Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

High-Performance AEM LTE with Advanced Membranes, Ionomers and PGM-Light Electrodes

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EE0008833 p185

June 7, 2:45 PM (20 + 10 minutes)

Type of Presentation: Oral

Annual Merit Review

NREL Transforming ENERGY | BERKELEY LAB Bringing Science Solutions to the World | Sandia National Laboratories | INL Idaho National Laboratory | Lawrence Livermore National Laboratory

Project Overview

Project Partners

Paul A. Kohl, Georgia Tech (Lead organization)
Barr Zulevi, Pajarito Powder
William Mustain, University of South Carolina
Chris Capuano, NEL Inc.

Project Vision

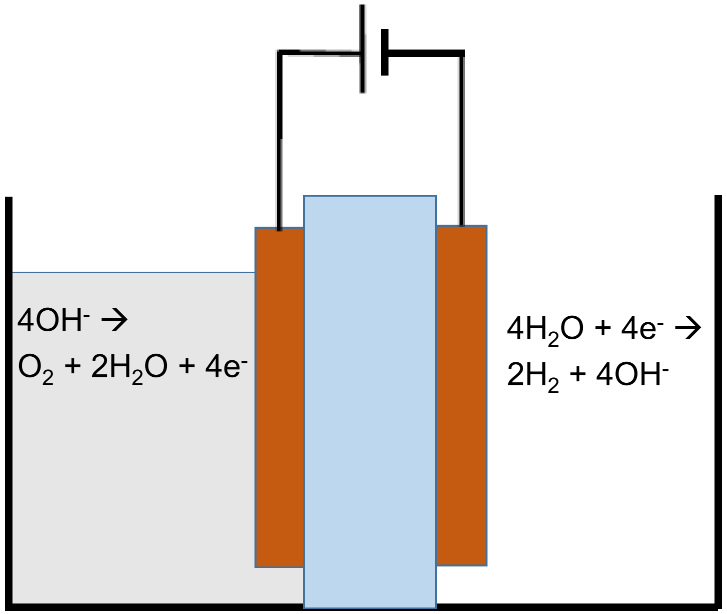
To enhance and *combine state-of-the-art alkaline polymer electrolyzer components* into one optimized membrane electrode assembly (MEA) system to achieve the DOE targets for low temperature electrolysis (LTE).

Project Impact

Low temperature alkaline electrolysis has the potential to lower the overall cost of electrolysis-driven hydrogen by (i) lowering the applied voltage, (ii) lowering the cost of catalysis and membranes, and (iii) meeting/improving the lifetime compared to acid-based LTE cells.

Award #	**DE-EE0008833**
Start/End Date	01/01/2020 – 5/30/2023 Includes Covid NCE
Total Project Value*	$1.25M (DOE + Cost Share)
Cost Share %	20%

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



Approach- Summary

Project Motivation

There is a significant need to reduce the cost and improve durability of LTE systems to enable affordable H_2 at large scale. Team members have demonstrated top-performing AEM LTE components. This project gives us the opportunity to combine and further enhance components, cells and systems.

Key Impact

Metric	State of the Art	Expected Advance
Operating voltage	*1 A/cm^2 @ 2 V*	*1 A/cm^2 @ 1.75 V*
Low (or no) PGM catalyst	*Not available yet*	*OER and HER low PGM or PGM-free at* 1 A/cm^2 at 1.75 V
Durability	Not demonstrated	<4 mV/1000 h

Barriers

(i) Low AEM stability at high voltage and T
(ii) Low AEM conductivity
(iii) Poor AEM mechanical strength
(iv) Catalyst cost
(v) Catalyst stability
(vi) Poor catalyst adhesion
(vii) Quality electrode fabrication missing
(viii) High operating voltage

Partnerships

Georgia Tech: Hydroxide conducting polymers.
South Carolina: Electrode design and fabrication.
Pajarito: Optimized PGM and non-PGM catalysts.
NEL Hydrogen: Large format testing, systems design and techno-economic analysis.

Approach - Innovation

Combined Partner Contributions:

Georgia Tech has developed the highest conductivity for a mechanically and chemically stable hydroxide conducting membrane for electrochemical devices.

Pajarito Powder has created outstanding PGM-free (and PGM) catalysts and has evaluated ionomers for electrode fabrication.

University of South Carolina has developed world-best electrodes and MEA fabrication methods.

Nel Inc. has extensive system-level integration of and cost modeling

Budget Period 1 Decision Point:

Cell Voltage < 1.7 V cell and < 20 mV/1000 h degradation extrapolated from 100 h tests.

Budget Period 2 Decision Point:

LTE performance at cell voltage of 1.65 V and <10 mV/1000 h degradation with an operating cost < $10/gge (using $0.025/kWh electricity).

Budget Period 3 Milestones and Goals:

Milestone 3.1 Materials scale-up with performance within 10% of that obtained previously using small scale synthesis.
Milestone 3.2 PGM-free AEM MEA demonstrates performance of <1.75 V LTE at 1 A/cm^2.
Milestone 3.3 Complete cost analysis for commercial-scale prototype resulting in a H_2 production cost of <$2/kg H_2.
Milestone 3.4 Durability testing at 1.75 V at 1 A/cm^2 with a degradation rate of <4 mV/1000 hr.
End of project goal: **1 A/cm^2 at <1.75V, (ii) <4 mV/ 1000 hr degradation (extrapolated from 100 h test), Path to $2/gge**

Relevance & Impact

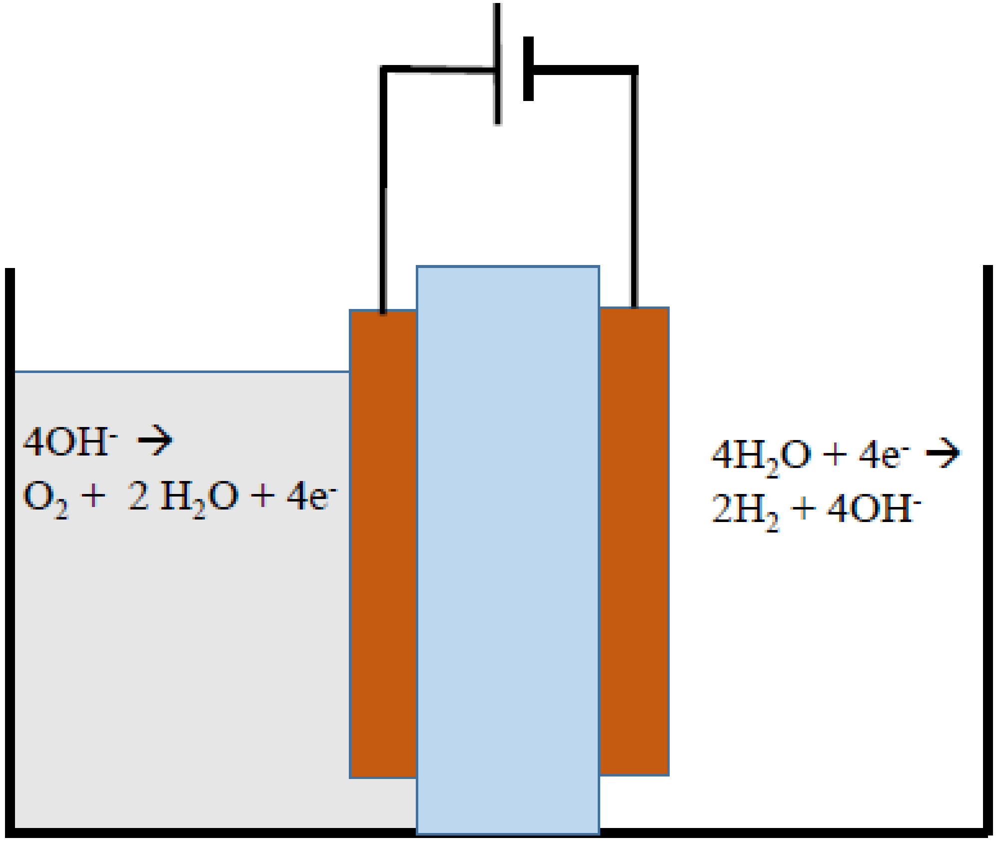
- Alkaline low temperature electrolysis (LTE) systems enjoy several advantages over acid-based LTE systems including facile (iridium free) oxygen evolution reaction (OER) kinetics, hydrocarbon (not perfluorinated) membranes, and use of common metals (SS and Ni, not Pt/Ti) in BOP.

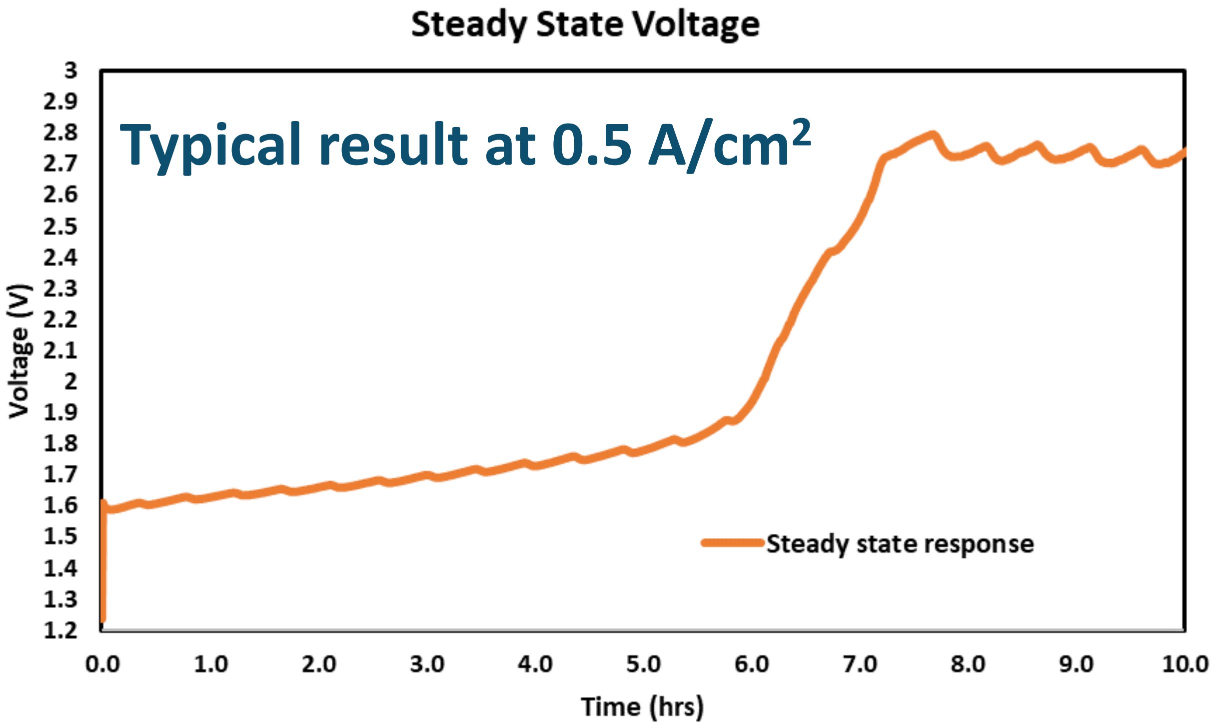
- System-level benefits can only be realized when the contributing parts are each optimized. The approach here is to take state-of-the-art components and work-out (optimize) each to achieve system-level advances with are greater than the sum of the parts for each components.

- Optimization of a single component (e.g., catalyst, membrane, ionomer, electrode fabrication method) produces sub-optimized solutions which are unlikely to meet the full objective of (i) performance: 1 A/cm^2 1.75 V, (ii) durability: 4 mV/1000 h degradation and (iii) cost: $2/gge.

Accomplishments

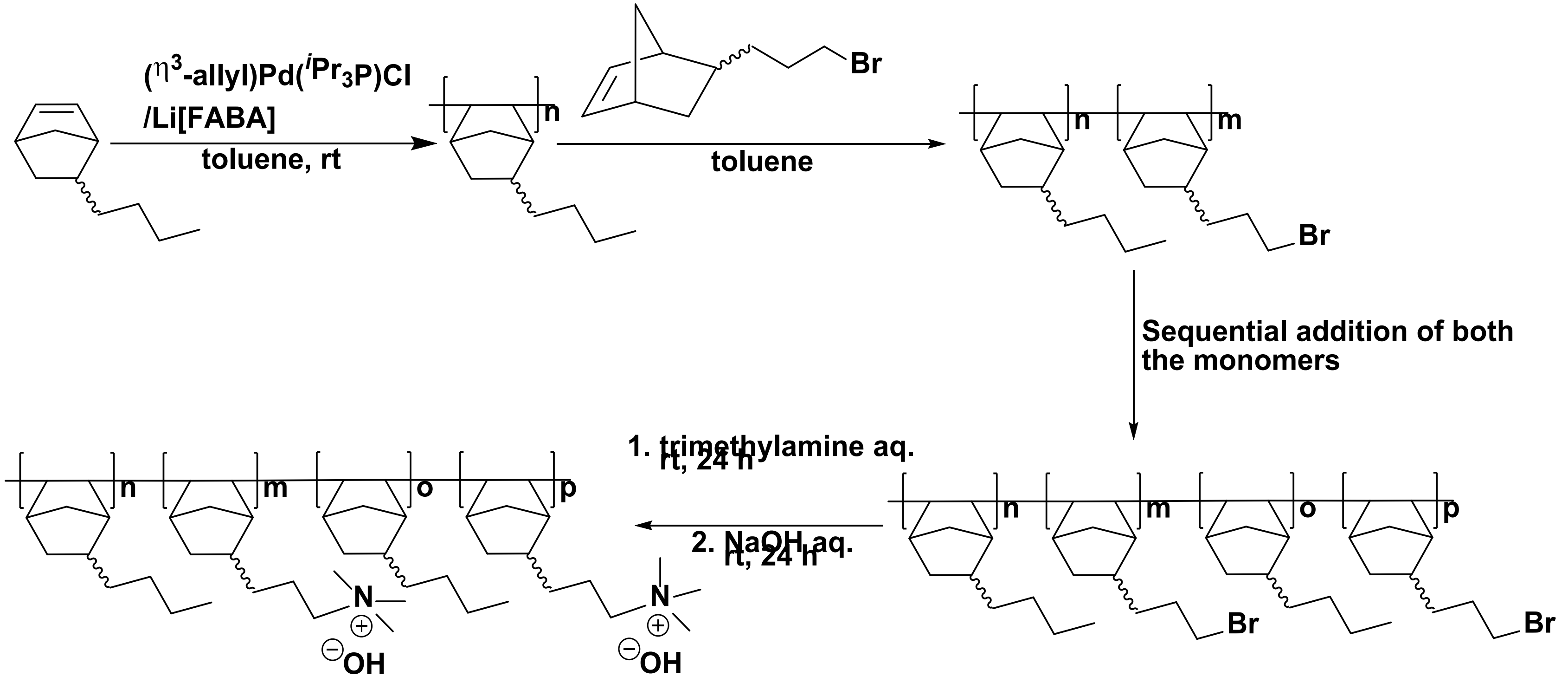
Initial Results in 2019: Unstable MEA & Degrading Catalyst





Accomplishments: High Conductivity, High Stability Membranes

Barriers
(i) Low AEM stability at high voltage and T
(ii) Low AEM conductivity
(iii) Poor AEM mechanical strength
(iv) Catalyst cost
(v) Catalyst stability
(vi) **Poor catalyst adhesion**
(vii) **Quality electrode fabrication missing**
(viii) High operating voltage



- Vinyl addition PNB, sp^3 carbons are chemically stable
- High Tg gives mechanically stable thin films
- Low molecular weight monomers => high IEC (4 meq/g) and conductivity (>200 mS/cm)
- Low-cost monomers from dicyclopentadiene, now at 10 kg scale with plans for 100 to 1000 kg scale

Contributes to Milestone 3.1: Materials scale-up, and Milestone 3.4: Durability

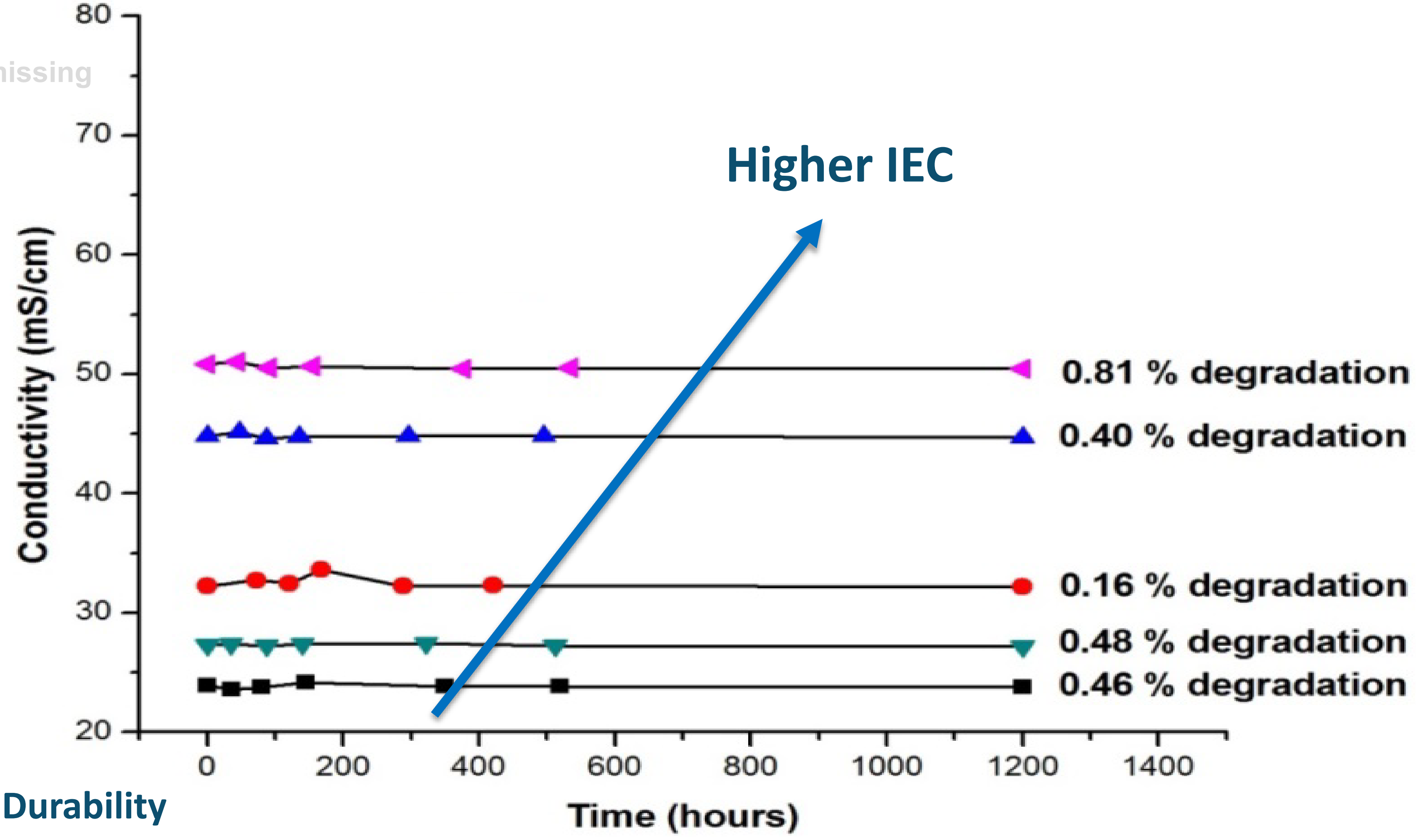
M. Mandal, G. Huang and P. A. Kohl, *J. Membr. Sci.*, 2019, *570–571*, 394-402.

Accomplishments: Membrane Accelerated Aging at 80ºC in 1 M KOH

Barriers

(i) Low AEM stability at high voltage and T
(ii) Low AEM conductivity
(iii) Poor AEM mechanical strength
(iv) Catalyst cost
(v) Catalyst stability
(vi) **Poor catalyst adhesion**
(vii) **Quality electrode fabrication missing**
(viii) High operating voltage

<1% degradation in >1200 hours



Contributes to Milestone 3.4: Durability

M. Mandal, G. Huang and P. A. Kohl, *J. Membr. Sci.*, 2019, *570–571*, 394-402.

Accomplishment: Low Cost OER Catalyst Development

PAJARITO POWDER

Barriers
(i) Low AEM stability at high voltage and T
(ii) Low AEM conductivity
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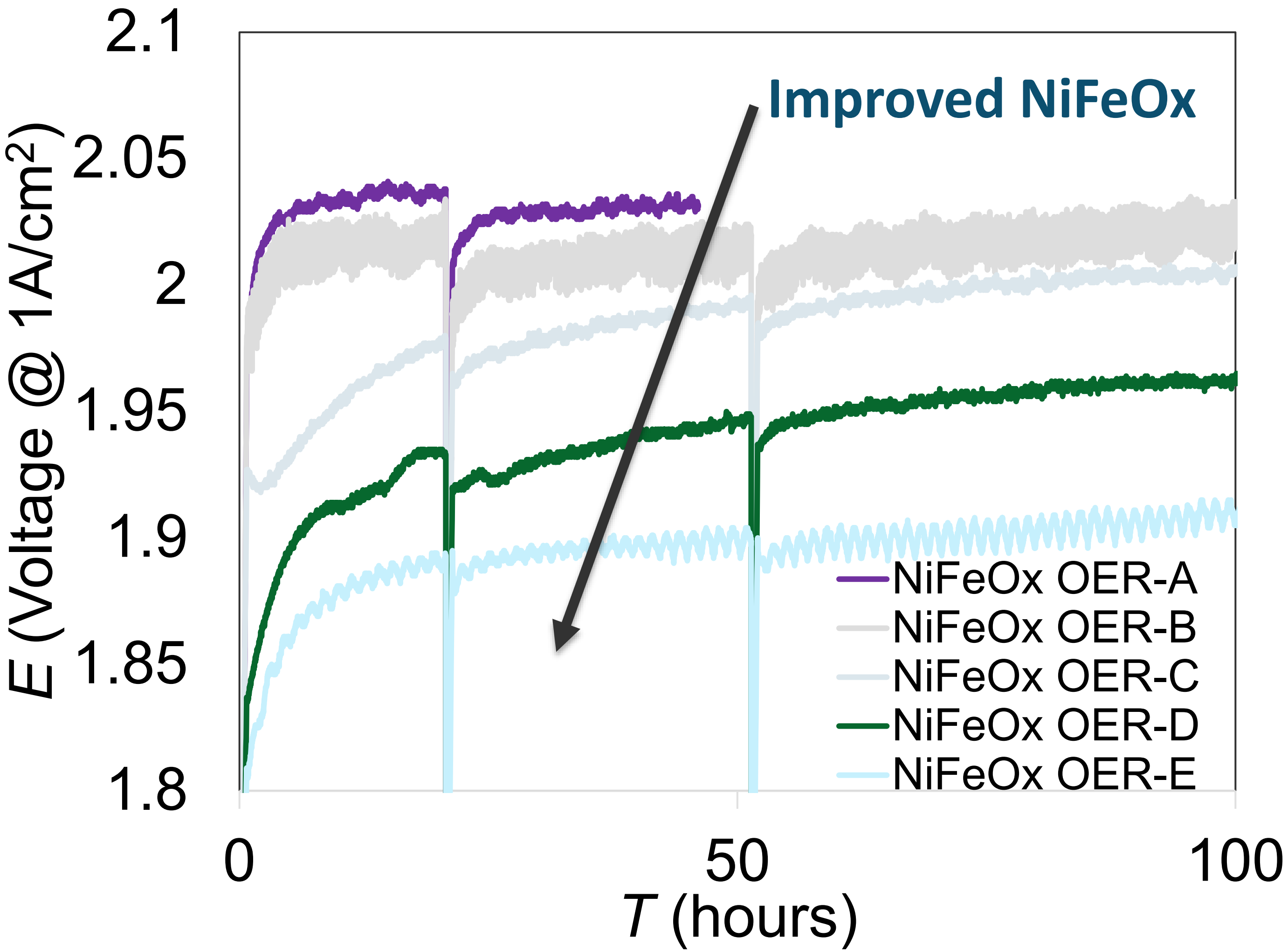
- Improved steady-state performance w/ NiFeOx OER catalyst
  - 140 mV improvement
  - Batch scale-up from 2 g to 50 g
- PbRuOx is no longer used due to degradation and heavy metal content



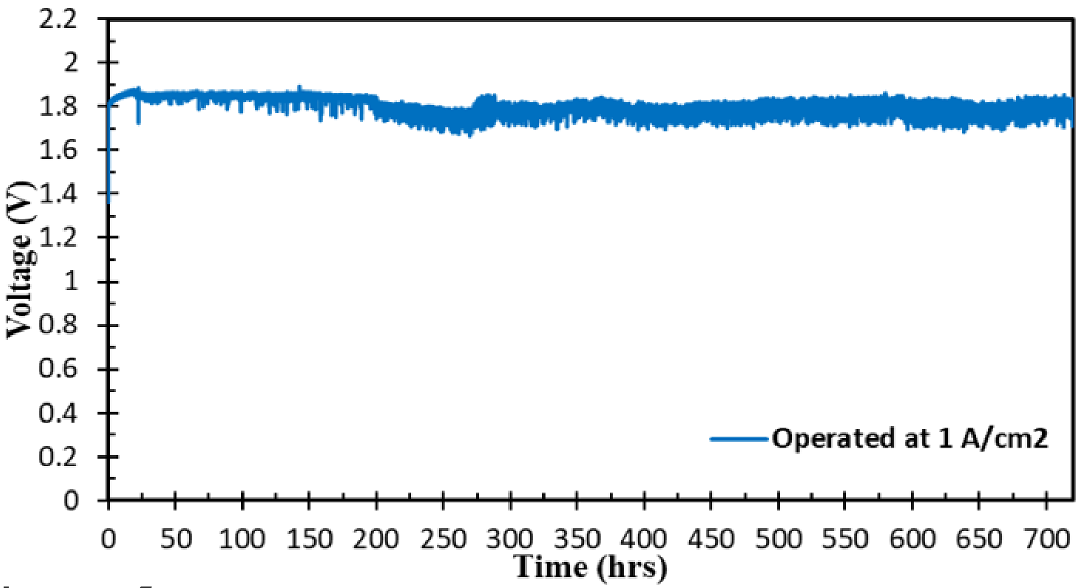
Anode: 3mg/cm² NiFeOx OER catalyst on SS PTL
Cathode: 1mg/cm² 30%PtNi/C on Carbon GDL
60°C cell temperature, 1M KOH fed to anode

Contributes to Milestone 3.2: PGM free

Contributes to Milestone 3.4: Durability

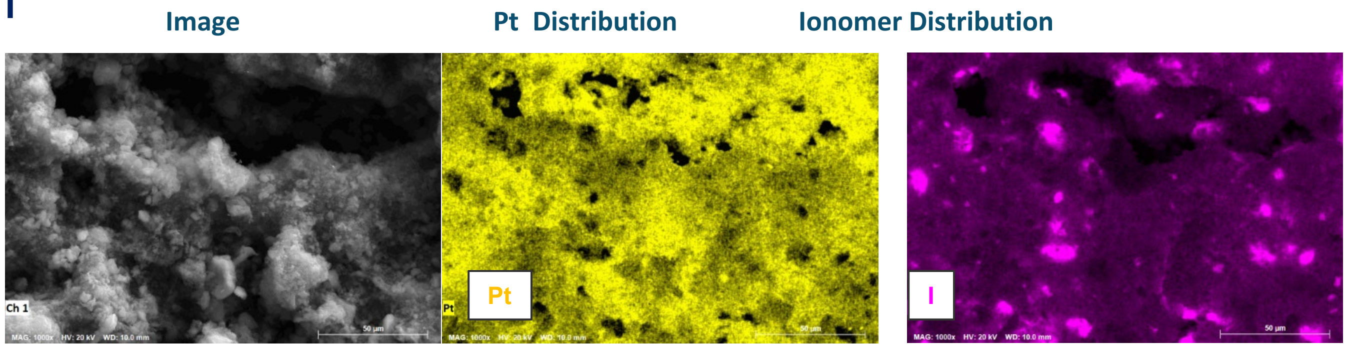
Accomplishment: Anode Optimization Using Insoluble Ionomer

- Ionomer Properties[1]
  - Particle-cast process
  - IEC and degree of cross-linking
- Statistical DoE Optimization[2]
  - Catalyst type, loading, adhesion
  - Ionomer loading
  - PTL type



- DOE-predicted composition had high performance
- PTL was the most statistically significant parameter
- Relaxed design allowed for first long-term stable operation

Contributed to D1: <40 mV/1000 for 100 h



[1]G. Huang, W.E. Mustain, P.A. Kohl, et al., J. Electrochem. Soc., 167 (2020) 164514
[2]N. Ul Hassan, W. E. Mustain *et al.*, *Electrochim. Acta*, **409**, 140001 (2022)

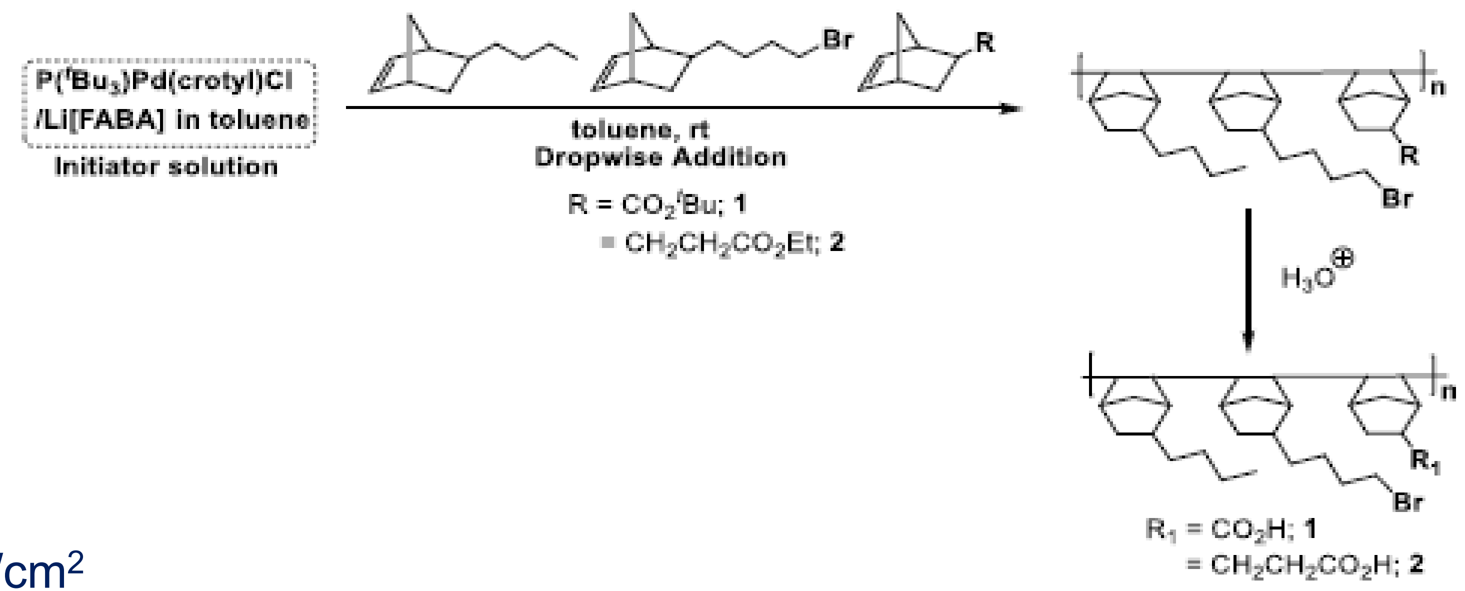
SEM Analysis via Josh Sugar, Sandia National Laborotory

Accomplishment: Creation of Self-Adhesive, Soluble Ionomers

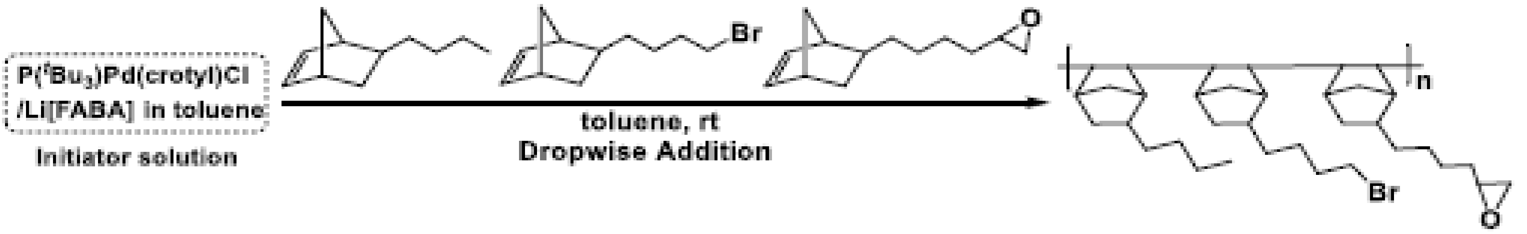
- ❖ Family of self-adhesive ionomers.
- ❖ Two-part system: adhesion between catalyst, PTL and ionomer.

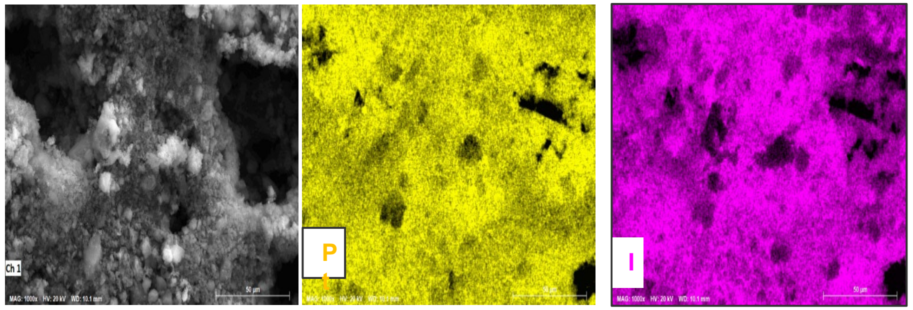
Contributes to Milestone 3.4: Durability at 1 A/cm^2

Terpolymer 1 and 2



Terpolymer 3

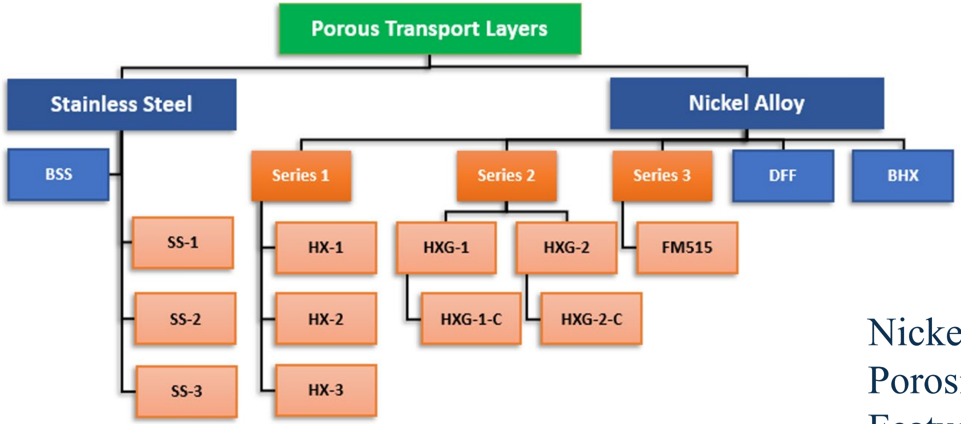




Chen, M., Mandal, M., Groenhout, K., McCool, G., Tee, M., Zulevi, B., and Kohl, P. A., “Self-Adhesive Ionomers for Durable Low-Temperature Anion Exchange Membrane Electrolysis, Journal of Power Sources, (2022).

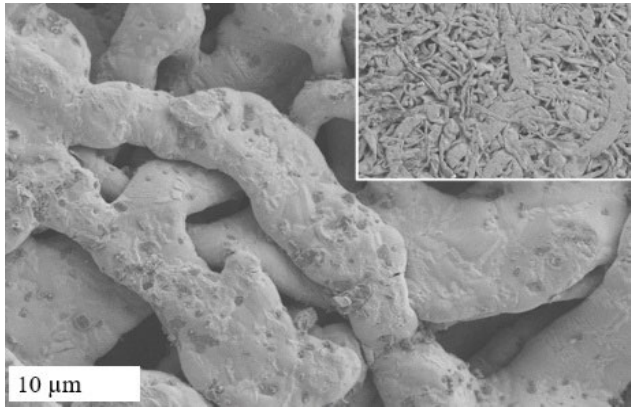
Accomplishment: Porous Transport Layer Optimization

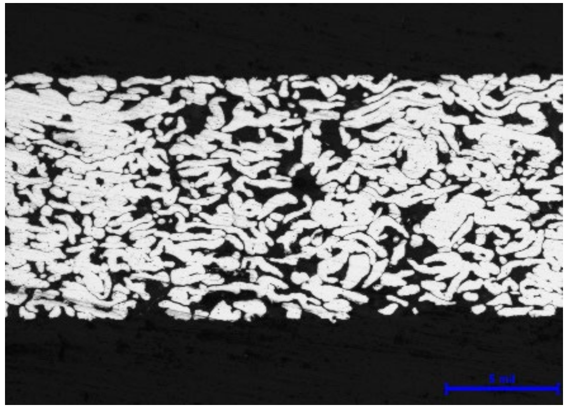
14 PTLs tested – 11 new, 3 commercial

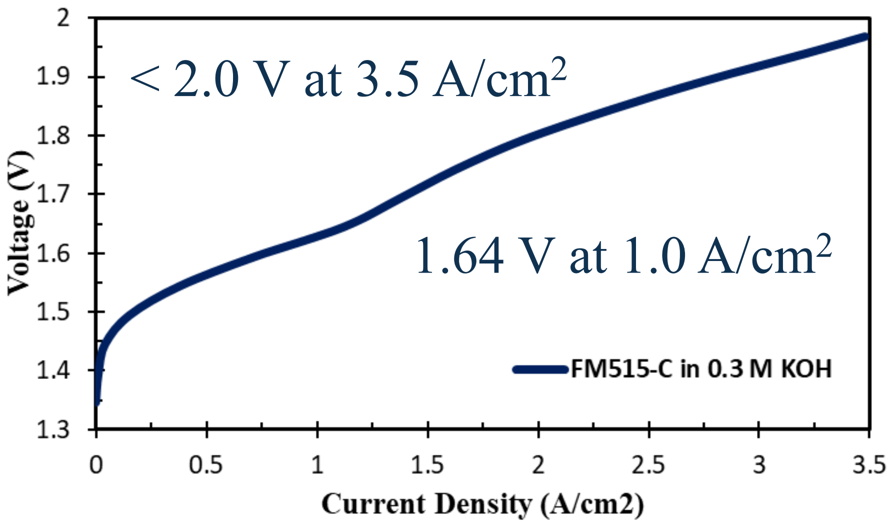


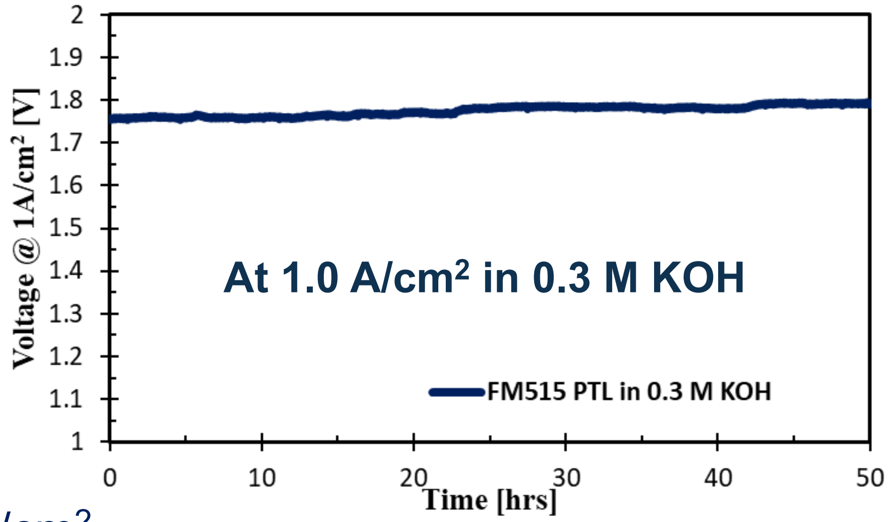
Nickel alloy (not SS)
Porosity: 35 – 40 %
Feature size: 10-15 µm
Thickness: 200 – 300 um

Best PTL now in pre-commercial stage
¼ the cost of previous “standard” PTL





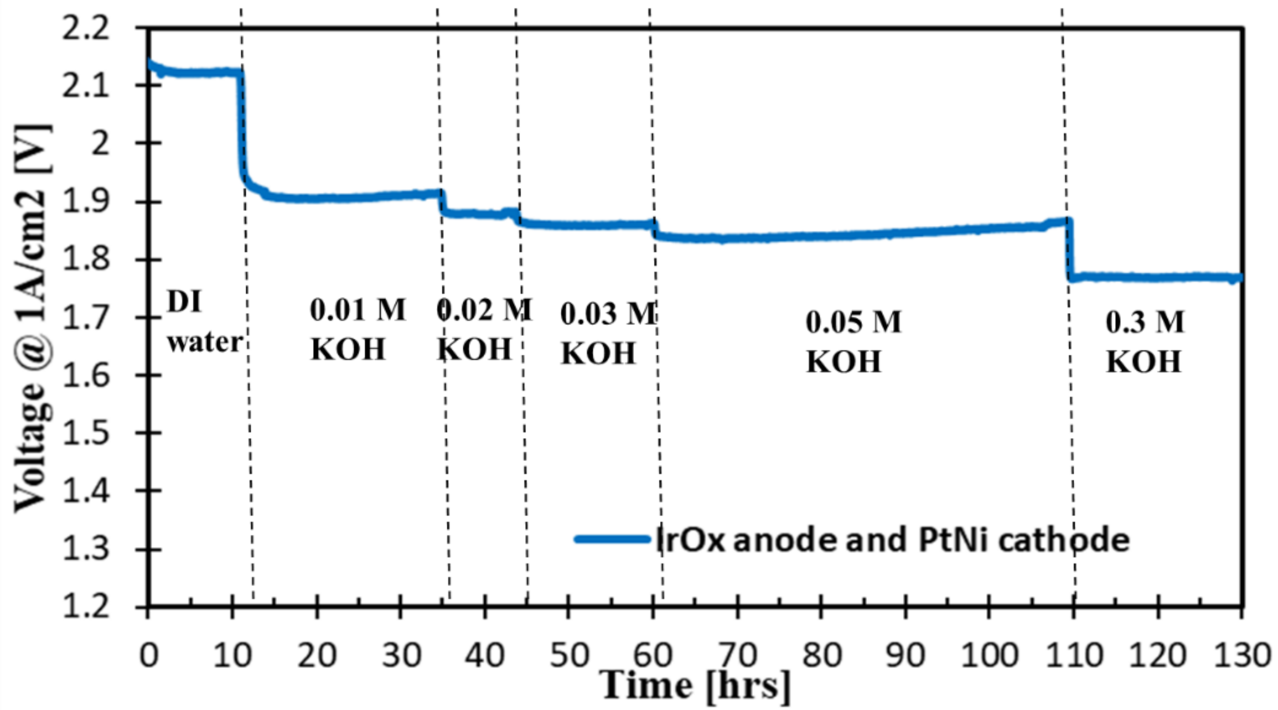


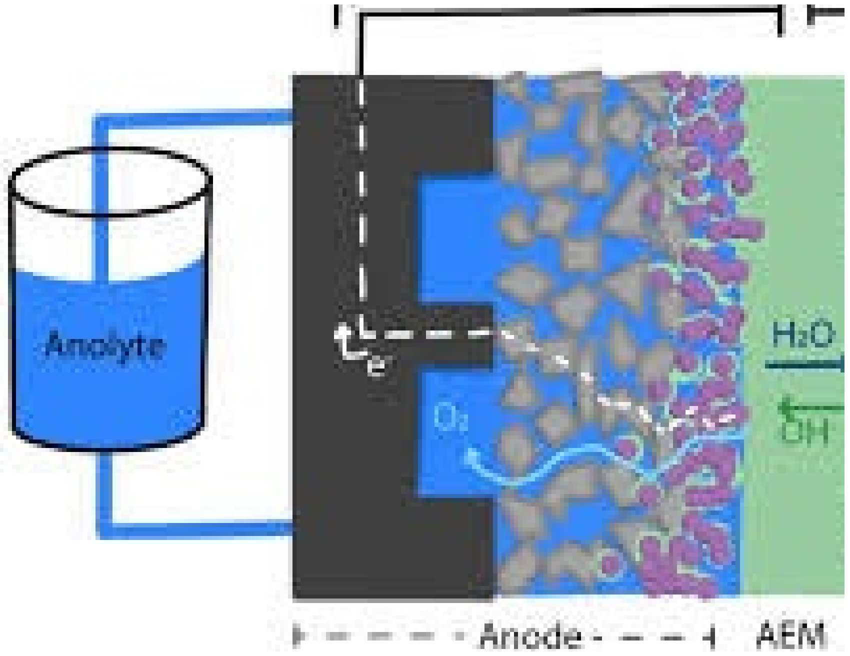


Contributes to Milestone 3.1: Scale-up and Milestone 3.4: Durability at 1 A/cm²

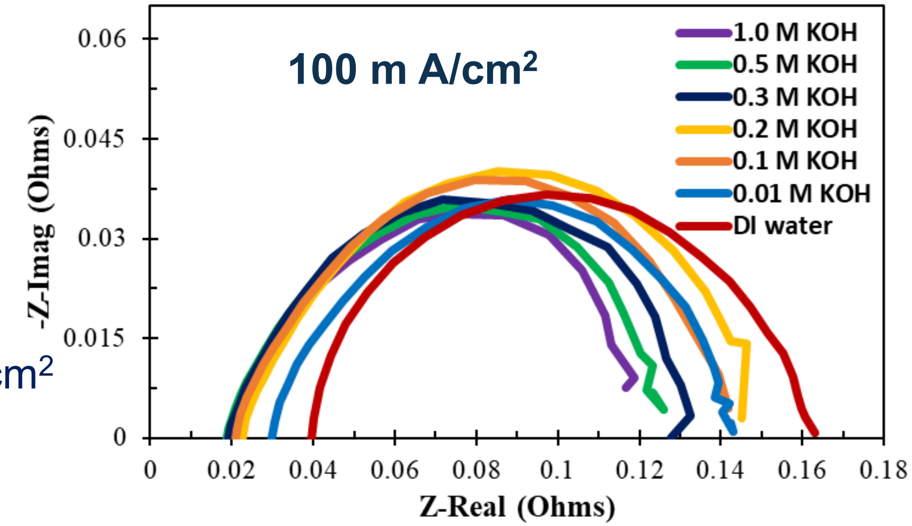
N. Ul Hassan, B. Zulevi, P.A. Kohl, W. E. Mustain *et al.*, J. Power Sources, 555 (2023) 232371

Accomplishment: DI vs KOH Aqueous Feed





- Presence of almost any salt enhances performance
- Voltage ($) penalty with DI water
- Little penalty in recirculation of dilute electrolyte vs DI water.

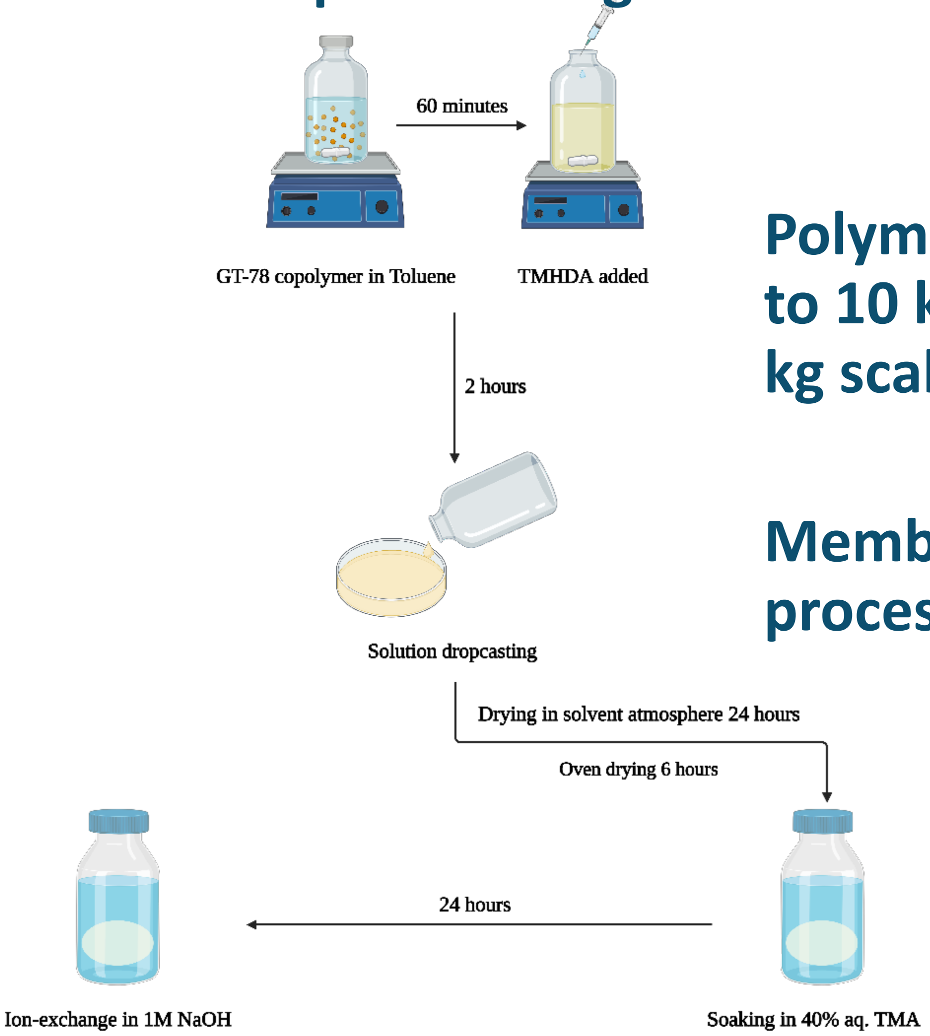


Contributes to Milestone 3.3: Cost Analysis, and Milestone 3.4: Durability at 1 A/cm^2

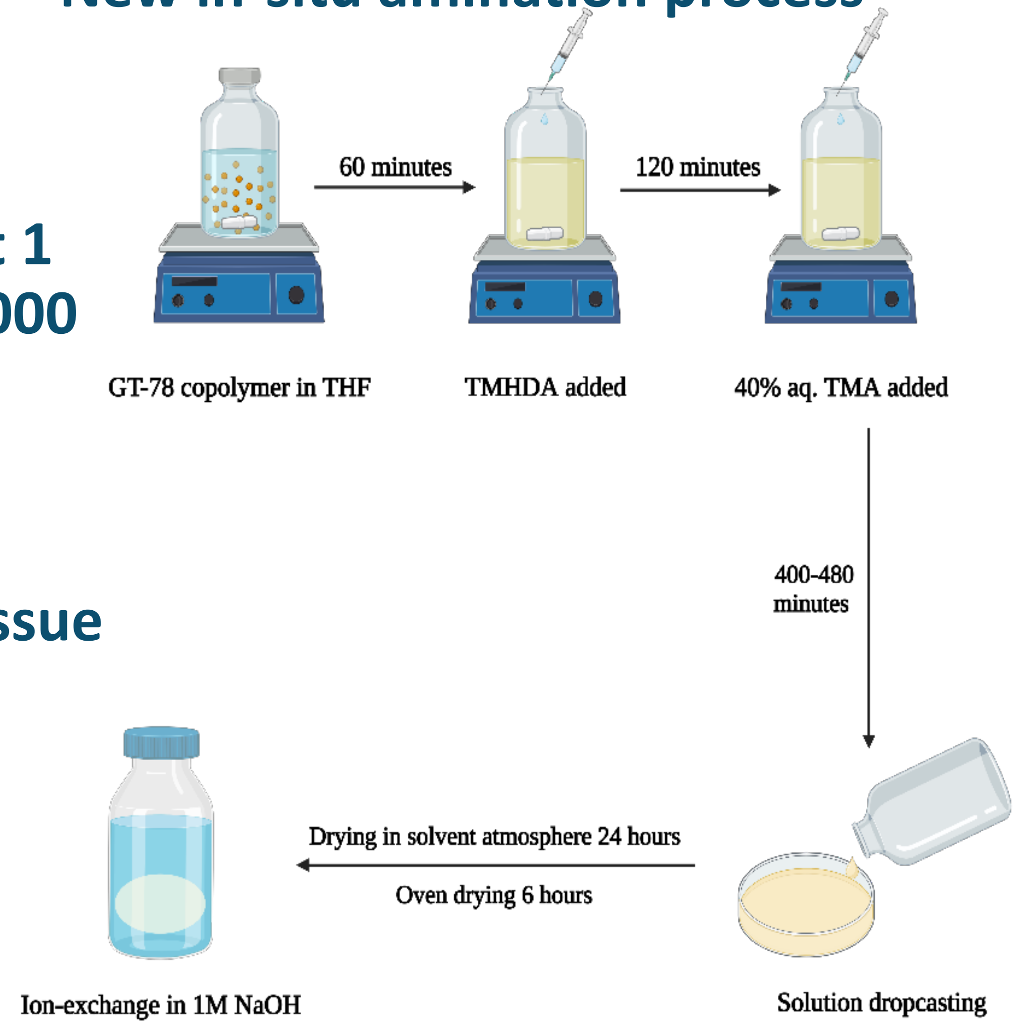
N. Ul Hassan, Y. Zheng, P.A. Kohl and W.E. Mustain, J. Electrochem. Soc., 169 (2022) 044526

Accomplishment: Membrane Scale-up and Manufactuability

Current post-casting amination



New in-situ amination process

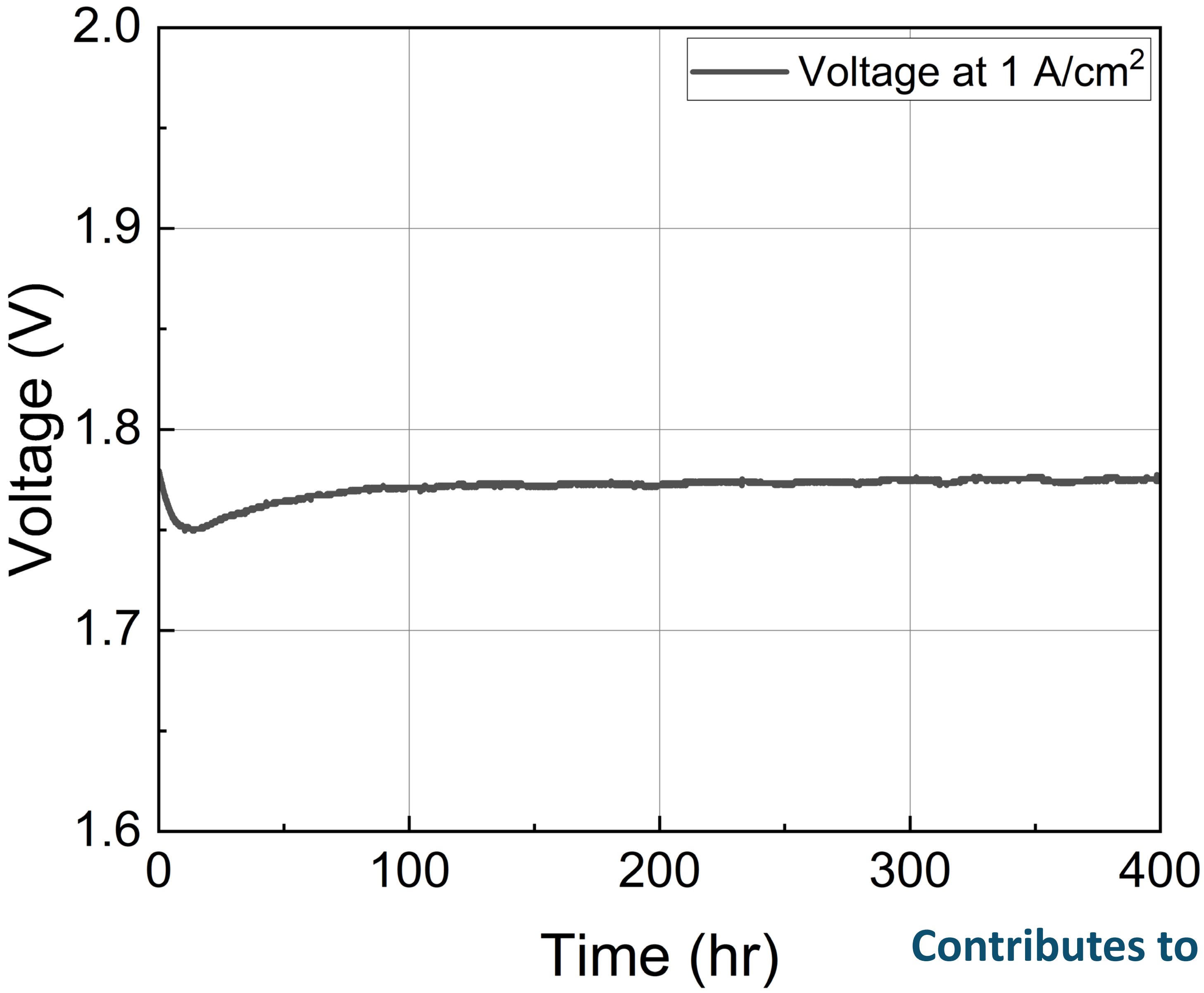


Polymers produced at 1 to 10 kg scale. 100-1,000 kg scale evaluated

Membrane post-processing is a scale issue

Contributes to Milestone 3.1: Scale-up

Accomplishment: Recent Performance Summary



Electrolysis at 1 A/cm_2 using:

- Self-adherent ionomer/NiFeOx anode
- Ni-based anode PTL
- Self-adherent ionomer/Pt_3Ni cathode
- Carbon paper cathode PTL
- 30 um thick Pention® membrane
- 0.1 M KOH water feed at anode

After break-in (130 hr to 400 hr)

Slope = **0.03 uV/hr (30 uV/1000 hr)**

Intercept = **1.772 V**

Contributes to Milestone 3.4: Durability at 1 A/cm^2

Accomplishments: Cost Analysis Comparisons

Variable	PEM Baseline	AEM (1000 mA/cm^2)	AEM (1500 mA/cm^2)
Cathode Catalyst	PGM	Low-PGM	Low-PGM
	1.0 mg/cm2	1.0 mg/cm^2	1.0 mg/cm^2
Anode Catalyst	PGM	Non-PGM	Non-PGM
	1.0 mg/cm^2	1.0 mg/cm^2	1.0 mg/cm^2
Flowfield Composition	Titanium	316L SS	316L SS
Electricity Cost ($/kWh)	$ 0.02	$ 0.02	$ 0.02
Capacity (%)	100	100	100
Current Density (mA/cm^2)	2000	1000	1500
Cell Potential (V)	1.84	1.77	1.83
Kg/Day delivered	450	450	450
Operating Temp (^{o}C)	50	50	50
Output pressure (bar)	30	30	30
$/kg Cost Percentage	**100%**	**103%**	**100%**
Efficiency (LHV)	66.8%	69.4%	67.2%

- 1500 mA/cm^2 scenario shows the gap closed with PEM.
- Cost of operation with dilute KOH water feed is insignificant compared to higher electricity cost with DI.

Contributes to Milestone 3.3: Cost Analysis

Collaborative Effectiveness: Leveraging of the EMN Nodes

Advanced Microscopy Node (Sandia National Laboratories)

- FIB/SEM and TEM studies to (i) if material in the cell is rearranging during use causing loss of electronic/ionic conduction paths, (ii) if chemical/structural reactions are occurring that cause the evolution of new and existing phases that change activity, and (iii) if the activity of the catalyst is changing and degrading performance.

Multiscale Modeling of Water Splitting Devices Node (LBNL)

- System level modeling will be performed including three-dimensional electrode structure, double layer effects (possible source of LTE instabilities w/o added salt), ohmic losses and concentration overpotential.

In Situ Testing Capabilities and Accelerated Aging (NREL)

- Small-scale cells developed within this project will lead to prototype size scale-up and durability testing at NREL.

Technology Transfer Activities

- AEM: Pending patents on polymers for membranes filed and licenses available. Currently sold as Pention®. Current scale is 1-10 kg/batch with 100 kg scale planned. Large-scale manufacturing (up to 10,000 tonnes/yr) is being evaluated.
- Pending patents on polymers for self-adhesive ionomers filed and licensing available. Ionomers are available commercially. Large-scale manufacturing is available.
- Optimized nickel-PTL is in commercial evaluation.
- Evaluation of technology for use by NEL.

Summary and Future Prospects (project has ended)

- Durability: <4 mV/1000 hr (400 uV/100 h) Demonstrated (Actual: 30 uV/1000 hr at 1.77 V for 270 hr at 1 A/cm^2)
  - Future evaluations must be done thoughtfully. Changes are small (e.g., 2 mV/1000 hr at 2 A/cm2 corresponds to 0.0001 ohm cm^2 change in area resistance per 100 h run).
  - Distinguish between degraded materials (catalyst, ionomer, PTL, AEM) and harmless conditioning of Ni, SS or other components (which have one-time resistance changes).
- Manufacturability: Many individual steps need to be taken to achieve high-volume supply chain.
  - Polymers can be produced at kg (to tonne) scale without loss of performance.
  - Self-adhesive ionomers in electrodes demonstrated.
  - Scale-up AEM R2R fabrication without post-casting treatments demonstrated.
  - Excellent PTLs can be produced.
  - Stable catalysts have been demonstrated.
  - Optimization needed many areas to squeeze out voltage and transport losses.
- Hydrogen cost target: Fighting for every mV
  - Cost advantages over PEM (Fe/Ni vs Ir, hydrocarbon vs perfluorinated, and SS/Ni vs Pt/Ti) are real.
  - Need to increase current density: 1.5 to 2.0 A/cm^2
  - Optimize OER and HER electrode fabrication and recipes for lowest overpotential.
  - Catalyst conductivity can probably be improved.
  - Adjust salt content for best performance vs degradation (long duration testing needed): little impact on cost.

Questions?

Contact us by email:

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