Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Scalable Elastomeric Membranes for Alkaline Water Electrolysis

Yu Seung Kim
Los Alamos National Laboratory
5/20/2020

Project ID p159

Project Overview

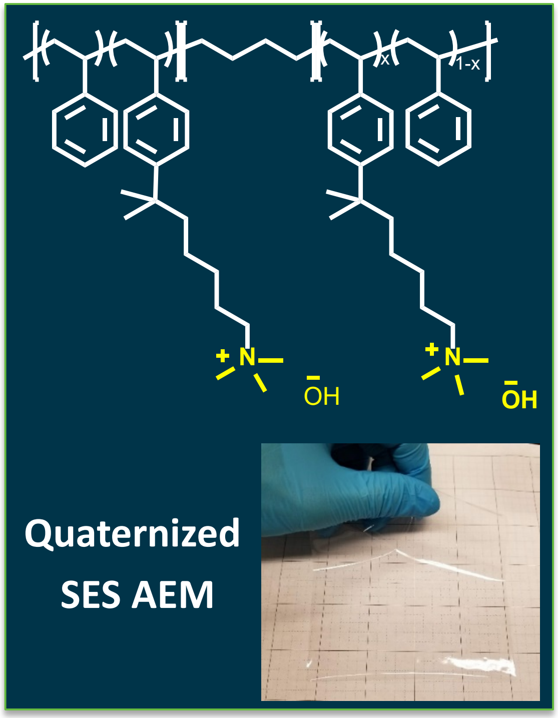
Project Partners

PI, Yu Seung Kim, Los Alamos National Laboratory
Co-PI, Chulsung Bae, Rensselaer Polytechnic Institute
Co-PI, Kathy Ayers, Proton Onsite

Award #	2.2.0.401
Start/End Date	10/01/2017 – 09/30/2020
Total Project Value* Cost Share %	$1.1M (DOE + Cost Share) 10%

Project Vision

Preparing advanced alkaline hydroxide conducting SES materials and demonstrating the performance and durability in alkaline membrane water electrolysis.



Project Impact

This technology will bring the alkaline membrane-based water electrolysis technology to a maturity level at which it can be further developed by industry for commercialization.

** this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Approach: Summary

Project Motivation

Current AEM electrolyzers performance and durability is low compared to PEM electrolyzers. In this project, we are aiming to develop economically viable polymer electrolytes that exhibit substantially improved performance and durability of alkaline membrane electrolyzer.

Barriers

- Alkaline stability
- Hydroxide conductivity
- Mechanical properties
- Performance of AEM electrolyzer
- Durability of AEM electrolyzer

Key Impact

Metric	State of the Art	Expected Advance
OH conductivity (mS/cm)	*30-40*	*40*
% Loss conductivity after 300 h, 1 M NaOH, 80 °C	*30*	*< 5*
Tensile toughness (MPa × % elongation)	2000	3000

Partnerships

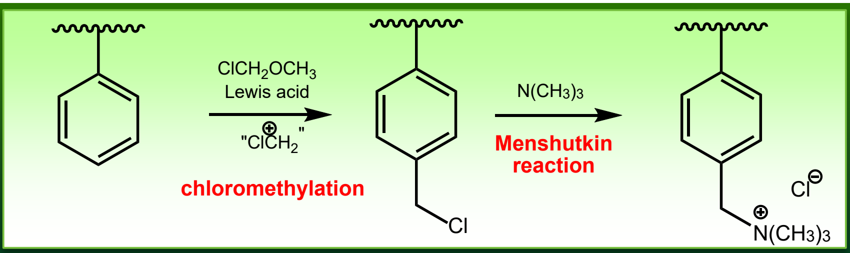
- Yu Seung Kim (LANL): Project managing, ionomer development, electrochemistry & AEM electrolyzer testing.
- Chulsung Bae, Sangwoo Lee (RPI): AEM synthesis & characterization
- Kathy Ayers (Proton Onsite): AEM electrolyzer testing (from the 2nd year)

Approach- innovation (AEM)

Synthesize highly conductive, alkaline stable styrene-ethylene-styrene block copolymer by inexpensive acid catalyzed route.

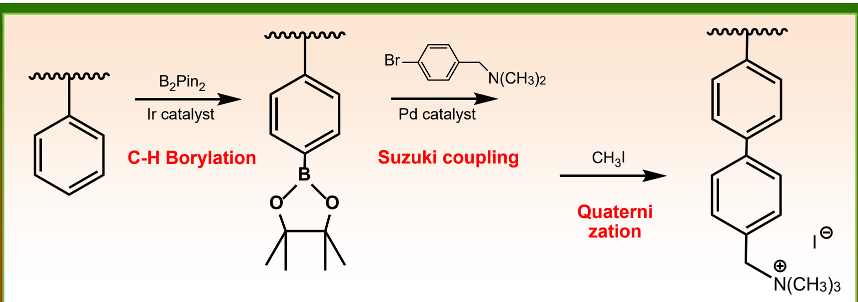
Conventional Chloromethylation

- Low level of functionalization & gelation
- Only allow benzyl ammonium functionalization
- Toxic and expensive reagents



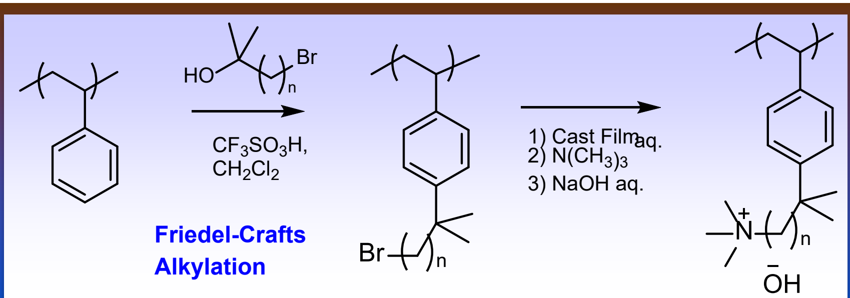
Metal-catalyzed coupling (M-Cat)

- Good control of IEC (1.5 meq./g)
- High hydroxide conductivity (40 mS/cm)
- Excellent chemical stability
- Not practical due to expensive metal catalysts



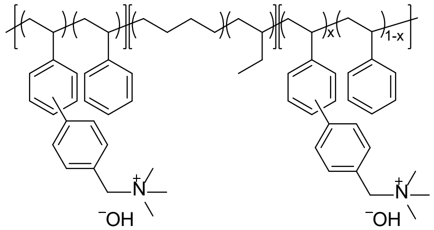
Acid catalyzed (Proposed)

- IEC, conductivity and chemical stability are similar to that from metal-catalyzed coupling
- Multi-cation structure is feasible
- No use of expensive metal catalysts

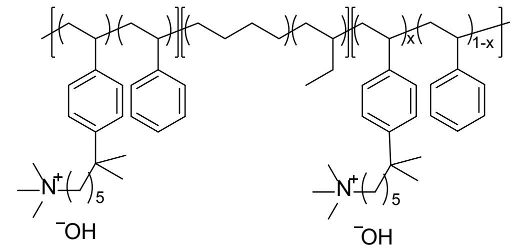


Approach: innovation (AEM)

Before the project



From the project



Approximate total chemical cost for a 6 in x 6 in membrane (45 micron thickness) is based on the laboratory chemical sources

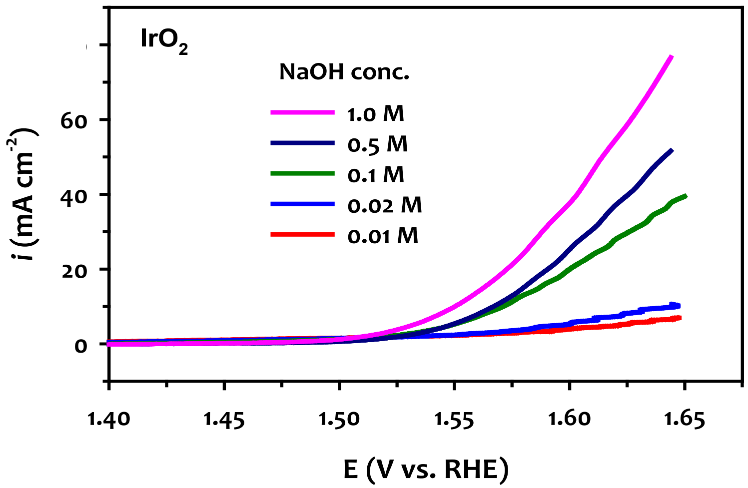
SEBS-TMA via Suzuki Coupling		
Reagent	**Quantity (g or mL)**	**USD**
4-bromobenzyl bromide	1.63 g	$1.71
$HNMe_2$ aq. solution	1.32 mL	$0.04
dioxane	3.25 mL	$0.17
diethyl ether	26.0 mL	$0.25
SEBS	0.86 g	$0.21
B_2Pin_2	2.14 g	$2.51
$[IrCl(COD)]_2$	0.0845 g	$13.6
dtbpy	0.0672 g	$0.58
THF anhydrous	8.62 mL	$0.44
$CHCl_3$	4.31 mL	$0.17
K_2CO_3	0.683 g	$0.01
$Pd(dppf)Cl_2$-CH_2Cl_2	0.0414 g	$0.90
THF anhydrous	8.27 mL	$0.42
$CHCl_3$	31.0 mL	$1.25
Dimethyl sulfate	1.05 mL	$0.08
N,N-Dimethylacetamide	83.9 mL	$3.22
Total cost for 1 g polymer		**$25.61**

SES-TMA via Friedel-Crafts Alkylation		
Reagent	**Quantity (g or mL)**	**USD**
6-bromohexanoic acid	0.935 g	$1.81
Sulfuric acid	0.0751 mL	<$0.01
methanol	5.67 mL	$0.09
ethyl acetate	4.25 mL	$0.05
MeMgBr_ether solu.	4.25 mL	$0.37
THF anhydrous	4.25 mL	$0.22
diethyl ether	11.3 mL	$0.11
SEBS	0.838 g	$0.20
triflic acid	0.585 g	$1.73
CH_2Cl_2 anhydrous	16.8 mL	$0.63
Toluene	16.8 mL	$0.29
TMA-water solution	2.96 mL	$0.13
Total cost for 1 g polymer		**$5.62**

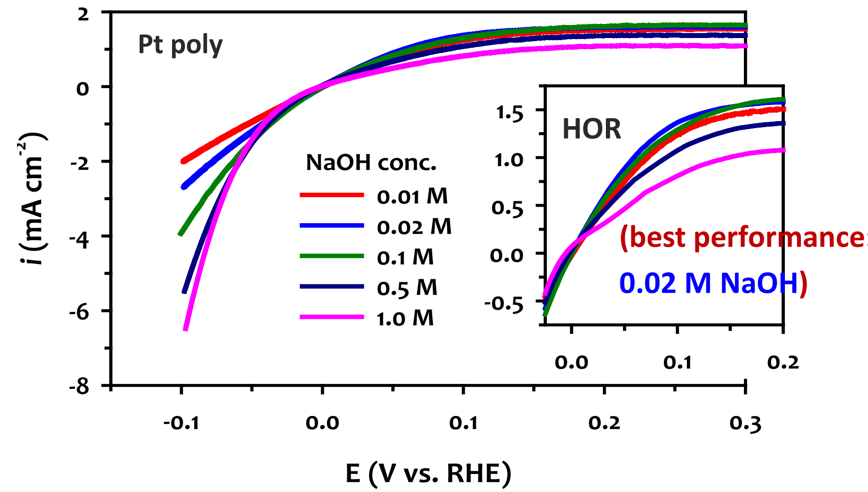
Approach- innovation (Ionomer)

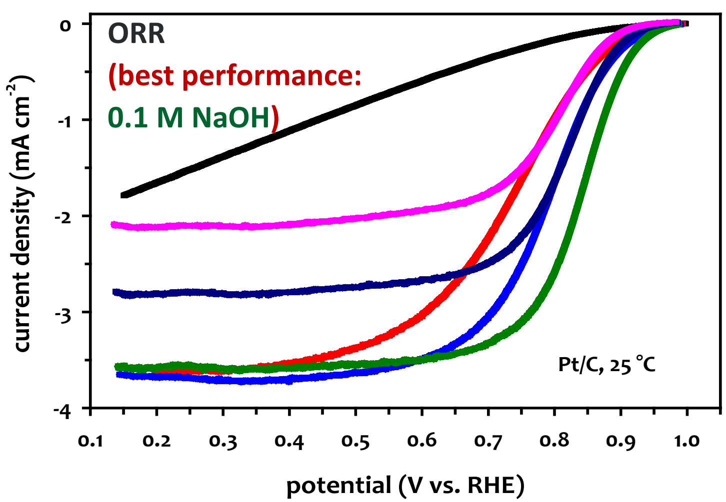
Identify the performance limiting factor of AEM electrolyzer

OER (best performance: 1.0 M NaOH)



HER (best performance: 1.0 M NaOH)





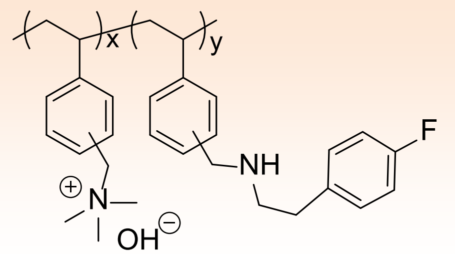
Key finding From Year 2 research:

For AEM electrolyzers, an ionomer with higher ion-exchange capacity is more desirable, but for AEM fuel cells, an ionomer with intermediate IEC may perform better.

Approach: Innovation (ionomer & device)

Ionomer: High quaternized aryl ether-free polystyrene (LANL)

- Phenyl group free polymer backbone
- No unsubstituted phenyl group in the side chain to minimize phenyl group oxidation
- High achievable IEC (3.3 meq. g^{-1})



TMA-45, IEC = 2.0 meq. g^{-1}
TMA-53, IEC = 2.4 meq. g^{-1}
TMA-62, IEC = 2.9 meq. g^{-1}
TMA-70, IEC = 3.3 meq. g^{-1}

Tech validation: AEM electrolyzer performance/durability (Proton Onsite)

- 28 cm2 test with non-PGM anode in 1 wt.% K_2CO_3

Control AEM supply: SNL (HydroGEN Consortium)

- Supply quaternized Diels-Alder poly(phenylene) for ionomer and durability study

AEM electrolyzer characterization/ modeling: LBNL (HydroGEN Consortium)

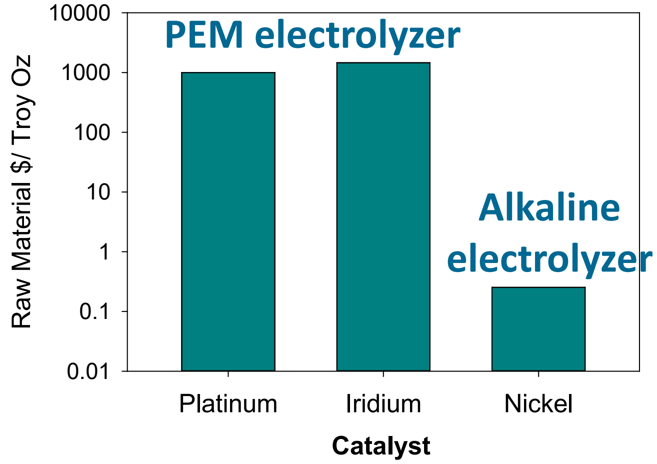
- AEM characterization
- Ionomer pH effect modeling & microelectrode

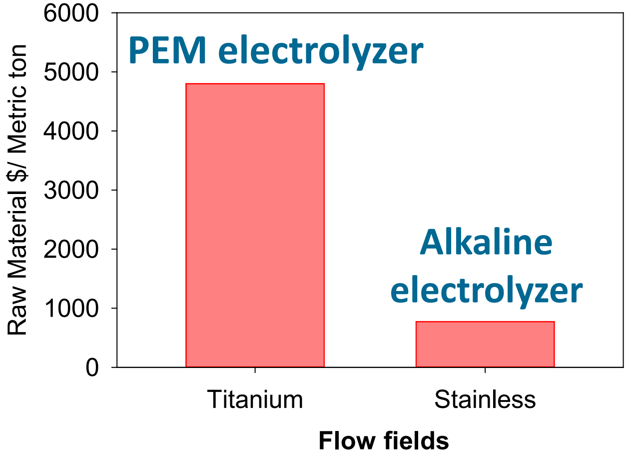
Tech validation: AEM electrolyzer performance (NREL) (HydroGEN Consortium)

- pH effect on AEM electrolyzer performance

Relevance and Impact

- Benefits of AEM electrolyzer over PEM electrolyzer





- Technical challenges of AEM electrolyzers
  - Low performance and durability are two technical challenges for AEM electroyzers. This project focuses on developing alkaline stable AEMs and ionomers to improve AEM electrolyzer performance and durability

- Node utilization and other types of resources
  - Node utilization: modeling, Ionomer thin film study, electrochemical measurement (SNL, LBNL, and NREL)
  - Other types of resources: Alkaline Membrane Fuel Cell Project (FCTO)

Current budget period Go/No-Go milestone(s)

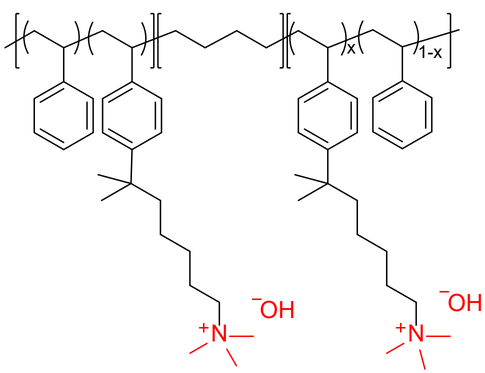
Milestone Name/Description	Criteria	End Date
Down select AEMs	Hydroxide conductivity: > 40 mS cm^{-1} at 30°C. Less than 5% loss in hydroxide conductivity after 300 h, 1 M NaOH treatment at 80°C. Mechanical toughness (mechanical strength (MPa) x % elongation) > 1400 at 50°C, 90% RH	12/31/2019
Down select anion exchange ionomer	AEM electrolyzer using the down selected ionomer needs to meet the target performance of electrolyzer (2 A/cm^2 at 1.8 V)	3/31/2020
AEM electrolyzer performance (in pure water)	Target performance: electrolyzer (2 A/cm^2 at 1.8 V) using RPI AEM and LANL ionomer	6/30/2020
AEM electrolyzer durability using the down-selected materials **300 h AEM electrolyzer durability test at LANL and Proton Onsite**	Identify major durability limiting factor of alkaline membrane water electrolysis at 80°C. Target electrolyzer durability: < 0.1 mV/hr degradation rate over 300 hr during continuous run of alkaline membrane electrolyzers at 1000 mA/cm^2	9/30/2020

Accomplishments: AEM Development – SES based (RPI)

Decision criteria – needs to meet the criteria simultaneously

1. **Hydroxide conductivity**: > 40 mS cm^{-1} at 30°C.
2. **Stability**: <5% loss in conductivity after 300 h, 1 M NaOH treatment at 80 °C.
3. **Toughness:** strength (MPa)×% elongation > 1400 at 50 °C, 90% RH

SES25-TMA-1.7



Styrene block: 25%, x = 100

Crystallinity: 21% (LBNL)

AEM characterization
LBNL node support
(see Backup slide 1)

Down selected AEM

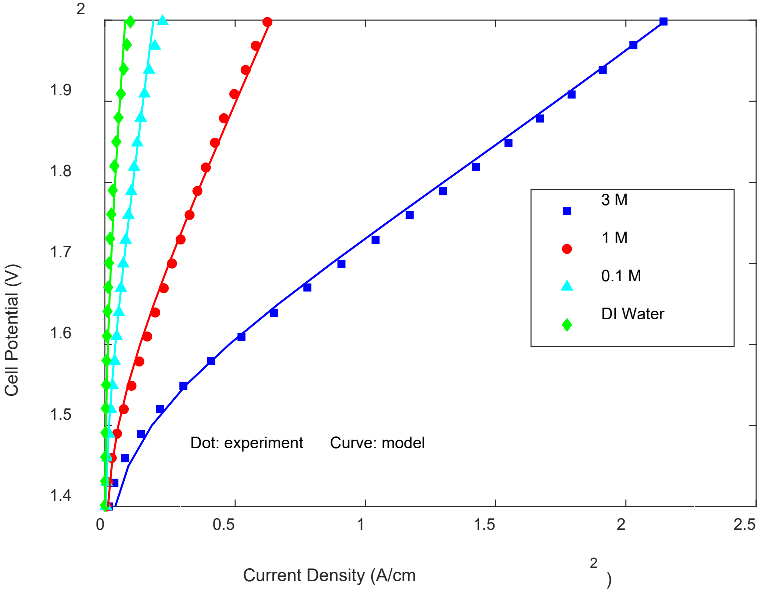
Samples	IEC [a] (mequiv./g)	OH^- σ (mS/cm)[b] at 80 °C	OH^- σ (mS/cm) at 80 °C[b]			Toughness[d]
			0 h	300 h[c]	% loss	
SES25-TMA-1.7	1.71	42	63	64	0	2091
Reinforced XL100-SEBS18-TMA-1.7	0.77	26	67	65	3	4820

[a]IEC values were measured by Mohr titration method (average of two experiments). [b]All OH^- σ were measured in water under argon atomosphere. [c]After alkaline test in 1 M NaOH Solution at 80 °C. [d]Mechanical toughness (strength (MPA) % elongation) measured at 50 °C, 90% RH.

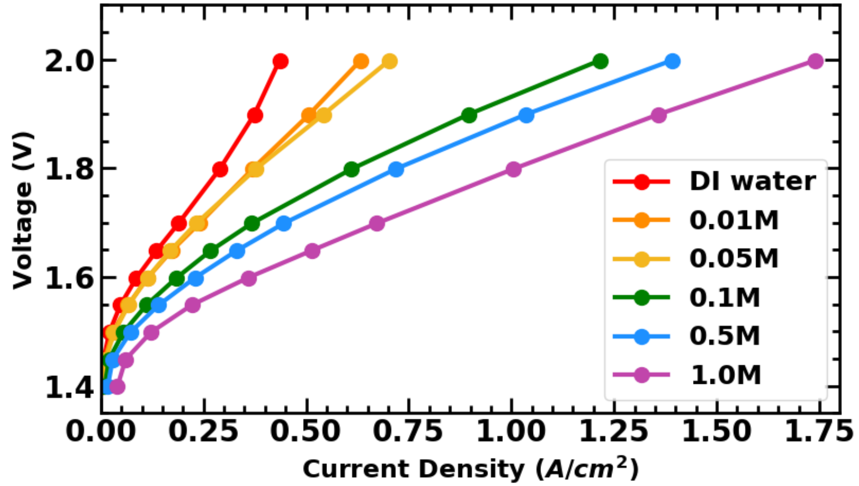
*** Meet the 12/31/2019 milestone**

Accomplishments: pH effect on AEM electrolyzer performance (Node Support)

Modeling electrolyte concentration effects (LBNL)



Experimental validation (NREL)



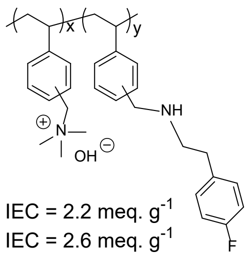
Electrolyte (60°C): DI water, 0.01M, 0.05M, 0.1M, 0.5M, 1M
AEM soaked in 1% KOH for 4 hours
Pt/C: 0.36 mg_{Pt}/cm^2 IrO_2: 0.75 mg_{Ir}/cm^2

- LBNL performed modeling work based LANL AEM electrolyzer data
- NREL performed experimental validation using LANL MEAs
- SNL provided control AEM for experiments
- AEM electrolyzer performance increases with increasing KOH conc.

More information on pH effect (see Backup slide 2,3)

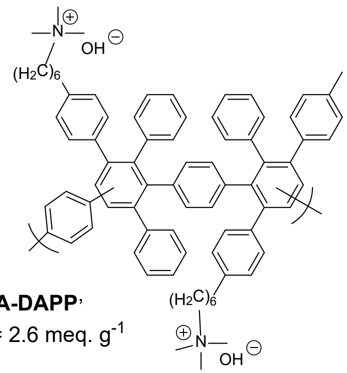
Accomplishments: Ionomer Development – polystyrene (LANL)

Ionomer (LANL)



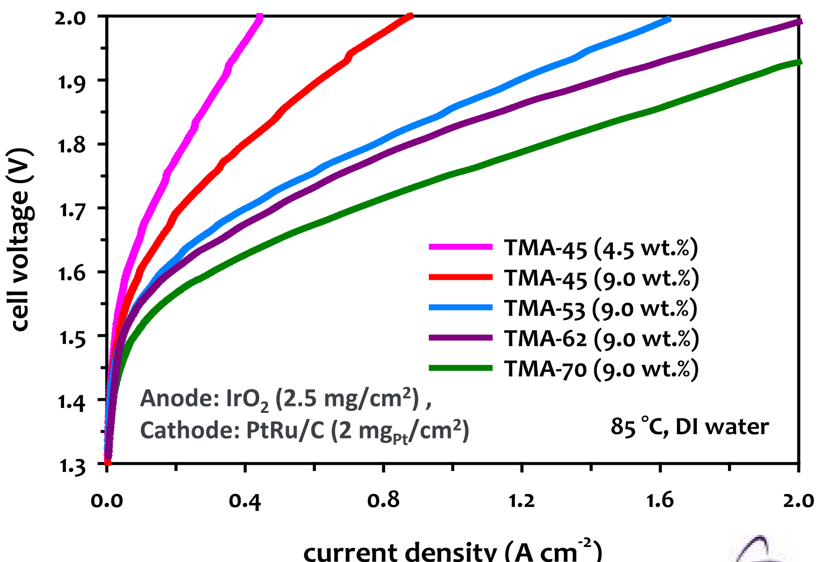
TMA-45, IEC = 2.2 meq. g^{-1}
TMA-53, IEC = 2.6 meq. g^{-1}
TMA-62, IEC = 2.9 meq. g^{-1}
TMA-70, IEC = 3.3 meq. g^{-1}

AEM (SNL, HydroGEN node)

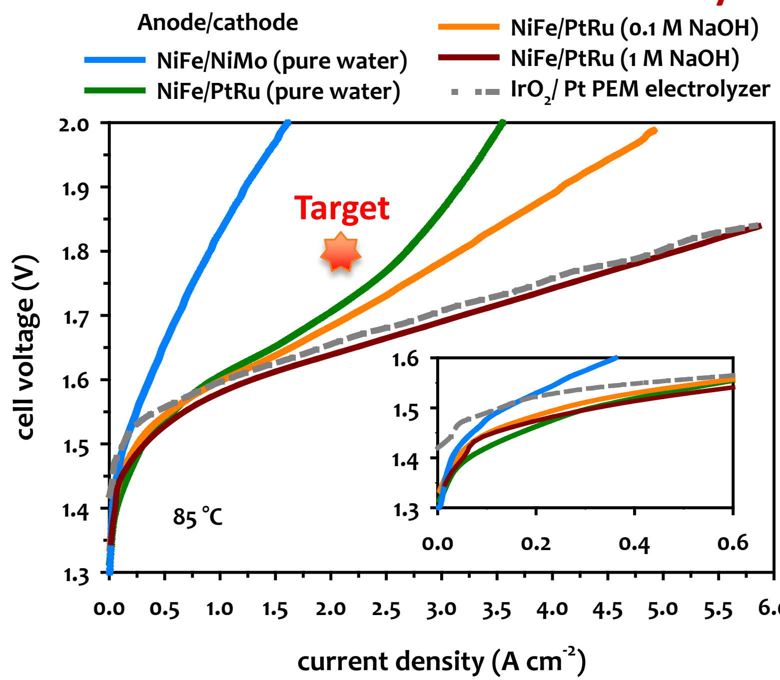


HTMA-DAPP,
IEC = 2.6 meq. g^{-1}

PGM catalysts



PGM-free catalysts



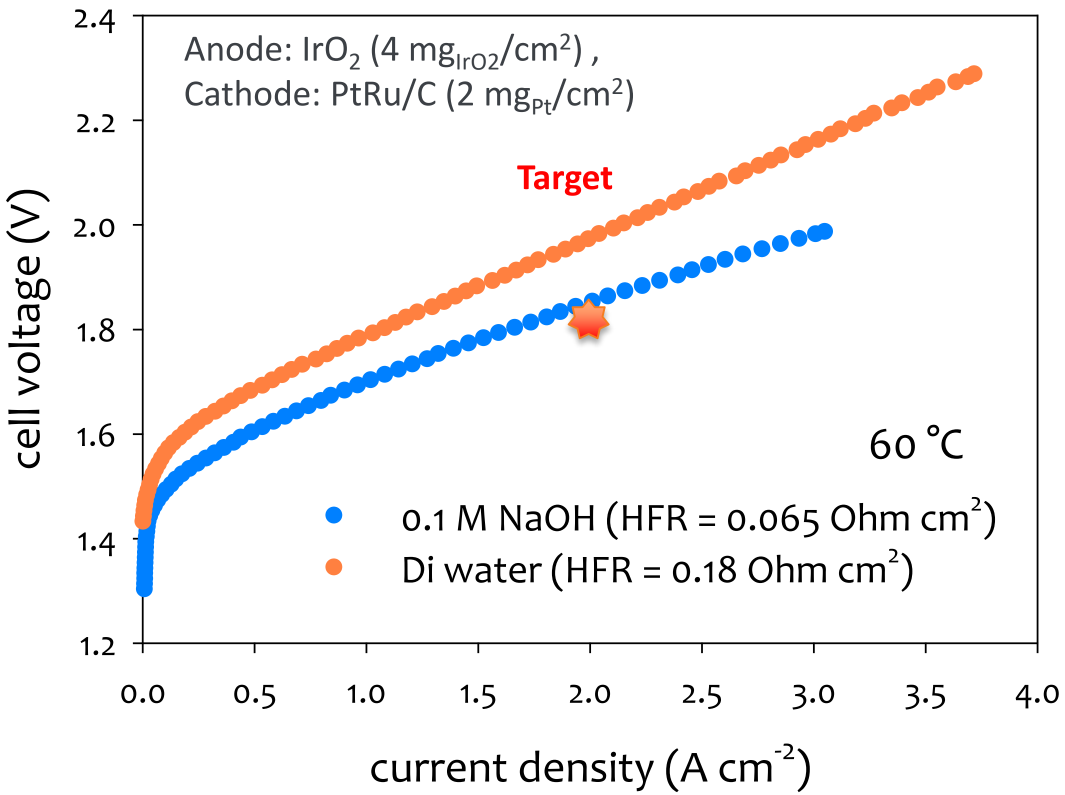
Target ionomer performance using pure water: 2 A/cm^2 at 1.8 V

Meet the 03/31/2020 milestone with a PGM-free anode catalyst

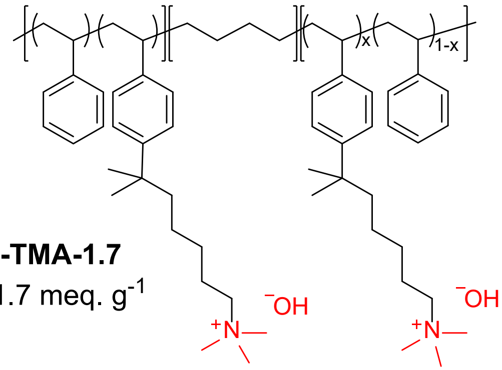
Los Alamos NATIONAL LABORATORY · PAJARITO POWDER FUEL CELL CATALYSTS · Sandia National Laboratories · WASHINGTON STATE UNIVERSITY

Accomplishments: AEM water electrolyzer performance

PGM catalysts

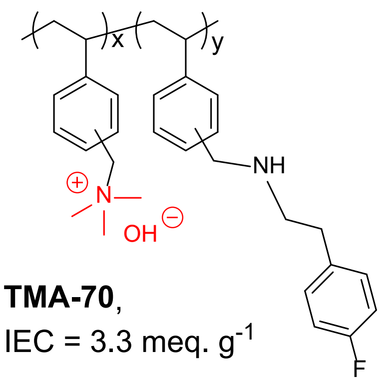


AEM (RPI)



SES25-TMA-1.7
IEC = 1.7 meq. g^{-1}

Ionomer (LANL)

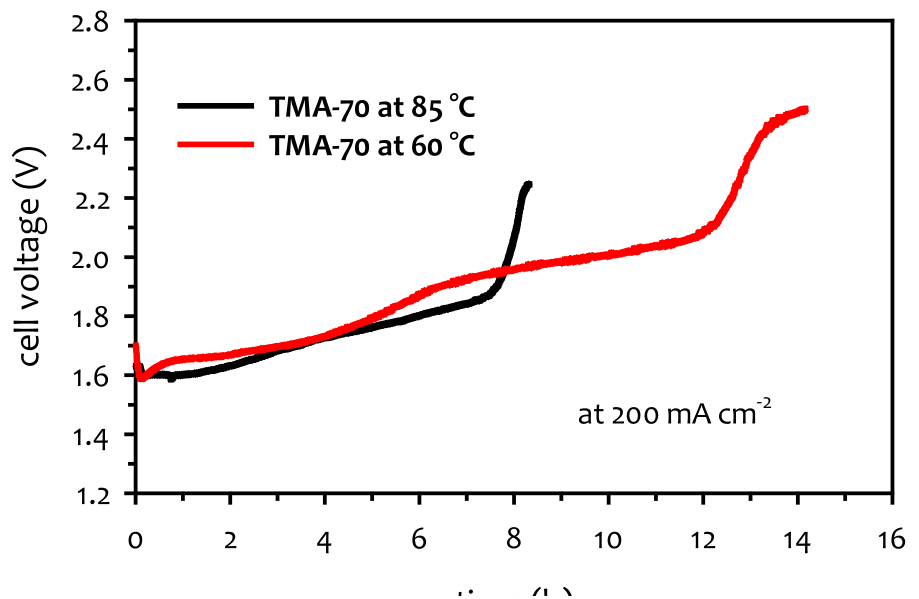


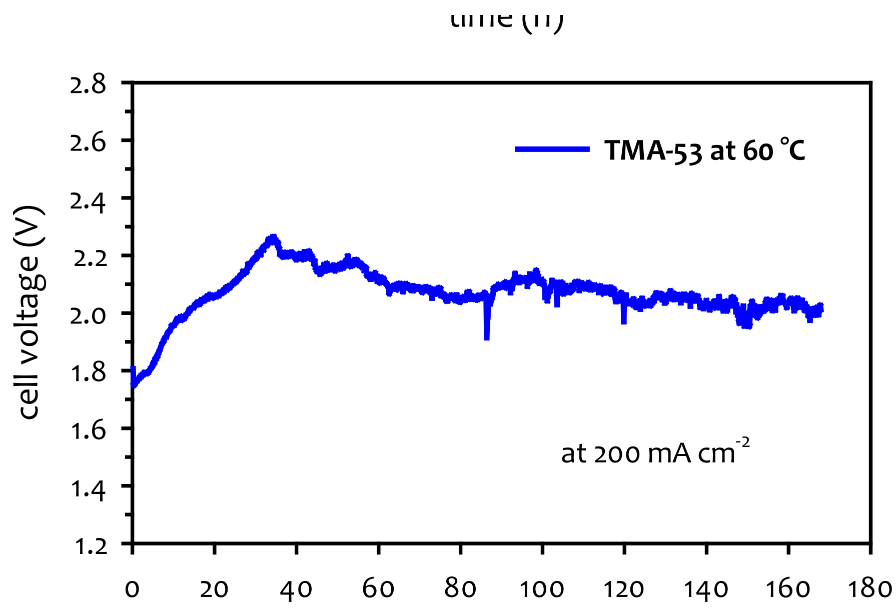
TMA-70,
IEC = 3.3 meq. g^{-1}

Target performance: electrolyzer (2 A/cm^2 at 1.8 V)

*** Approaching to the 06/30/2020 milestone**

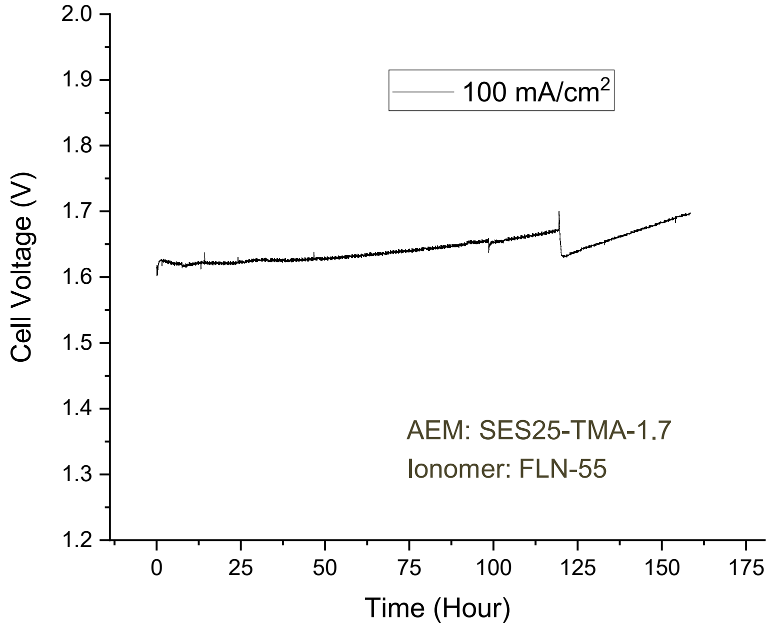
Accomplishments: Durability of polystyrene ionomers

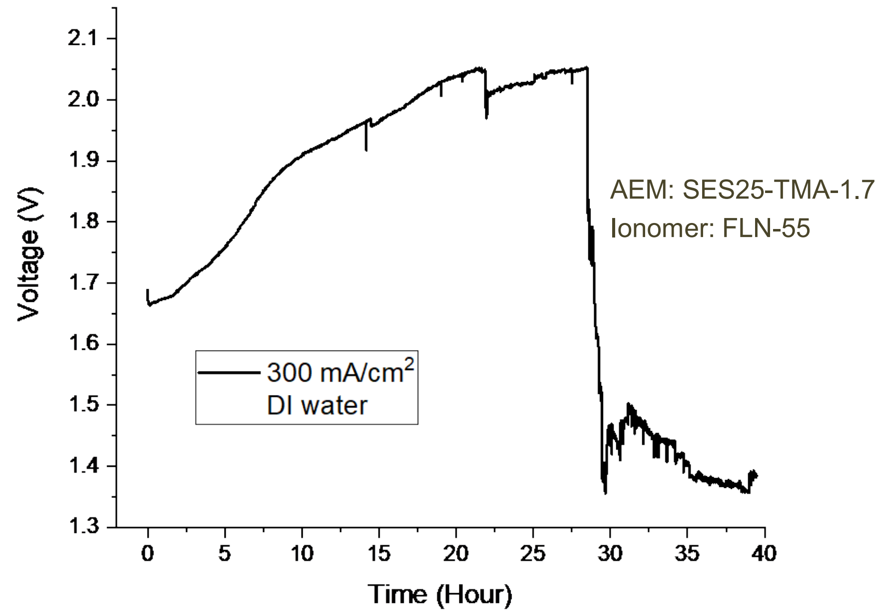




- LANL polystyrene ionomers have limited durability.
- Higher operating temperature and higher IEC of the ionomer → more degradation.
- Major degradation mechanism: Ionomer washing due to the high IEC.

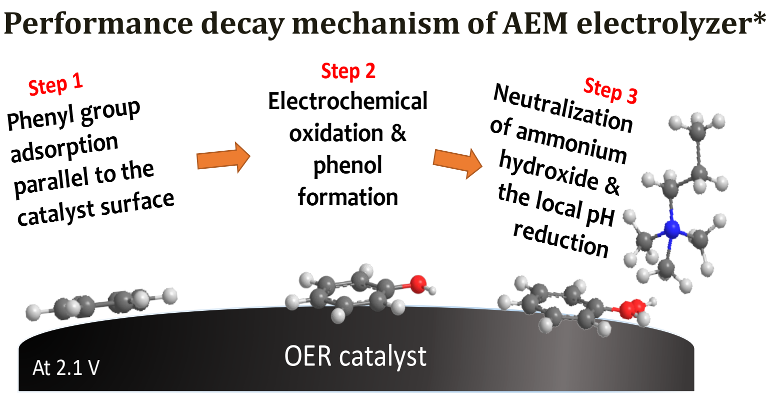
Accomplishments: Impact of current density on durability



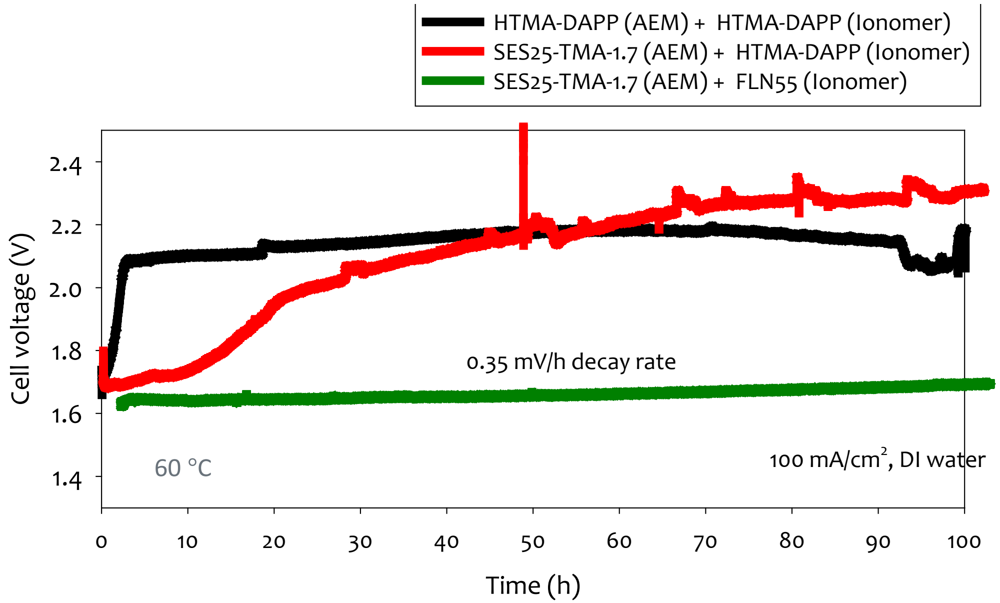


- Lower durability with higher current density
- Catalyst binding capability may be a key issue

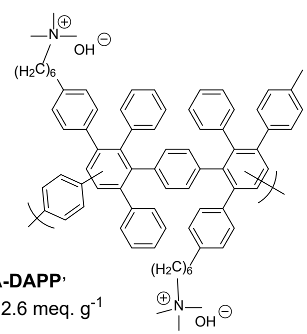
AEM water electrolyzer performance loss mechanism



Performance decay of AEM electrolyzer over time

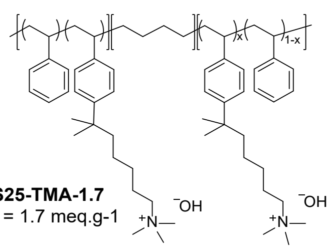


Control AEM & Ionomer (SNL)



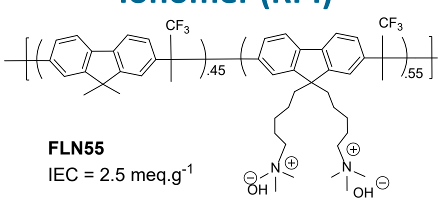
HTMA-DAPP
IEC = 2.6 meq. g^{-1}

AEM (RPI)



SES25-TMA-1.7
IEC = 1.7 meq.g-1

Ionomer (RPI)



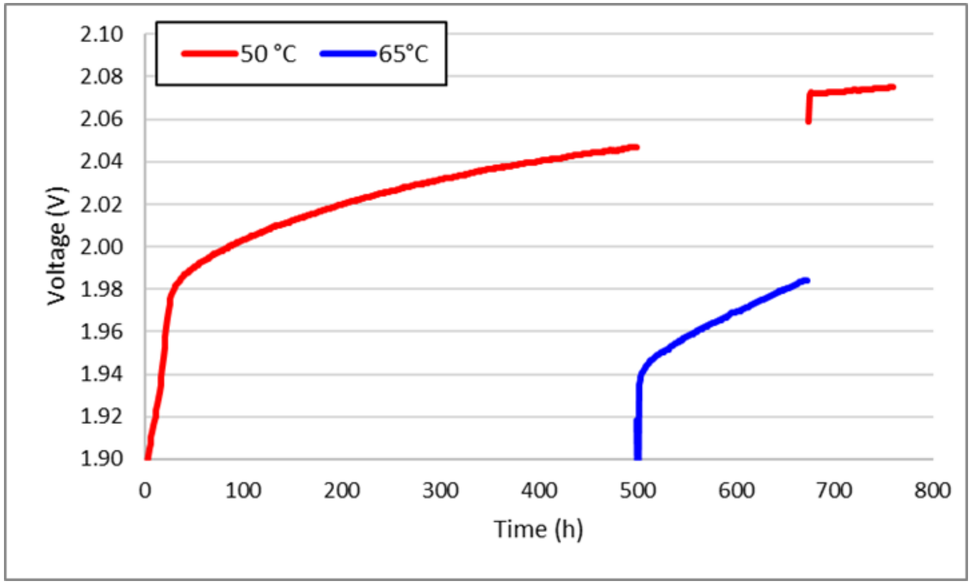
FLN55
IEC = 2.5 meq.g^{-1}

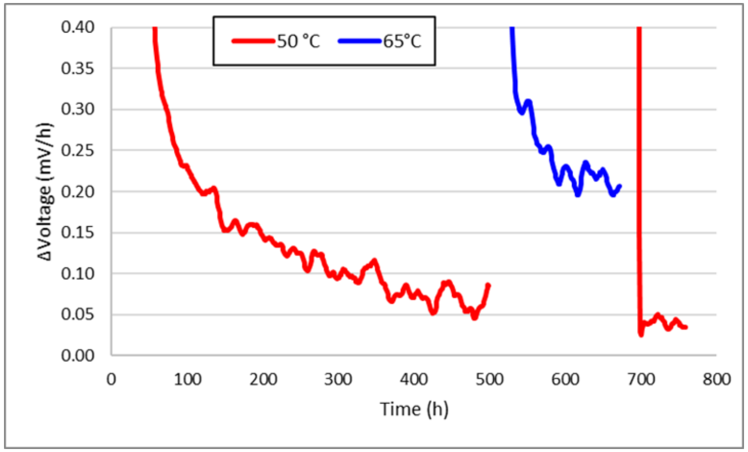
Highlight: Achieved 0.35 mV/h decay at 1.6 V for with pure-water feed AEM electrolyzer

End-of-life performance and N_2 diffusion data is available (Backup slide 5)

Accomplishments: AEM water electrolyzer durability

$28\ cm^2$ stability data with SNL (control) AEM





- Voltage degradation was taken as the slope over the previous 25 hours
- The voltage loss at 50°C: 50 μV/h while the decay at 65°C: 200 μV/h

Current density = 0.5 A/cm^2

Temperature = 50/65 °C (as indicated)

Pressure: 100 psi gauge

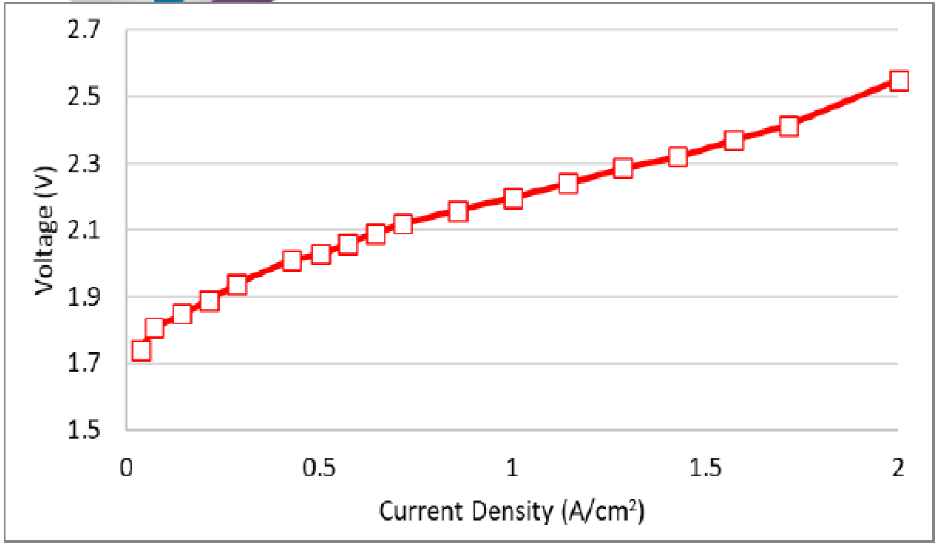
Non-PGM anode electrolyzer stack lasted > 750 h

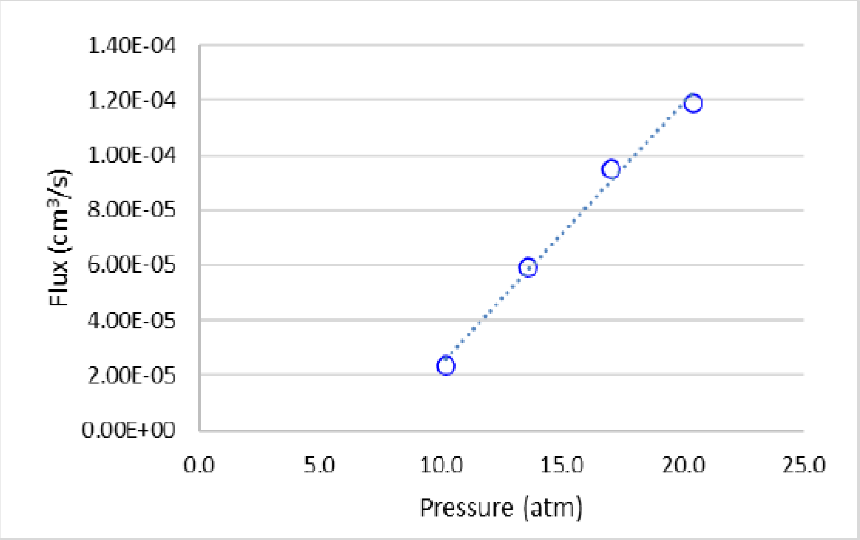
Target electrolyzer durability: < 100 μV/hr for 300 h at 1.0 A/cm^2

*** On-track 09/30/2020 milestone**

End-of-life performance and N_2 diffusion data is available (Backup slide 5)

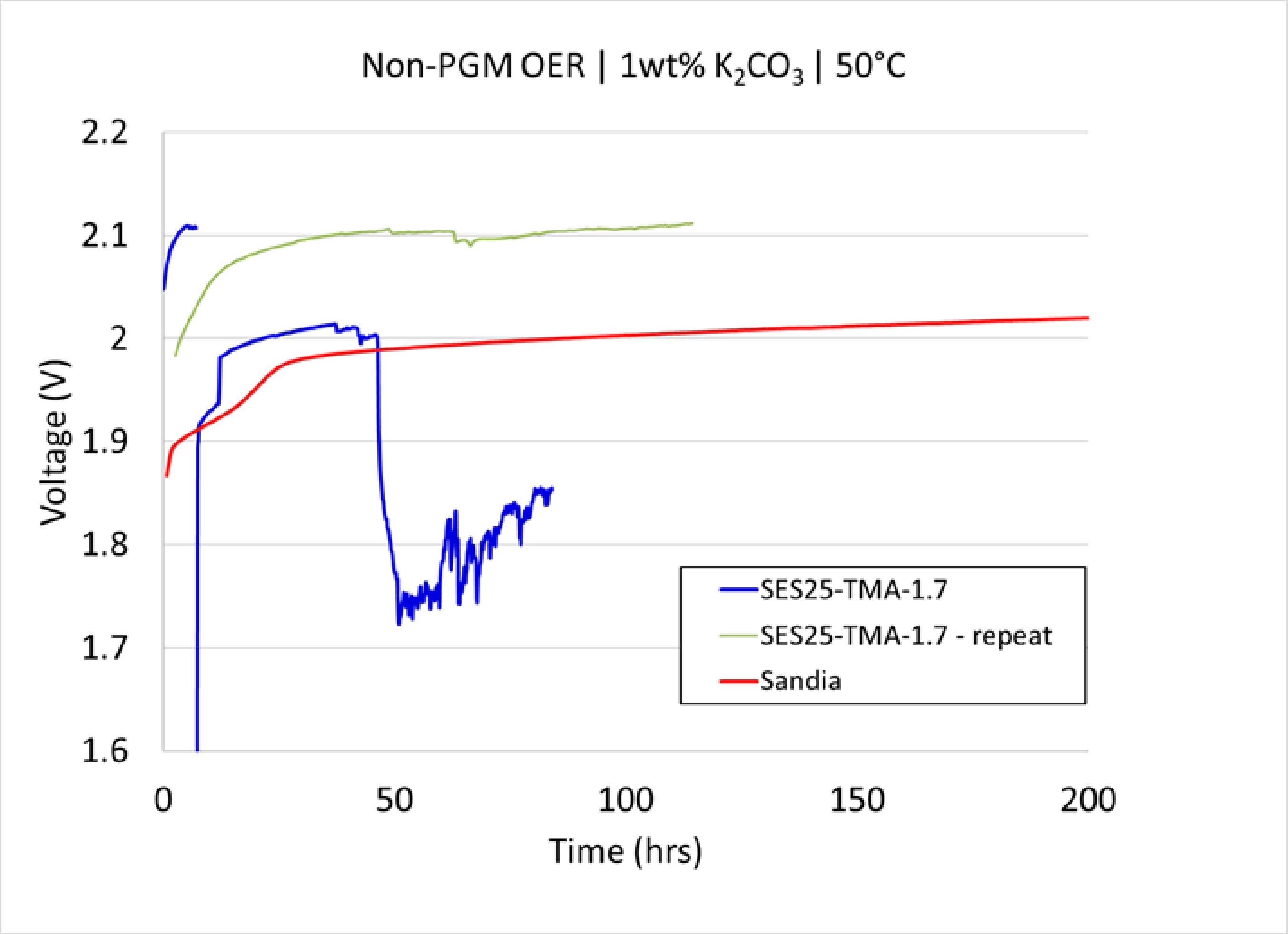
28 cm^2 – End of life measurements





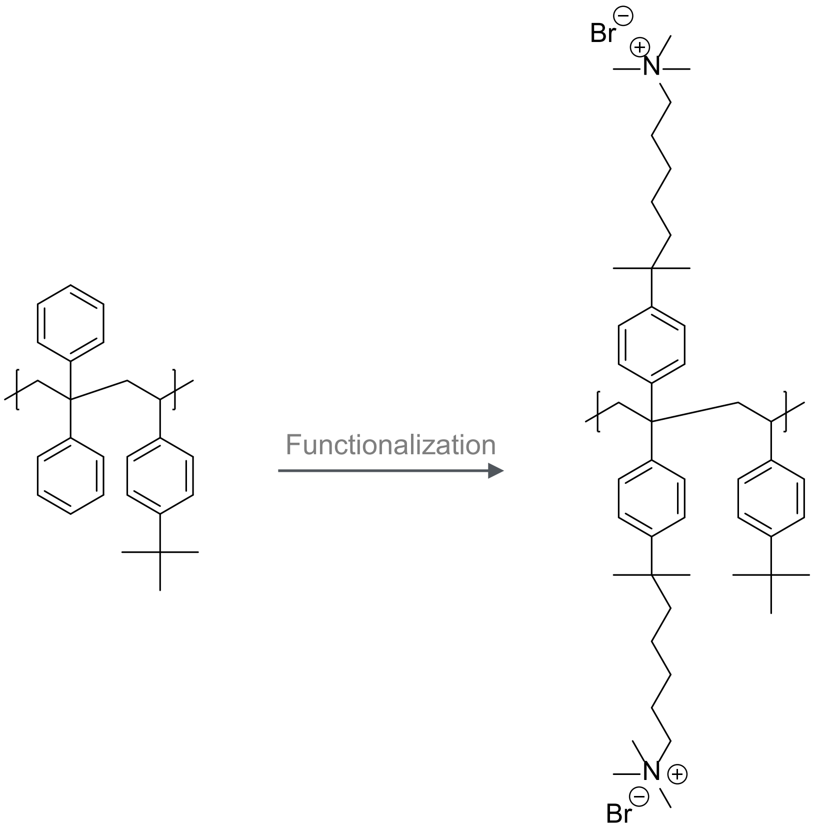
- **At the end of the test the stack did not show signs of cross cell leak or electronic short failures**
- **Stack was able to run with current up to 2 A/cm^2**
- **The nitrogen diffusion rate is normal, but the y-intercept is not at the origin.**

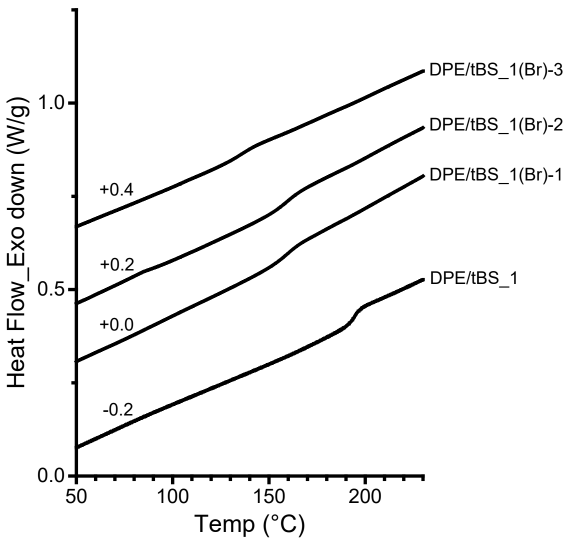
AEM water electrolyzer durability update with SES AEM



Accomplishments: Approach to increasing durability

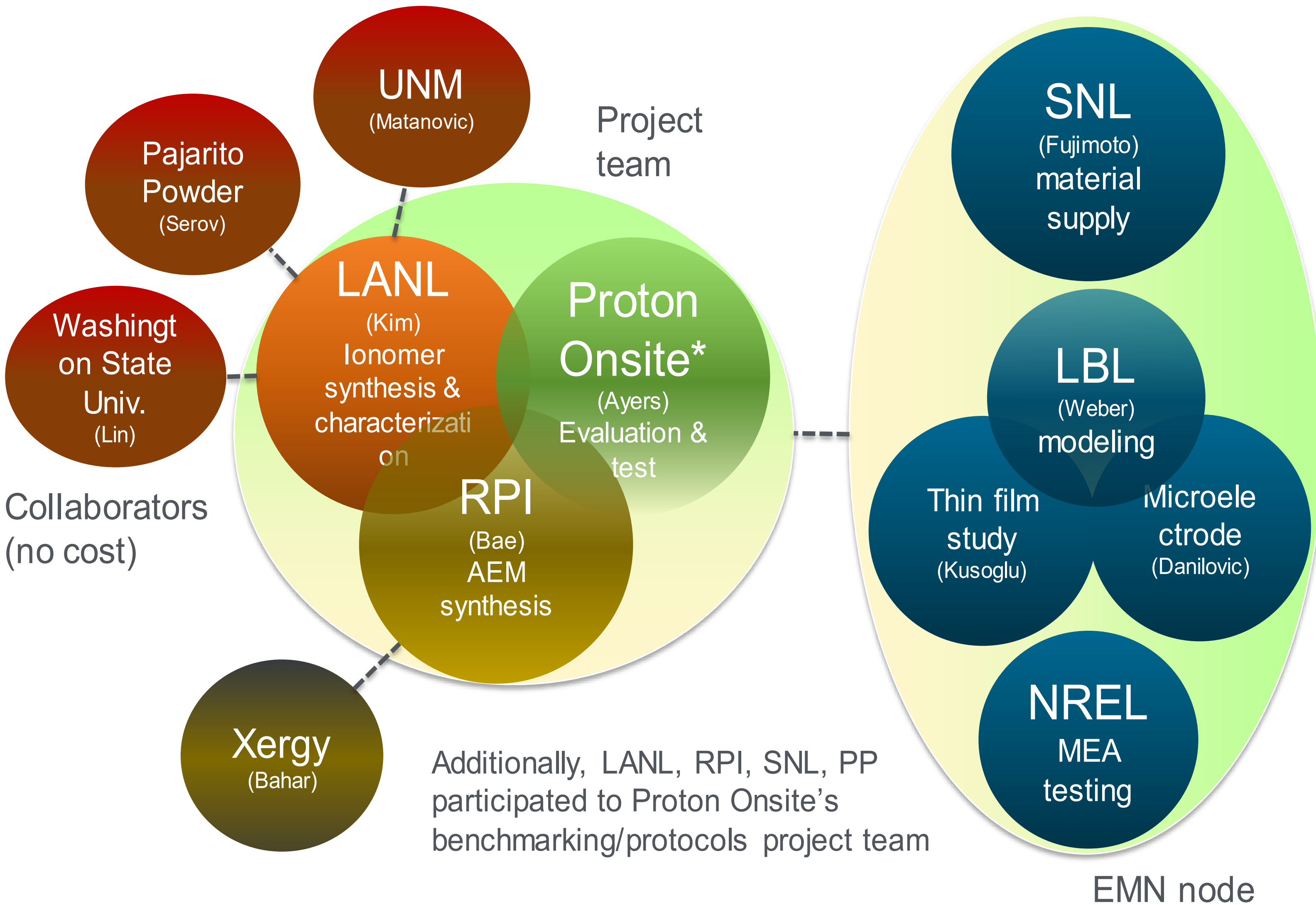
- No phenyl group in the polymer backbone
- High IEC but low water uptake
- Alkyl ammonium side chain instead of benzyl ammonium





Polymer	DoF (phenyls)	Projected IEC (Cl^-)	Mn (kg/mol)	T_g (°C)
DPE/tBS_1	n/a	n/a	205	194.5
DPE/tBS_1(Br)-1	0.32	1.36	239	159.4
DPE/tBS_1(Br)-2	0.35	1.50	245	159.4
DPE/tBS_1(Br)-3	0.72	2.24	247	135.0

Collaboration: Effectiveness



Proposed Future Work

By the end of September 30, 2020 (the last year) with current budget.

Institution	Proposed scope	Budget ($)	Intended outcome
RPI	Provide down-selected SES AEMs for durability study	30K	Support LANL and Proton durability test
LANL	Provide ionomer for durability study	30K	Support LANL durability test
LANL	MEA durability testing including using PGM-free catalysts	50K	Meet the 9/30/2020 durability milestone
Proton	MEA performance/durability	50K	Tech validation
SNL	Provide the control AEMs for durability study	50K	Support LANL and Proton durability test
LBNL	AEM characterization & thin film electrode study	60K	Support RPI AEM development
LBNL	Microelectrode study	40K	Support LANL MEA development
NREL	Complete the pH effect of electrolyzer performance	50K	Support LANL MEA development

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

Project Summary

Objective:	Preparing scalable polystyrene-based materials and demonstrating the performance and durability in alkaline membrane water electrolysis.
Relevance:	Aiming to make AEM electrolyzer system competitive to PEM electrolyzers in terms of performance and durability. AEM electrolyzers can utilize PGM-free catalysts, as well as low-cost metal flow fields which account for more than 70% of the stack cost.
Approach:	Preparing highly alkaline stable SES block copolymer AEM and polyolefinic ionomeric binder which minimizes the undesirable interaction with electrocatalysts.
Accomplish-ments (FY 19)	▪ Prepared polyolefinic SES block copolymer which showed no chemical degradation for 300 h in 1 M NaOH at 80 °C, hydroxide conductivity > 60 mS/cm at 80 °C and mechanical toughness. ▪ Developed AEM electrolyzers that exhibited > 2 A/cm^2 at 1.8 V using pure water and PGM-free anode catalyst layer. ▪ Demonstrated > 750 h stack durability with 50 μV/h at 50 °C and 100 psi gauge using PGM-free anode.
Collaborations:	LANL team (LANL, RPI and Proton Onsite) works together with 5 EMN nodes at three different National Labs (LBNL, SNL and NREL). Additional interactions with WSU, Pajarito Powder, UNM, and Xergy (no cost).

Publications and Presentations

Publications:

- Highly quaternized polystyrene ionomers for high performance anion exchange membrane water electrolysers, Dongguo Li, Eun Joo Park, Wenlei, Zhu, Qiurong Shi, Yang Zhou, Hangyu tian, Yuehe Lin, Alexey Serov, Barr Zulevi, Ehren Donel Baca, Cy Fujimoto, Hoon Chung, Yu Seung Kim, *Nature Energy*, 5, 378-385 (2020).
- Phenyl Oxidation Impacts the Durability of Alkaline Membrane Water Electrolyzer, Dongguo Li, Ivana Matanovic, Albert S. Lee, Eun Joo Park, Cy Fujimoto, Hoon T. Chung, and Yu Seung Kim, *ACS Applied Materials & Interfaces*, 11, 10, 9696-9701 (2019).

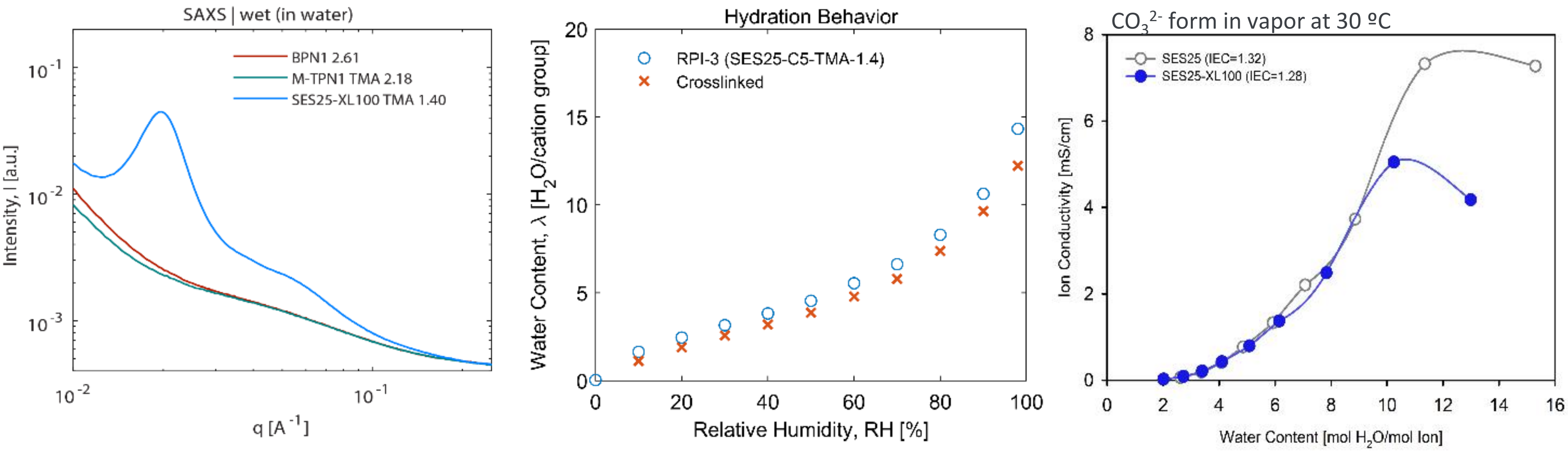
Presentation:

- Electrolyte Oxidation Limits the Life of Alkaline Membrane Water Electrolyzer, Y. S. Kim, D. Li, I. Matanovic, A. S. Lee, H. T. Chung, I01-1406, 235th ECS Meeting, May 26-30, 2019, Dallas, TX, USA.
- Phenyl Oxidation at Oxygen Evolution Potentials – Impact on Alkaline Membrane Electrolyzer Durability, D. Li, Y. S. Kim, 2019 MRS Fall Meeting & Exhibit, December 1-6, 2019, Boston, Massachusetts, USA.

Technical Backup Slides

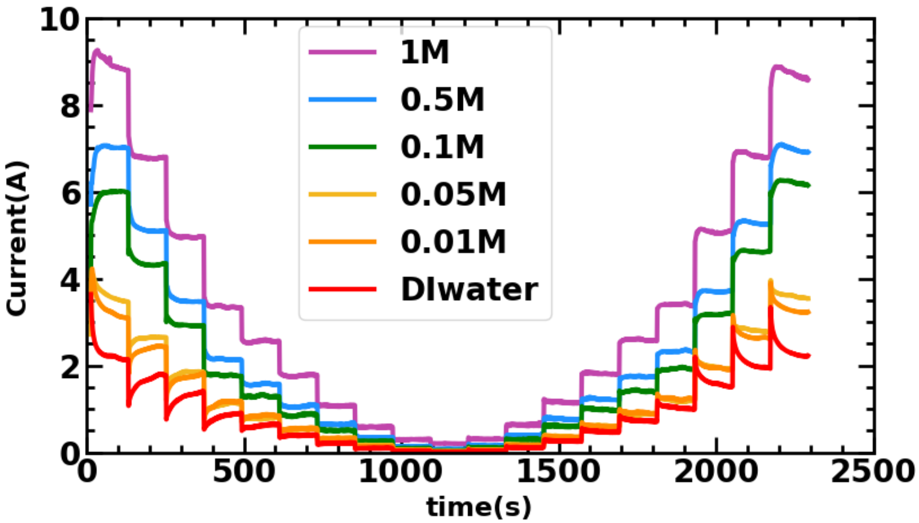
Characterization of Crosslinked SES AEMs

- Crosslinked SES (XL) membrane exhibits a phase-separated structure
  - The SES25-XL100 shows a clear phase-separation with long-range order (with peaks ca. 30 and 10 nm spacing) while the other polymers lack an apparent phase-separation, exhibiting a broader shoulder
- Crosslinking reduces water uptake at high RH and in water, but only slightly
- Crosslinked SES shows similar conductivity in vapor (compared to un-crosslinked), but deviates at high RH or in liquid water
  - conductivity decreased at high water content, possibly due to ion dilution by excessive water
  - In liquid, XL has lower water content but comparable conductivity (XL: 5.2 vs. 5.94 mS/cm)

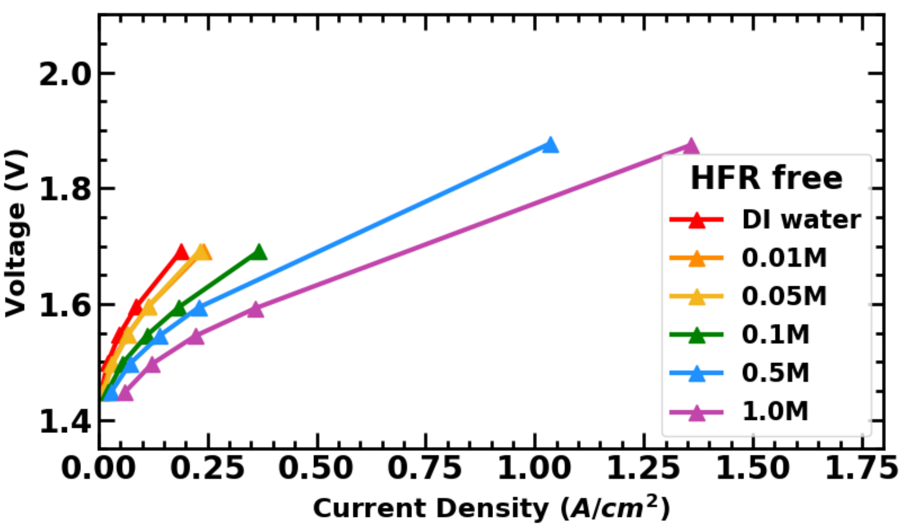


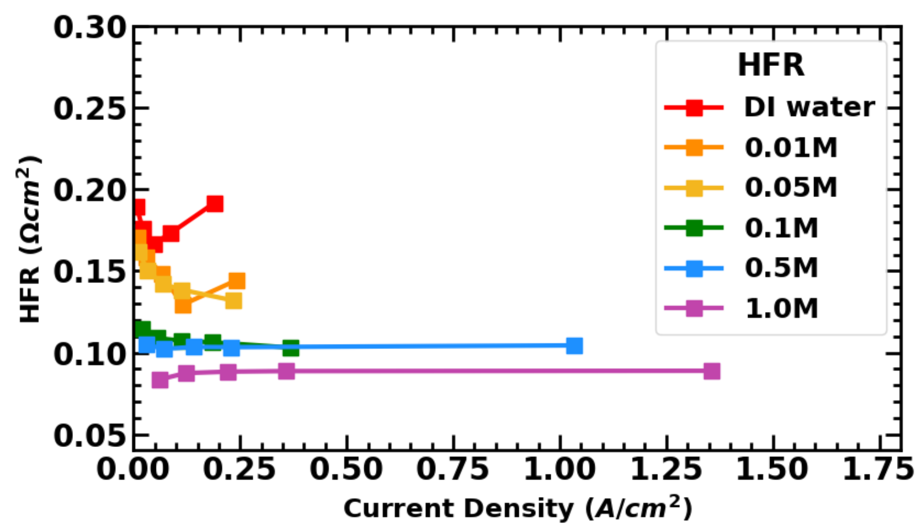
Current vs. Time: Concentration Comparison

Electrolyte (60°C): DI water, 0.01M, 0.05M, 0.1M, 0.5M, 1M
LANL Membrane soaked in 1% KOH for 4 hours
Pt/C: 0.36 mg_{Pt}/cm^2 IrO_2: 0.75 mg_{Ir}/cm^2
Frequency: 1Hz – 100,000Hz

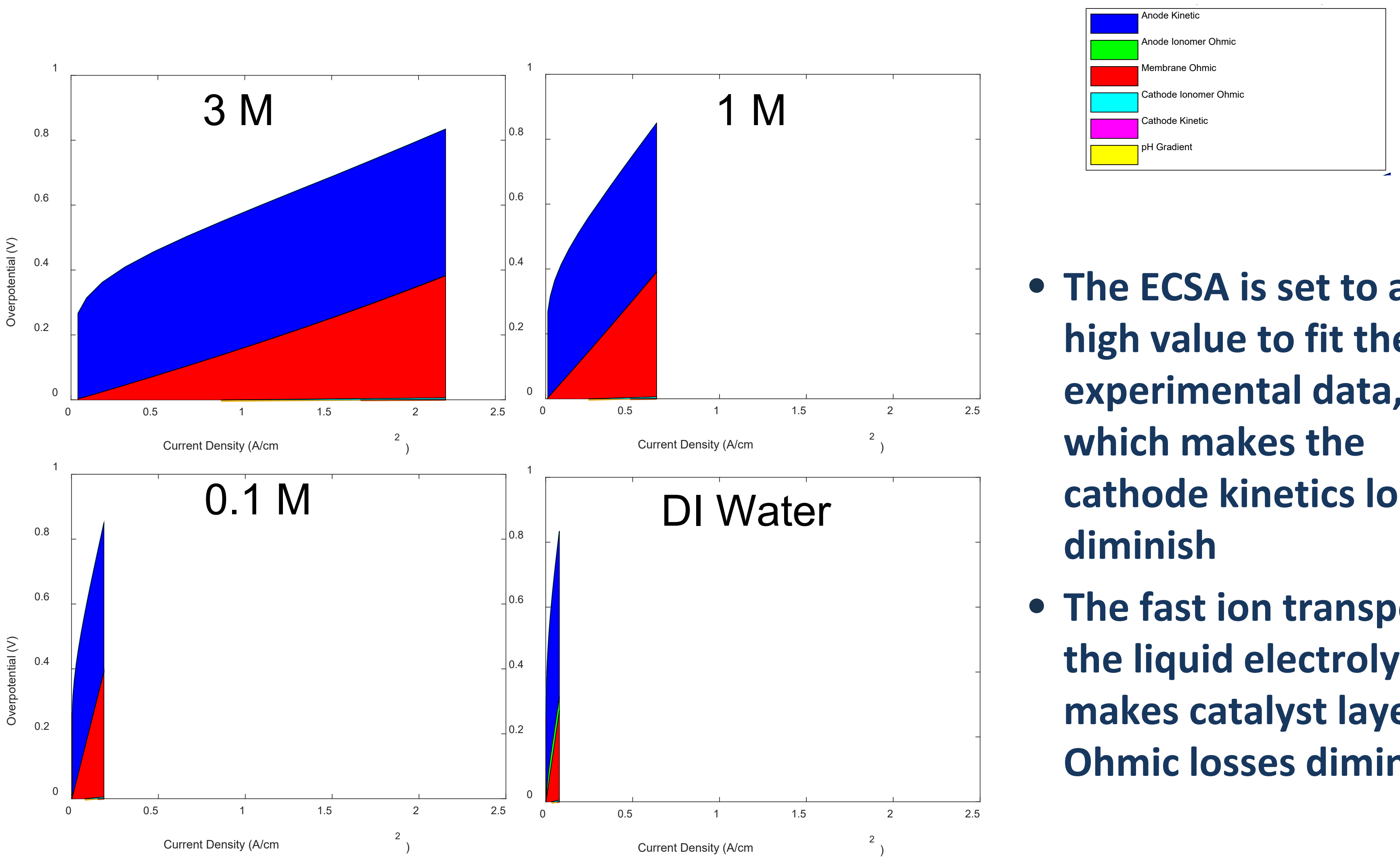


- Performance increases with concentration as expected
- Stepping current down
  - Concentrations ≤ 0.05 M approach equilibrium from a lower current density
  - Concentrations ≥ 0.5 M approach equilibrium from a higher current density
- Stepping current up
  - Reverses equilibrium behavior



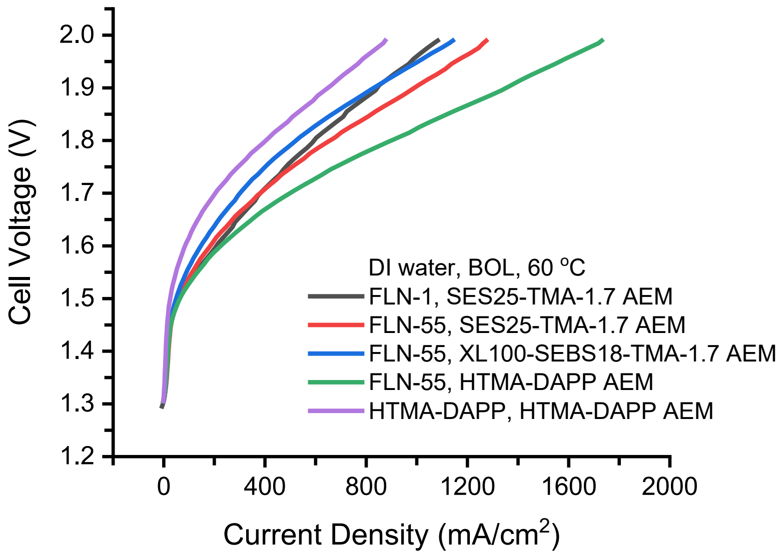


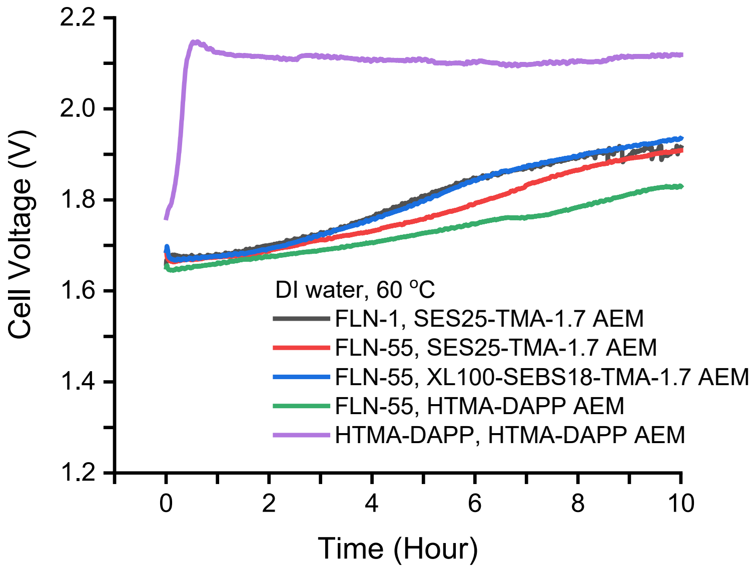
Applied voltage breakdown (AVB)



- **The ECSA is set to a very high value to fit the experimental data, which makes the cathode kinetics loss diminish**
- **The fast ion transport in the liquid electrolyte makes catalyst layer Ohmic losses diminish**

Durability study using different materials





- Better initial performance for HTMA-DAPP AEM probably due to decreased thickness.
- Much faster decay at the constant current density of 300 mA/cm² vs. 100 mA/cm².
- Similar initial performance and durability for FLN ionomers.
- Lower initial performance and much faster voltage increase at the beginning of life test for HTMA-DAPP ionomer due to the rapid phenol formation.