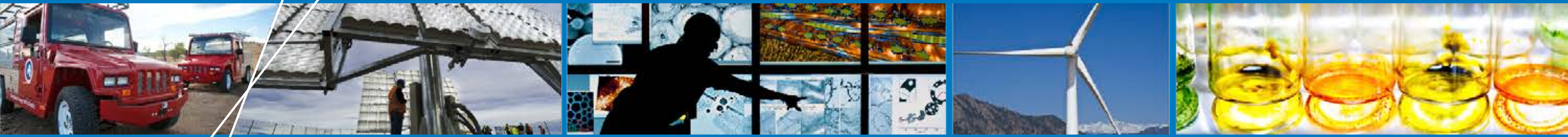
AMFC Workshop 3 Overview



Bryan Pivovar

National Renewable Energy Laboratory (NREL)

Sheraton Grand

Phoenix, AZ

April 1, 2016

Agenda

8:30 - 8:50 am	AMFC Challenges–Anion Exchange Membrane: **Chulsung Bae (RPI)**
8:50 - 9:15 am	AMFC Challenges-Electrocatalysis: **Yushan Yan (U. Delaware)**
9:15 - 9:30 am	BREAK
9:30 - 10:00 am	AMFC Challenges–Membrane Electrode Assembly: **Yu Seung Kim (LANL)**
10:00 -10:20 am	AMFC Challenges-System/Other Issues (Water/Carbonate): **Miles Page (Elbit Energy)**
10:20 -12:00	BREAKOUT SESSION
	Session 1: Research Challenges/R&D Needs
	AEM – Leader: **Michael Hickner, ORNL (Estrella Main Room)**
	MEA/System – Leader: **Adam Weber, LBNL (Ahwatukee A Room)**
	Catalysts – Leader: **Jacob Spendelow, LANL (Ahwatukee B Room)**
12:00 -1:20 pm	LUNCH – ON YOUR OWN
1:20 – 2:20 pm	Joint Session – Out Brief from Breakout Session 1
2:20 – 2:45 pm	AMFC Status: **Dario Dekel (Technion – IIT)**
2:45 - 3:00 pm	BREAK
3:00 – 4:10 pm	BREAKOUT SESSION
	Session 2: Status, Protocols, Milestones
	AEM – Leader: **Michael Hickner, ORNL (Estrella Main Room)**
	MEA/System – Leader: **Adam Weber, LBNL (Ahwatukee A Room)**
	Catalysts – Leader: **Jacob Spendelow, LANL (Ahwatukee B Room)**
4:10 – 5:00 pm	Joint Session – Out Brief from Breakout Session 2
5:00 pm	Concluding Remarks: **David Peterson (DOE)**

Rationale for Workshop

- **AMFCs materials have advanced rather significantly and remain an area of high technical interest**
- **The field has lacked standardization, baselines, or a clear understanding of current status. This impacts setting research priorities.**
- **Workshop goals:**
  - Define *major technical challenges and R&D needs for AMFC technology (Breakout Session 1)*
  - Develop consensus on *Status, Protocols, Milestones for AMFC technology (Breakout Session 2)*

Overview

- **While the field is much better understood than it was a few years ago, it is still necessary to provide an overview of AMFCs**
- **Our 4 world leading speakers in the area will provide depth in the most critical areas, this talk looks to provide highlights and fill in some missing areas and then focus on Breakout Sessions and desired outcomes.**

2011 AMFC Workshop Findings

Table 1. Select Highlights of Breakout Sessions

Breakout Session	Key Highlights
Anion Exchange Membranes – Stability	Membrane stability with Tokuyama membranes has been demonstrated to a level at or near commercial impact. AEM stability remains inferior to proton exchange membranes under conditions relevant to fuel cell operation.
Anion Exchange Membranes – Transport/Conductivity	Conductivity of AEMs is significantly lower than acid membrane analogues. Relatively little transport property data exist for AEMs, but water transport is likely to be an even larger issue in AMFCs than PEMFCs.
Electrocatalysis in High pH Environments	Oxygen reduction under basic conditions using high-performance, durable, non-precious electrocatalysts has been reasonably demonstrated, leaving anode catalysis as the primary concern in stark contrast to acidic systems.
MEA Issues	The most promising AMFC performance and durability reported to date has focused on H_2 as a fuel, and is now commonly achieved without the addition of free electrolyte. Performance of single cells has increased significantly with ~500 mW/cm^2 performance reported and durability in the thousands of hours.
System Issues	System issues will depend on system-specific requirements, but work in this area is necessary to determine how much improvement is needed in each of the other areas to produce viable devices. CO_2 from air or fuel has a major impact on system design and performance.

http://energy.gov/eere/fuelcells/alkaline-membrane-fuel-cell-workshop

2011 AMFC Workshop Findings

Table 1. Select Highlights of Breakout Sessions

Breakout Session
Anion Exchange Membranes – Stability
Anion Exchange Membranes – Transport/Conductivity
Electrocatalysis in High pH Environments
MEA Issues
System Issues

Combined at this Workshop (Anion Exchange Membranes – Stability; Anion Exchange Membranes – Transport/Conductivity)

Combined at this Workshop (MEA Issues; System Issues)

3 Break Out Sessions

Membranes
Electrocatalysts
MEAs

http://energy.gov/eere/fuelcells/alkaline-membrane-fuel-cell-workshop

Breakout Session 1

Major technical challenges and R&D needs for AMFC technology

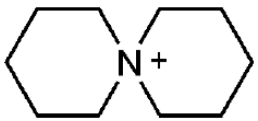
Recent Advances

Perhaps the most exciting advance in the AEM area in the past decade has come from the high hydroxide stabilities of covalently tetherable cations recently reported.

benzyltrimethyl ammonium ($BTMA^+$) stability at 80°C of less than 10% degradation after 5,000 hours.

M Sturgeon, C Macomber, C Engtrakul, H Long, and B Pivovar, J. Electrochem. Soc., 162 (4) F366-F372 (2015).

6-azonia-spiro[5.5]undecane
20x improvement.

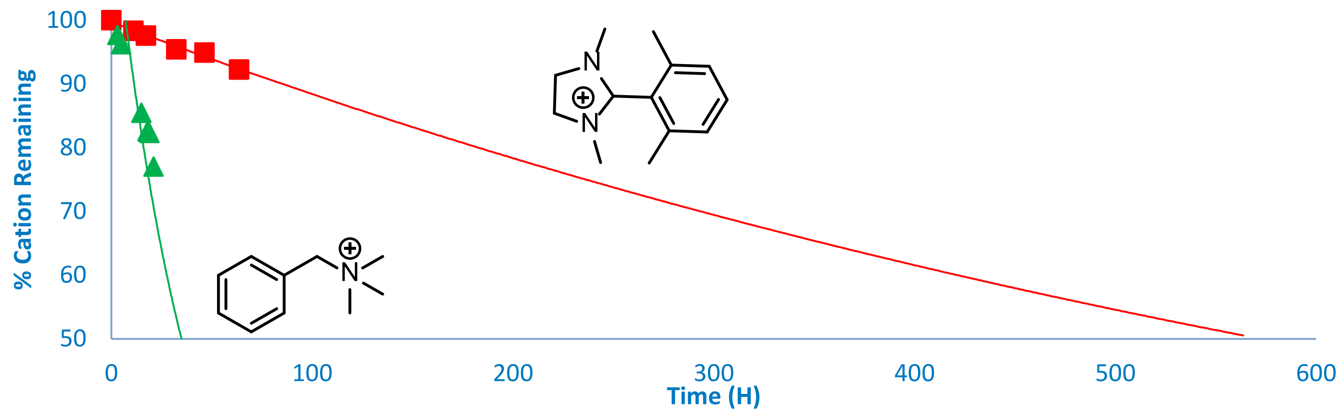


6-azonia-spiro[5.5]undecane

Marino, M.G. and K.D. Kreuer, Chemsuschem, 2015. **8**(3): p. 513-523

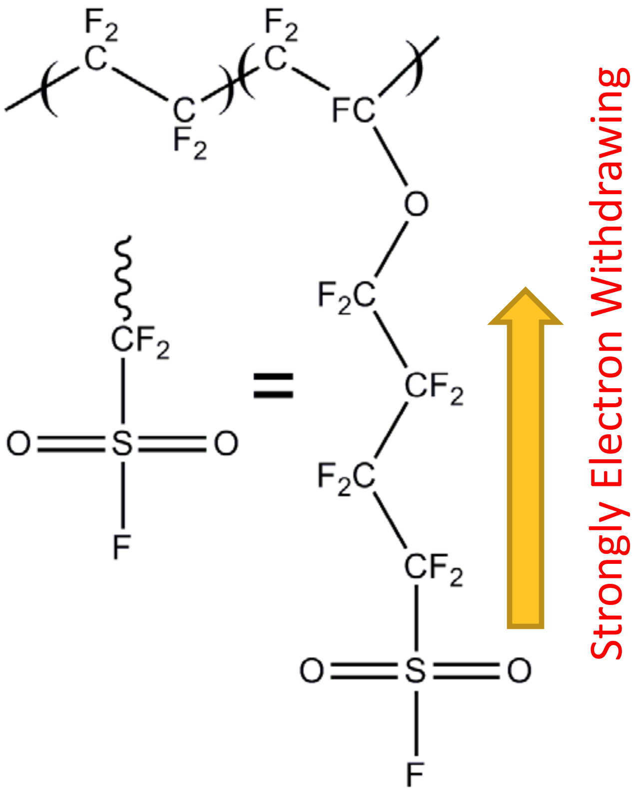
Our results suggest benzyl imidazole is ~100x more stable than BTMA.

0.1M cation in 2M KOH(aq) @ 140 °C

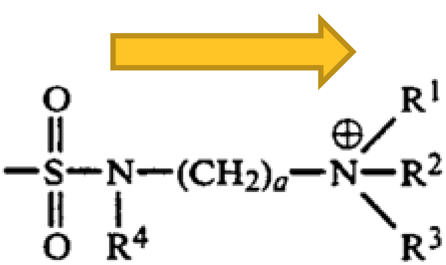


Research Needs

AEMs



Electron Deficient



Backbone and tether stability remain concerns.

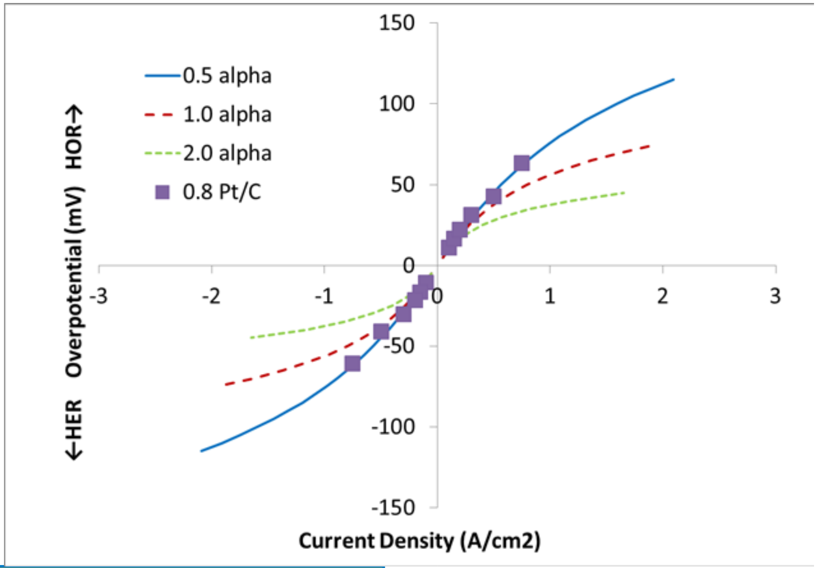
Can PF linking strategies be developed that have stability

Can straight hydrocarbon polymers withstand operating conditions and provide desired properties (conductivity, mechanical properties)

Research Needs

Electrocatalysis

Electrocatalysis - Hydrogen reactions are the concern rather than oxygen reaction (PEM).



Reference	Catalyst	$i_{o,HOR}$ (mA/cm²)
Strmcnik et al., 2013	Pt/C	~1.0
"	Pt(0.1)Ru(0.9)/C	>6.5
Durst et al., 2014	Pt/C	1.0
Wang et al., 2014	Pt/C	0.3
"	Pt(0.6)Ru(0.4)/C	0.7
St. John et al., 2015	Pt/C	0.49
"	Pt(0.8)Ru(0.2)/C	1.42

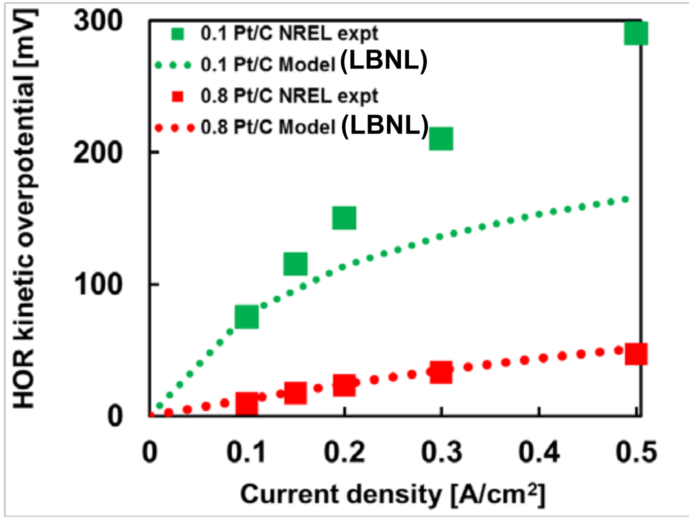
Research Needs
MEAs/Systems

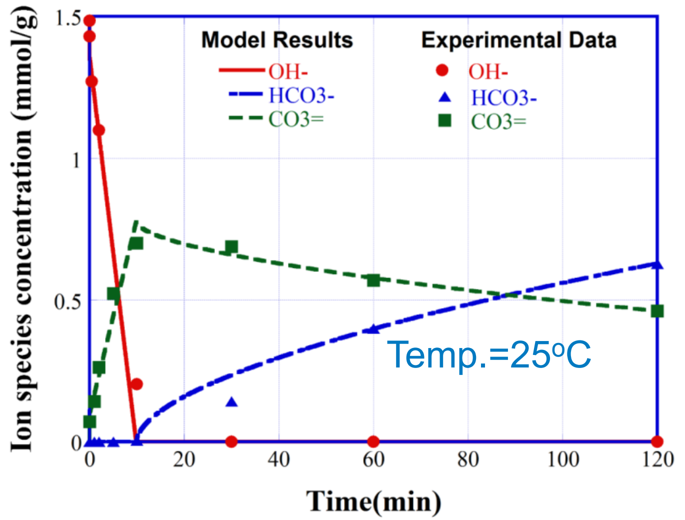
Electrode Fabrication – Optimized performance, ionomer solutions.

Cell Performance/Durability - Optimization, diagnostics and quantification of losses.

Water Management – A more significant issue in AMFC than PEMFCs. Impacts operating temperatures.

Carbonate – CO_2 a major concern for performance and operating conditions.





Experimental data from Yanagi, H. and K. Fukuta, ECS Transactions, 2008. **16**(2): p. 257-262.

Breakout Session 2

Status, Protocols, Milestones for AMFC technology

Target/Status Tables for AEMs and AMFCs

Table 3.4.12 Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Units	2005 Status [a]		Stack Targets	
		Cell	Stack	2010	2015
Platinum group metal (pgm) total loading [b]	mg PGM / cm^2 electrode area	0.45	0.8	0.3	0.2
Cost	$ / kW	9	55 [c]	5 [d]	3 [d]
Durability with cycling					
Operating temp ≤80°C	hours	>2,000	~2,000 [e]	5,000 [f]	5,000 [f]
Operating temp >80°C	hours	N/A [g]	N/A [g]	2,000	5,000 [f]
Electrochemical area loss [h]	%	90	90	<40	<40
Mass activity [j]	A / mg Pt @ 900 $mV_{iR\text{-}free}$	0.28	0.11	0.44	0.44
Specific activity [j]	μA / cm^2 @ 900 $mV_{iR\text{-}free}$	550	180	720	720

Table 3.4.13 Technical Targets: MEAs

Characteristic	Units	2005 Status [a]	2010	2015
Operating temperature	°C	<80	<120	<120
Inlet water vapor partial pressure	kPa	50	<1.5	<1.5
Cost [b]	$ / kW	60 [c]	10	5
Durability with cycling				
At operating temp of ≤80°C	hours	~2,000 [d]	5,000 [e]	5,000 [e]
At operating temp of >80°C	hours	N/A [f]	2,000	5,000 [e]
Unassisted start from low temperature	°C	-20	-40	-40
Performance @ ¼ power (0.8V)	mA / cm^2 mW / cm^2	200 160	300 250	300 250
Performance @ rated power	mW / cm^2	600	1,000	1,000
Extent of performance (power density) degradation over lifetime [g]	%	5 [h]	10	5
Thermal cyclability in presence of condensed water		Yes	Yes	Yes

The information in Tables like these is helpful for both quantifying the status of a technology and setting research goals.

Protocol's similarly beneficial.

Status, Protocols, Milestones

AEMs

Table D-4 Membrane Mechanical Cycle and Metrics (Test using a MEA) Table revised December 10, 2009		
Cycle	cle 0% RH (2 min) to 90°C dewpoint (2 min), single cell 25-50 cm^2	
Total time	**Until crossover >2 mA/cm^2 or 20,000 cycles**	
Temperature	**80°C**	
Relative Humidity	**Cycle from 0% RH (2 min) to 90°C dewpoint (2 min)**	
Fuel/Oxidant	**Air/Air at 2 SLPM on both sides**	
Pressure	**Ambient or no back-pressure**	
Metric	Frequency	Target
Crossover*	**Every 24 h**	**$\leq$2 mA/cm^2**
Shorting resistance**	**Every 24 h**	**>1,000 ohm cm^2**

*** Crossover current per USFCC "Single Cell Test Protocol" Section A3-2, electrochemical hydrogen crossover method.**

**** Measured at 0.5 V applied potential, 80°C and 100% RH N_2/N_2. Compression to 20% strain on the GDL.**

AEMs – PEM developed protocols may be inappropriate

What are most appropriate metrics? (conductivity, mechanical properties)

What are most appropriate test conditions? (OH^- form, vs Cl^- form, T, RH)

What about durability? (Specific durability tests, anything beyond chemical?)

Status, Protocols, Milestones
Electrocatalysis

Table E1 Electrocatalyst Cycle and Metrics

Cycle	Triangle sweep cycle: 50 mV/s between 0.6 V and 1.0 V. Single cell 25-50 cm^2	
Number	30,000 cycles	
Cycle time	16 s	
Temperature	80°C	
Relative Humidity	Anode/Cathode 100/100%	
Fuel/Oxidant	Hydrogen/N_2 (H_2 at 200 sccm and N_2 at 75 sccm for a 50 cm^2 cell	
Pressure	Atmospheric pressure	
Metric	Frequency	Target
Catalytic Mass Activity[a]	At Beginning and End of Test minimum	$\leq$40% loss of initial catalytic activity
Polarization curve from 0 to $\geq$1.5 A/cm^2 [b]	After 0, 1k, 5k, 10k, and 30k cycles	$\leq$30 mV loss at 0.8 A/cm^2
ECSA/Cyclic Voltammetry[c]	After 10, 100, 1k, 3k, 10k, 20k and 30k cycles	$\leq$40% loss of initial area

a. Mass activity in A/mg @ 150 kPa abs backpressure at 857 mV iR-corrected on 6% H_2 (balance N_2)/O_2 {or equivalent thermodynamic potential}, 100% RH, 80°C normalized to initial mass of catalyst and measured before and after test.
b. Polarization curve per protocol in Table E3.
c. Sweep from 0.05 to 0.6 V at 20 mV/s, 80°C, 100% RH.

ORR – 0.6-0.9V cycling may be fine to just take PEM as this replicates operating conditions, but is this an issue for AMFCs?
What about support corrosion?
What about HOR? What should be catalyst activity target or assessment condition for HOR?

Status, Protocols, Milestones
MEAs/Systems

Table E3 Polarization Protocol

Test Point #	Current Density	Anode Inlet H2% (balance N2)	Anode H2 Stoich	Anode Dewpoint Temp	Anode Inlet Temp	Anode Pressure outlet	Cathode Inlet O2%	Cathode Inlet N2%	Cathode O2 Stoich	Cathode Dewpoint Temp	Cathode Inlet Temp	Cathode Pressure Outlet	Cell/Stack control Temp	Test pt. Run Time	Set Point Transit time
	[A/cm2]	inlet/dry	[-]	[°C]	[°C]	[kPaabs]	inlet/dry	inlet/dry	[-]	[°C]	[°C]	[kPaabs]	[°C]	min	s
Break-in															
B1	0.6	100%	1.5	59	80	150	21%	79%	1.8	56	80	150	80	20	0
Reduction															
R1	0	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	1	0
R2	0	100%	1.5	59	80	150	0%	100%	1.8	59	80	150	80	Until V> 0.1V	0
Polarization curve															
P1	0.2	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P2	0.4	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P3	0.6	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P4	0.8	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P5	1	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P6	1.2	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P7	1.4	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P7	1.6	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P8	1.8	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P9	2	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P10	1.8	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P11	1.6	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P12	1.4	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P13	1.2	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P14	1	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P15	0.8	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P16	0.6	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P17	0.4	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P18	0.2	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P19	0.1	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P20	0.05	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P21	0.02	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P22	0.05	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P23	0.1	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0
P24	0.2	100%	1.5	59	80	150	21%	79%	1.8	59	80	150	80	3	0

Stoichs for points below 0.2A/cm2 at 0.2A/cm2 equivalent flow

Specific cell protocols exist for PEM performance and durability testing.

For AMFC, what reactants should be used (O_2 or CO_2 free air), what stoich, temperature, humidification, break-in procedure, etc.

How can comparisons be made easily between groups.

Workshop Deliverables

- **Report to DOE**
  - Define *major technical challenges and R&D needs for AMFC technology (Breakout Session 1)*
  - Develop consensus on *Status, Protocols, Milestones for AMFC technology (Breakout Session 2)*

3 Break Out Sessions

Membranes
Electrocatalysts
MEAs

- Thank you all again for your participation
- We look forward to an interesting and productive Workshop.