NATIONAL RENEWABLE ENERGY LABORATORY

Innovation for Our Energy Future

Alkaline Membrane Fuel Cell Workshop Welcome and Overview

Bryan Pivovar

National Renewable Energy Laboratory

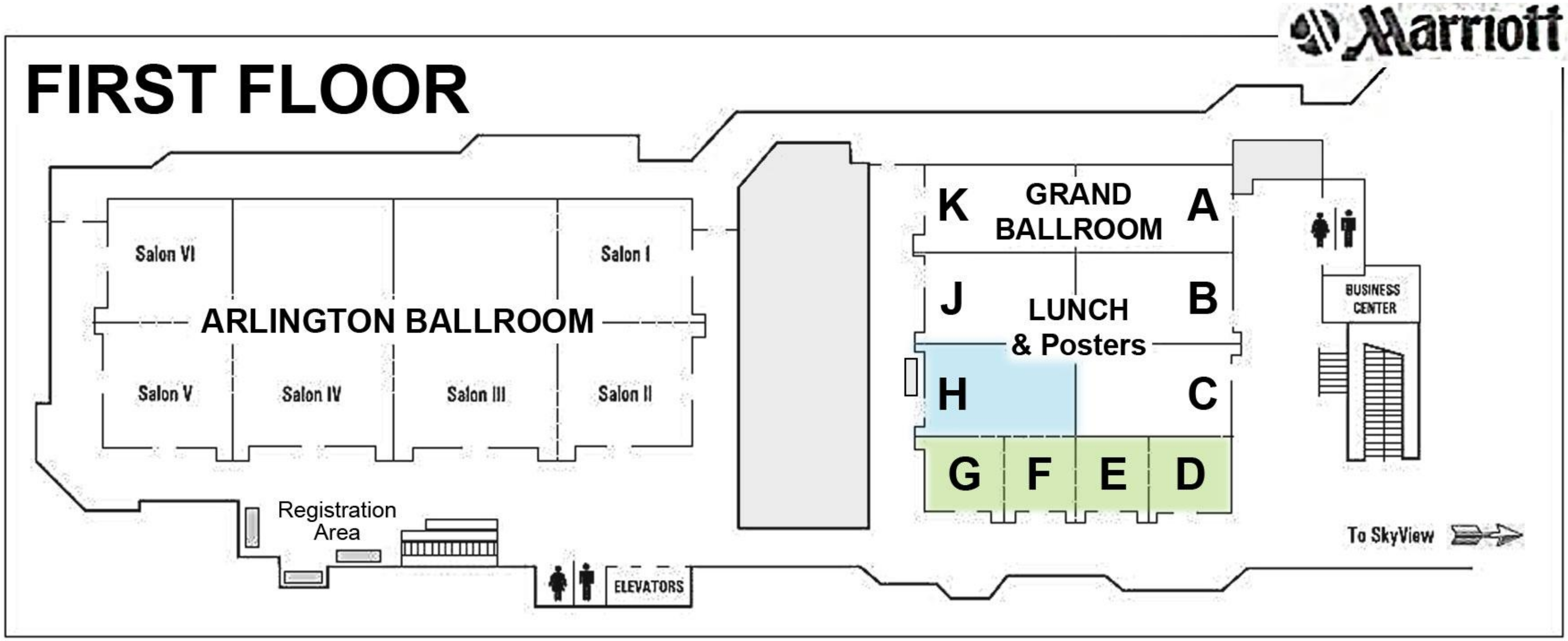
AMFC Workshop

May 8, 2011

Welcome

- Your participation is appreciated
- Date of Workshop

Meeting Location



2011 Alkaline Membrane Fuel Cell Workshop

Workshop Agenda

SUNDAY, MAY 8, 2011

1:00 pm - 1:15 pm	**Welcome and Opening Remarks** (Salon H)
1:15 pm - 1:45 pm	**Workshop Overview: Dr. Bryan Pivovar, NREL** (Salon H)
1:45 pm - 2:15 pm	**Alkaline Membrane Research Overview:** **Prof. Andy Herring, Colorado School of Mines** (Salon H)
2:15 pm - 2:45 pm	**Alkaline Electrocatalysis Research Overview:** **Prof. Sanjeev Mukerjee, Northeastern University** (Salon H)
2:45 pm - 3:15 pm	**AMFCs: Tokuyama Perspective:** **Kenji Fukuta, Tokuyama Corp.** (Salon H)
3:15 pm - 3:45 pm	**Break**
3:45 pm - 4:15 pm	**AMFCs: CellEra perspective:** **Shimshon Gottesfeld, CellEra, Inc.** (Salon H)
4:15 pm - 4:30 pm	**Move to Breakout Sessions**
4:30 pm - 6:00 pm	**Breakout Sessions** (Salons D-H)

MONDAY, MAY 9, 2011

8:00 am - 9:45 am	**Breakout Sessions** (Salons D-H)
9:45 am – 10:15 am	**Break**
10:15 am - 12:00 pm	**Joint Session Outbrief from Breakout Sessions** (Salon H)

Rationale for Workshop

Significant advances recently in the area of Alkaline Membrane Fuel Cells

Property	Status
Conductivity[a]	40 mS/cm
Membrane Chemical Stability[b]	> 95%
Electrocatalysis [c]	Non-precious validated
Fuel Cell Durability[d]	~200 mW/cm^2, 800 hours 50 mW/cm2, >3000 hours
Fuel Cell Peak Power Density[e]	~500 mW/cm^2

[a] Measured in liquid water, OH^- form, room temperature; [b] Stability after 1,000 hours in >2M OH- at 80°C; [c] examples presented with performance and durability compared to Pt; [d] At min. voltage of 0.5V for efficiency; [e] Using CO_2-free air and/or O_2.

Generating increased interest, as reflected by the >100 Workshop pre-registrants.

2011 Alkaline Membrane Fuel Cell Workshop

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.

Anion Exchange Membrane (AEM) Fuel Cell

Varcoe et al. ECS Transactions, 16 (2) 1819-1834 (2008)

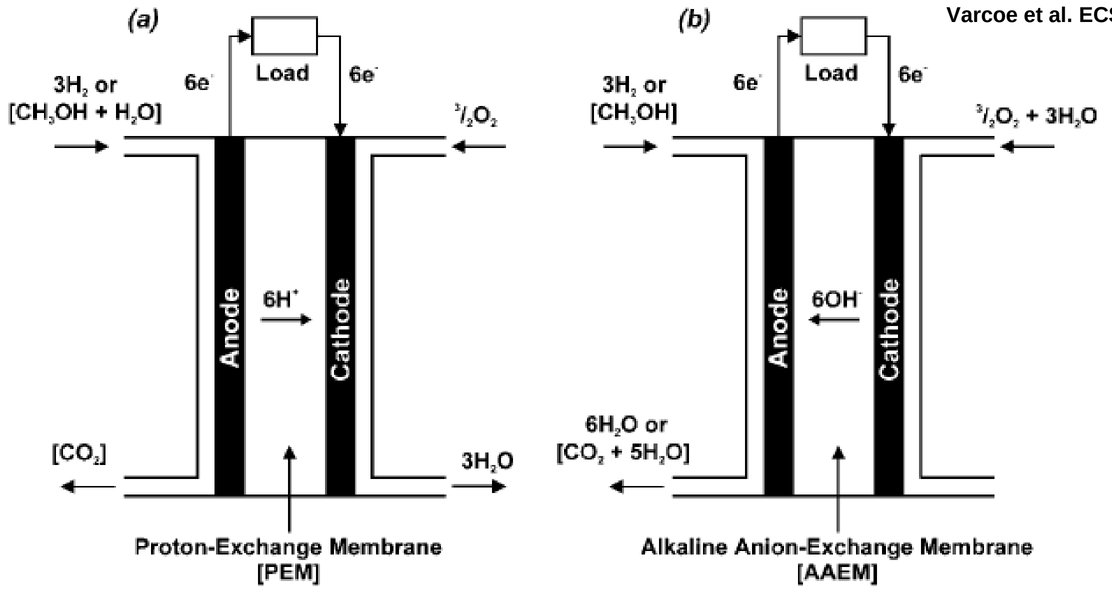


Fig. 1 A schematic of (a) a proton-exchange membrane and (b) an alkaline membrane fuel cell both fuelled either with H_2 gas or directly with methanol. The stoichiometric ratio of reactants and products are shown in each case.

	Acidic	Alkaline	Carbonate
Oxygen	$2\ H^+ + O_2 + 2\ e^- \rightarrow H_2O$	$H_2O + ½\ O_2 + 2\ e^- \rightarrow 2\ OH^-$	$H_2O + ½\ O_2 + 2\ e^- + CO_2 \rightarrow 2\ CO_3^{2-}$
Hydrogen	$H_2 + \rightarrow 2\ H^+ + 2\ e^-$	$H_2 + 2\ OH^- \rightarrow 2\ H_2O + 2\ e^-$	$H^+ + O_2 + e^- \rightarrow H_2O$
Methanol	$CH_3OH + H_2O \rightarrow 6\ H^+ + 6\ e^- + CO_2$	$CH_3OH + 6\ OH^- \rightarrow 5\ H_2O + 6\ e^- + CO_2$	$CH_3OH + 3\ CO_3^{2-} \rightarrow 2\ H_2O + 6\ e^- + 4\ CO_2$

AEM Fuel Cell Potential Advantages

Catalysis

- Non-precious catalysis
- Improved anode/cathode kinetics/durability
- C-C bond electrochemistry, fuel choices

System Issues

- Electro-osmotic drag in opposite direction
- Materials choices/ durability

Membrane vs. free electrolyte

- Tolerance to carbonate
- Liquid water tolerance/ electrolyte migration
- Differential pressures, thinner membrane
- Corrosion
- System design simplification

2006 AMFC Workshop Findings

Breakout Group	Key Recommendations
Anion Exchange Membrane/Cation Stability and Conductivity	**Improve cation stability** – current generation materials have had significant limitations due to chemical stability of the cations, explore different classes and novel cations, explore degradation mechanisms and dependence on temperature and water content. **Improve conductivity** – conductivity in these systems is significantly lower than in acid membrane systems, the role of cation basicity, water content and membrane morphology need to be related to conductivity and carbonate formation needs further investigation.
Electrocatalysis in High pH Environments	**Catalysts for complex fuel oxidation** – the ability of alkaline systems to effectively utilize complex fuels like ethanol is a significant advantage over related systems, how they do this and whether or not they can be effectively expanded to include more complex fuels (like gasoline) is an area that needs further investigation.
Utilizing Anion Exchange Membranes in Fuel Cells	**MEA fabrication** – current generation cells only obtain system useful performance with the addition of free electrolyte, research to improve performance of cells without free electrolyte are required for many applications.
System Considerations/Needs	**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.

* Taken from Army Research Office Report, from Alkaline Membrane Fuel Cell Workshop, Phoenix, AZ, Dec 11-13, 2006.

These findigns parallel this Workshop's Breakout Sessions

2006 AMFC Workshop Agenda

Monday, Dec. 11

7:30	- 7:45	Opening Remarks Dr. Robert Mantz, ARO/ Dr. Bryan Pivovar, LANL
7:45	- 8:15	Army Power Needs Dr. Cynthia Lundgren, Army Research Laboratory
8:15	- 9:15	Workshop Overview Dr. Bryan Pivovar, Los Alamos National Laboratory

Tuesday, Dec. 12

8:00	- 8:30	Alkaline Fuel Cells Overview, Mr. Peter Nor, Astris Energi Inc.
8:30	- 9:00	Alkaline Membrane Fuel Cells, Prof. Robert Slade, University of Surrey
9:00	- 9:30	Catalysis in Alkaline Environments, Prof. Andrzej Wieckowski, University of Illinois
9:30	- 10:00	Alkaline Membrane Fuel Cells at ACTA, Dr. Xiaoming Ren, ACTA spa
10:00	- 10:30	Morning Break
10:30	- 11:00	Alkaline Membrane Stability, Prof. Thomas Davis, University of South Carolina
11:00	- 11:30	Cation Stability in Alkaline Environments, Dr. James Boncella, Los Alamos National Laboratory
11:30	- 12:00	Hydroxide/Carbonate Interactions, Dr. Lawrence Pratt, Los Alamos National Laboratory
12:00	- 1:00	Lunch
1:00	- 1:30	Aqueous Carbonate Fuel Cells, Prof. Elton Cairns, University of California - Berkeley
1:30	- 2:00	System Considerations for Alkaline Membrane Fuel Cells, Dr. Jerry Martin, Mesoscopic Devices
2:00	- 2:15	Charge to Breakout Groups
2:15	- 2:45	Afternoon Break
2:45	- 5:00	Breakout Groups

Wednesday, Dec. 13

8:00	- 10:00	Breakout Groups
10:00	- 10:30	Morning Break
10:30	- 12:00	Joint Session Out Brief from Breakout Groups

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2011 Alkaline Membrane Fuel Cell Workshop

Power Ranges (Needs)

Transportation: Power density (conductivity)

Stationary: Lifetime

Portable: Fuel?

Backup power

Materials handling

From W – kW scale

Carbonate Formation

Carbonate

- From fuel (often) or from air
- Buffered free electrolytes systems can mitigate

$$CO_2 + H_2O + CO_3^{2-} \Longleftrightarrow 2HCO_3^- \quad (C)$$

$$CO_3^{2-} + H_2O \Longleftrightarrow HCO_3^- + OH^- \quad (D)$$

$$H_2O \Longleftrightarrow H^+ + OH^- \quad (E)$$

$$CO_2 + OH^- \Longleftrightarrow HCO_3^- \quad (F)$$

$$CO_2 + 2OH^- \Longleftrightarrow CO_3^{2-} + H_2O \quad (G)$$

$$CO_2 + H_2O \Longleftrightarrow H_2CO_3 \quad (H)$$

$$H_2CO_3 + OH^- \Longleftrightarrow H_2O + HCO_3^- \quad (I)$$

$$H_2CO_3 + 2OH^- \Longleftrightarrow 2H_2O + CO_3^{2-} \quad (J)$$

Y. Wang et al., *Electrochem Comm.*, 5 (2003) 662.

Early (pre 2006) high reported performances often add electrolyte to liquid fuel solutions (KOH, K_2CO_3).

- Buffer effect, but free electrolyte issues

Aqueous Carbonate Fuel Cells

Concentration Profiles in O_2 Reduction

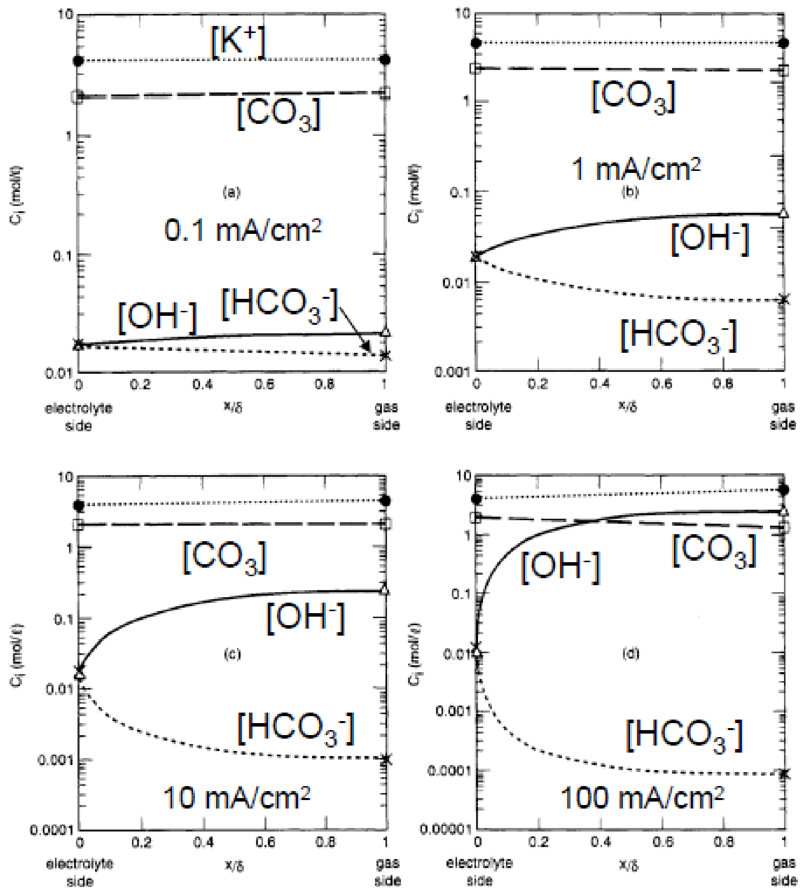


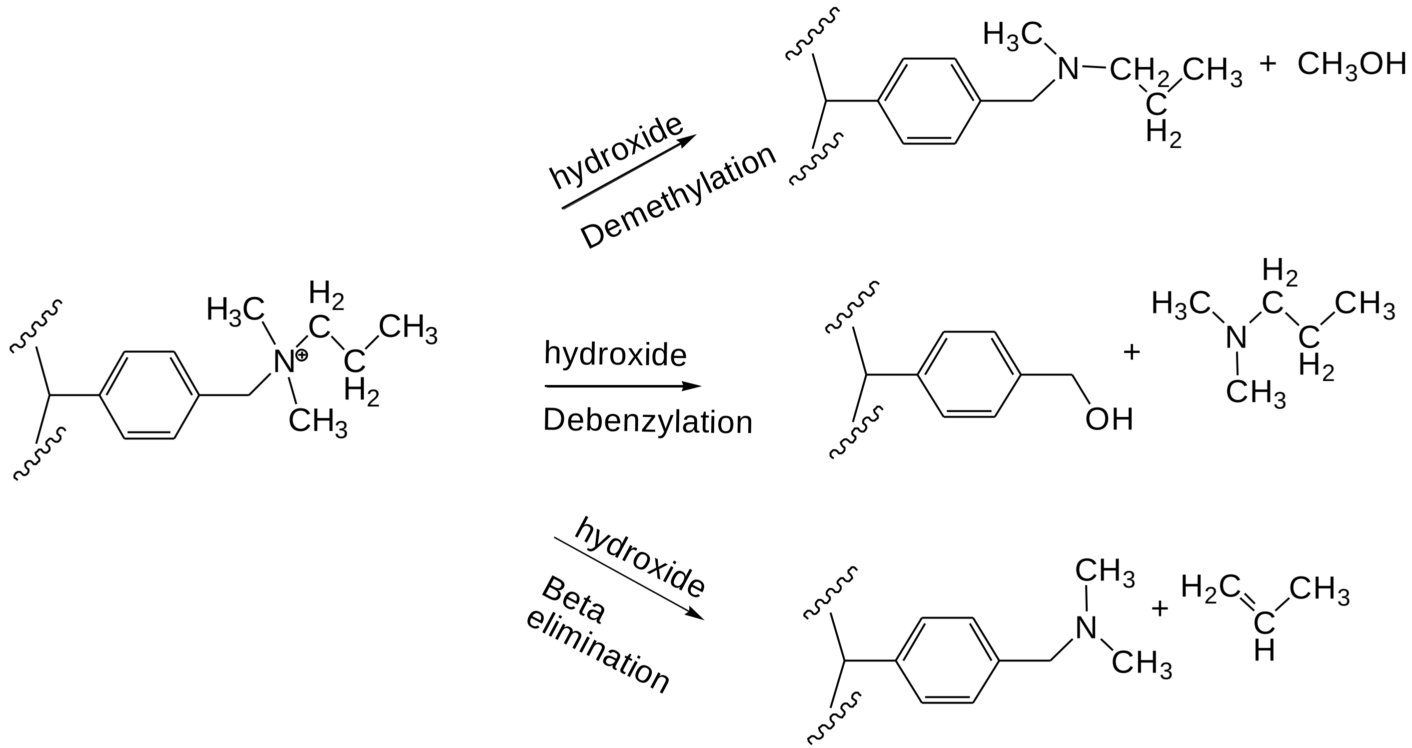
Figure 3. Predicted ionic concentration profiles for 2 M K_2CO_3 electrolyte and pure oxygen at several current densities: (a) 0.1, (b) 1, (c) 10, and (d) 100 mA/cm^2. (— △) C_{OH^-}; (- - - ×) $C_{HCO_3^-}$; (— —□) $C_{CO_3^{2-}}$; (· · · ●), C_{K^+}.

Modeling studies show that hydroxide can accumulate to high concentrations at current densities of 100 mA/cm² and higher.

Cs_2CO_3 should be an acceptable electrolyte for H_2/Air cells

* Taken from E Cairns, Aqueous Carbonate Fuel Cell Presentation, Alkaline Membrane Fuel Cell Workshop, Phoenix, AZ, Dec 11-13, 2006.

Alkaline (Anion Exchange) Membrane - Stability



Traditional anion exchange membrane cations degrade by these routes. Has been suggested that lifetimes of ~ 1000 hours at 50-60 C could be achieved, early reports did not approach this stability.

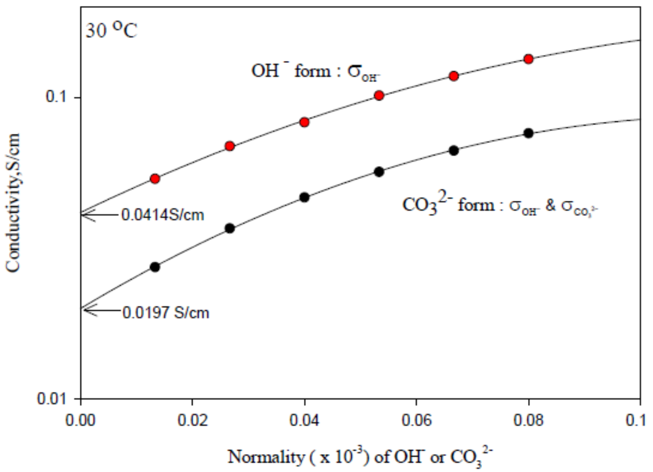
Alkaline (Anion Exchange) Membrane - Conductivity

Protons vs. Anions

*Cussler, Diffusion, 1997.

Ion	Infinite Diffusion Coefficient* (10^{-5} cm^2/s)
H^+	9.3
OH^-	5.3
CO_3^{2-}	0.9

Yu Seung Kim, 2010 DOE AMR presentation, available at http://www.hydrogen.energy.gov/pdfs/review10/fc043_kim_2010_o_web.pdf



At similar concentrations/mobilities, significantly increased ohmic losses should be expected.

Findings in membranes have reasonably reflected what might be expected (data at right, plus Tokuyama data shown in later presentation).

Electrocatalysis

Half reactions

- Hydrogen
- Oxygen
- Other anode fuels

Non-precious

- Examples will be presented, but baselining still required particularly of overpotential losses

Durability

- Under conditions of relevance (time, temperature, potential)

MEA performance (2006)

Membrane	IEC (meq g^{-1})	Electrolyte in Electrode	Anode Catalyst	Cathode Catalyst	Temp (°C)	Peak Power Density ($mWcm^{-2}$)	Current @ 0.5V ($mAcm^{-2}$)	OCV (V)
AAEM*	1.14	none	4 mg cm^{-2} Pt	4 mg cm^{-2} Pt	50	1.6	4	1.05
AAEM*	1.14	crosslinked aminated poly(benzyl chloride)	0.5 mg cm^{-2} Pt/C	0.5 mg cm^{-2} Pt/C	50	55	110	1.07
AAEM*	1.14	crosslinked aminated poly(benzyl chloride)	0.5 mg cm^{-2} Pt/C	4 mg cm^{-2} Ag/C	50	49	80	0.94
AAEM*	1.14	crosslinked aminated poly(benzyl chloride)	0.5 mg cm^{-2} Pt/C	4 mg cm^{-2} Au/C	50	24	40	0.85
ETFE-based AAEM	1.42	crosslinked aminated poly(benzyl chloride)	0.5 mg cm^{-2} Pt/C	0.5 mg cm^{-2} Pt/C	50	90	175	0.98
ETFE-based AAEM	1.42	crosslinked aminated poly(benzyl chloride)	0.5 mg cm^{-2} Pt/C	0.5 mg cm^{-2} Pt/C	60	110	230	0.96
Epichlorohydrin-based AEM	0.5-0.6	none	0.13 mg cm^{-2} Pt/C	0.13 mg cm^{-2} Pt/C	25	20	35	1.2
Epichlorohydrin-based AEM	0.5-0.6	poly(acrylic acid) and 1 M KOH	0.13 mg cm^{-2} Pt/C	0.13 mg cm^{-2} Pt/C	25	43	80	1.1

* Taken from AMFC Workshop Report, Alkaline Membrane Fuel Cell Workshop, Phoenix, AZ, Dec 11-13, 2006.

As of 2006, low power densities and no real durability data exist

- **Still a lack in durability data (particularly in literature), but a few examples will be presented here.**
- **Power density greatly enhanced.**

Breakout Groups

Session 1 (Salon D): Anion Exchange Membranes – **Stability –** 20 signed up for session; Leader: Jim Boncella, LANL   Scribe: Clay Macomber, NREL

Session 2 (Salon E): Anion Exchange Membranes - **Transport/Conductivity** - 21 signed up for session; Leader: Andy Herring, Colorado School of Mines   Scribe: Joe Elabd, Drexel

Session 3 (Salon H): **Electrocatalysis** in High pH (non-precious, complex fuels) - 26 signed up for session; Leader: Sanjeev Mukerjee, Northeastern   Scribe: Jacob Spendelow, DOE

Session 4 (Salon F): **MEA Issues** (ionomer solutions, electrode performance/durability) - 22 signed up for session; Leader: Dario Dekel, CellEra   Scribe: Doug Wheeler

Session 5 (Salon G): **System Issues** (carbonate, specific materials, water management) – 10 signed up for session; Leader: Anil Trehan, CommScope   Scribe: Huyen Dinh, NREL

Anion Exchange Membranes – Stability

Consider (Primary):

Stability of Alkaline Membranes (How long do today's materials last, what is reasonable intermediate target, what is ultimate goal – compare to PEMs)

Importance/Effect of conditions (Temperature, Hydration, Counterion, Peroxide?, Mechanical, RH cycling, other?)

Cations: Traditional/Alternative or Advanced

Membranes: Backbones (systems explored, impact on durability)

(Secondary):

Issues that crossover with Session 2 (for example impact of Water Uptake or phase separation on stability)

Anion Exchange Membranes - Transport/Conductivity

Consider (Primary):

Conductivity (Today's materials, targets, impact of counterion, comparison with PEMs)

Water transport (Today's materials, targets, impact of counterion, comparison with PEMs)

Water Uptake (Today's materials, targets, impact of counterion, comparison with PEMs)

Membrane Chemistries and how they impact structure and transport properties

(Secondary):

Issues that crossover with Session 1 (for example impact of Water Uptake or phase separation on stability)

Electrocatalysis in High pH (non-precious, complex fuels)

- State of the art non-precious anode and cathode catalysts
- Performance and durability in high pH
- What different approaches are being employed, with what kind of results, what are the merits and needs of specific approaches
- How does non-precious performance compare to Pt
- Comparisons between acid and alkaline performance (durability)
- Breaking down differences between ORR, HOR, and more complex (MeOH, EtOH, etc) anode reactions

MEA Issues (ionomer solutions, electrode performance/durability)

Fuel Cell Performance and Durability (today's, targets, comparisons with PEMs)

Specific issues critical to performance and durability (importance of fabrication, operating conditions)

Materials improvements of importance (membrane temperature stability, improved electrode structures)

Importance of operating conditions (temperature, humidification, fuel)

What are rates of performance loss and how do performance losses over time manifest themselves (ohmic, catalytic, delamination, catastrophic – membrane failure, other)

Issues involved with MEA fabrication and performance (AEMs much different typically than PEM materials and availability)

System Issues (carbonate, specific materials, water management)

- Applications/Power Range (portable, stationary, back-up, motive)
- Comparison to competing technologies
- Integration issues
- Fuel choice
- Operating conditions
- Carbonate concerns (tolerance, scrubbing, electrochemical purge, other?)

Workshop Deliverables

Report provided to DOE/ARO

- Assess the state of alkaline membrane fuel cell technology (Includes quantifying status in various areas of performance for AMFC materials, systems)
- Identify limitations
- Performance potential
- **Key research needs**
- Research timeframe/ level of effort

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 [i]	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.

Thank you all again for your participation

We look forward to an interesting and productive Workshop.