State-of-the-Art Performance and Durability of AEMFCs

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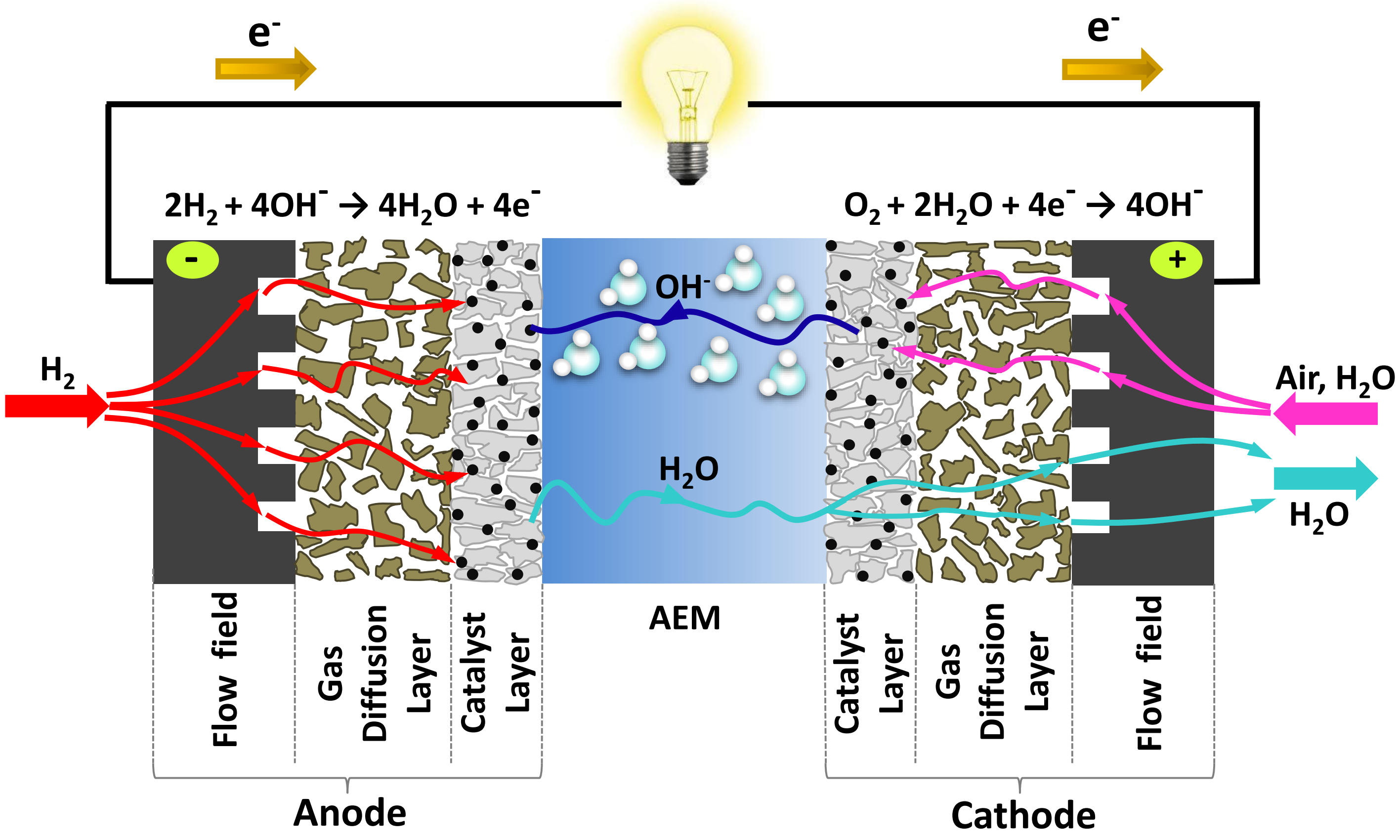
AEMFCs Operate Fundamentally Different than PEMFCs



[2]M. Gerhardt, L. Pant and A. Weber, 233rd ECS Meeting, Seattle 2018

[1]A. Roy, J. Peng and T. Zawodzinski. 233rd ECS Meeting, Seattle 2018

Figure adapted from D.Dekel. J. Power Sources, 375 (2018) 158-169.

Published in: W.E. Mustain, *Current Opinion in Electrochemistry*, **12** (2018) 233-239, DOI: 10.1016/j.coelec.2018.11.010

- Reaction: 6 H_2O Molecule Swing Between the Anode and Cathode
  - Water gradient
  - Electro-osmotic drag
    - 2-8 H_2O molecules per OH- [1]
  - Gas phase H_2O cannot support ORR [2]
- Backdiffusion is Critical
  - Low H_2O flux membranes = low performance
    - In general not reported by membrane makers
    - Helpful to develop H_2O transport metric/target
- Convective Water Removal
  - Where to remove water from?
  - Backpressure vs. no backpressure
    - Total volume of water and rate - increasing backpressure reduces evaporation
  - High vs. low flowrates
    - Flowfield and CL design

4 Pillars for High Performing AEMFCs

1. Anion Exchange Membrane
   - Excellent Alkaline Stability
   - High Conductivity
   - High Water Uptake and Mobility

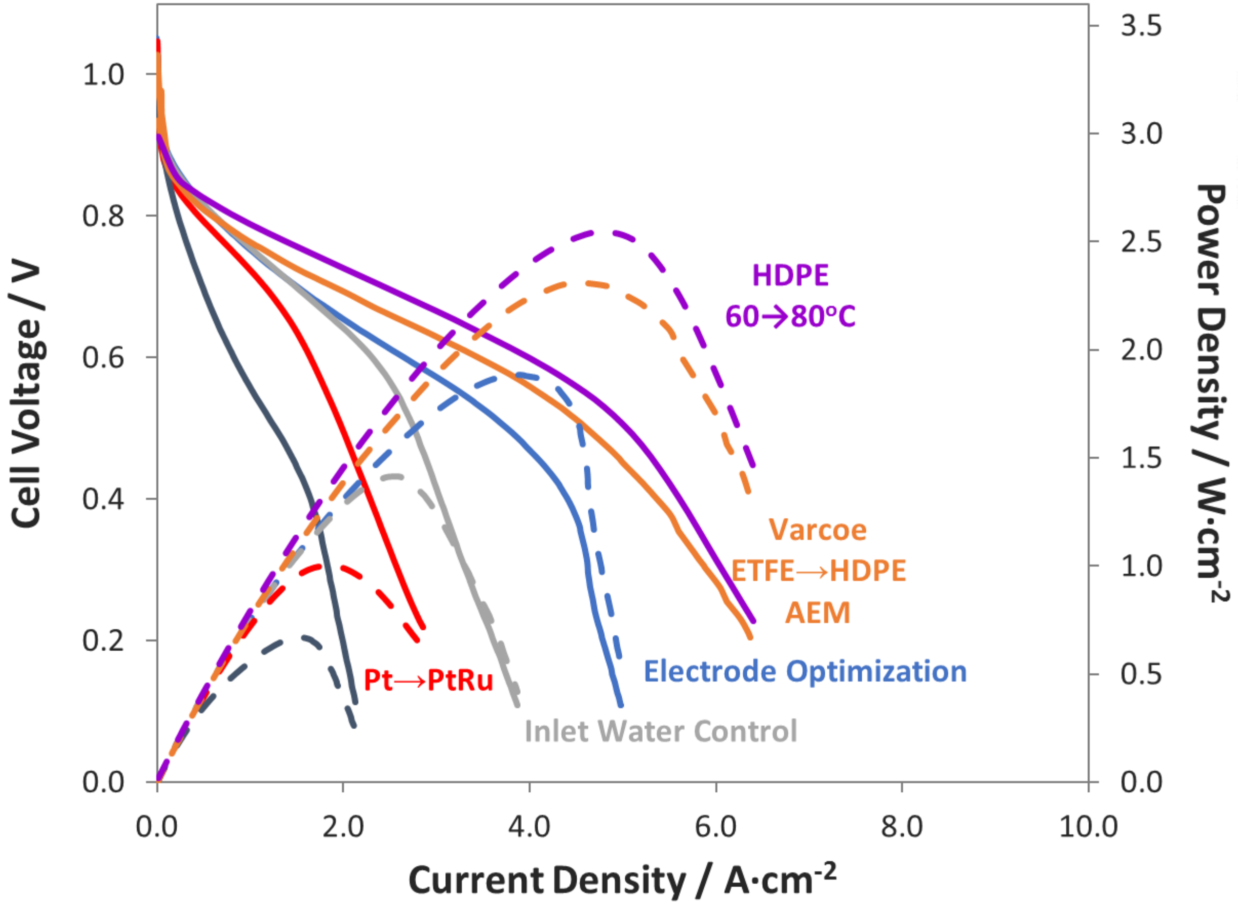
2. Control over the content and balance of water
   - Membrane with rapid H_2O transport
   - Optimized operation parameters
     - Flowrates, backpressure, gas dew points
   - Control over electrode composition and structure

3. Electrodes
   - PtRu/C and Pt/C have sufficient activity
     - Can we reduce loading and cost? PGM-free?
   - Ionomer (typically linked to AEMs)
     - Success with powder and solubilized forms
     - High ionic conductivity
     - Chemically robust at high and low λ
     - Low adsorption onto catalyst surface
   - Electrode Development – Integration and Optimization

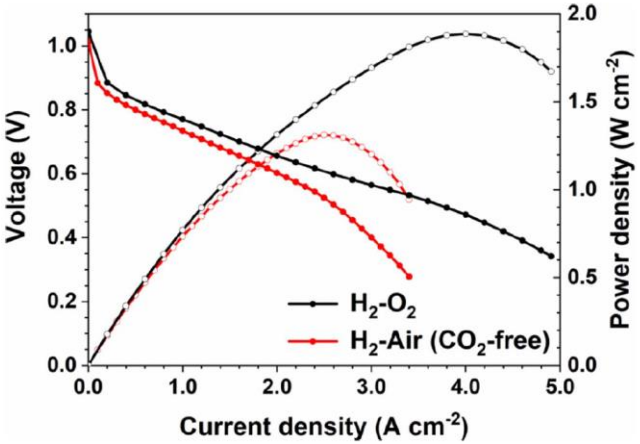
4. Minimizing exposure to CO_2 and managing negative effects

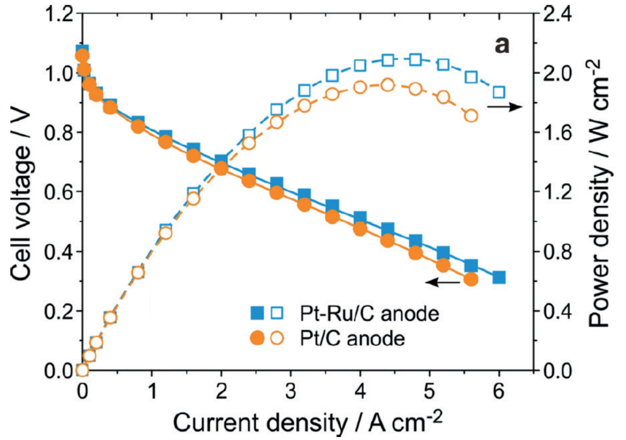
Systematic Improvement in the Achievable Peak Power Density and Current Density in AEMFCs

High Stoich H_2/O_2 (CO_2-free), no backpressure

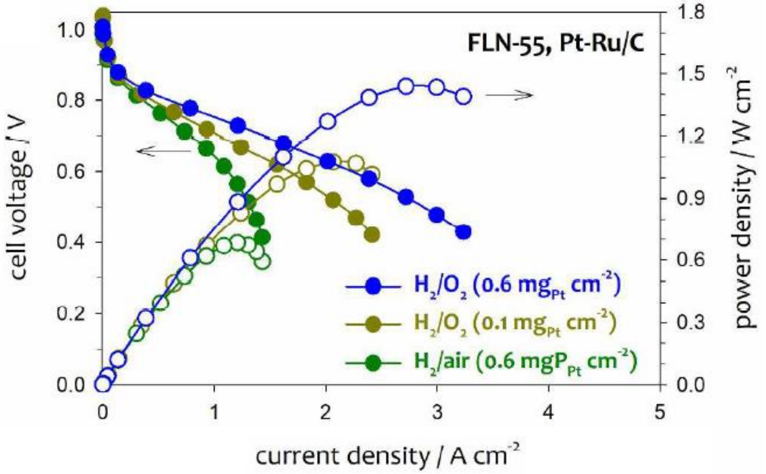


Q. Li, L. Zhuang et al., *Angew. Chemie Int. Ed.*, **131** (2018) 1456-1450





T. Wang, Y. Yan et al., *J. Electrochem. Soc*, **166** (2019) F3305-3310



S. Maurya, YS Kim et al., *Energy. Environ. Sci*, **11** (2018) 3283-3291

Y. Wang, L. Zhuang, et al, *Energy Environ. Sci*, **8** (2015), 177-181

T.J. Omasta, J. Varcoe, B. Pivovar, W.E. Mustain et al, *Energy Environ. Sci*, **11** (2018), 551-558

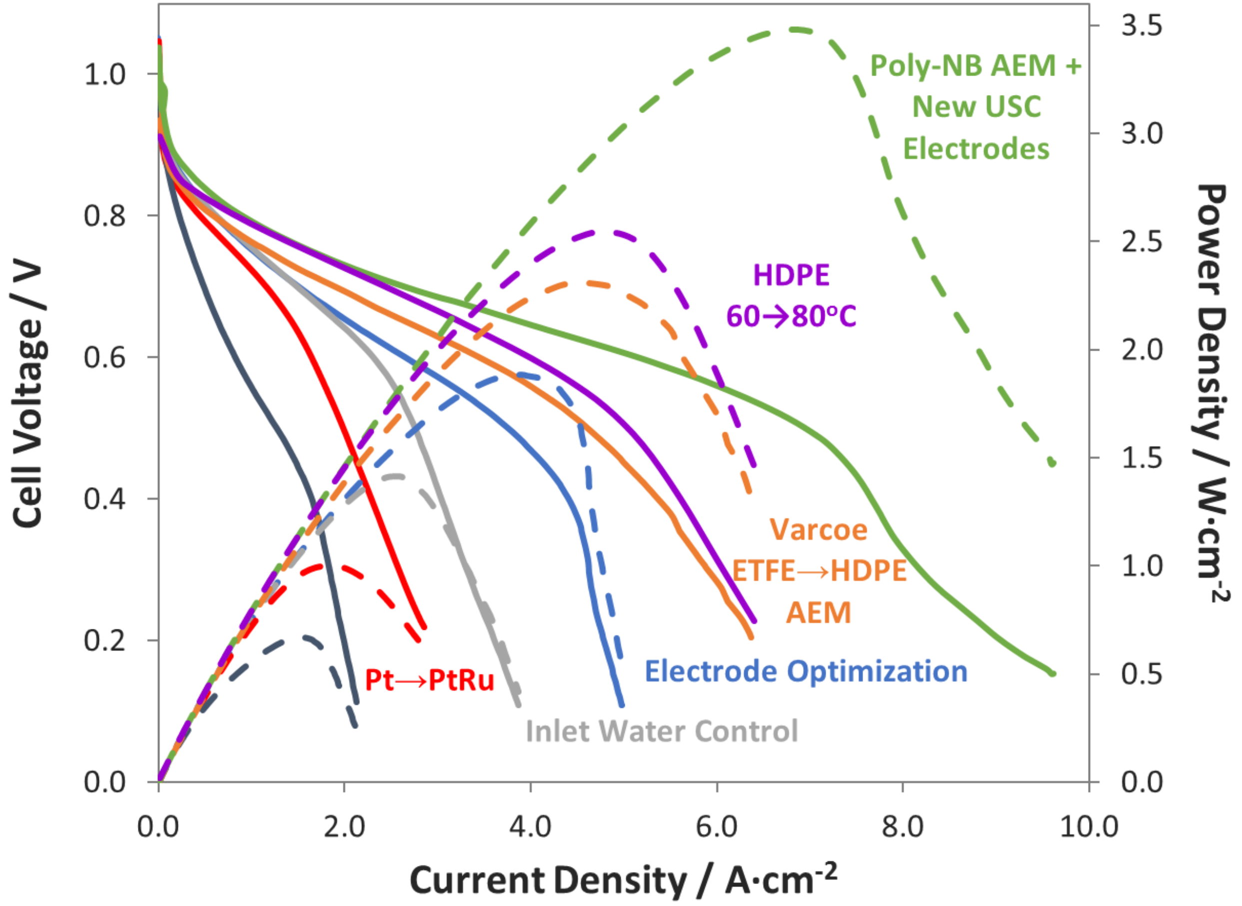
G. Huang, B. Pivovar, W.E. Mustain and P.A. Kohl et al. *J. Electrochem. Soc.* Accepted.

T.J. Omasta, J. Varcoe, W.E. Mustain *et al.*, *J. Power Sources*, **375** (2018) 205

L. Wang, X. Peng, W.E. Mustain, J.R. Varcoe, *Energy Environ. Sci.*, 12 (2019) 1575-1579

Systematic Improvement in the Achievable Peak Power Density and Current Density in AEMFCs

High Stoich H_2/O_2 (CO_2-free), no backpressure



- Very good performance has been achieved with multiple ionomer/catalyst approaches
  - We now know it is possible to achieve very high power in AEMFCs
  - How to do it with each AEM/ionomer system is NOT the same
    - e.g. some want high flowrate and low P, some what low flowrate and high P, etc
    - Can be different even w/same AEM new ionomer
    - Have spent a lot of $$ on AEMs, almost zero on electrode and catalyst layer design/integration
  - We will need to remember this when developing performance metrics

Y. Wang, L. Zhuang, et al, *Energy Environ. Sci*, **8** (2015), 177-181

T.J. Omasta, J. Varcoe, B. Pivovar, W.E. Mustain et al, *Energy Environ. Sci*, **11** (2018), 551-558

G. Huang, B. Pivovar, W.E. Mustain and P.A. Kohl et al. *J. Electrochem. Soc.* Accepted.

T.J. Omasta, J. Varcoe, W.E. Mustain *et al.*, *J. Power Sources*, **375** (2018) 205

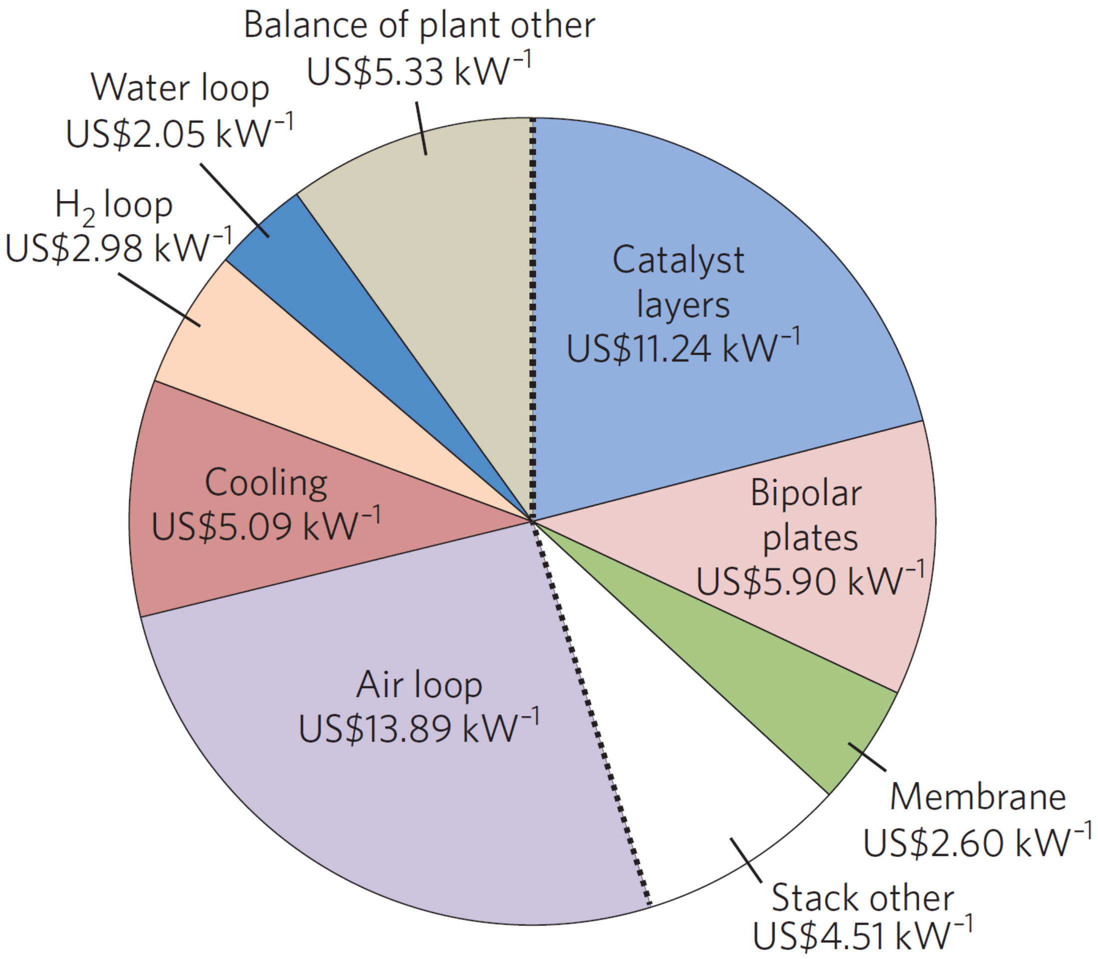
L. Wang, X. Peng, W.E. Mustain, J.R. Varcoe, *Energy Environ. Sci.*, 12 (2019) 1575-1579

The Arms Race is Over

- There is no point in showing that 3.4 W/cm^2 can be exceeded operating on UHP H_2/O_2
- It is now time to focus on more practical issues
  - Realistic Stoichs (e.g. < 3 at the cathode)
  - PGM-free catalysts (ORR and HOR)
  - Air-operation
    - Transport – performance loss when switching from 100% →20 % O_2
    - Negative effects of CO_2
  - Performance Stability (not just materials)
- We also need to develop metrics and protocols that are AEMFC specific and platform (AEM/ionomer) flexible – though application relevant

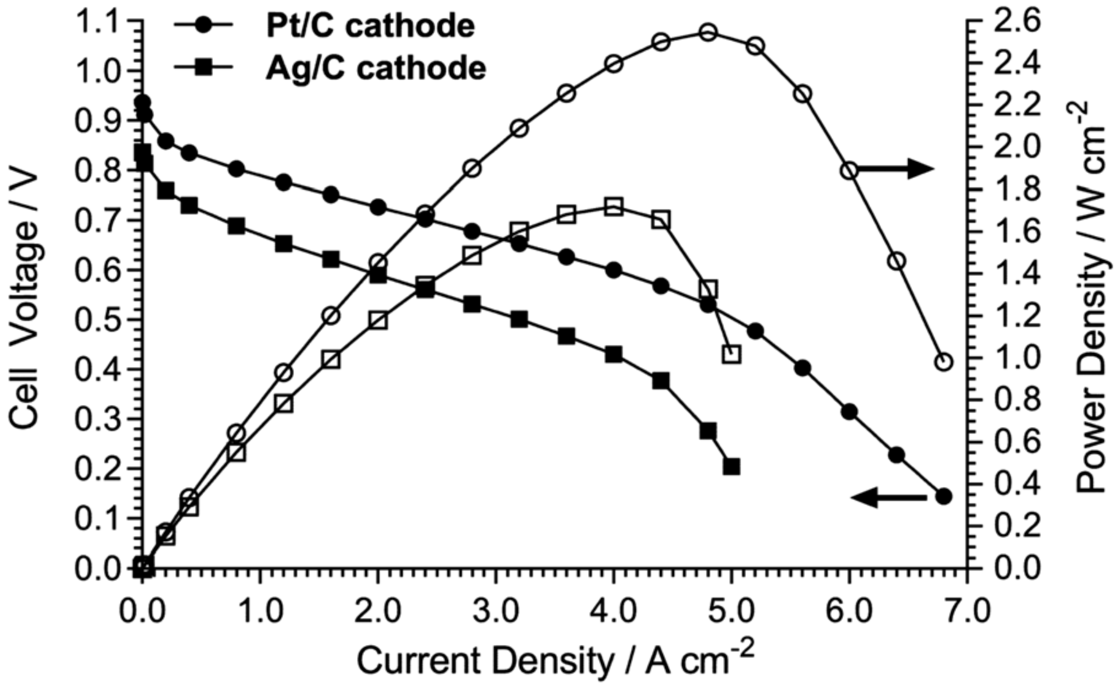
PGM-Catalysts for AEMFCs

- One of the main driving forces for the study of AEMFCs
  - In the long run, we most likely need to do better than PEMFCs
    - $< 0.125\ mg_{PGM}/cm^2$
- Much more success demonstrating PGM-free catalyst for ORR than HOR
  - Ionomer interactions
  - Stability issues
  - Etc.

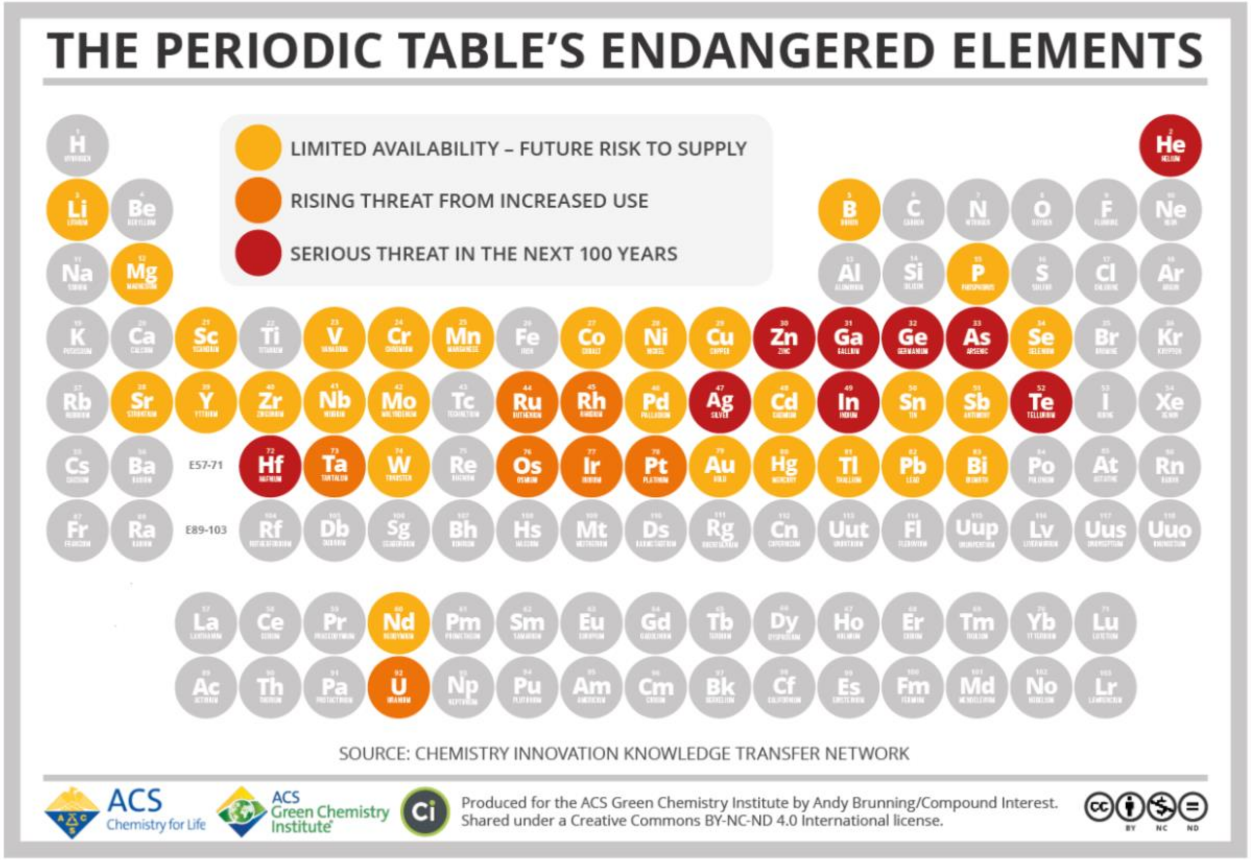


- Setzler, Yan, *et al.*, *Nat. Nanotechnol.*, **11** (2016) 1020

Ag as a PGM-free AEMFC Cathode



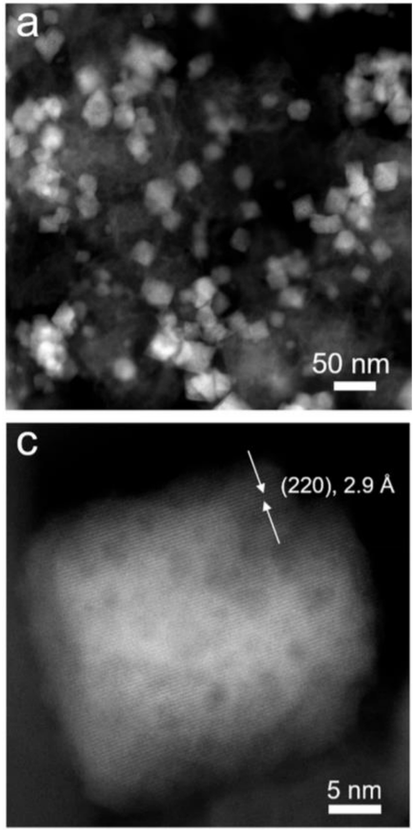
L. Wang, X. Peng, W.E. Mustain, J.R. Varcoe, *Energy Environ. Sci.*, 12 (2019) 1575-1579

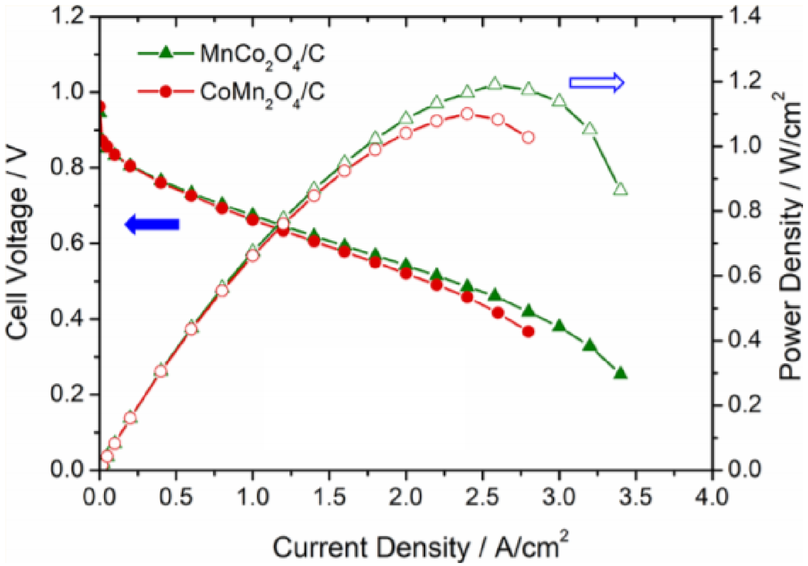


- Ag is a more endangered element than Pt and may not be the long-term PGM-free solution

Select Non-PGM ORR Catalysts in AEMFCs

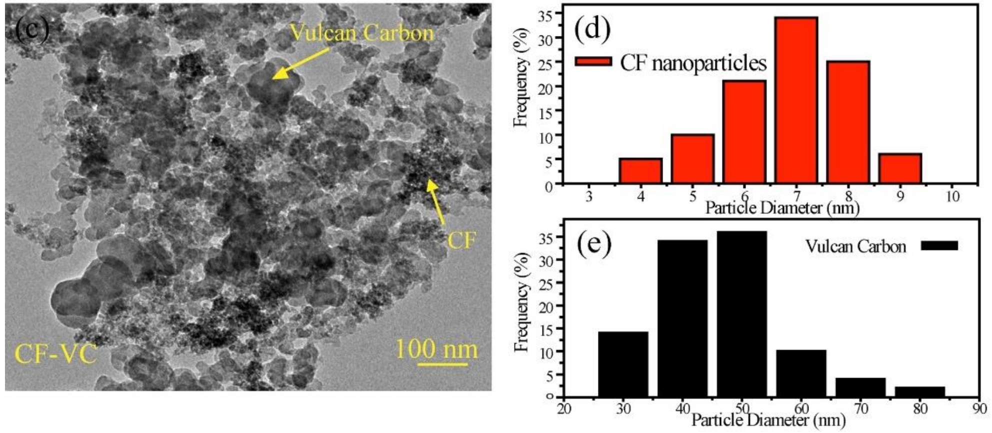
Mn-Co Spinel/HSC KB

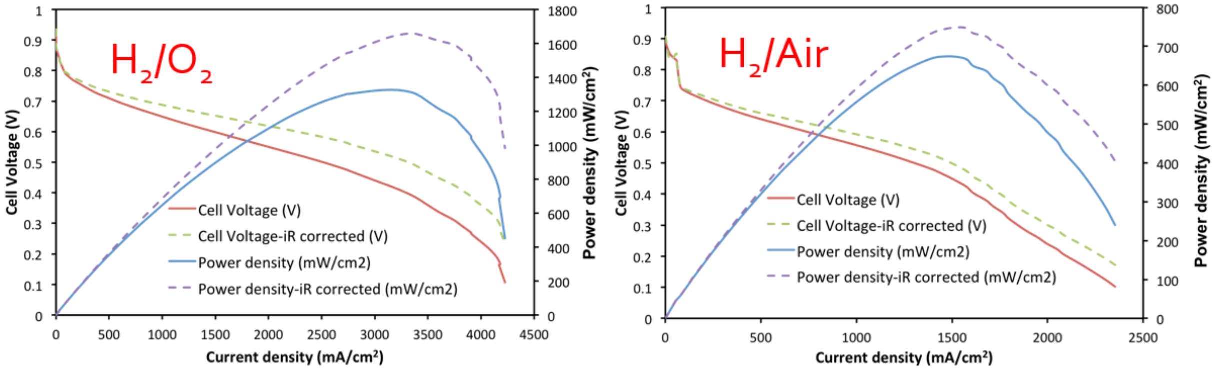




- Y. Yan, L. Zhuang, H.D. Abruna *et al.*, *ACS Energy Lett. 4 (2019) 1251-1257.*
- *Y. Wang, H. Abruna, L. Zhuang, et al., Nat. Commun., 10 (2019) 1506*

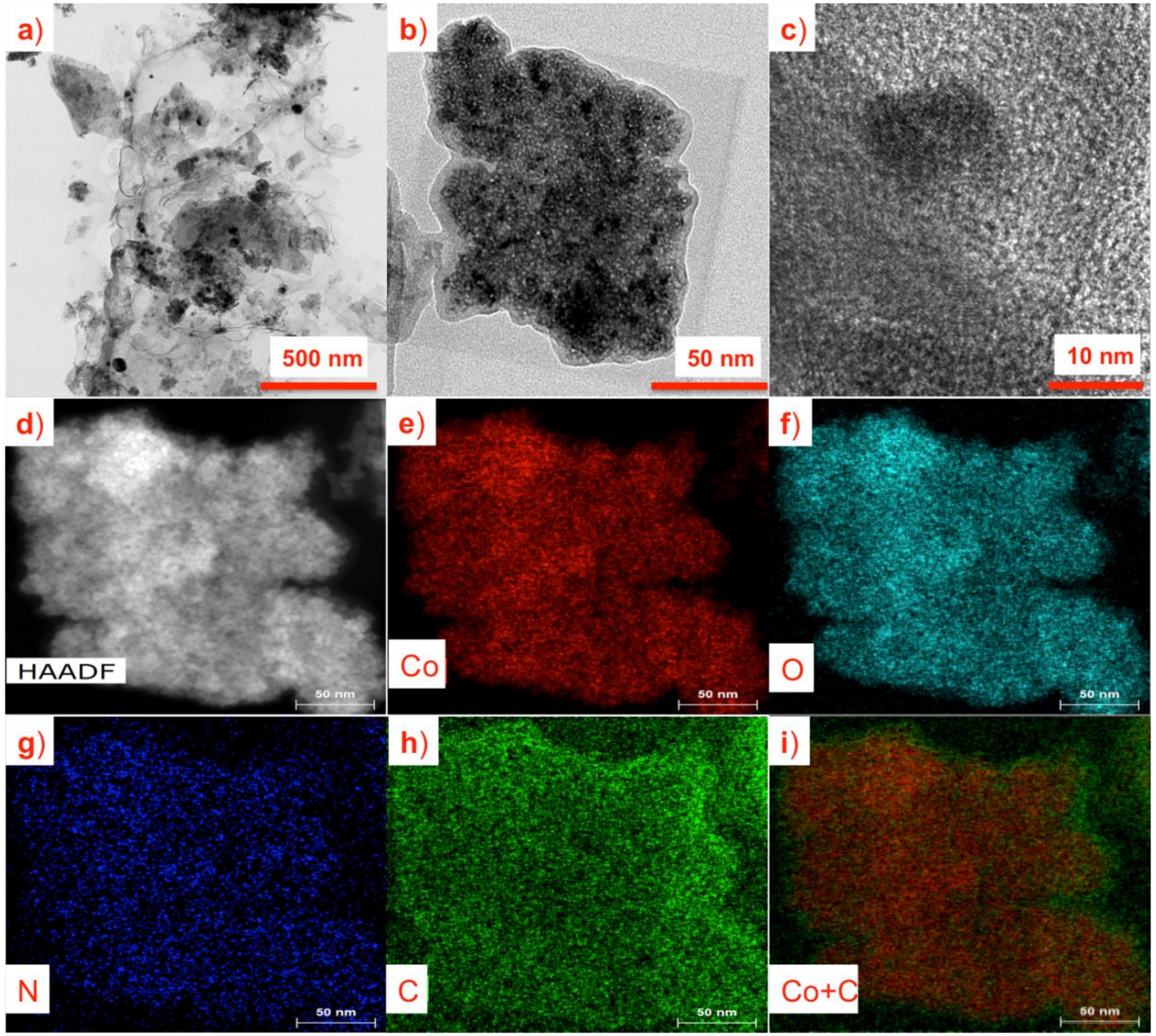
$CoFe_2O_4$/Vulcan



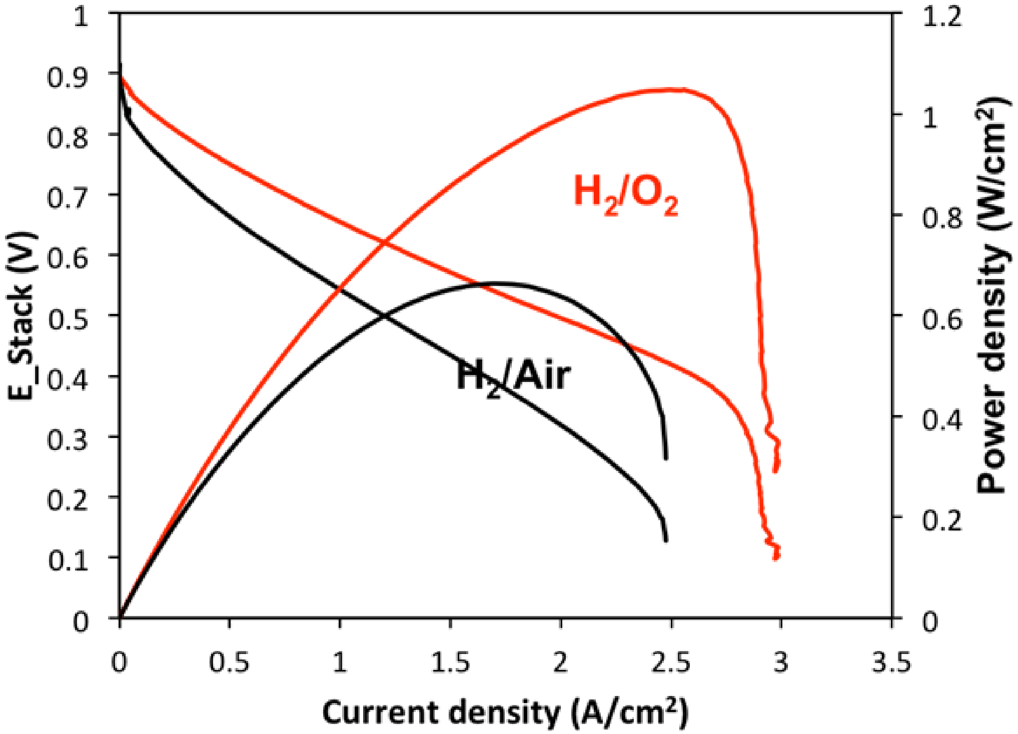


- X.Peng, W.E. Mustain et al.,, Catalysts, 9 (2019) 264.

Non-Precious Metal N-C-CoO_x Electrocatalyst for the ORR in AEMFCs

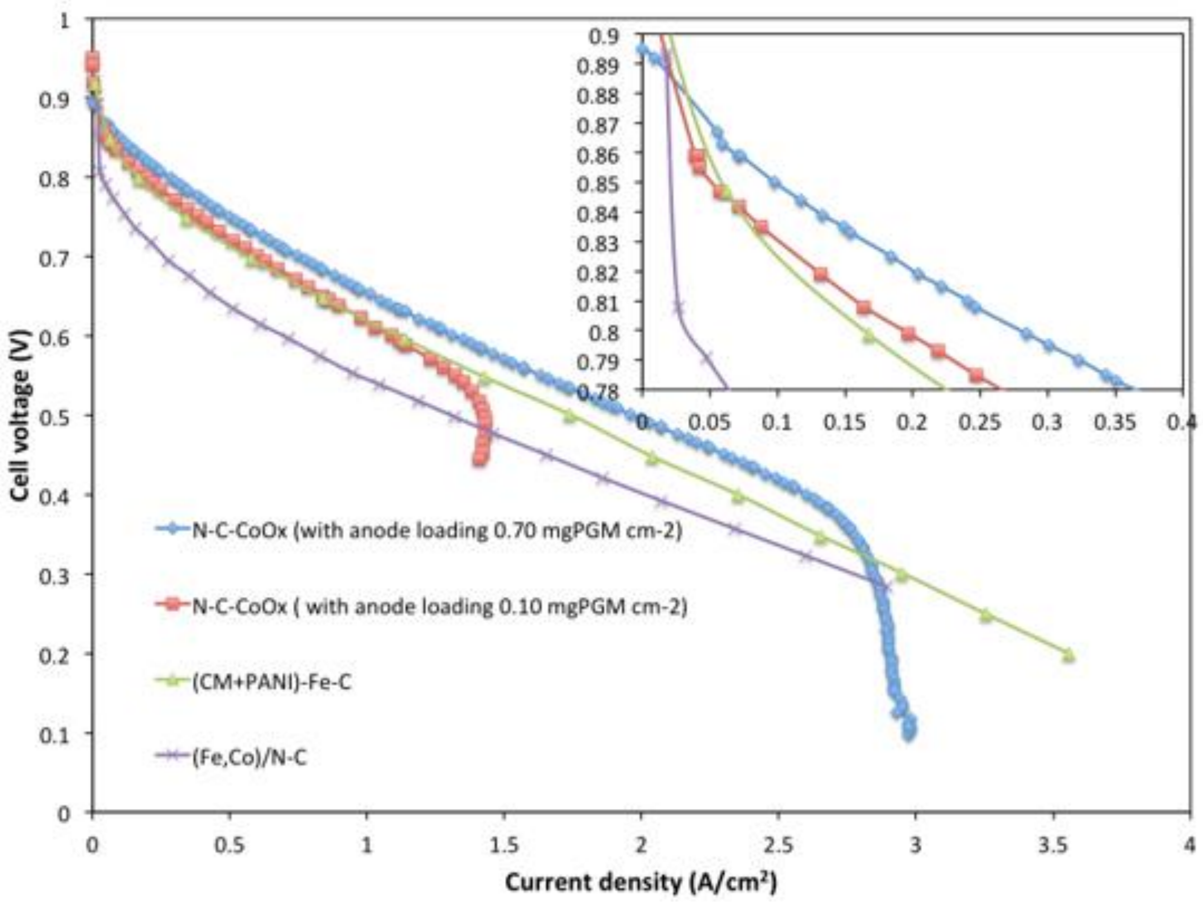


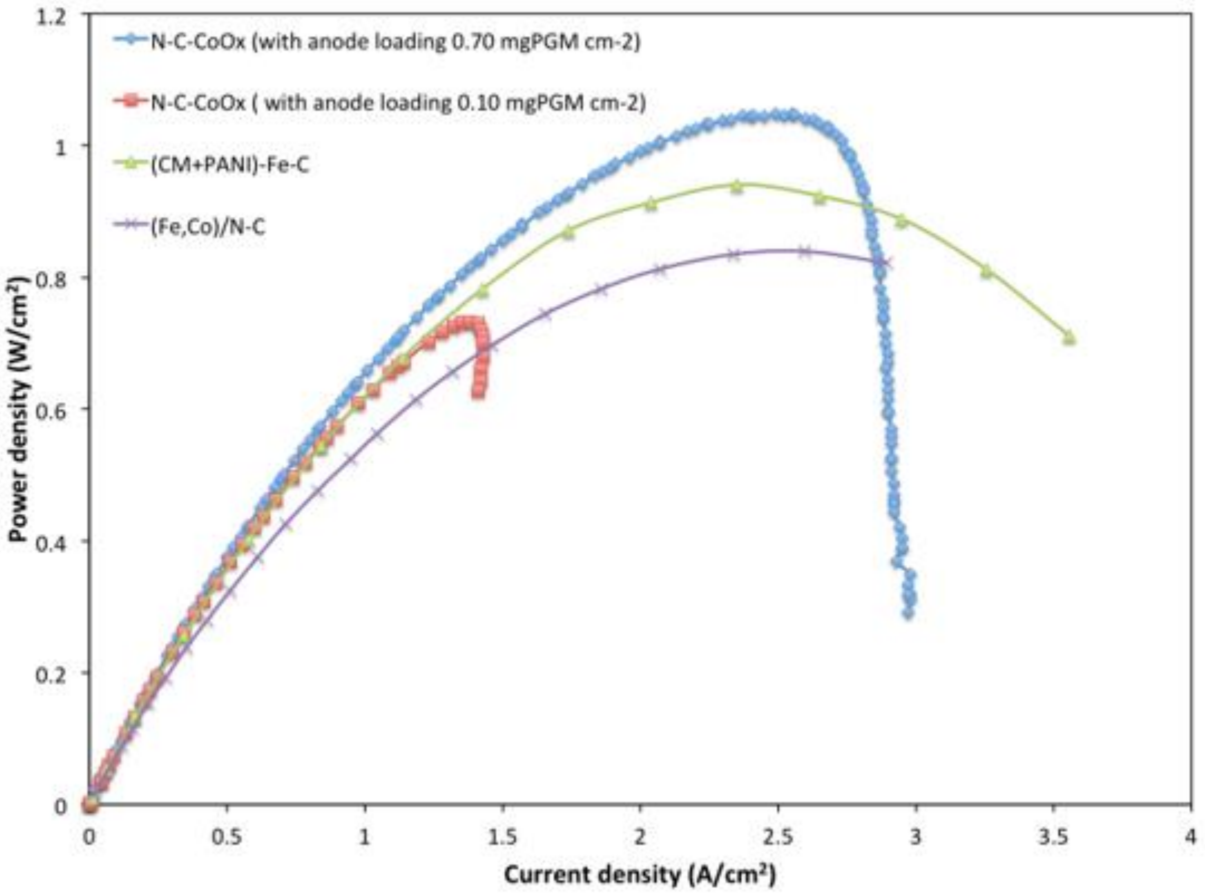
- 2-D planar structure
- CoO_x particles embedded in N-C



Xiong Peng, T J. Omasta, Emanuele Magliocca, Lianqin Wang, John R. Varcoe and W.E. Mustain. *Angew. Chem. Int. Ed*. **58** (2019) 1046-1051.

Comparing AEMFC and PEMFC Performance and Durability with PGM-free Cathodes





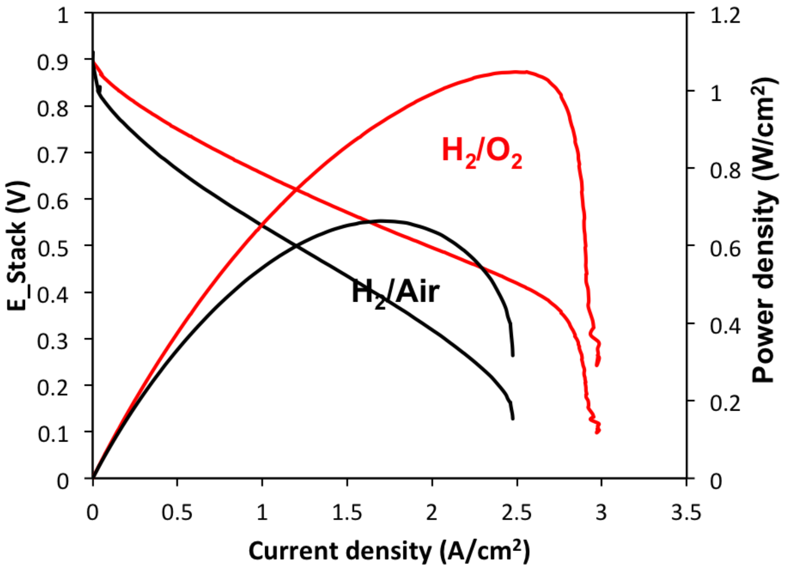
AEMFC (blue/red): Xiong Peng, W.E. Mustain, et al. *Angew. Chem. Int. Ed*. **58** (2019) 1046-1051.
PEMFC (green): H. T. Chung, P. Zelenay, et. Al. *Science* **357** (2017) 479–484
PEMFC (purple): J. Wang, S. Wei, et al., *J. Am. Chem. Soc.* **139** (2017) 17281–17284.

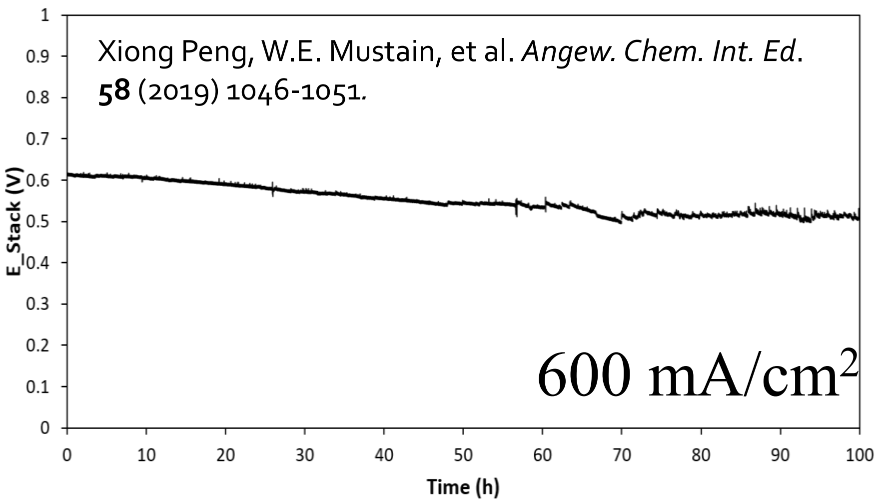
- H_2/O_2
- AEMFC@60^{o}C; PEMFCs@80^{o}C

Comparing AEMFC and PEMFC Performance and Durability with PGM-free Cathodes

AEMFC

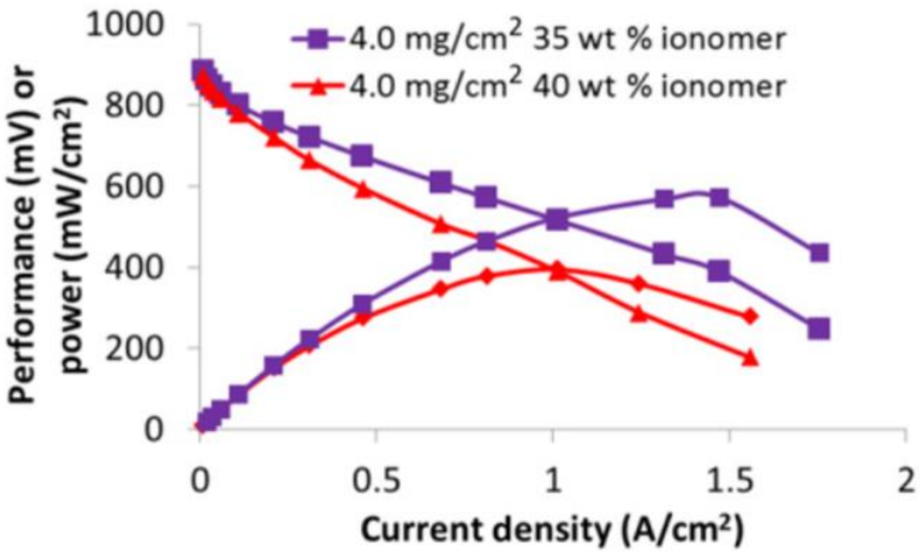
- H_2/air
- 60°C
- 2.4 mg/cm^2



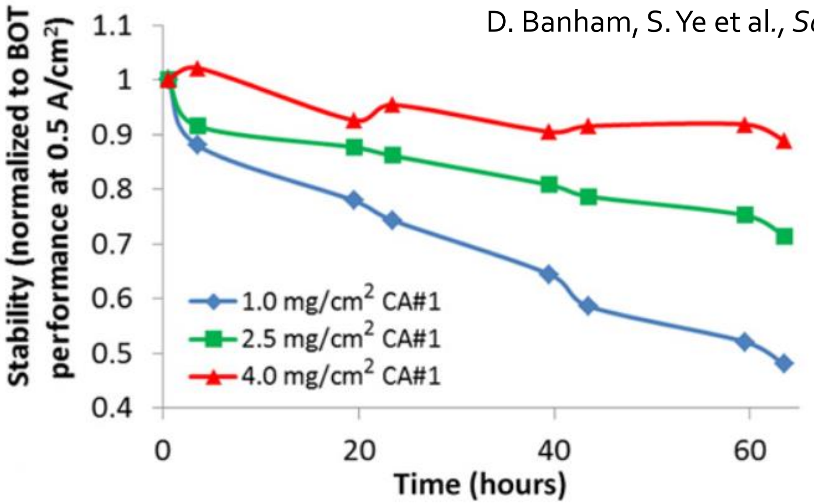


PEMFC

- H_2/air
- 75°C



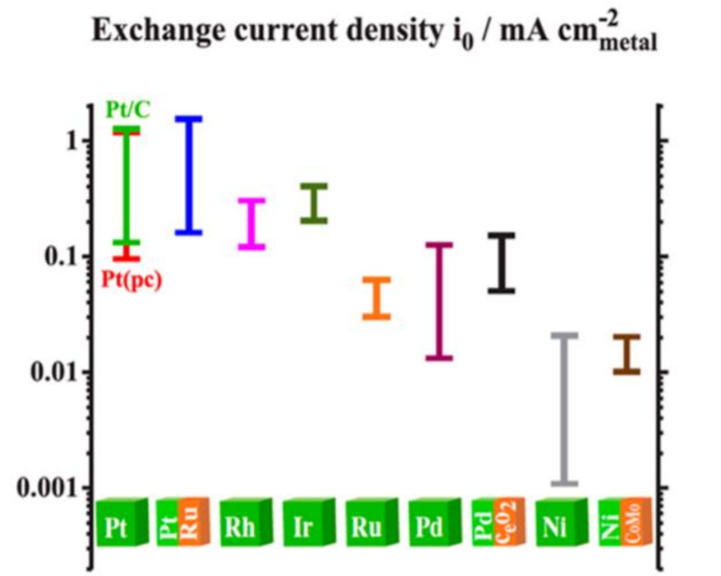
D. Banham, S. Ye et al., *Science Advances*, 4 (2018) 7180



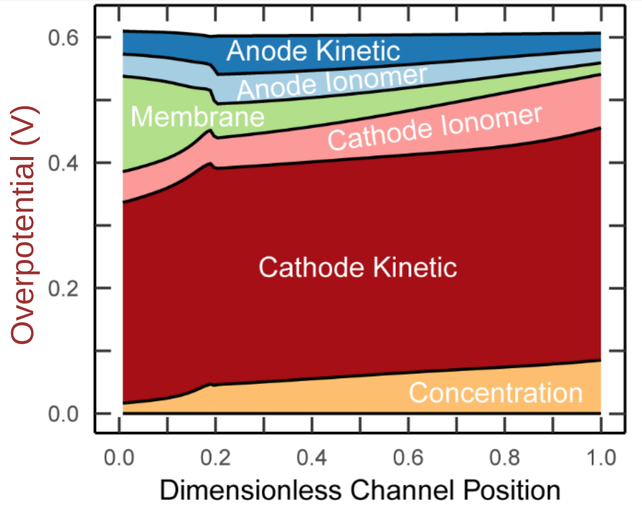
ORR Electrodes

- Good News: PGM free cathodes in AEMFCs are already competitive with PEMFCs
  - Reasonable peak power with both oxygen (~1.2 W/cm^2) and air (~0.7 W/cm^2)
- Electrode integration is incredibly important for these catalysts
  - We need PGM-free specific approaches and designs
  - Even the highest peak power in the literature (1.4 W/cm^2) was achieved with a catalysts that had MUCH lower intrinsic acitivity than SOA

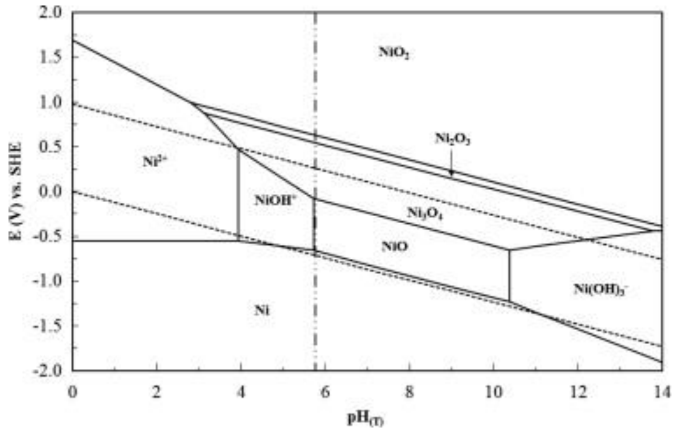
Hydrogen Oxidation Reaction

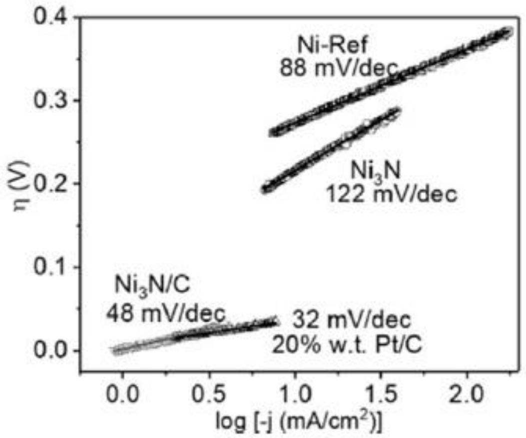


E.S. Davydova, S. Mukerjee, F. Jaouen and D.R. Dekel, *ACS Catalysis*, **8** (2018) 6665-6690



M.R. Gerhardt, L.M. Pant and A.Z. Weber, *J. Electrochem. Soc.*, **166** (2019) F3180-F3192

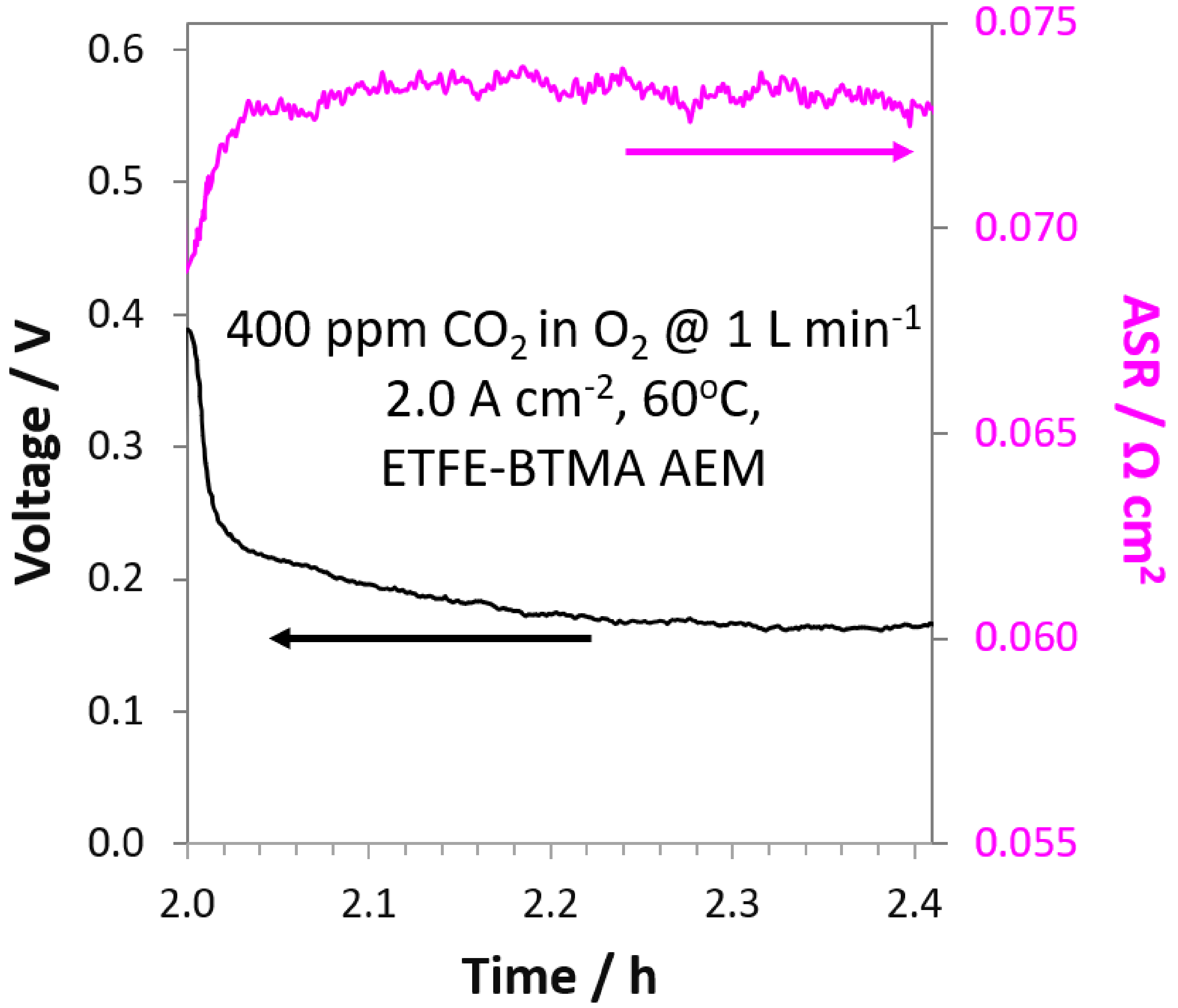




W. Ni, X. Hu et al., *Angew. Chemie Int. Ed.*, **58** (2019) DOI: 10.1002/anie.201902751

- HOR exchange current density is still several orders of magnitude higher than ORR
  - Importance of the HOR overpotential is very overstated
  - Though still higher than PEMFC
- Suggests that non PGM options might be usable
- There are no practical Pt-free catalysts for alkaline HOR today
  - All known chemistries are either inactive or oxidize in MEAs
    - e.g. NiFe, NiMo, etc.

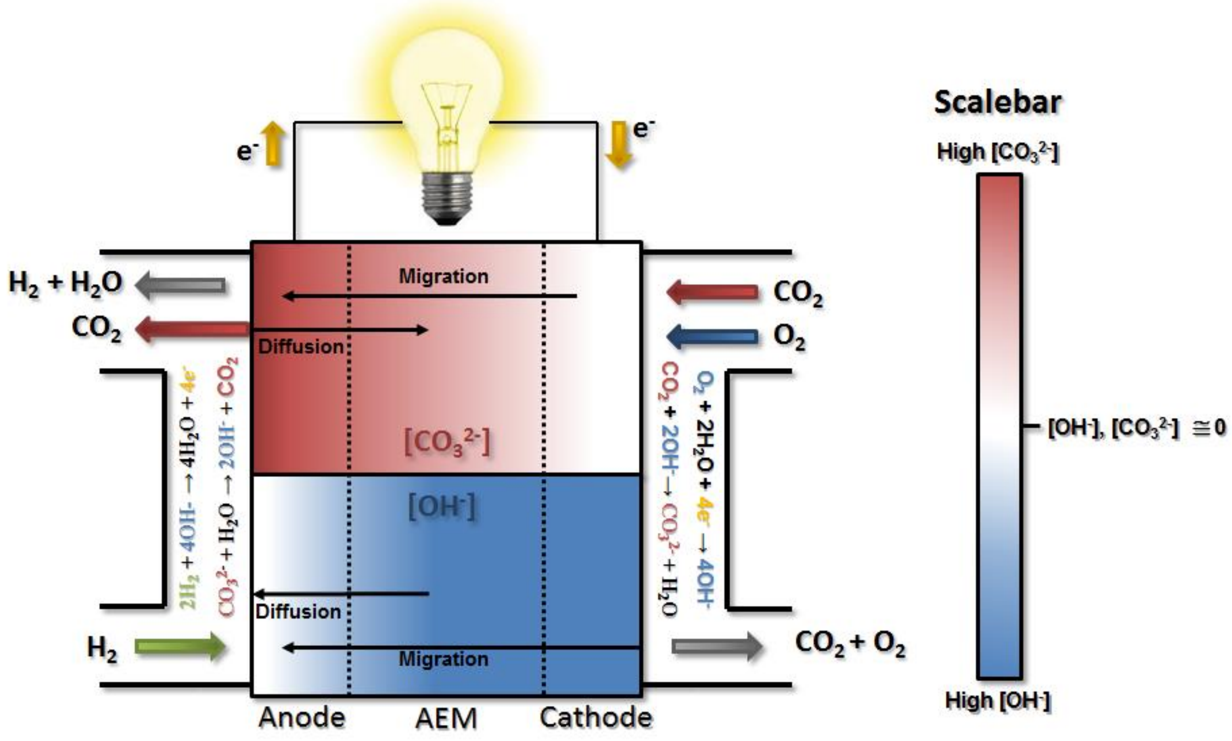
Reality: AEMFC CO_2/Carbonation has Significant Negative Effects on Performance



Y. Zheng, J.R. Varcoe, B. Pivovar and W.E. Mustain et al., *Submitted for Review*.

- Even at high current density, the total voltage loss from feeding CO_2 is ~200 mV
- 2 <u>Very</u> Common Misconceptions
  - The cell can sufficiently "self-purge" carbonate at high current densities
  - The primary mechanism for performance loss is reduced conductivity
    - Here ΔR_Ω is ~ 8 mOhm; $\Delta V = i^*\Delta R_\Omega = 16$ mV
- There are other mechanisms in play that need to be discussed

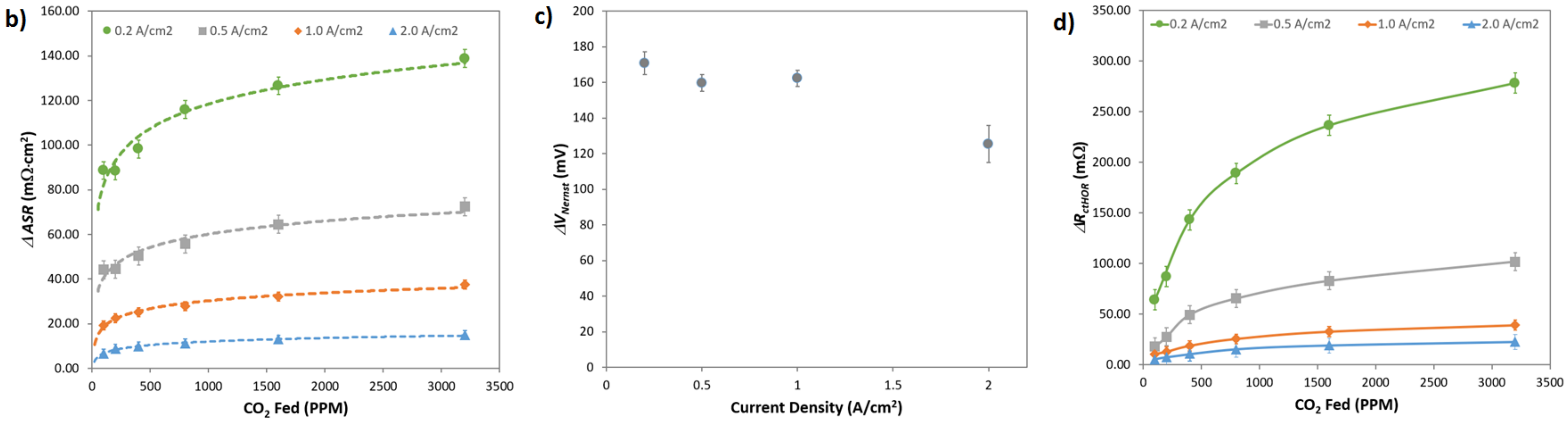
3 Mechanisms for Carbonate-Related Voltage Loss in AEMCs



- Carbonate moves by migration from cathode → anode (some back diffusion)
  - Mechanism 1: conductivity drops, ASR increases (ΔASR)
- Under normal operating voltages, CO_3^{2-} does not directly react with H_2 and Carbonate accumulates in the anode
  - Mechanism 2: Anode pH increases, ΔV_{nernst}
  - Mechanism 3: Low a_{OH-} and $t_{OH-} < 1$
    - Effectively "shuts off" parts of the anode, increasing the effective current density and increasing R_{ctHOR}

Y. Zheng, J.R. Varcoe, B. Pivovar and W.E. Mustain et al., *Submitted for Review*.

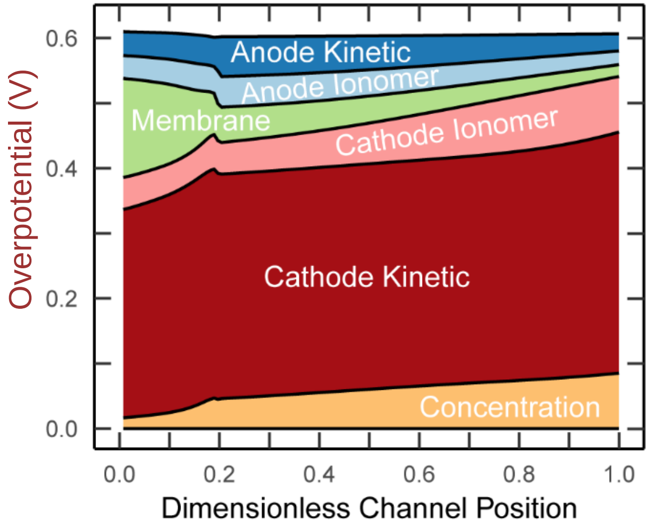
Quantified Contributions to CO_2-Related Voltage Loss in AEMFCs, 60°C

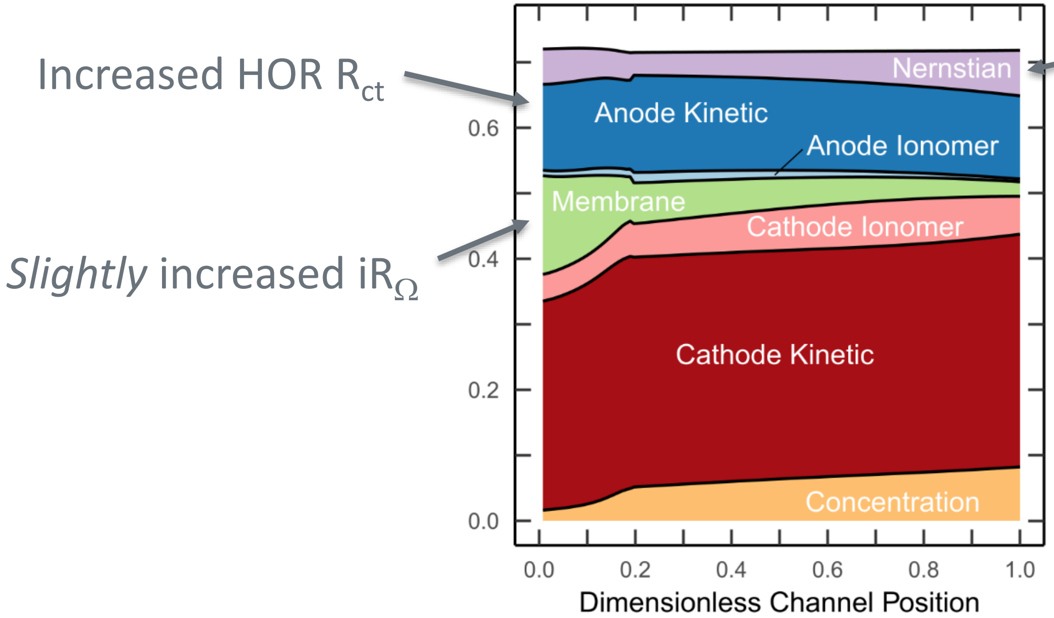


- Resistances follow a rational trend – with decreasing CO_2 concentration and increasing current density preferred
- CO_2-related overpotential is dominated by the Nernstian and kinetic contributors

Previous Work Extensively Investigating These Mechanisms Have Mostly Been Computational

- U. Krewer, D. Dekel et al., Electrochim. Acta, 263 (2018) 433-446.
- M.R. Gerhardt, L.M. Pant and A.Z. Weber, J. Electrochem. Soc, 166 (2019) F3180-F3192



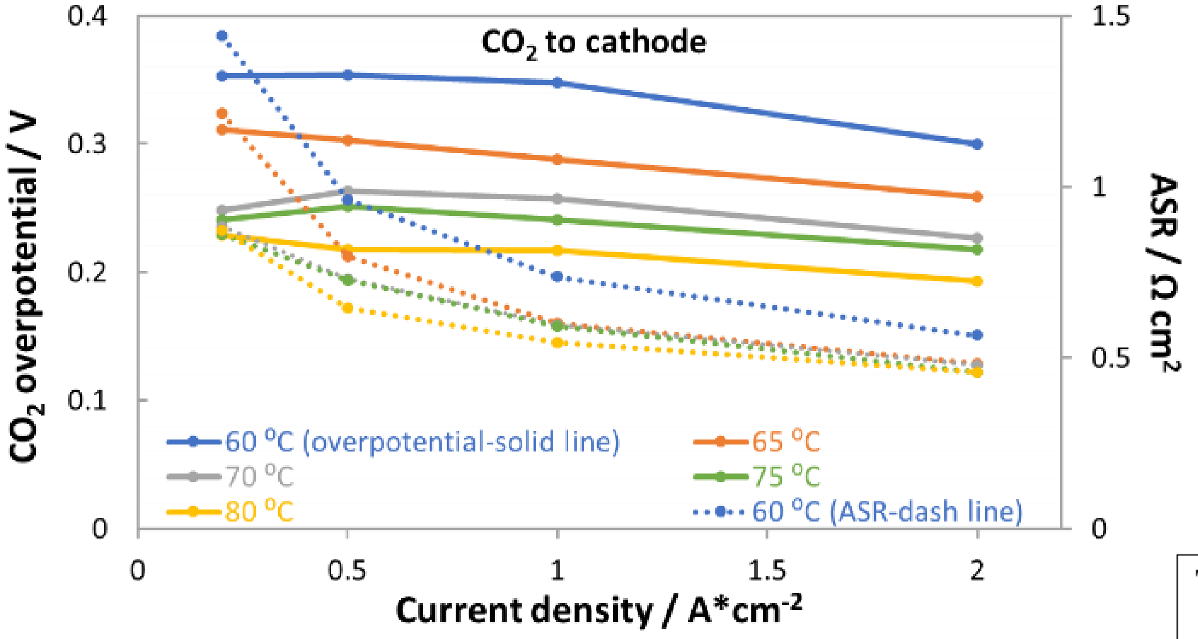


Models run with at 60 °C with H_2 and air (w/ and w/o 400 ppm CO_2 at 50% RH and 0.72 A/cm^2, 1.2x stoich flow

- Unfortunately, these models have not yet been validated with high fidelity experimental data – but we have reach out to A. Weber to do just that.

Increasing the Temperature Can Help to Reduce CO_2-Related Voltage Losses in AEMFCs

LDPE-BTMA AEM



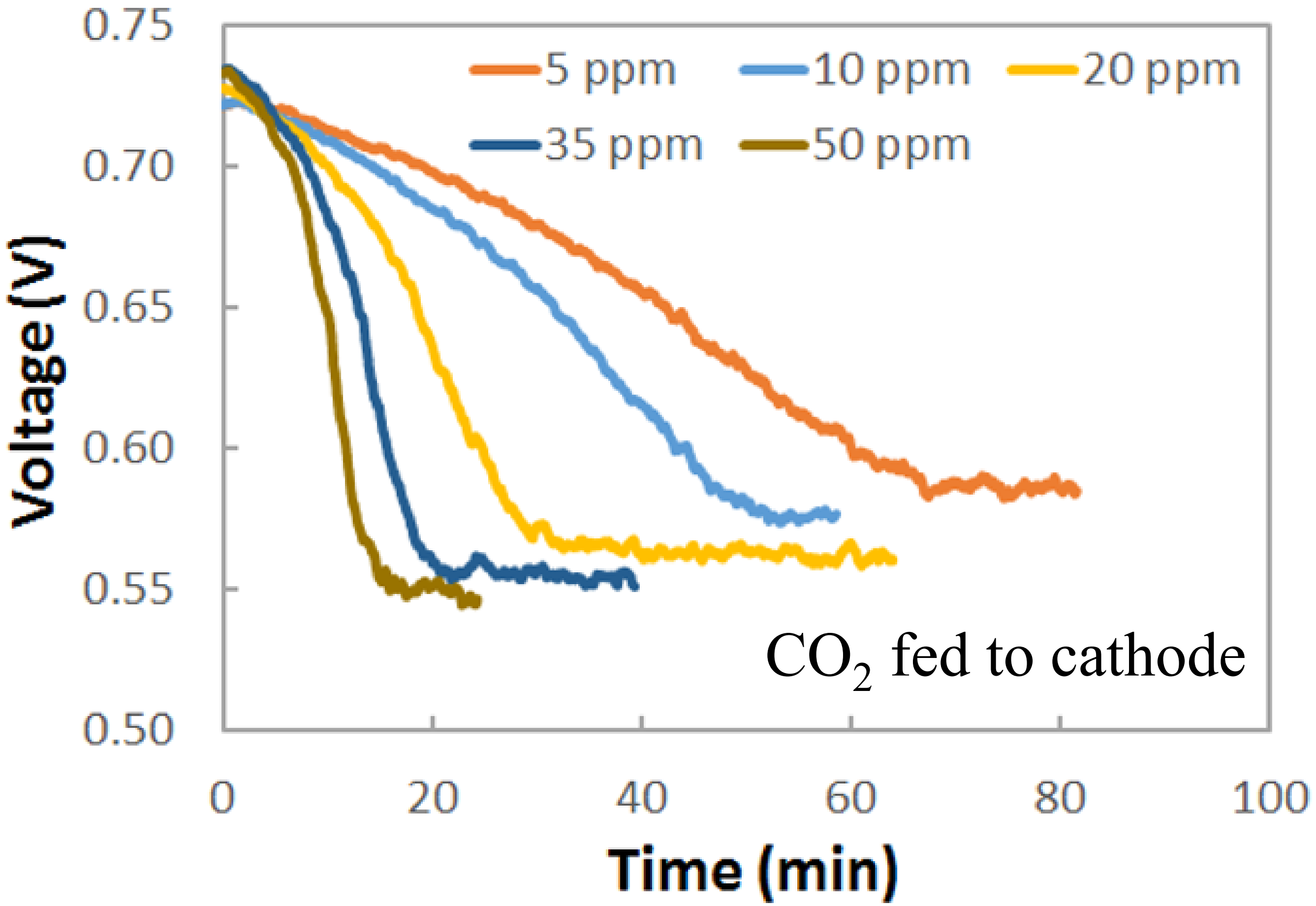
Temperature (℃)	60	65	70	75	80
Carbonate in AEMFC (μmol)	17.9	12.4	12.4	11.5	11.4
Degree of Carbonation (%)	34.0	23.7	23.6	21.9	21.6

- Increasing temperature decreases the amount of carbonate in the system
- Reduces both the ASR and ΔV_{Nernst}

Temperature (°C)	ΔASR (mΩ cm²)	ΔV_{Ohmic} (mV)	ΔV_{Nernst} (mV)	R_{ctHOR} (Ω)	V_{ctHOR} (mV)
60	22.6	22.6	226	17.0	84.8
65	17.6	17.6	177	18.0	90.2
70	16.9	16.9	150	18.2	91.1
75	18.2	18.2	134	17.7	88.5
80	15.9	15.9	113	17.2	85.9

Lower Threshold?

1.0 A cm^{-2}; 60 °C; ETFE-BTMA AEM

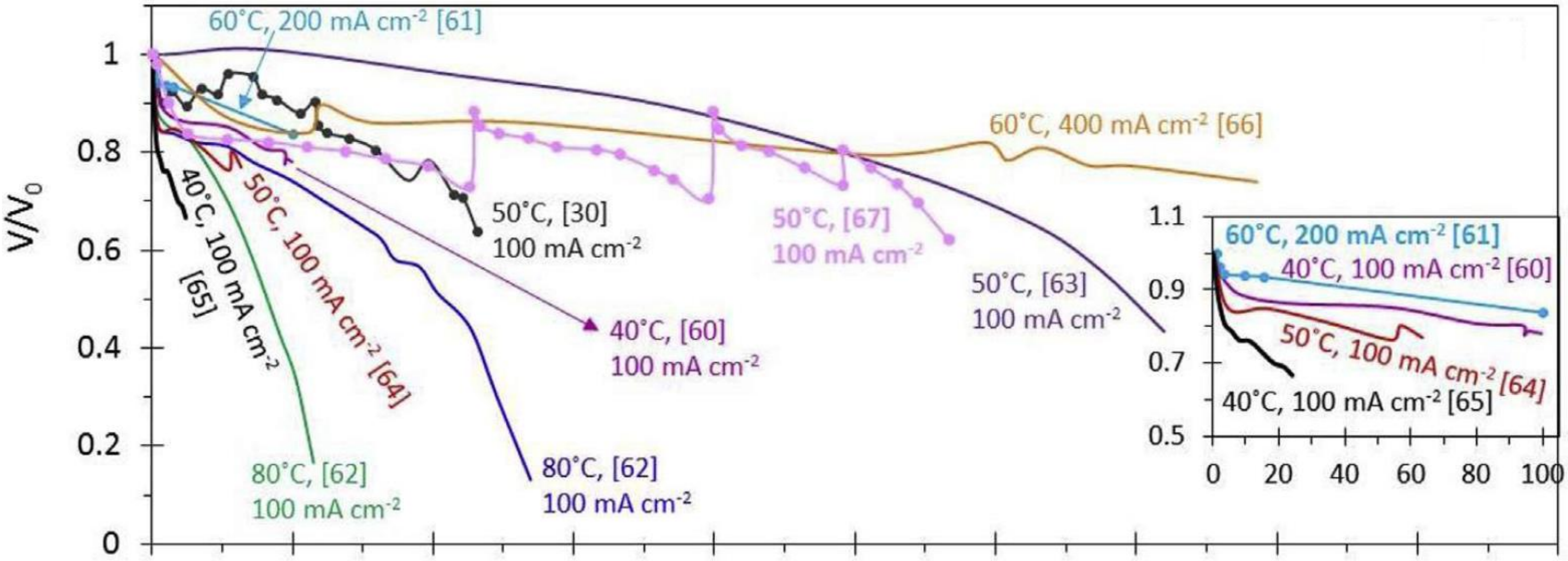


- At 2.0 A/cm², 80°C, and 10 ppm cathode CO_2, the CO_2-related voltage loss was reduced to 90 mV
- Anecdotal evidence that this may not be the case for all systems
- The AEM an ionomer BOTH have an impact on carbonate content and CO_2 overpotential

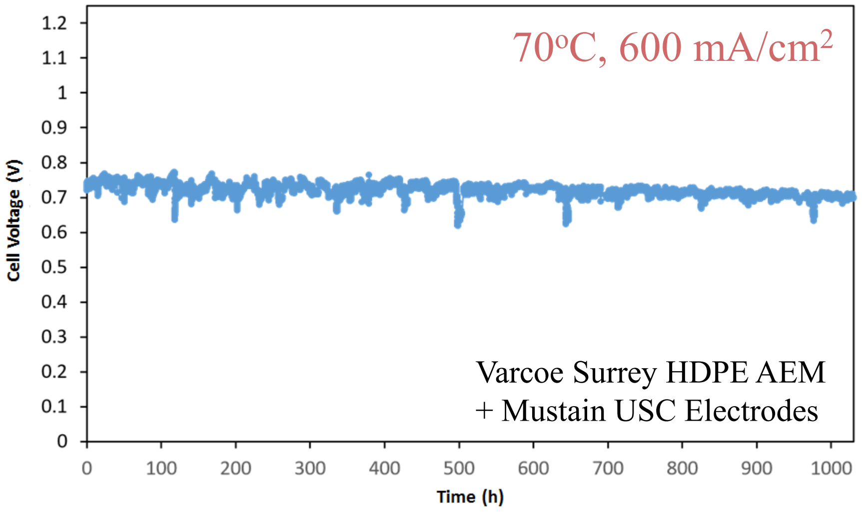
Y. Zheng, J.R. Varcoe, B. Pivovar and W.E. Mustain et al., *Submitted for Review*.

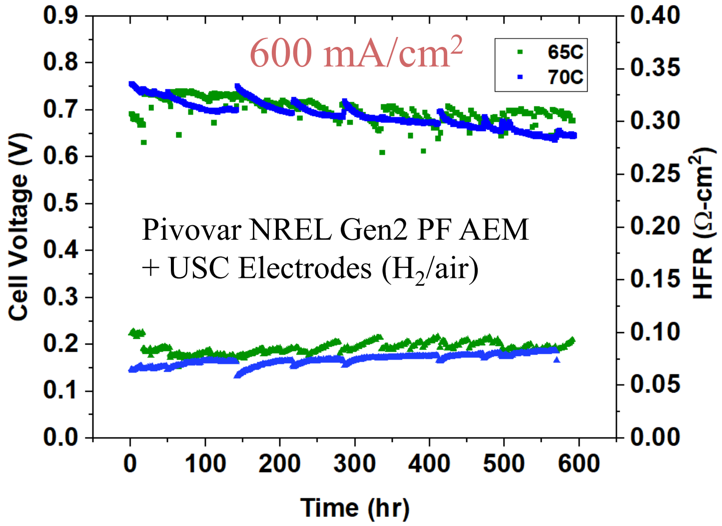
AEMFC Durability – Late 2017/Early 2018

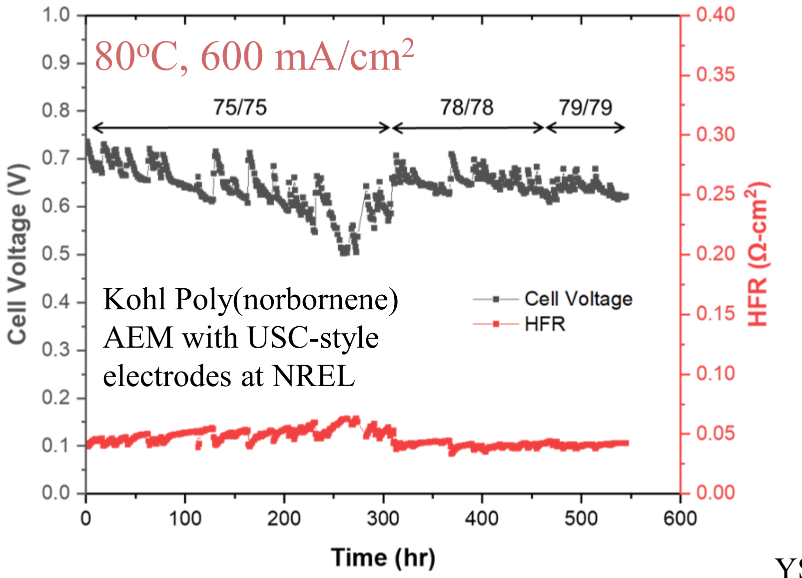
- D. Dekel, *J. Power Sources*, **375** (2018) 158-169.

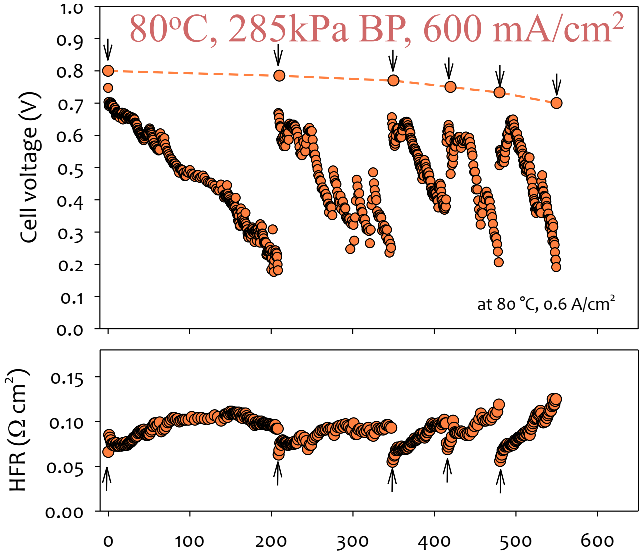


State-of-the-Art AEMFC Longevity







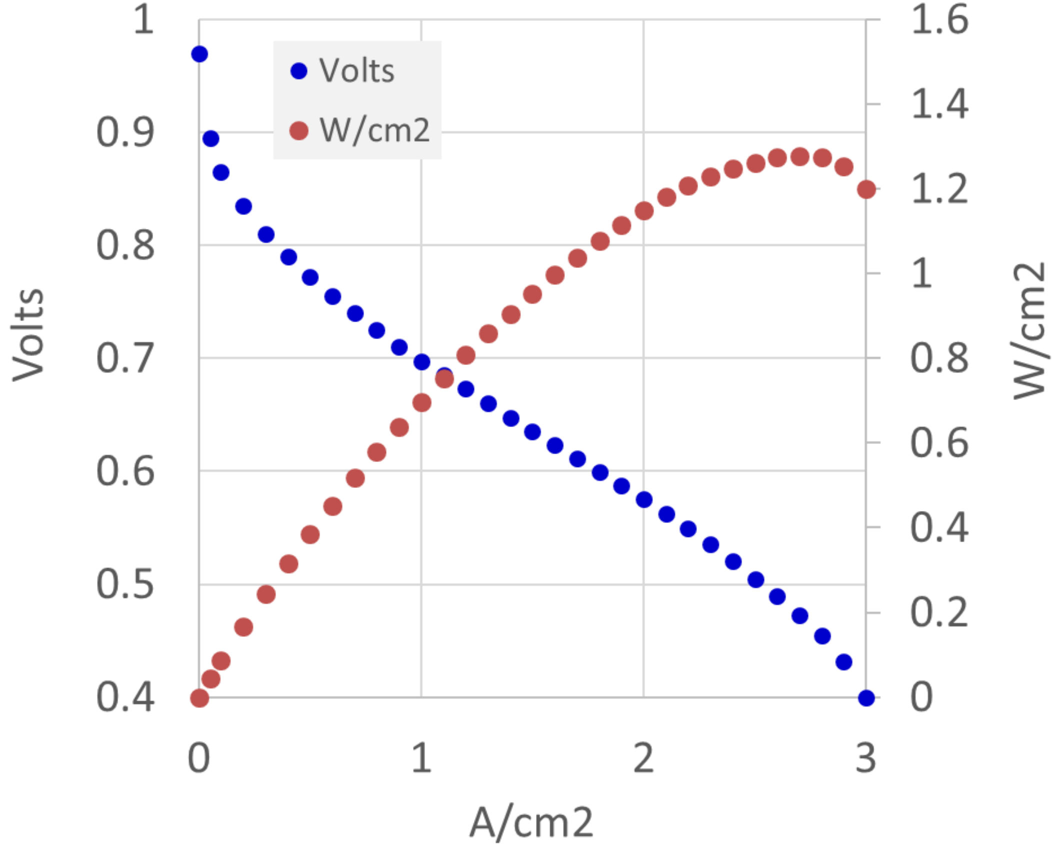


YS Kim, quaternized poly(biphenylene) AEM, FLN anion exchange ionomer

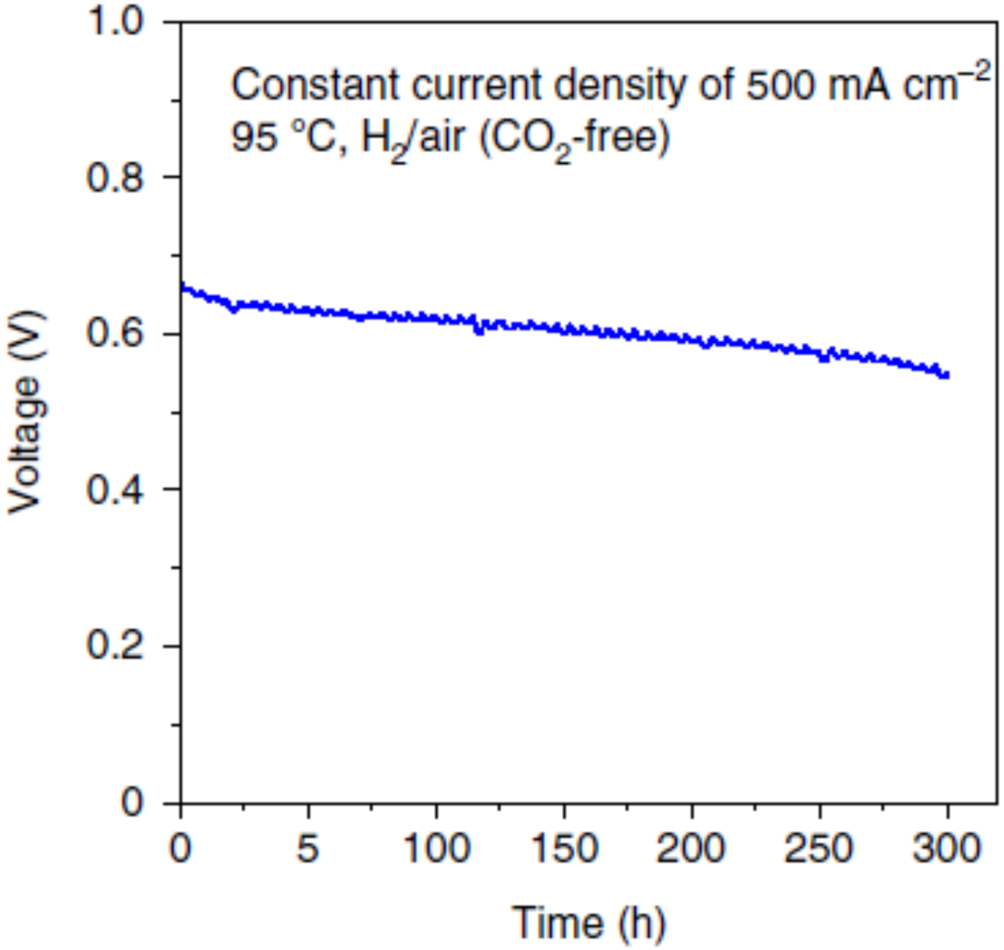
- AEMFCs are now routinely operated in several groups and systems for 500+ hours and ~10% voltage decay
  - Significantly improved over 1-2 years ago
- Top AEMFC durability is 1000h with ca. 5% voltage degradation

Where We Are Commercially: PO-CellTech

- H_2/Air [CO_2-free], 80°C, P_{ca}=2bar_a
- ~0.1mg/cm² Pt "cost equivalent"
- 5cm²



PAP ionomer/membrane*

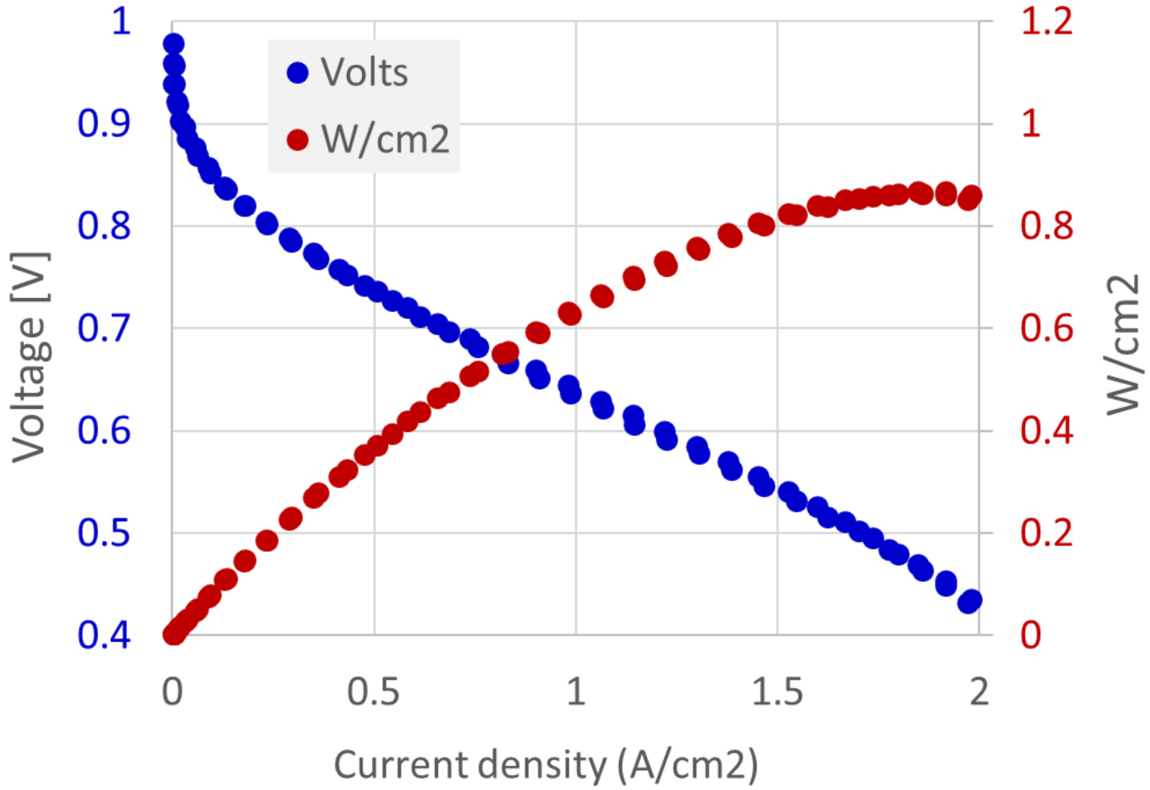


Slide Material C/O Miles Page, PO-CellTech

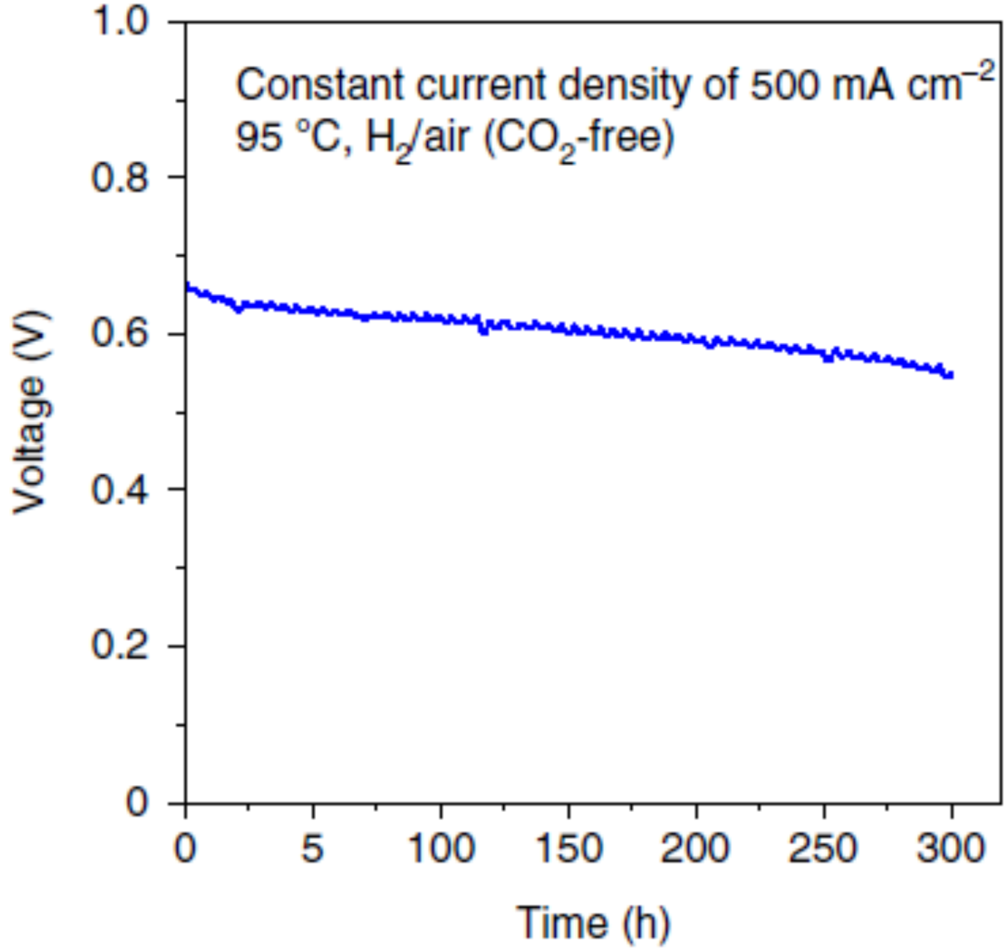
* Wang, J. *et al.*, Nature Energy 2019, 4, 392-398

Where We Are Commercially: PO-CellTech

- H_2/Air [CO_2-free], 80°C, P_{ca}=2bar_a
- ~0.1mg/cm² Pt "cost equivalent"
- 300cm²



PAP ionomer/membrane*



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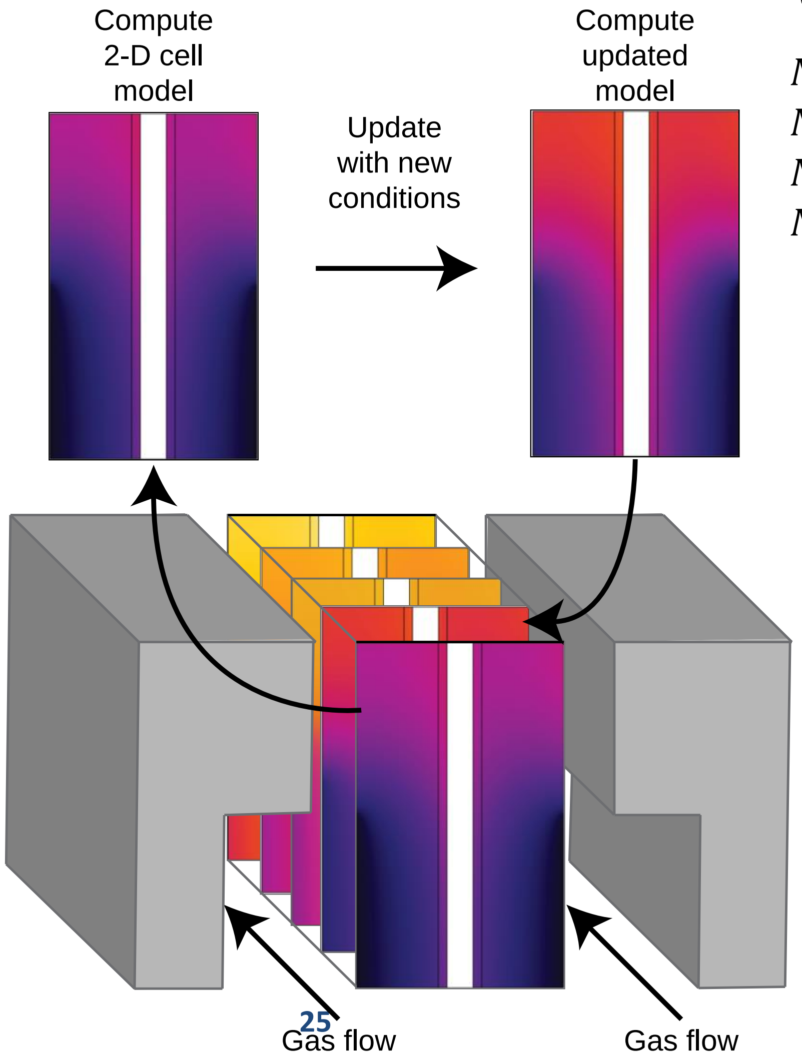
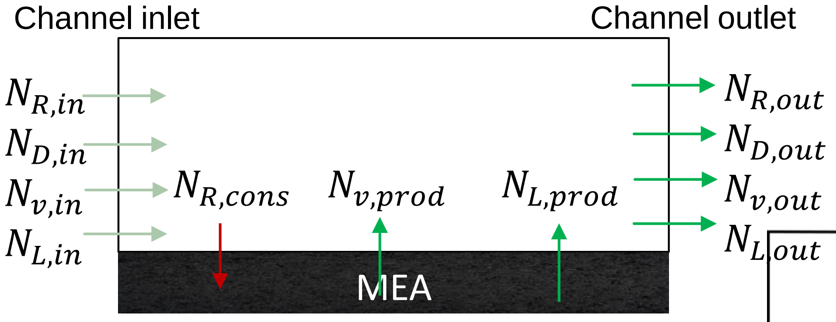
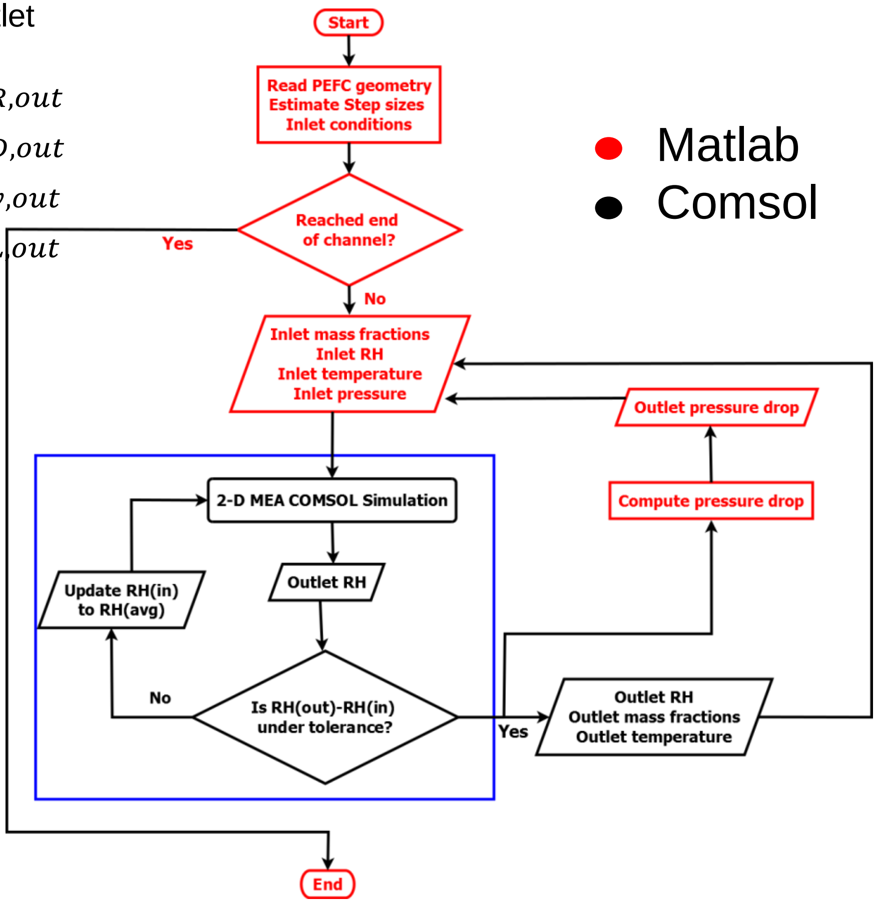
* Wang, J. *et al.*, Nature Energy 2019, 4, 392-398

There is a Significant Need to Better Link Modeling with Experiments







- Matlab
- Comsol

Models use air cathode, H_2 anode, 50% RH.
Cell voltage of 0.6 V, temperature 60 °C.
Air flow rate is 2.4x H_2 flow rate (same stoich)

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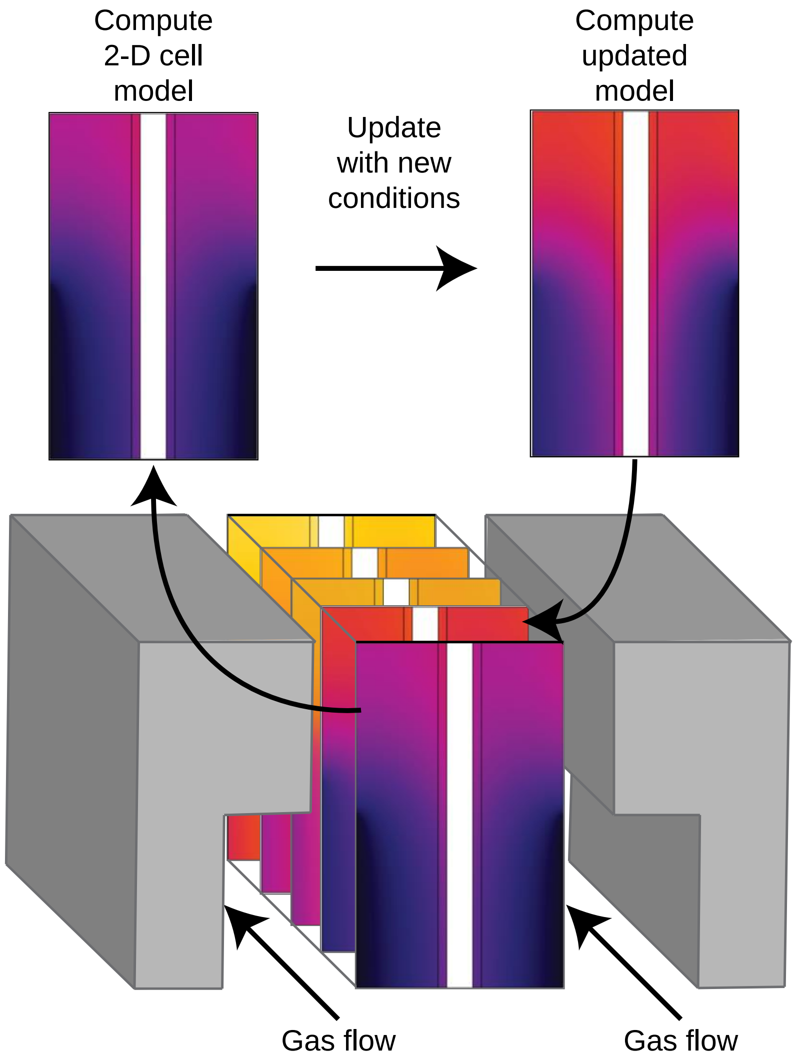
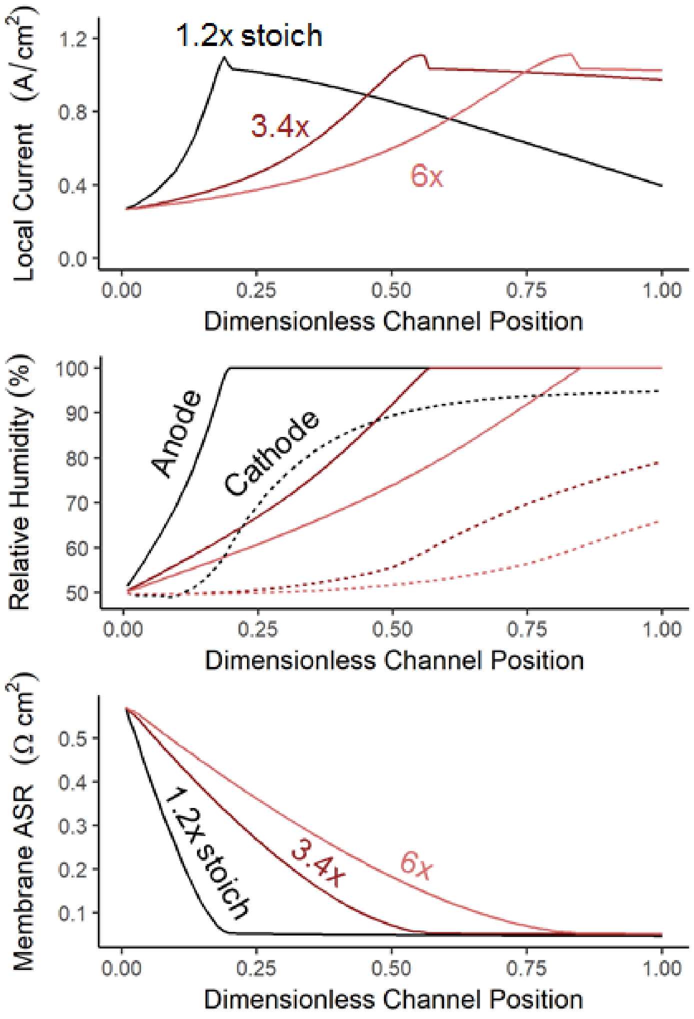
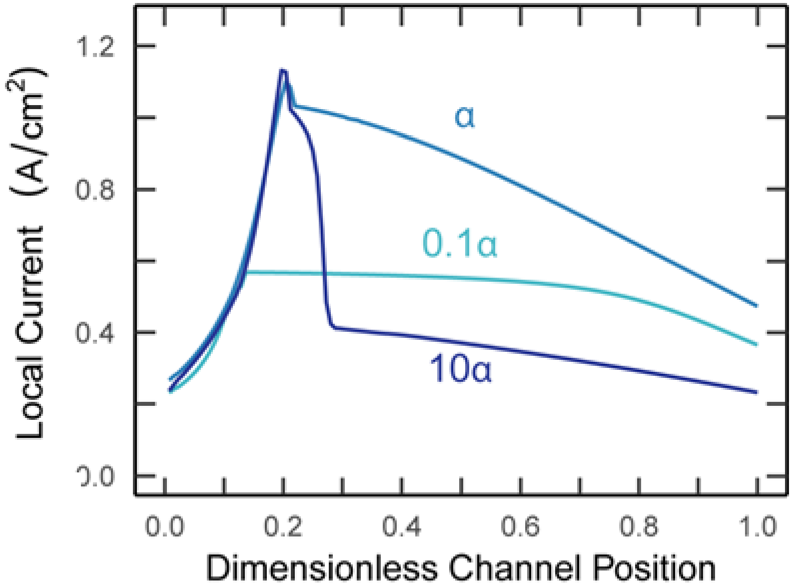
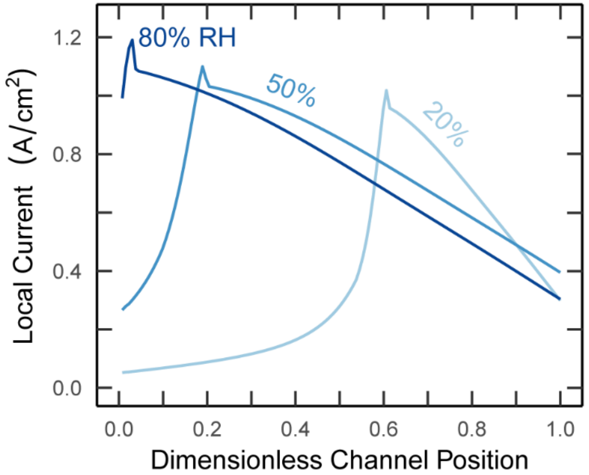
Increase flow rates to mitigate flooding









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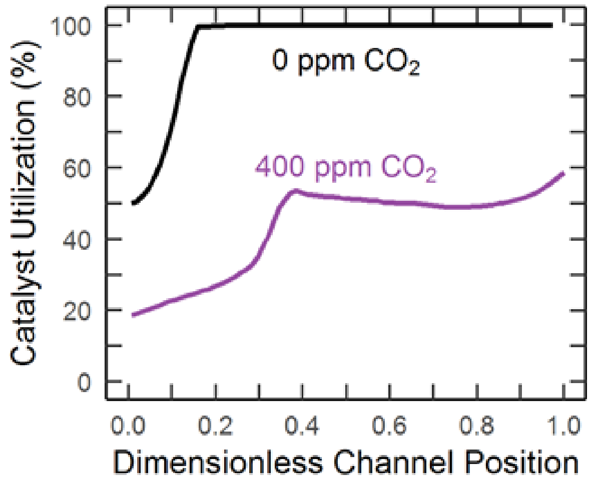
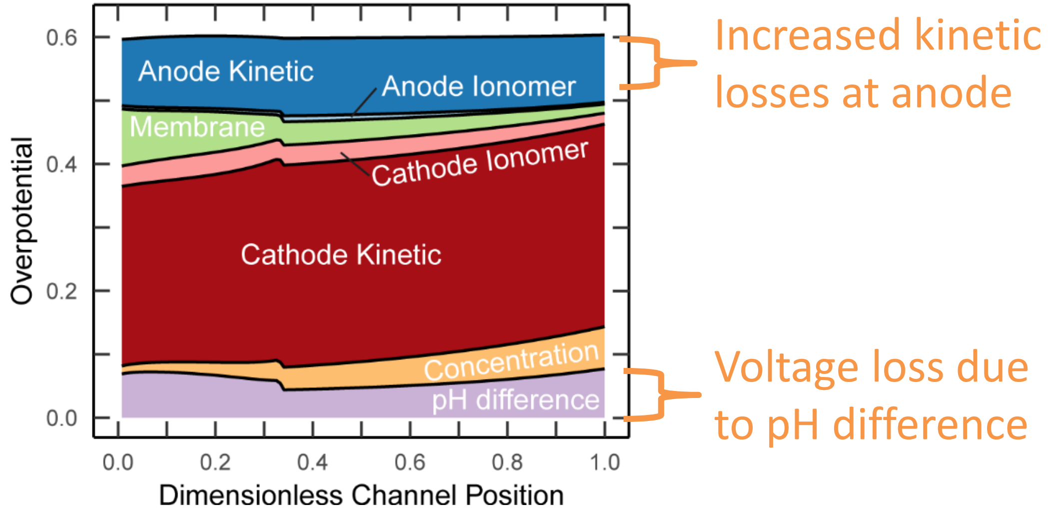
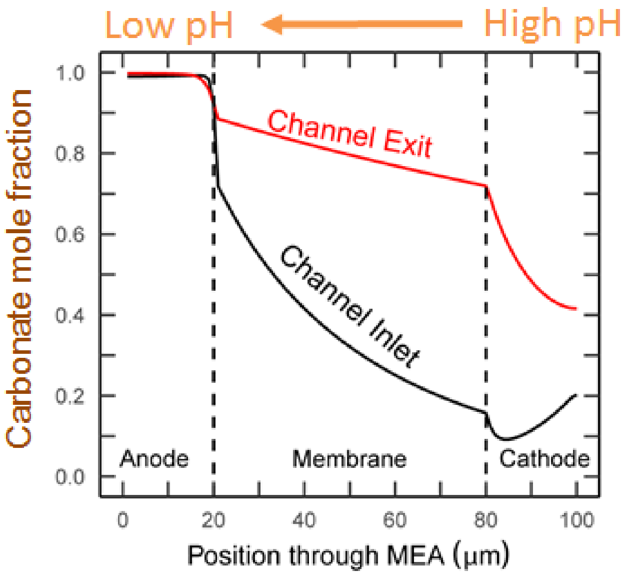
Insights into the Effects of CO_2







- CO_2 accumulation at the anode
  - Leading to low catalyst utilization and higher charge transfer resistances
- It is very difficult to decouple the charge transfer and Nernstian contributors experimentally, but that can be done with high accuracy with validated models
- Models can help experimentalists to iterate on viable operating conditions, determine the efficacy of proposed solutions and more rapidly explore the design space for optimized conditions

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Recommendations

- Transition from focusing exclusively on materials to a more balanced approach that targets integration and performance
  - e.g. AMFC-PAD-type consortia
    - This would be REALLY helpful to the community and could grow the technology quickly
- Create opportunities to marry experimental and modeling groups to better understand electrode-level and cell-level dynamics
  - And to look at practical hurdles for deployment
    - Air operation (PGM and PGM-free), water management (and targets), and CO_2

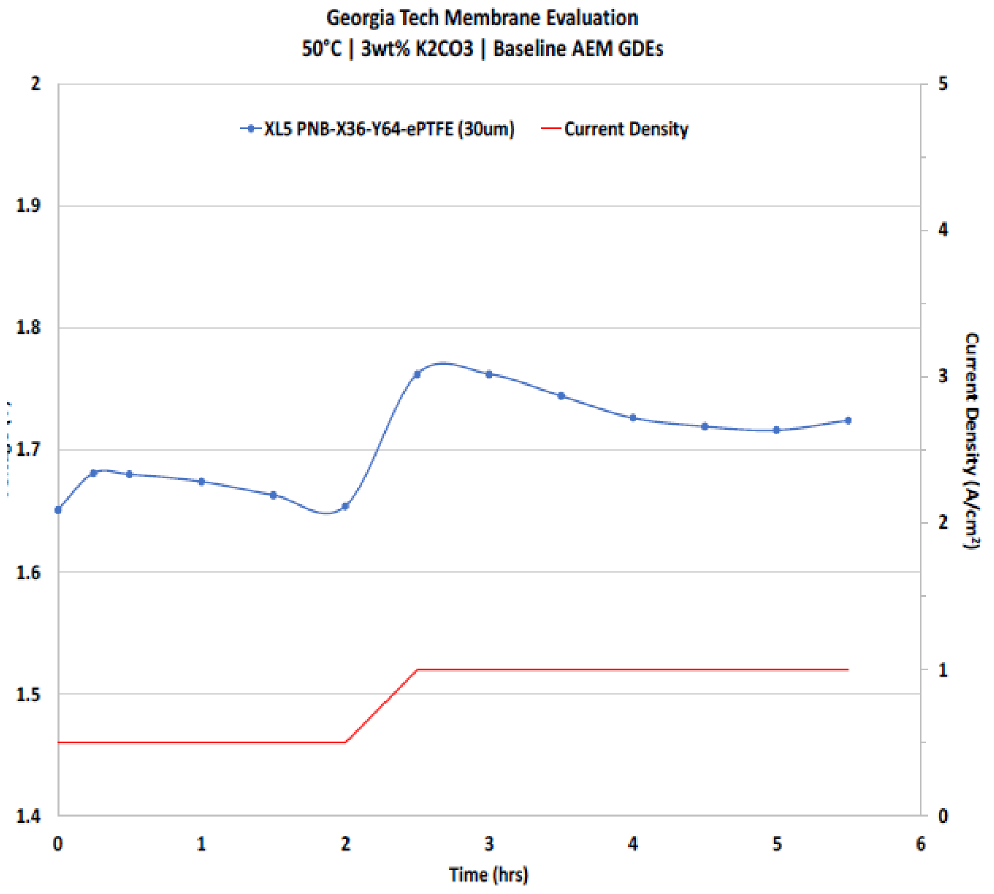
More Recommendations

- Develop a membrane metric for minimum water transport rate
  - Conditions TBD

- Start to design systems specifically for AEMFCs (not adjusted PEMFCs)
  - Start the discussion around targets considering where AEMFCs have real advantages vs. PEMFCs
  - Develop an operating window of interest for AEMFCs to be evaluated
    - Range of stoichs, operating T, operating P, defined CO_2 condition, range of operating dew points that can be accommodated at anode/cathode

One Slide on Low T Electrolysis (LTE)

- An area where AEMs can clearly make an improvement over PEMs
  - Collaboration between Georgia Tech, and Proton Onsite/NEL and Pajarito has already have shown operating voltage 150 mV lower than PEM-equivalent
    - This is without combining literature-best materials and electrode engineering/optimization
- Challenges
  - Durability not yet demonstrated
  - Bicarbonate addition to water
  - Scaleup of catalysts and AEMs



Slide Material C/O Paul Kohl, Georgia Tech

Thank You

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