Innovative Concepts

Resonance-Stabilized Anion Exchange Polymer Electrolytes

Yu Seung Kim

yskim@lanl.gov

Los Alamos National Laboratory

UNCLASSIFIED

Project Objectives

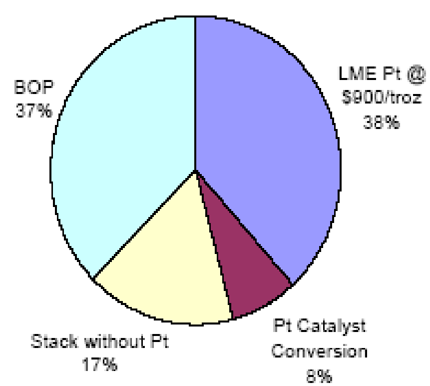
- **Technical Barriers: Fuel cell commercialization is a cost issue. Pt is the primary driver for cost.**
- **Technical Cost Target: $50/kW for fuel cell system.**
- **Objective: Reduce fuel cell cost by developing alkaline fuel cell system*.**

Economies of Scale   Impact of Commodity Materials

Approximately 46% of the 2005 high volume cost comes from Pt commodity cost and will not be subject to economies of scale.

2005 Key Assumptions		
Power density	mW/cm²	600
Cell voltage	V	0.65
Net power	kW_e	80
Gross power	kW_e	90
Production volume	units/yr	500,000
Pt cost	$/g ($/troz)	29 (900)
Pt loading	mg/cm²	0.75
Stack Quality Control (QC) and conditioning **not included**		

Fuel Cell System Cost—80 kW Direct H_2 (108 $/kW[1], $8,640)

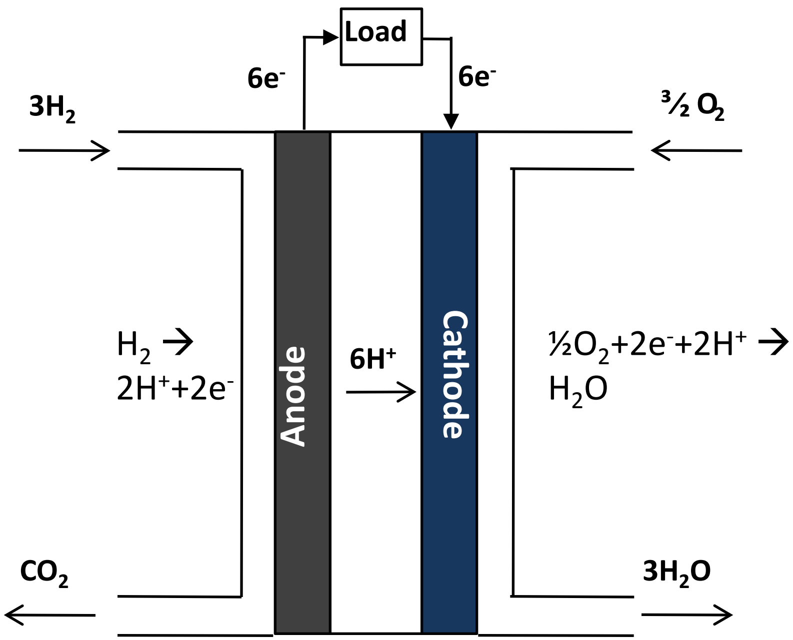


[1] kW of net power

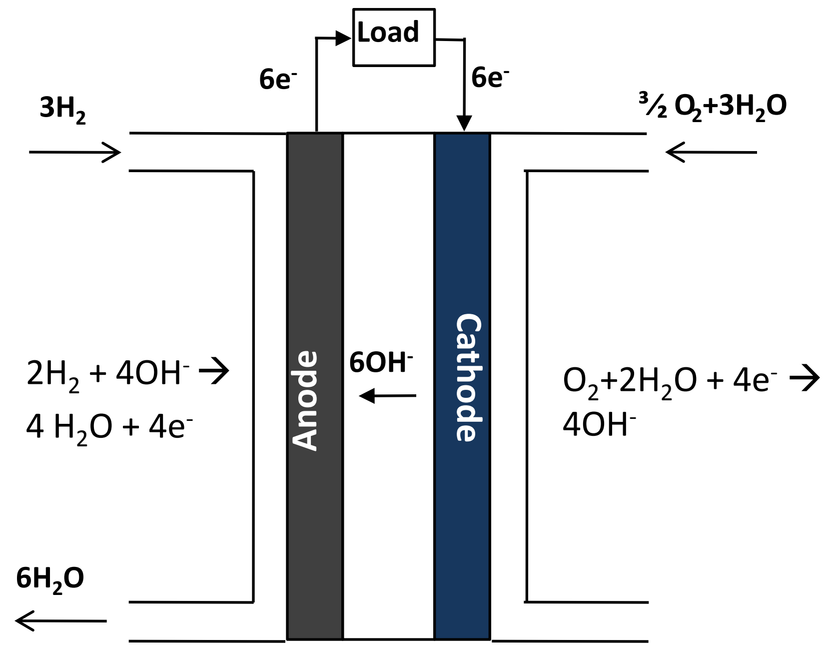
However, with time performance improvements will lower the grams Pt/kW_{net} over time.

Average Pt cost is over S 1,100/ounce last 6 month

PEMFC vs. AFC



Proton-Exchange Membrane
[PEM]



Alkaline Anion-Exchange Membrane
[AAEM]

No precious metal catalyst is needed in AFC!!

> **"Nitrogen-containing carbon nanotubes can act as a metal-free electrode with a much better electro-catalytic activity….. than platinum for oxygen reduction in alkaline fuel cells"** From Liming Dai et al. Science, 323, 760, Feb. 2009.

See other refs. 1) Lu et al. PNAS, 105, 52, 20611 (2008), 2) Lefevre et al. Science, 324, 71 (2009)

Technical Barriers for Alkaline Fuel Cells

ISSUES	Technical Barriers	Current Status	Technical Target
Stability	Fast degradation of AEM at high PH conditions	1M KOH 30 days [1]	> 500 h at 80^oC in 1 M KOH solution
Conductivity	Significantly low due to low mobility of OH^-, carbonate formation etc.	27 mS/cm (20^oC) [1] 34 mS/cm (50^oC) [2]	> 50 mS/cm at 80^oC
Electrode Processing	Poor solubility of AEM and lack of understand electrode structure	196 mW/cm^2 H_2/O_2 80^oC [1] 130 mW/cm^2 H_2/O_2, 50^oC [3] 94 mW/cm^2, H_2/O_2 50^oC [2]	> 200 mW/cm^2 H_2/air at 80^oC.

1. Y. Yan et al., *Angewandte Chem*. **121**, 6621-6624, (2009).
2. Varcoe et al., *Chem. Mater*. **19**, 2686-2693, (2007).
3. Varcoe et al., *Electrochem. Comm*. **8**, 839-843, (2006).

Approach –Guanidine Base AEM

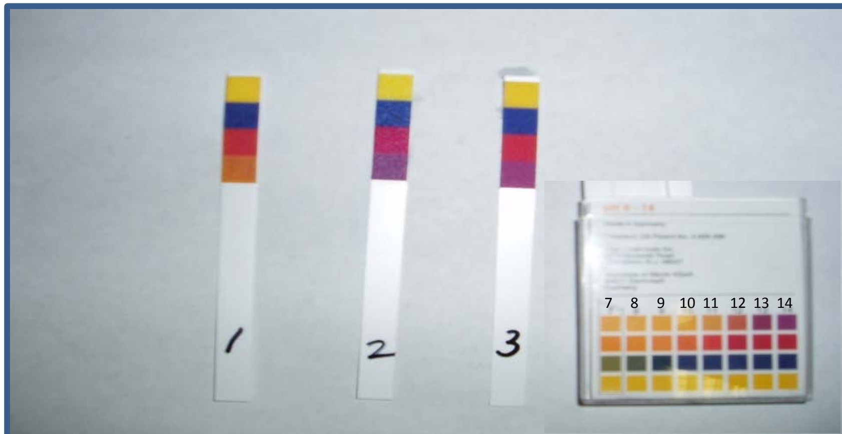
Advantage

- **High stability due to high basicity**
- **High conductivity due to resonance structure**
- **Excellent processibility due to solubility**
- **Commercially available and cheap material (~ $300/kg, Aldrich)**

Disadvantage

- **Polymer degradation due to high cation basicity**

Guanidine Base AEM



1: Triethylamine: H_2O (1:1 v/v)
2: Tetramethylguanidine: H_2O (1:1 v/v)
3: 1 M NaOH

Approach – Perfluorinated Electrode

Learning from PEMFC

- Electrode using hydrocarbon Ionomers were never broken!!!
- Perfluorinated membrane has high H_2 crossover

Ideal Combination

- Hydrocarbon membrane + Perfluorinated ionomer

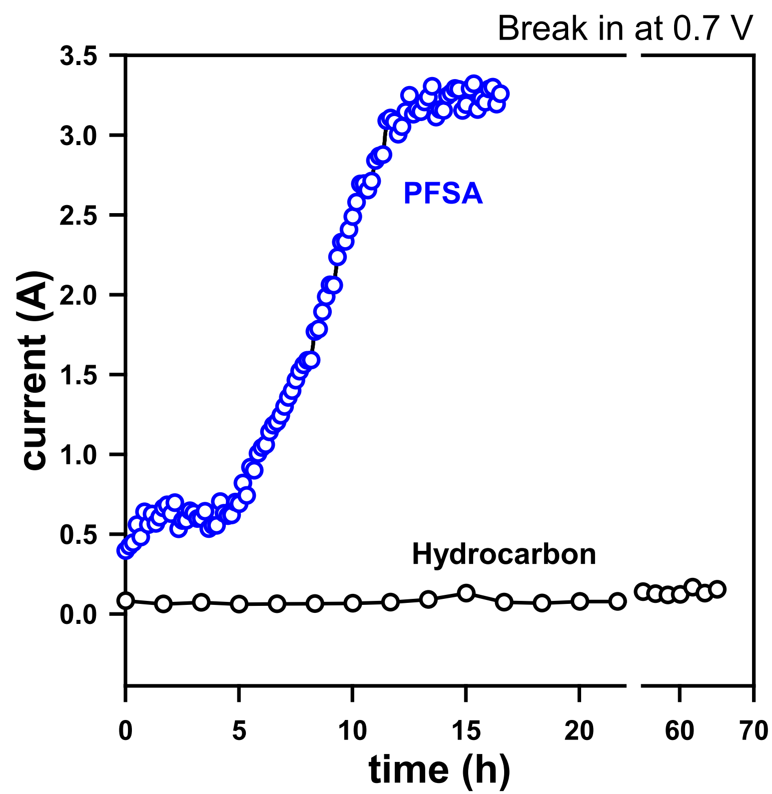
Dissimilar MEA structures

- Interfacial resistance issue

LANL US Patent Applications 20060240301
LANL US Patent Pending (2008)
JPL US Patent 6391486 (2002)

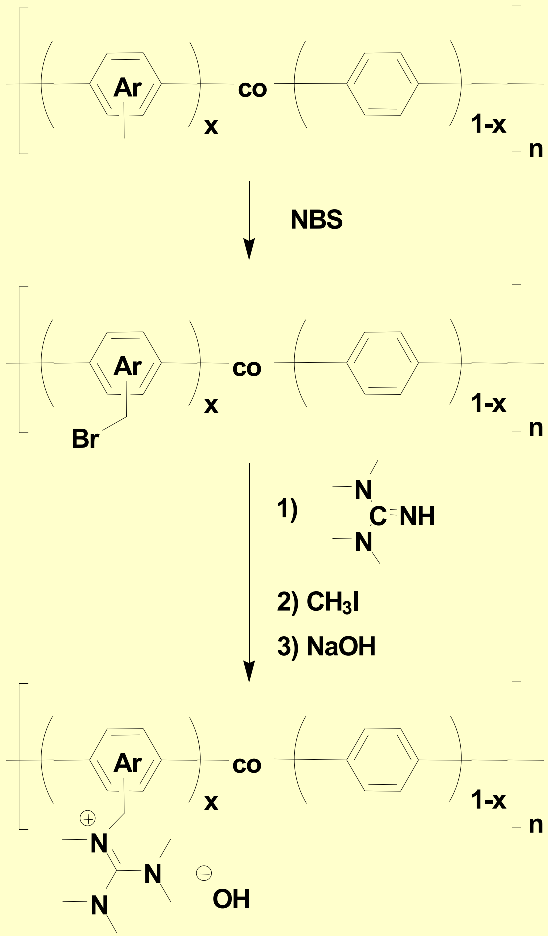
- Catalyst dispersion issue

LANL US Patent Pending (2009)



Fuel cell break-in: 80°C under fully humidified conditions
Catalyst: 20% Pt/C: 0.2 mg/cm^2
Data: high temperature working group meeting, 2009 DOE AMR Meeting

Examples



Polymer Synthesis

Cation Synthesis*
if necessary

* Derek H.R. et al. Organic Syntheses, coll. Vol.9, p. 101 (1997)

Project Timeline

September 1, 2009 — **Program start, kickoff meeting**

March 1, 2010 — Milestone: High MW Guanidine Base Hydrocarbon Membrane

DOE annual review

September 1, 2010 — Milestone: Highly Efficient Non-precious Metal catalyst

March 1, 2011

DOE annual review — Milestone: Electrode Formulation & MEA Processing

November 30, 2011 — **Program end** — Milestone: Hardware Delivery to DOE

Milestone	High MW Guanidine Base Hydrocarbon Membrane	Highly Efficient Non-precious Metal catalyst	Electrode Formulation & MEA Processing	Hardware Delivery to DOE
Decision Criteria	$[\eta]_{NMP}$: >0.7 *M*w: 50,000 g/mol Stability : > 500 h at 80°C in 1 M KOH	H_2 oxidation: < 30 mV higher than 0.1 mg pt/cm² O_2 reduction: < 50 mV higher than 0.1 mg pt/cm²	No HFR change* During 100 h fuel cell test	Max. power density: 200 mW/cm² H_2/air & Durability: > 800 h under steady-state operation

* Pivovar et al. *J. Electrochem. Soc.* (2007) Vol.154, p.B739

Go-No-Go Decision Point

September 1, 2009 | March 1, 2010 | September 1, 2010 | March 1, 2011 | November 30, 2011

March 1, 2010 — **Polymer Electrolytes**

September 1, 2010 — **Electro catalyst**

June 1, 2011 — **MEA**

Criteria

Film formable(50 μm thick)
σ= 0.05 S/cm at 80°C

Water uptake
< 60% at 30°C

Durability
>500 h in 1 M KOH

Criteria

H_2 oxidation
< 30 mV higher than
0.1 mg pt/cm^2

O_2 reduction
< 50 mV higher than
0.1 mg pt/cm^2

Criteria

Maximum power density
200 mW/cm^2 H_2/air (Pt)
150 mW/cm^2 H_2/air (non-Pt)

Durability
Less than 10 % performance
degradation after 500 h
H_2/O_2 fuel cell test

Organizations, Tasks and Budget

Organization	Tasks	Budget
Los Alamos National Lab. PI: Y.S. Kim	• PFSA ionomer synthesis • Electrode processing	FY 1: 300 K FY 2: 300 K
Sandia National Lab. PI: C. Fujimoto	• Hydrocarbon ionomer synthesis • Guanidine base synthesis	FY 1: 200 K FY 2: 200 K
Jet Propulsion Lab. PI: S.R. Narayan	• Electro-catalyst synthesis and characterization • MEA fabrication	FY 1: 150 K FY 2: 150 K