulsung Bae, *Macromolecules* **2019**, *52*, p. 2139