

#### "Fuel-cell System for Hand-Carried Portable Power"

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<u>Outline</u>



**Brief General Introduction to Power Sources** 

Borohydride Fueling and the Hydrogen – Air Fuel cell

Other Research projects at ASU

1-Regenerative Borohydride Fuel Cell, RBFC (NASA)

2-Reformed Hydrogen Fuel Cell, RHFC (Boeing)

3-Proton Conducting Membranes (ARO, NASA)

4-Oxygen Reduction on Steel and Ni alloy (DoE)

5-SAM Electrocatalysts (ARO)



### Introduction to Power Sources

ENERGY CONVERSION VS. ENERGY STORAGE



Driving Force: Substantially decreased size, weight, and cost with improved application lifetime, safety, environmental compliance and increased mobility.



#### **Commercial Portable Power Requirements**



WINtech & Applied Nano Bioscience Centers at ASU

**Trend in Portable Electronic Products** 







### **Projection of Energy on Body per Year**





#### **Categories of Fuel Cells and Applications**

Solid Oxide Fuel Cell Large Power utility, Hydrocarbon Fuel, T = 700°C, Seals

<u>RHFC HT-PEM, MC and Phos Acid</u> Residential Power, Impure  $H_2$ , T = 190°C, Low V<sup>cell</sup>

<u>Nafion PEM</u> Automotive&Backup utility, pure  $H_2$ ,T = RT to140°C, cost

<u>DMFC as battery replacement</u> Hand – Carried Portable Power, MeOH/Water, RT, stability, cost

Nafion PEM with Borohydride as battery replacement Hand – Carried Portable Power, NaBH<sub>4</sub>/water, RT,opportunity



### **Conclusion for Approach to Portable Power**

- Hydrogen-Air PEM Fuel Cell
  - Reliable
  - Maintainable
  - Affordable
- Hydrogen source
  - traditional fuel problem proposed to be solved by generating hydrogen using a microfluidic reactor

- to generate hydrogen (H<sub>2</sub>) gas by catalytic (Ru) hydrolysis of alkaline aqueous sodium borohydride (NaBH<sub>4</sub>) solution

- to send resulting gaseous  $H_2$  to anode and borax (NaBO<sub>2</sub>) solution to waste receptacle (volume vacated by NaBH<sub>4</sub> hydrogen storage solution).



### Hydrogen: the universal fuel

A transition to hydrogen as a major fuel in the next 50 years could fundamentally transform the U.S. energy system, creating opportunities to increase energy security through the use of a variety of domestic energy resources for hydrogen production while reducing environmental impacts, including atmospheric  $CO_2$  emissions and criteria pollutants.

The National Academies Committee on Alternatives and Strategies for Future Hydrogen Production and Use

February 2004



### Sodium Borohydride System Overview

### **Diagram of ASU Room Temperature** <u>H<sub>2</sub>-generator fed Fuel Cell System</u>





- H<sub>2</sub> generation:

via low-temp catalytic NaBH<sub>4</sub> hydrolysis

Ru catalyst NaBH<sub>4</sub> + 4 H<sub>2</sub>O  $\longrightarrow$  4 H<sub>2</sub> + NaB(OH)<sub>4</sub>





#### First Order Estimation of Efficency for Low Temperature Borohydride Fuel Cell System Objective is for 1W to 10W for 9,000 hours (1year).

Efficiency Breakdown	GOAL		Today		
System Component	Efficiency		Efficiency	Comments	
Fuel Input Volume	95%		95%	Fuel loss (fresh cartridg w/ 1 year half life used within a month).	
Liquid Pump	99%		90%	Piezo- or echem- pump (milli-liters/minute); mW's parasitic loss.	
Air Pump	95%		80%	Miniature Air pump/fan (100 sccm) 0.1 W parasitic loss.	
Yield of H <sub>2</sub>	98%		98%	At least 98% hydrolysis; depends on rate of $H_2$ generation	
Anode polarization	98%		98%	Voltage losses. Operating potential ~ 0.04V vs NHE (ideal is zero)	
Cathode Polarization	75%		70%	Operating potential ~ 0.8V vs NHE (Ideal is 1.23V); decay < 10 microV/hour	
Water Return Subsystem	99%		90%	If needed, same as liquid pump	
Anode/Cathode collection	95% 90% Current collector sheet resistance < 0.2 Ohm cm <sup>2</sup>		Current collector sheet resistance < 0.2 Ohm cm <sup>2</sup>		
Membrane IR Loss	95% 90%		90%	Proton conductivity > 0.01 S cm <sup>-1</sup>	
Total Elec. Loss, R-internal	95% 90%		90%	At max power where R-load = R-internal, then iR loss is $j^2$ times R-internal	
DC-DC Converter	90%	80% Assumes stack voltage of 0.7 to 2.8V.			
Gas/Liquid Separation	100%	100% 100% Passive devices			
Net System Efficiency	49%		24%	25 to 45 % is reasonable	
				Areal power density = 0.1 (passive air) 0.35 W/cm <sup>2</sup> (active) at 0.8V per cell.	
NET POWER DENSITY	100	W/liter	**	Volumetric power density =100 W/I	
<b>NET ENERGY DENSITY 1000</b> Wh/I <b>**</b> For NaBH <sub>4</sub> -30		For NaBH <sub>4</sub> -30; 2500Wh/I x Efficiency = System Energy density			
				System Energy density=~1250Wh/l, ignoring V(Fuel Cell)	
				If 10% total volume is Fuel Cell, then System Energy Densit is ~1000Wh/l.	



## Fuel Cell



### Fuel cell

### - best alternative to batteries for man portable power



<u>Fuel cells are similar to batteries but:</u> -Have higher energy density for \* for longer application life than a battery of same size <u>Or</u> \*same application life with smaller lighter fuel cell than the battery that's replaced

-Allow instant chemical recharge

<u>Room temperature fuel cell ideal for:</u> -portable applications -close proximity to people!

Schematic Diagram of a Conventional Fuel Cell



### **Actual Fuel Cell Hardware**





### **Electrode / Membrane Interface in a MEA**



Interfacial region between bulk solid polymer electrolyte (SPE) membrane and the active-layer of Pt-catalyzed gas-fed porous electrode.



#### **Effect of Electrode Preparation on MEA Performance**



Polarization curves for 3 MEAs with different amounts of Nafion.  $O_2$  /  $H_2$  flows: ~15 : 20 sccm. T=22°C. Ambient pressure.

Red: Blue: Black:

no Nafion (too little)
13 mg Nafion (too much)
4.5 mg Nafion (just right)
in 50 mg of electrode(2.3 cm <sup>2</sup> )

#### **Conditions**

Nafion117 membrane E-TEK V2 ELAT Electrode Pt loading=0.5mg/cm<sup>2</sup>.

 $A^{active} = 1 cm^2$ .

Electrodes hot pressed on membrane for 2 minutes at 120°C and 2800 lbs.





Performance of Fuel Cell fed hydrogen and oxygen in time. Pt Loading = 0.5 mg/cm<sup>2</sup>. 4.5 mg Nafion per 50 mg electrode.



### <u>An attractive add on:</u> Buckyball Proton Conducting membrane

 $\sigma_{\rm H+}$  of C60(OH)<sub>12</sub> = 10<sup>-5</sup> S cm<sup>-1</sup> at ~ 25 °C  $\sigma_{H+}$  of C60(OH)<sub>6</sub> (OSO<sub>3</sub>H)<sub>6</sub> = 10<sup>-2</sup> S cm<sup>-1</sup>

Simplifies fuel cell water handling since no water transferred with proton
Allows "dead ending" of hydrogen!!



### **Conclusions on Fuel Cell**

### \*Room temperature hydrogen-oxygen fuel cell provides ~ 0.1W/cm<sup>2</sup>

\*MEA consisting of Nafion 117 with E-TEK ELAT electrode is suitable for developing system

Need a fuel !!



# Hydrogen Generator

"A Safe, Portable Hydrogen Generator Using Aqueous Borohydride Solutions", S.C. Amendola, S.L. Sharp-Goldman, M. Saleem Janjua, M.T. Kelly, P.J. Petillo, and M. Binder (Millennium Cell LLC) Joint International Meeting of theECS and ISE - Honolulu, Thursday, October 21, 1999. Battery/Energy Technology Joint General Session, Battery Division/ Energy Technology Division.



## **Description of fuel system**

- H<sub>2</sub> storage in sodium borohydride (NaBH<sub>4</sub>) solution, 2200 Wh/Kg for 30wt% NaBH4, 3wt% NaOH in 67wt% H2O
- > Catalytic reactor releases  $H_2$  at ambient T and P,
- > Low power pumps to move liquid fuel,
- > Orientation independent

Gas – Liquid separator membrane.



### **Fuels and Relative Energy Density**



Volumes of different Fuels equivalent to ~10 Watt-hours of Electrical Energy at 100% Chemical to Electrical Conversion Efficiency.



### **Preparation of Ru Catalyst for H<sub>2</sub> Generation**



Solution soaked  $RuCl_3$  on alumina pellets, decanted, air dried. Samples were heated under 5% hydrogen, balance helium. Heated at 100°C/hr to 150°C or 700°C; no dwell and 6 hour dwell.



### **Alumina Geometries for supporting Ruthenium Metal**



- Catalyst support features: High surface area (220m<sup>2</sup>/g) g-alumina with total pore volume of 0.62cc/g.
- Improved packing of catalyst bed with spherical alumina support



### <u>Elemental Analysis by EDAX</u>



2 wt.% Ru on alumina 6 hour dwell time



5 wt.% Ru on alumina no dwell time

5 wt.% Ru on alumina 6 hour dwell time



### **First Generation Hydrogen Reactor**



Fuel mixture composition: 30 wt% NaBH4, 4.3 wt% NaOH, 67 wt% H2O Provides 2250 Watt-hour per liter of mixture at 100% conversion efficiency *Mass of Ru estimated at 52mg!* 





Effect of catalyst heat treatment in forming gas





• Note: No GAS OUT was observed when Ru on alumina was replaced by equivalent weight of alumina only.



**Catalytic Hydrogen Generation (cont.)** 

Effect of rinsing catalyst with water



#### Effects of Rinsing Catalyst in DI Water

\* Weight % of Ru in ruthenium-on-alumina pellet is <u>4.6 wt%.</u> by EDAX and volume of colored cross-section



### **Hydrogen Generating Reactor**



Expected to flood chamber and generate gas and collect at top

Only utilized Catalyst on bottom

So evaluated catalyst activity to optimize Ru utilization in reactor!

Fuel mixture composition: 30 wt% NaBH4, 4.3 wt% NaOH, 67 wt% H2O

Mass of Ru in reactor estimated at 52mg!

### **Catalyst Characterization**





#### **Calibration of Apparatus**

Apparatus for: H2 flow by weight of water displacement



BH<sub>4</sub> solution and catalyst

Displaced water

#### Rate of hydrogen generation = k x catalyst area x [NaBH<sub>4</sub>]

k = rate constant, [NaBH4] near constant. Effect of catalyst area???



### **Catalyst Characterization**

#### Rate of Hydrogen Generation Based on Different Catalyst Weight



WINtech & Applied Nano Bioscience Centers at ASU



### **Catalyst Characterization (con't)**

no loss catalytic activity in time









### **Orientation Independence**

H<sub>2</sub> Generation Actual through **Orientation Independent Gas/Liquid Separating Membrane** H<sub>2</sub> Generator 62 sccm of hydrogen 70 Ru catalyst (below membrane) H<sub>2</sub> generated (sccm) 50 30 Celgard 4560 G/L OUT IN Area membrane = 3cm<sup>2</sup> 10 Catalyst mass = 0.8mg 0 0.2 **Celgard Membrane** 0.4 0.6 0 (Gas/Liquid Separator) NaBH<sub>4</sub> flow (sccm)



### **Conclusions on Catalytic Hydrogen Generator**

- Stable hydrogen storage solution
  - -30% NaBH<sub>4</sub> solution initially stores 2250 Wh/l -1/2 life of pH 14 solution is > 1 year (450 days).
- Active and Stable Hydrogen Generating Catalyst Catalyst activity is stable for thousands of hours
- $H_2$  generation rate is proportional to catalyst area Based on the cost of Ru metal and estimates of Ru used, Cost for Ru in H<sub>2</sub> generator would be < \$0.50 Watt.
- Celgard membrane is gas/liquid separator for gravity independence



### **System Conclusions**

Fuel-cell package projected to give > 4x application life of same sized battery-pack as a result of:

energy dense H<sub>2</sub> storage (E<sup>d</sup> > 2200 Wh/liter or kilogram)
 compact & orientation-independent H<sub>2</sub> generator
 reliable and efficient H<sub>2</sub> - air fed fuel cell.

Low temperature is compatible with hand-carried portables.

- Safe: H<sub>2</sub> storage solution is
  - nontoxic, nonflammable
  - liquid alkaline borohydride storage cartridge leaks slowly
     pressurized tank of H<sub>2</sub> is hazardous & lost nearly instantly.
- Fuel cell system is cost competitive with batteries at < \$10/Watt.



### **Future Research on Room Temp System**

Refine H<sub>2</sub> generating reactor features: \* Ruthenium-coated titanium metal support \* New gas-liquid separating membranes \* effect of storage solution pH and additives

Integrate H<sub>2</sub> generator to Low-power piezo liquids pump & fuel cell

Integrate power and control electronics

Model system features using FEMLab software



### Schematic Diagram of H<sub>2</sub> Generator with Fuel Cell





#### *Liquid Pump Characterization* Piezo-Pump with 15 mm diameter PZT





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2-Reformed Hydrogen Fuel Cell, RHFC (Boeing Aircraft Corp.)

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5-SAM Electrocatalysts (US Army Research Office, ARO)



#### **1-Solar Regenerated Borohydride FuelCell**



<u>Conservative Approach</u> - Solar to Electric converter - Water Electrolyzer - H<sub>2</sub>, O<sub>2</sub> regeneration - PEM FuelCell

<u>Problem</u> - gas storage!

Educational Regenerative Fuel Cell System



Electrolytic Process for the Production of Alkali metal Borohydrides, UP Patent 3,734,842, H.B.Cooper May 22 (1973.

INVENTUR. HAL. B. H. COOPER

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generate:

Advantage

**1-Solar Regenerated Borohydride FuelCell** 



### **2-RHFC: 10-Watt Planar Stack**



Boeing Aircraft & NuElement Tacoma, WA





Polarization (I/V) Curve for PBI fuel cell in Standard Graphite Housing T=160°C, Hydrogen / Air, Teflon gasket, Pt loading = 1 mg/cm<sup>2</sup>



• Power per stack =  $0.6 V \times 200 mA/cm^2 \times 25cm^2$  per cell x 4 cells = 12 Watt



#### 2-Relative Performance of Graphite-housed PBI-MEA Fed pure H<sub>2</sub> versus simulated reformate

V-cell @ 200mA/cm<sup>2</sup> in *Graphite* Housing

after run in ceramic housing, T = 165 to  $180^{\circ}$ C, A = 2.62cm<sup>2</sup>, Pt loading = 1 mg/cm<sup>2</sup> Air fed cathode, H<sub>2</sub> fed anode except where indicated in figure.



Power per stack =  $0.6 V \times 200 mA/cm^2 \times 25cm^2$  per cell x 4 cells = 12 Watt



#### **3-Proton Conducting Membranes**

with Prof. C. Austen Angell, ASU Chem. Dept.



Polarization curves on Pt-catalyzed gas-fed electrodes in EAN-EA-H<sub>2</sub>PO<sub>4</sub> and 85% H<sub>3</sub>PO<sub>4</sub>. Flow H<sub>2</sub> = 40sccm, O<sub>2</sub> = 30sccm, E-TEK electrode area = 0.5cm<sup>2</sup>. Pt loading = 0.5 mg/cm<sup>2</sup>.



1320

450

#### 4-Corrosion...Surface FTIR of Steel



Electrochemical Fourier Transform Infrared (Echem-FTIR) reflectance surface spectroscopy method: (a) Electrochemical Infrared Reflectance Cell, (b) Reflectance Absorption Optics, (c) Infrared difference spectra for carbon steel in 1M KOH.



#### 4-Surface Voltammetry of Steel



Cyclic voltammogram for an ASTM A516 steel disk (A=0.3 cm2) in aqueous anaerobic 1M KOH solution (pH=14). Room temperature. Scan rate = 10 mV/sec.

Voltammetry peak assignments made from in situ FTIR experiments



#### 4- Oxygen Reduction on Steel and Ni alloy



Linear regression of the ring and disk data Yields plots of  $i_{dl}/(i_{dl}-i)$  versus  $\omega^{-1/2}$ which yield slopes, S<sub>2</sub>, and intercepts, I<sub>2</sub>.

Regression of the  $i_D/i_R$  versus  $\omega^{-1/2}$  plots yields slopes, S<sub>1</sub>, and intercepts, I<sub>1</sub>.

These S and I values can be used in the following expressions

 $k_{1} = S_{2} Z_{1} (I_{1} N - 1) / (I_{1} N + 1)$   $k_{2} = 2 S_{2} Z_{1} / (I_{1} N + 1)$  $k_{3} = Z_{2} S_{1} N / (I_{1} N + 1)$ 

Schematic of rotating ring disk electrode (left)

O<sub>2</sub> reduction current (right, bottom) on a steel disk

Peroxide  $(H_2O_2)$  oxidation current (right, top) on the Au Ring.



#### **Result of Rotating Ring Disk Electrode (RRDE) Study**

rate constants for oxygen reduction

**Rates constants for O<sub>2</sub> reduction at different potentials** 

**Oxygen Reduction Mechanism** 

	Potential versus SCE			
Rate Constant	0.85 (volts	(IS) 0.45		
(cm/s) k <sub>1</sub> (anodic)	360 x 10 <sup>-5</sup>	59 x 10 <sup>-5</sup>		
k <sub>2</sub> (anodic)	<sup>a</sup> 960 x 10 <sup>-5</sup>	<sup>b</sup> 230 x 10 <sup>-5</sup>		
k <sub>3</sub> (anodic)	<sup>a</sup> 950 x 10 <sup>-5</sup>	65 x 10 <sup>-5</sup>		

<sup>a</sup>Hydroxide (water) dominant product of O<sub>2</sub> reduction <sup>b</sup>Peroxide product of O<sub>2</sub> reduction



Solution peroxide



#### 5-Self Assembled Monolayer (SAM) of Electrocatalysts



SAM precursor for O, catalysis



Metal macrocycle tether anchor

Macrocycles can include: porphyrins, phthalocyanins, bi-nucleating ligands, etc.

Schematic diagram of SAM of catalyst on an inert metal surface

Schematic diagram of the precursor to SAM



### **5-Precursors to Electroactive SAMs**





#### **Model of Surface Catalyst**

#### 6-FHP

6-ferrocenylhexyl phosphonic acid

#### **Catalytic SAM Precusor**

#### Co-P

Co(II) 5-(4dihydroxyphosphorylphenyl) 10,15,20 tris(3,4dimethoxyphenyl) porphyrin



#### 5-Voltammetry of Ni with Electroactive Solution vs Surface Species



Voltammograms of Ni and Pt in 0.1 molar NaClO4 in 50% MeCN and 50% water under Argon.

- (a) Ni with 0.5 mM ferrocene present;
- (b) Pt with 0.5 mM ferrocene present;
- (c) Ni with no ferrocene in solution.

Scan rate: 100 mV/s; area of all electrodes: 2 cm2.

Voltammograms of a Ni electrode in 0.1 M NaClO4 in 50% MeCN and 50% water under Argon.

- (a) the first scan with 6-FHP on the Ni
- from 0.5 mM FHP solution in 7:3 CHCl3: CH3OH;
- (b) after continuous scanning 10 minutes;
- (c) after stored in electrolyte for 24.5 hours and retested;
- (d) bare Ni electrode.

Scan rate: 100 mV/s; Area of Ni: 2 cm2.

5-O<sub>2</sub> Reduction Catalyzed by SAM of Co-P on ITO



Voltammograms of ITO in 0.01 M triflic acid (a) with a SAM of Co-P under  $O_2$ , (b) with a SAM of Coporphyrin under Ar and (c) bare ITO under Ar. Scan rate 100 mV/sec. Electrode area = 2.7 cm<sup>2</sup>.

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**Prospects for Future Research** 

\* Further size reduction of Borohydride system using MEMS

\* Nanoporous supports with SAM of electrocatalysts

\* Biofuel cells & Biosensors

\* Develop new non-Pt Electrocatalysts (e.g., for H<sub>2</sub> oxidation)

\* Model Fuel Cells with FEM-lab



#### Arizona State University - BioDesign Institute



ASU AZ Biodesign Institute View from campus

GouldEvans LORD · AECK · SARGENT



#### Arizona State University – Flexible Display Center

