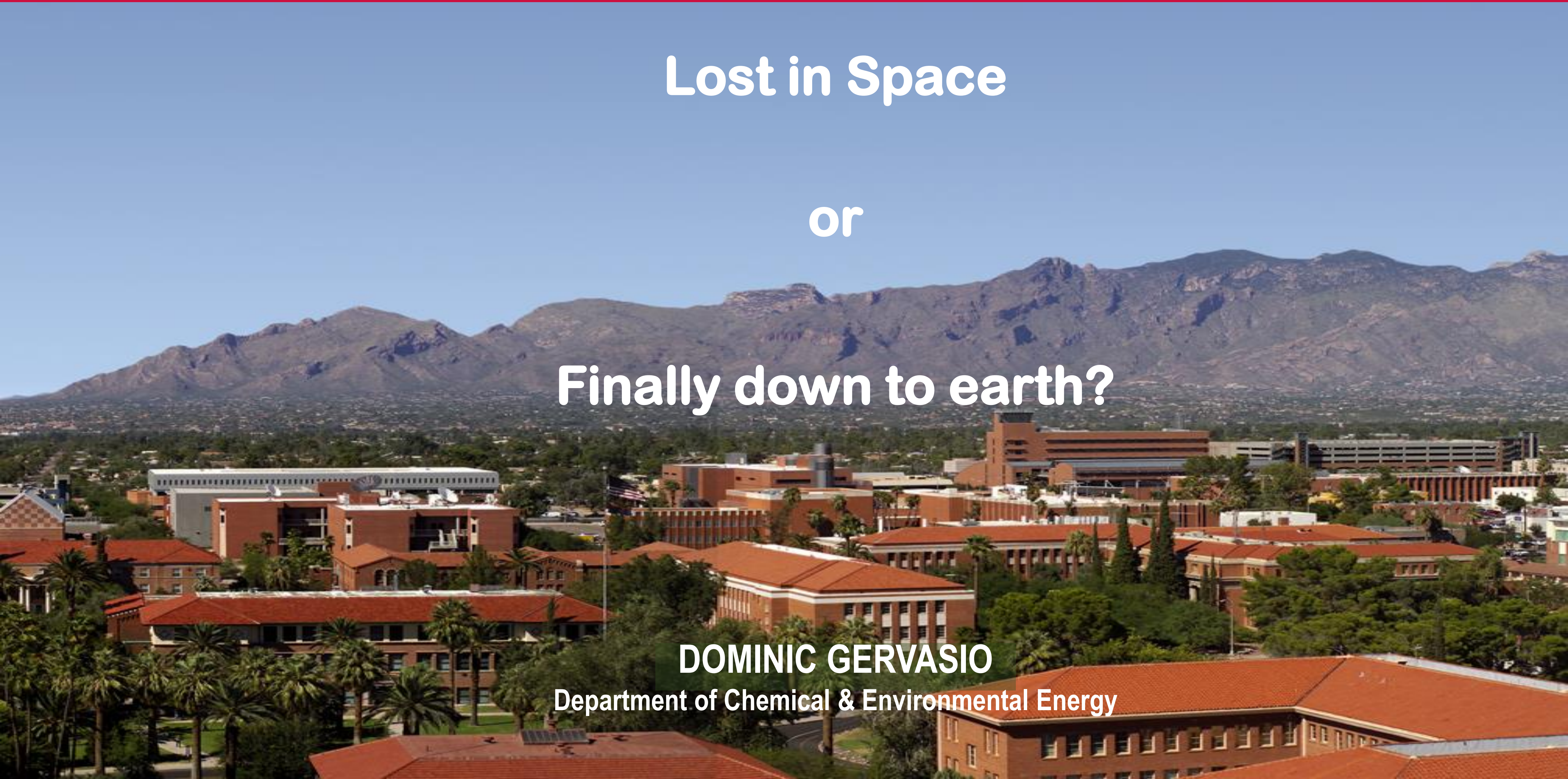
Fuel Cells Revisited



Lost in Space

or

Finally down to earth?

DOMINIC GERVASIO

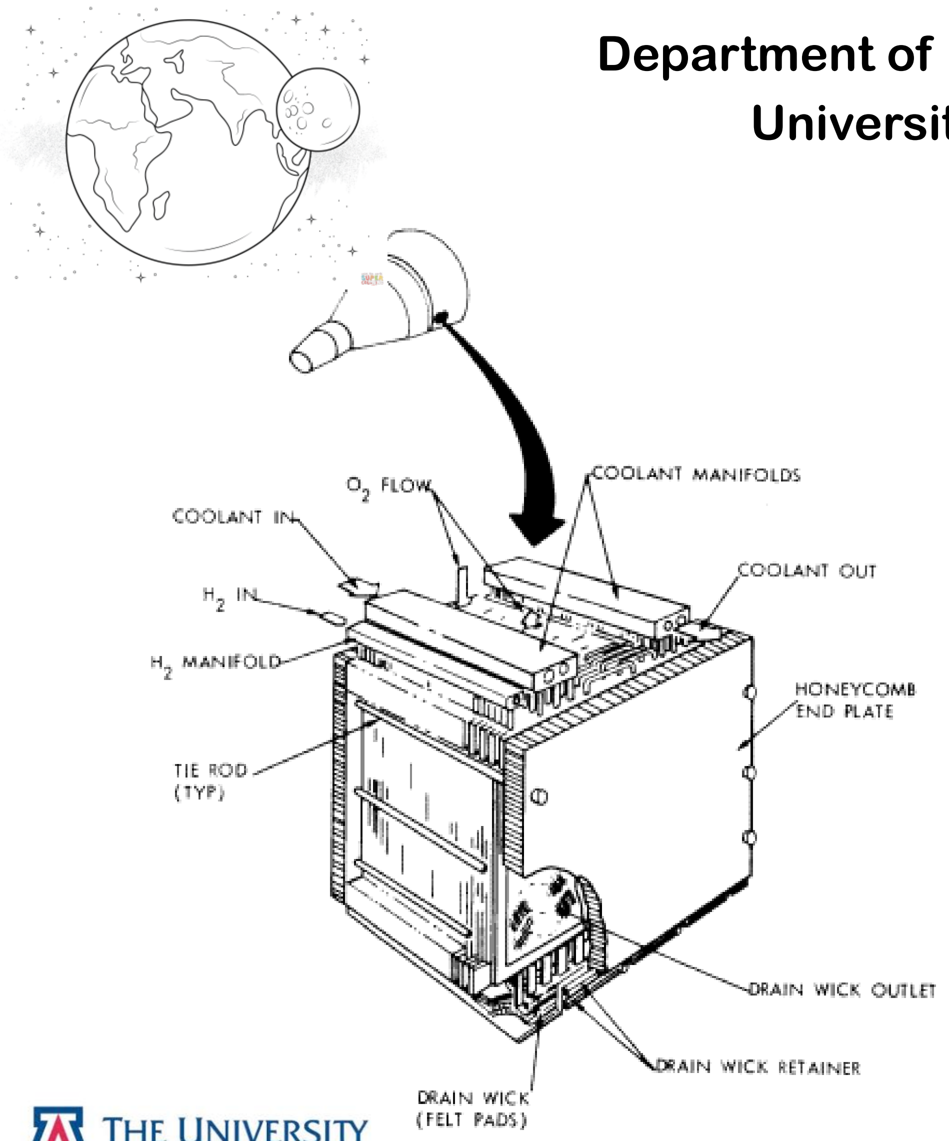
Department of Chemical & Environmental Energy

Fuel Cells Revisited: Lost in Space or finally down to earth?

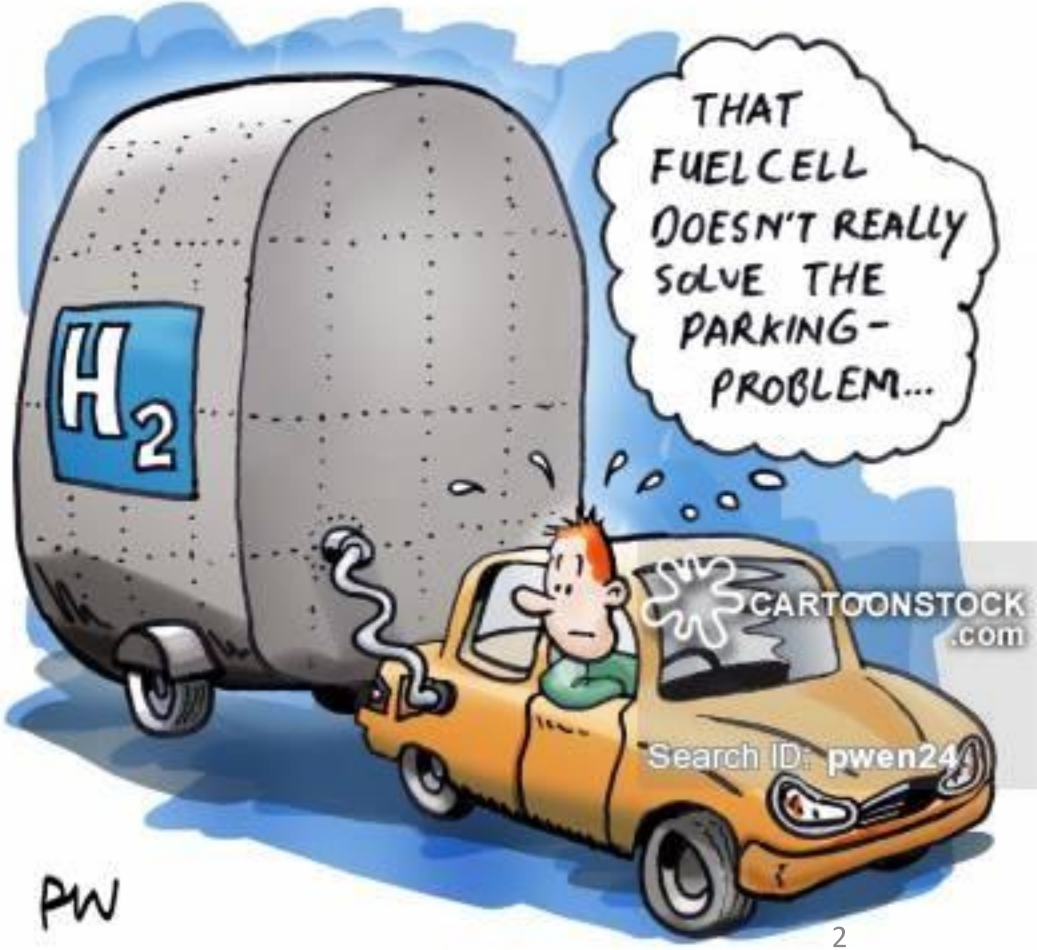
Dominic F. Gervasio

Department of Chemical and Environmental Engineering

University of Arizona, Tucson, Arizona USA



?



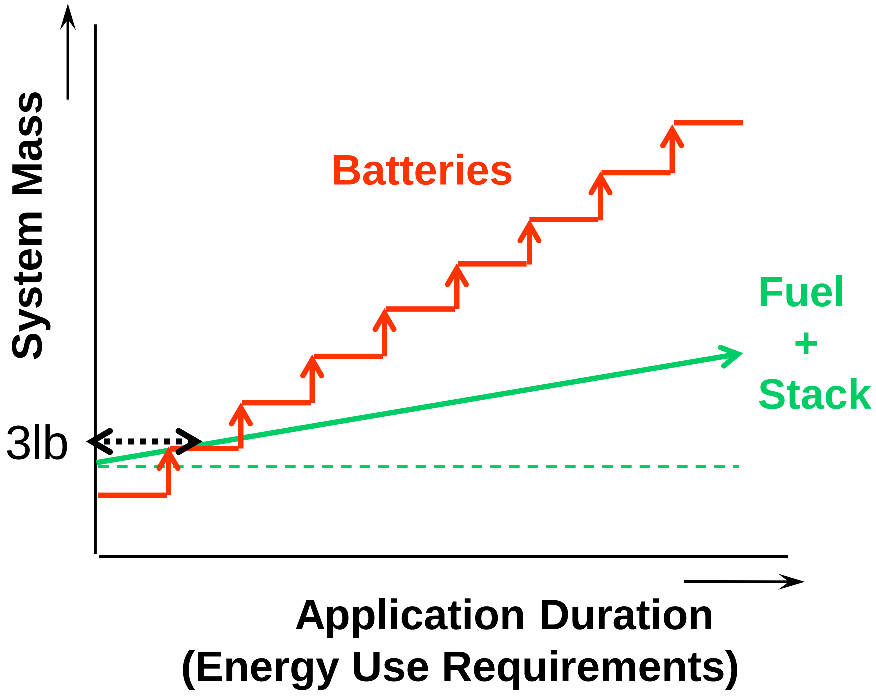
THE UNIVERSITY OF ARIZONA

Outline

- Fuel cell versus battery
- Evolution of fuel cells … in space…size and weight reduction
- Special consideration for earth-bound fuel cells… air not O_2
- **DUUHH*!!*** … A fuel cell power source is a ***system***
- *The* critical component – the electrolyte membrane
- Prospects for future development

Fuel cells and batteries are both DC power supplies…what's the difference?

Batteries: use dissimilar metals to generate cell voltage… simple, but metals are not energy rich
Fuel Cells: dissimilar fuels generate voltage…. fuels are energy rich, but *not simple to use on Earth*



Fuel	E^d (Wh/kg)
Hydrogen	33,000
Diesel Fuel	13,200
Methanol	6,200
$NaBH_4$-30%	2,500
TNT	1,400

Battery:	E^d (Wh/kg)
Rechargeable (est. max.)	200
Li/SO_2 Battery (primary)	176
Alkaline Battery (primary)	80
Nickel-Cadmium (secondary)	40

H_2 fuel cell
vs
Li battery

Energy rich fuels in fuel cells* give *lower size and weight* *with increasing application duration

Consequences ?

Gasoline versus battery powered car

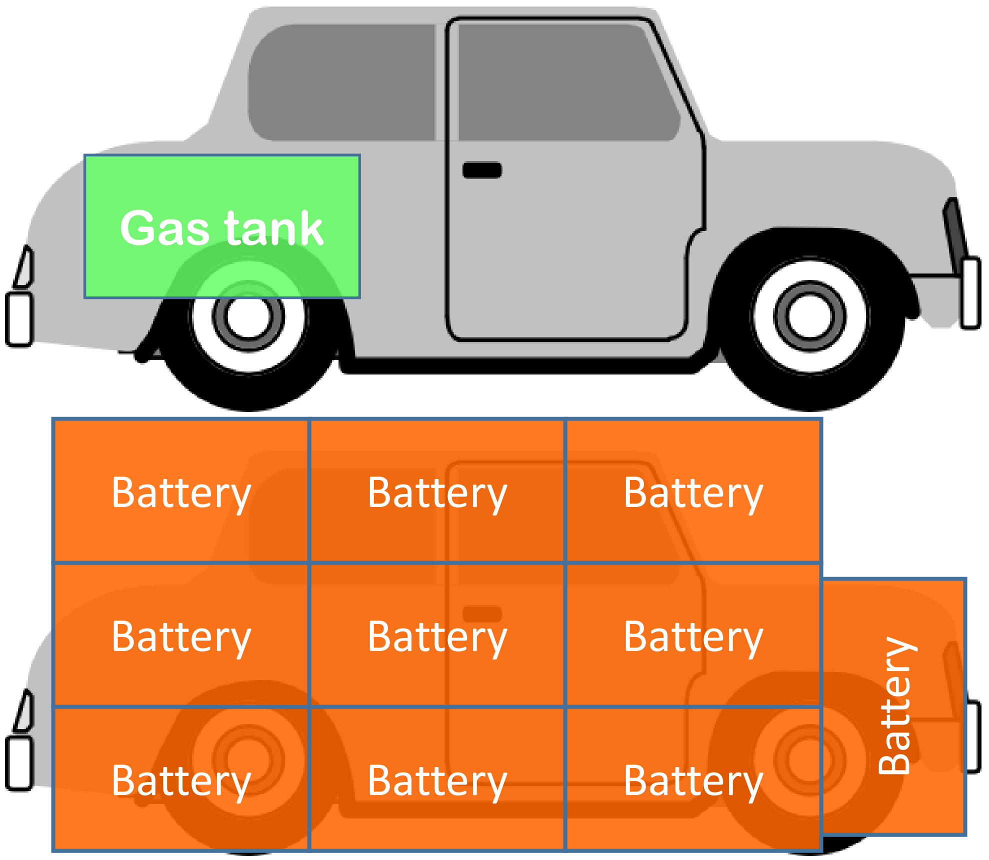
1. Gasoline is cheap compared to batteries

One gallon of gasoline equals 6.25 lbs 6.25 / 2.2046 lb/kg = 2.835 kilograms

13,200 Whr/kg x 2.835 kg/gal = 37422 Wh/gal x $3/gal = < $0.08 per kWh

Lithium battery > **$20/kWh** (or is equivalent to $750 per "gallon" of electricity) ; NOT counting cost of charging from grid

2. Gasoline gives more energy per kilogram compared to batteries



Gas Tank is 1/10 the size of car for 400 mile trip with quick refill (minutes)

Battery "Gas Tank" *is* size of car for 400 miles

There is nowhere

- to put your golf clubs
- or even for passengers to sit!

with slow refill (hours)

Battery only cars just won't do !

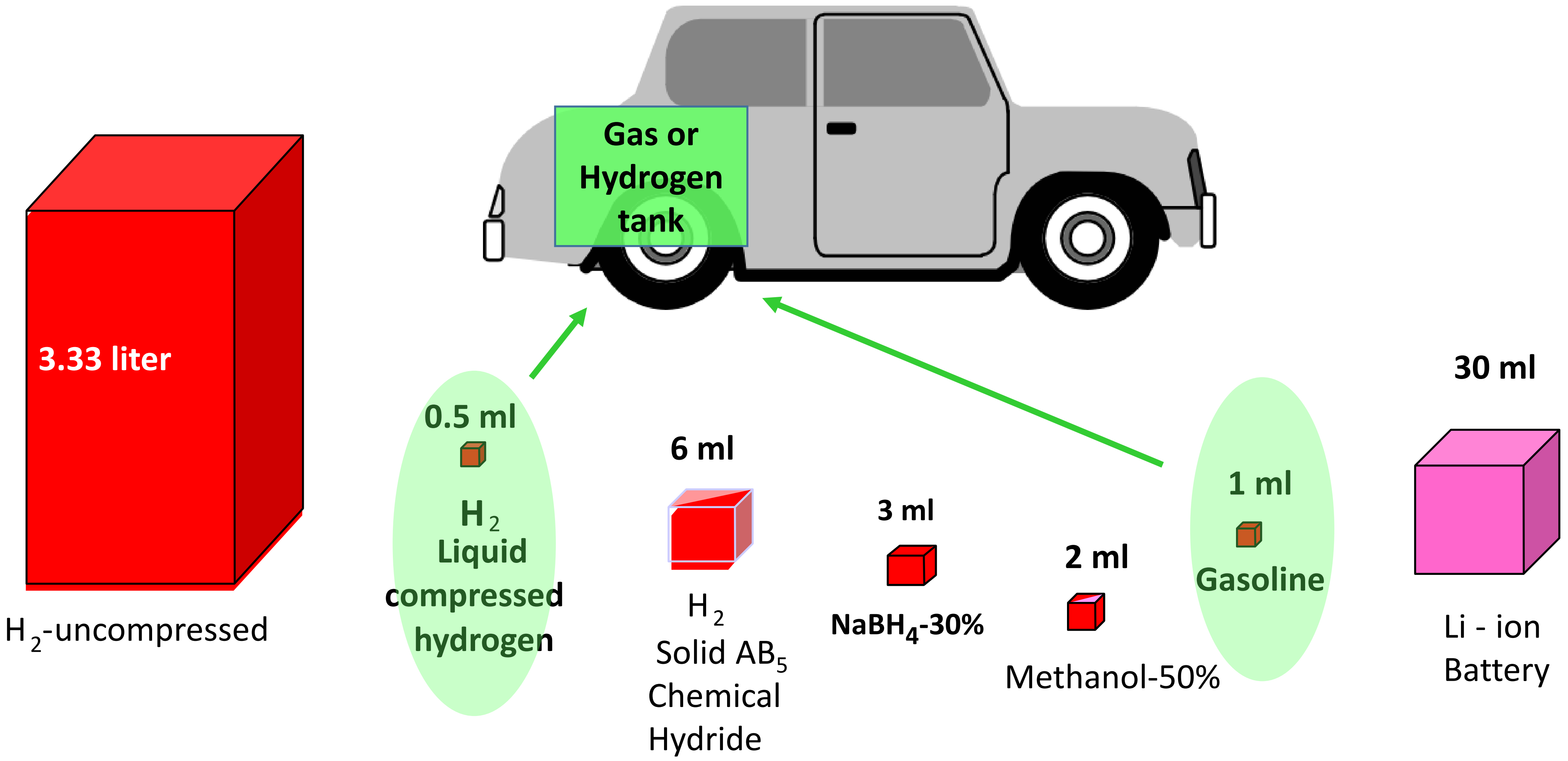
Q & A

Question: If a battery won't do as the primary power source substitute for an ICE powered car … then what can you use?

Answer: a fuel fed electric-powered car

… a Fuel-cell car

Hydrogen fuel used in fuel cells is comparable to gasoline



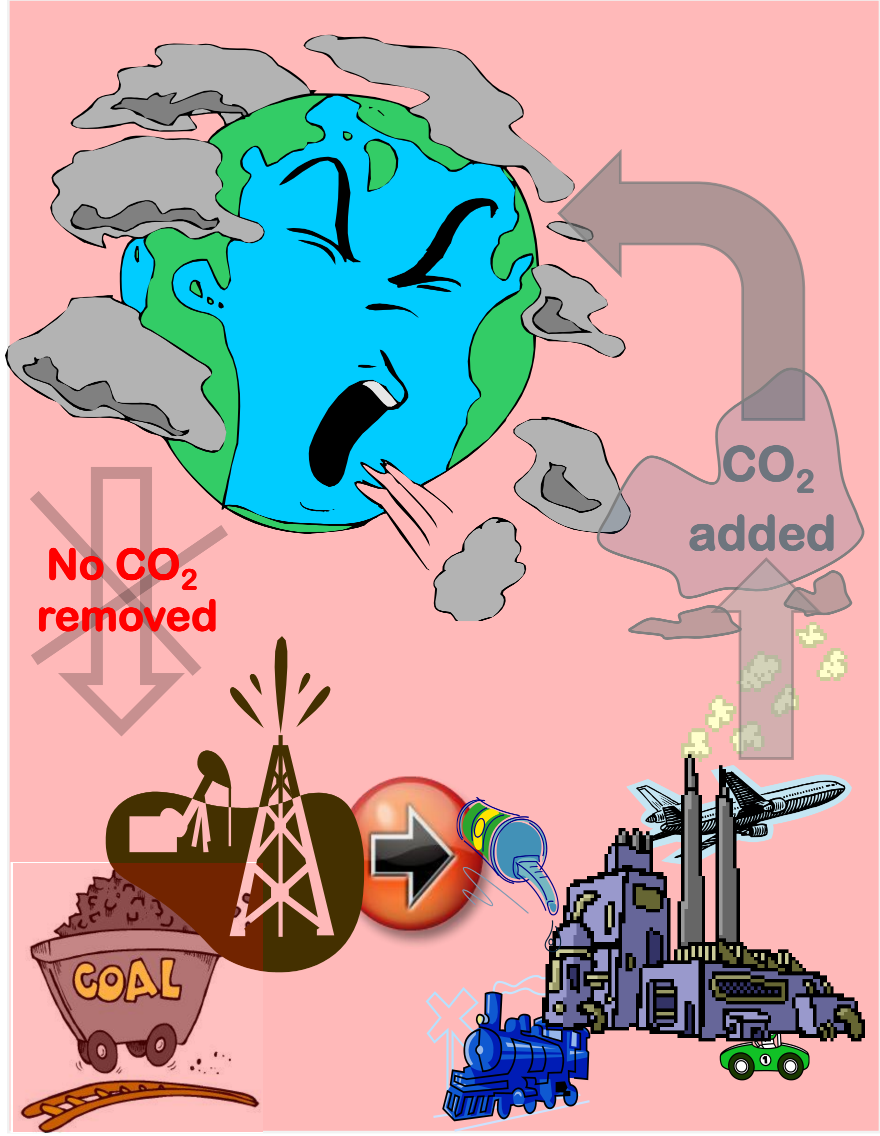
Volumes of different Fuels equivalent to ~10 Watt hours of Electrical Energy at 100% Chemical to Electrical Conversion Efficiency.

Another advantage of fuel cells … reduced pollution

Power from *non-renewable fossil fuel*

adds CO_2 to the atmosphere

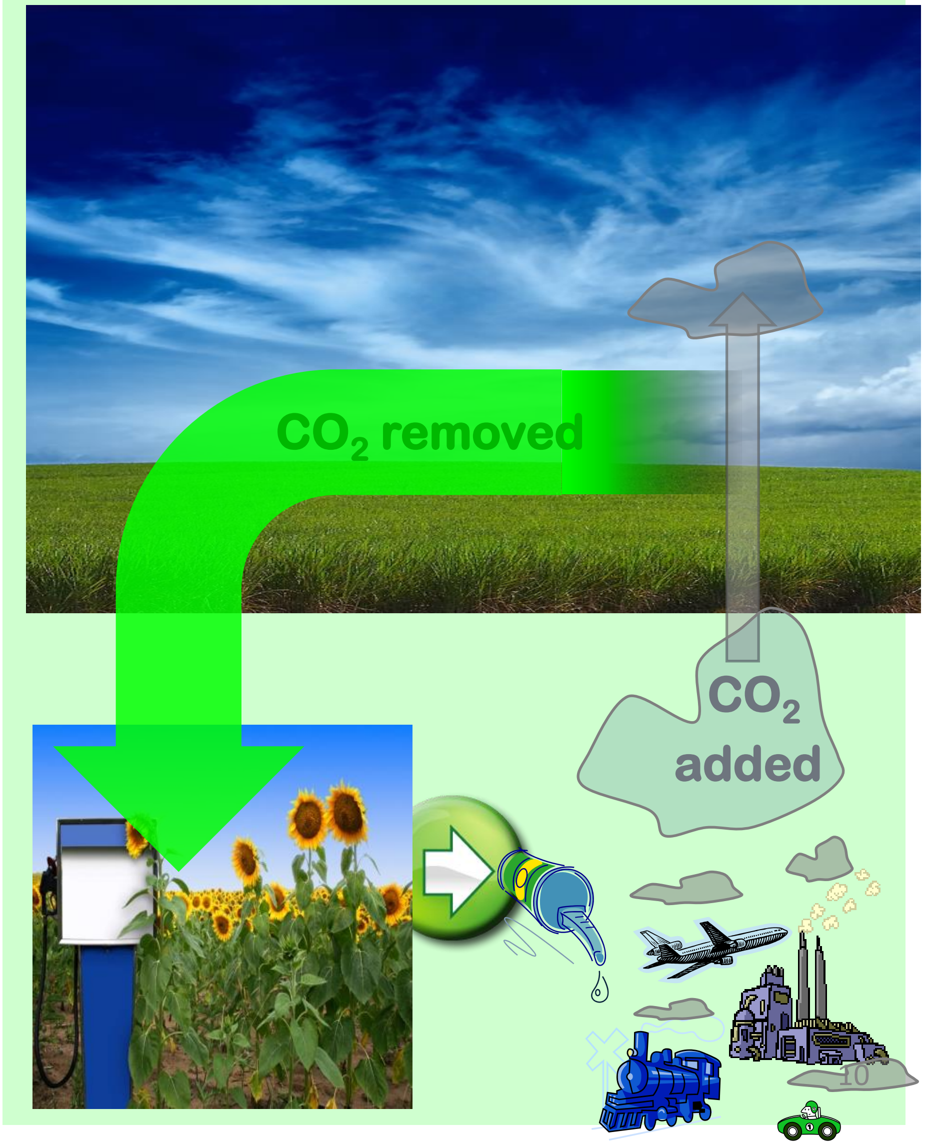
CO_2 levels continually increase



Power from *renewable bio fuel*

yields no added CO_2 in the atmosphere

Plants re-absorb CO_2 from atmosphere



Hydrogen can be derived from…

Renewable sources

- **Biomass**
- **Solar**
- **Wind**

… or from

- **nuclear driven electrolysis**
- **efficient reforming of hydrocarbons**

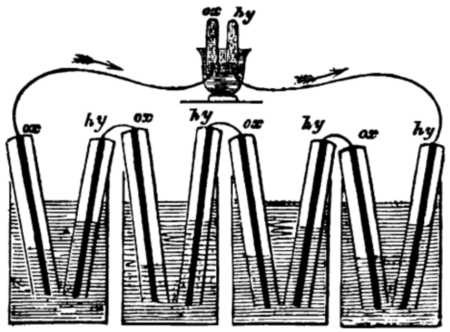
So an added benefit of hydrogen

Low pollution

Next **… evolution of fuel cell design**

Evolution of fuel cells

- Sir William Grove demonstrated the first fuel cell in 1839,
  - addition of electricity to Pt catalyzed electrodes in acidic water to make H_2 and O_2
  - and reaction of hydrogen anode and oxygen cathode to make water and ***generate electricity***



Grove

- In 1959, British engineer Francis Thomas Bacon successfully demonstrated a 5 kW stationary fuel cell using hydrogen and oxygen feeds with alkaline (aqueous KOH) electrolyte operating at 205 ° C (400 °F) and 414 N/cm^2 (600 psi)
  - stationary power supply for a welder, saw and lift
  - *but too heavy and too high pressure for space*

Bacon

- In 1965, the Gemini V spacecraft used the first fuel cell in space
  - 1 kilowatt proton exchange membrane (PEM) fuel cell
  - eliminated excess weight and volume lifted in orbit for 2 things:
    1. batteries for required electrical power
    2. drinking water for astronauts

first fuel cell in space (PEM) made by GE

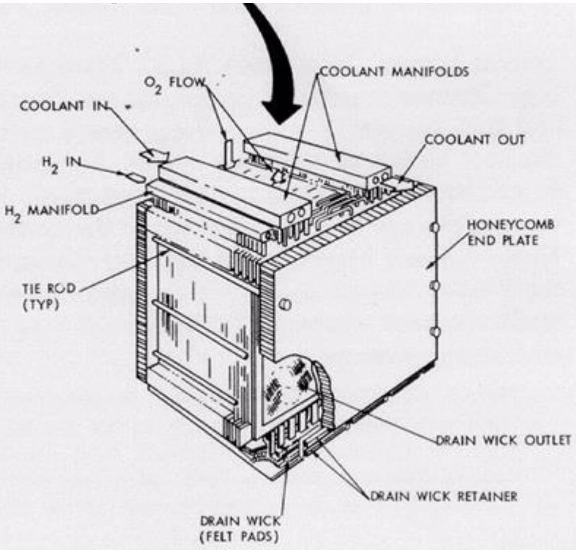
First fuel cell in space: PEM made by GE for the NASA Gemini program

- in 1965, the Gemini V spacecraft was the **first spacecraft to use fuel cells**
- pure hydrogen and oxygen reactants came from the propulsion system
- sulfonated polystyrene resin **polymer electrolyte membrane (PEM)**; with wicks to draw **water out of cell for astronauts' drinking water (1 kWh electrical energy → 1/2 L liquid H_2O)**
- so solved 2 problems: **eliminated weight and volume of i) batteries & ii) water lifted into orbit**
- fuel cell used **28 mg of platinum catalyst per cm^2** of electrode
- maximum power output per was about one kilowatt operated at about 65 °C
- 32 individual cells in series produced 23 to 26 volts per stack (efficiency = 60 to 70%) per module and 3 modules were used in each mission, needed 2 for mission and 1 to land

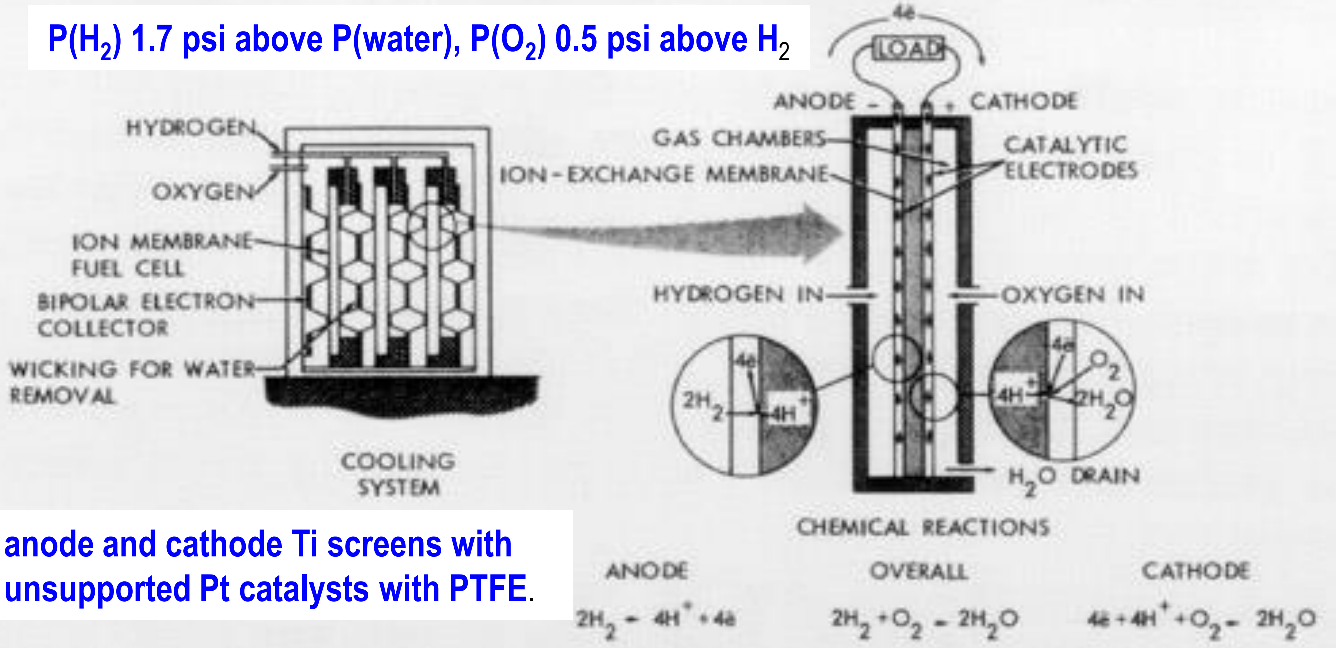
112 liter
= ~ 225 kg
= ~ 500 lb

Module: 47 x 37.5 x 63.5cm (18 1/2 x 14 3/4 x 25 in)

Heat generated by the fuel cell stack was removed by a circulating coolant.



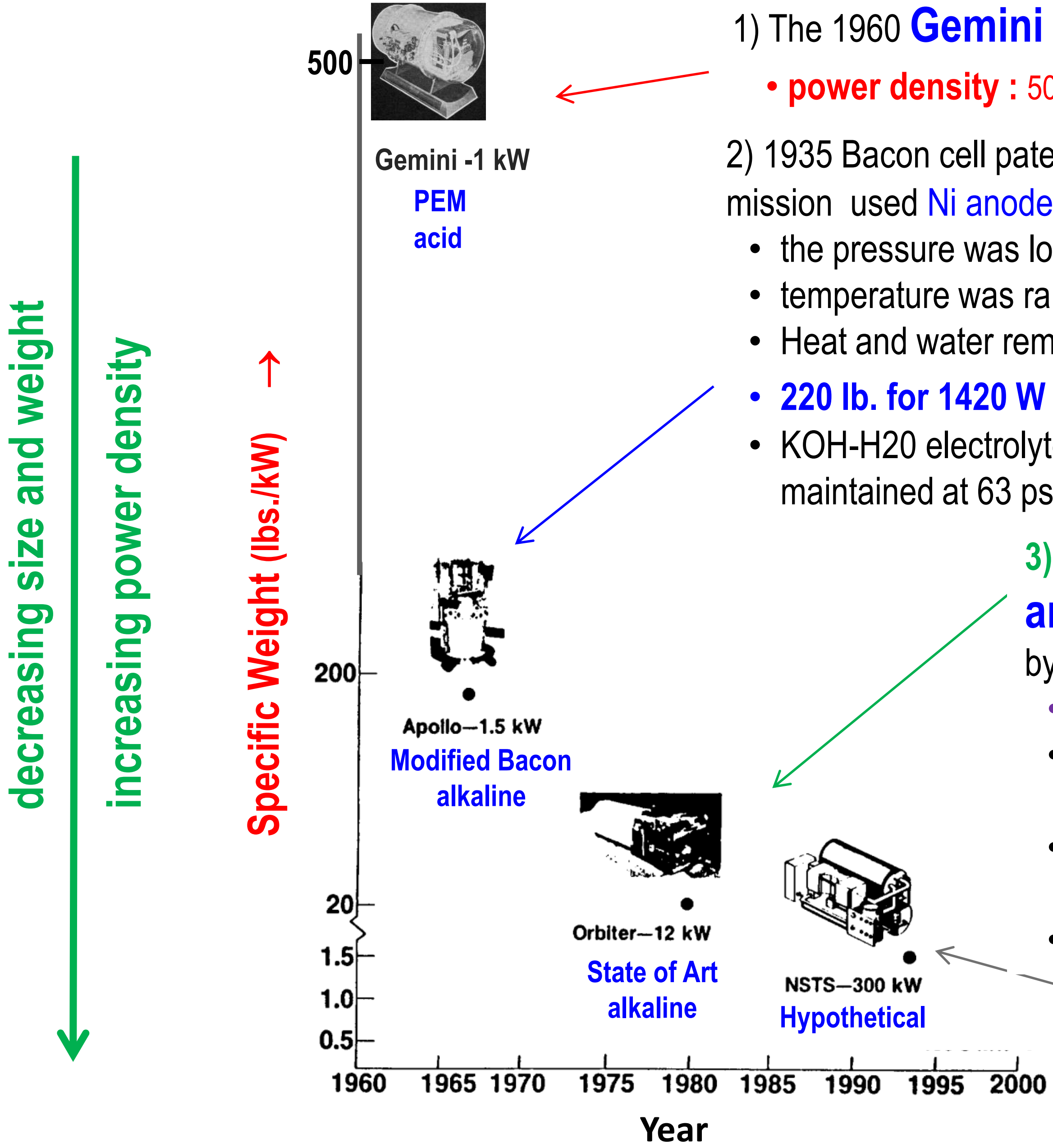
P(H_2) 1.7 psi above P(water), P(O_2) 0.5 psi above H_2



anode and cathode Ti screens with unsupported Pt catalysts with PTFE.

Fuel Cells For Space Science Applications , Kenneth A. Burke , National Aeronautics and Space Administration, Glenn Research Center, Cleveland, Ohio 44135 (2003)
https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20040010319.pdf

Lesson of space program – reduce the size and weight of fuel cells



1) The 1960 **Gemini** Pt catalyzed proton exchange membrane (PEM)fuel cell system

- **power density :** 500 pounds for 1 kW or 1 kW/250kg =0.004kW/kg; 1 kW/100 liter **= P^d = 0.01 kW/liter**

2) 1935 Bacon cell patent acquired by Pratt & Whitney (United Technologies) and modified for **Apollo** mission used Ni anode and Li-Ni cathode and KOH electrolyte

- the pressure was lowered from 600 to 50 psi; KOH concentration increased from 30 to 75%
- temperature was raised to 260 °C; a current density of 150 A/ft 2 the voltage was 0.87 V/cell
- Heat and water removed by hydrogen circulation; with glycol-water secondary coolant loop
- **220 lb. for 1420 W (P^d = 0.014 kW /kg)** Peak power was 2295 W at 20.5 V.
- KOH-H20 electrolyte solution was pressurized to 53.5 psia while each reactant gas cavity was maintained at 63 psia.

3) **7 kW average weighs 250 lb. (P^d = 0.062 kW/kg)** in **Space Shuttle and Orbiter** 32 percent KOH in an asbestos matrix operating pressure is 60 psia by using 20 mg/cm^2 Au Pt alloy catalyst on cathode and I0 mg/cm^2 Pt on anode.

- **Note: internal combustion engine** is about 450 lbs for 150 hp or **P^d =0.7 kW/kg**
- cell temperature reduced to 93 °C. required gold plated Ni screens upon which a catalyst layer and PTFE for gas passages to catalyst.
- heat generated is transferred to a fluorinated hydrocarbon dielectric liquid to the Orbiter's heat exchangers to a Freon coolant system
- 3'rd system still used TODAY;

4) A fourth hypothetical "regenerative system" (fuel cell/electrolyzer)

- has a marginally better alkaline fuel cell
- photovoltaic (PV) power to electrolyze water to regenerate hydrogen and oxygen so alkaline fuel cell can make electrical power during sundown.

After 60 years of fuel cell research for space… the 3rd alkaline fuel cell is still the best in space

But alkaline fuel cells

- ❑ require pure O_2; cannot use air with acid CO_2 which reacts with basic KOH making carbonate …which is not efficient at 200°C
- ❑ require pure H_2, compact liquid H_2 from cryogenic rocket fuel available in the cold of space … but H_2 gas voluminous on earth
- ❑ liquid electrolytes can leak under shock and vibration on earth … ionically shoring stack with drastic power reduction
- ❑ earth-bound fuel cells need to operate ten of thousands of hours,
    - alkaline fuel cell catalysis is more active in the *short term*…BUT decays after about 500 hours *!*

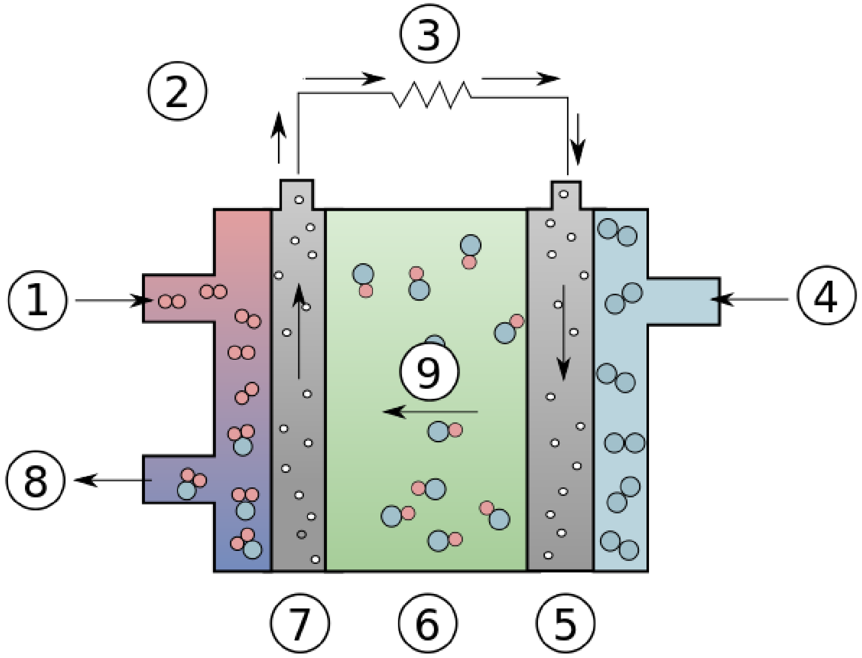


Diagram of an Alkaline Fuel Cell.

1: Hydrogen
2:Electron flow in wire
3:Load (light bulb, radio, etc.)
4:Oxygen
5:Cathode
6:Electrolyte (liquid aqueous KOH solution)
7:Anode
8:Water (produced by cell)
9:Hydroxyl Ions (OH^- from KOH)

Liquid alkaline fuel cell is not acceptable for earth-bound use

Let's get down to earth

For use on Earth …. its back to PEM fuel cells

Much has been learned from space fuel cells … where does this leave us for earth bound fuel cells?

To make medium sized (100kW) fuel cells for automotive and distributed generators, we need :

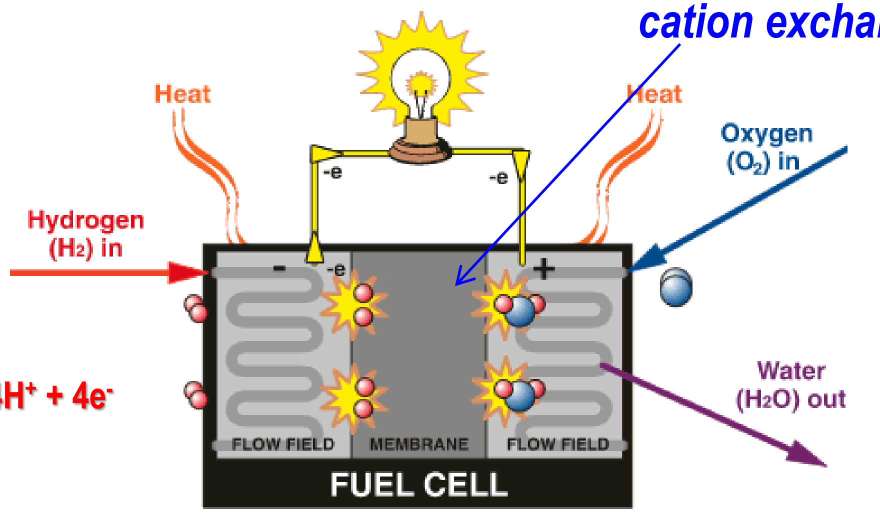
- hydrogen storage for the anode and an air-fed CO_2-tolerant cathode
- therefore a *polymer electrolyte membrane* (PEM) is required, which is either
  - an acidic (proton conducting) membrane electrolyte to reject CO_2 and have more stable Pt catalysts
  - or an alkaline (anion exchange) membrane electrolyte with low CO_2 solubility to preserve OH^- conduction in air

cation exchange membrane

The 2 kinds of *polymer electrolyte membrane* (PEM)

1) proton-exchange PEM, proton (H^+) passes through a cation exchange membrane
2) hydroxide-conducting PEM, hydroxide (OH^-) passes through anion exchange membrane

Anode:
$2H_2 \rightarrow 4H^+ + 4e^-$



Cathode:
O_2
+
$4H^+ + 4e^-$
↓
$2\ H_2O$

Wish list

- faster and temporally-stable and hopefully low-cost catalysts for H_2 oxidation and O_2 reduction
- water-free high-temperature ion-conductors (electrolytes) to
  1) minimize system bulk by shrinking radiator size
  2) further elimination of bulk, weight and parasitic losses by eliminating the use of a humidifier

in short… a tall order…seems impossible…or is it?

Comparison of PEM fuel cell systems

Attribute	Nafion PEM	High Temp. PEM	SOFC
Operating Temperature	25 to 80°C	140 to 200°C	700 to 900°C
Ambient Temp. Tolerance	freezes/dries out	invariant	invariant
Power (at ambient P)	0.1 to 0.35	0.12 to 0.2 *(new membranes)*	0.5 to 1 W/cm²
Water management	tricky	easy	easy
Gas feeds	needs humidified	dry	dry
Thermal management	difficult (dry out)	easy	moderate (900°C)
Radiator	large	small	small
Thermal Mechanical Stress	shrink/swell	small	large stress
Shock and vibration	tolerant	tolerant	intolerant
Cell Efficiency	60%	50% - 80% *(new membranes)*	65%
Electrolyte (ions)	Fixed ions	Fixed ions *(new membranes)*	Fixed ions
Electrolyte (solvent)	needs water	none	none
Membrane technology	mature	developing	developing
Material Cost	Nafion $700/m^2	< $ 1/10 Nafion stack	< $ 1/10 Nafion stack
Processing cost	low	low	high (seals)
Catalyst cost	$250/kW (Pt)	$250/kW(Pt) $10 (if non Pt)	$250/kW (Pt) $10 (if non Pt)
Combustion	toxic	non-toxic	does not burn
Operating life	1000 to 40,000h	20,000 h	? Thermal & Mechanical shock
Contaminant Sensitivity	sensitive	insensitive	insensitive
CO sensitivity	50ppm	2%	40%
Stack size	>100 W/kg	> 360 W/kg *(metal BPP)*	>100W/kg
Stack volume	> 200 W/liter	> 690 liter *(metal BPP)*	> 500 W/liter
Reformer size	large (CO clean up)	small	small
t (cold start to full power)	minutes (hydrate)	minutes *(heat up in metal BPP*	hours (heat up to Temp.)
Overall system	large, heavy	simpler, smaller	larger, heavy

red is bad green is good yellow is neutral

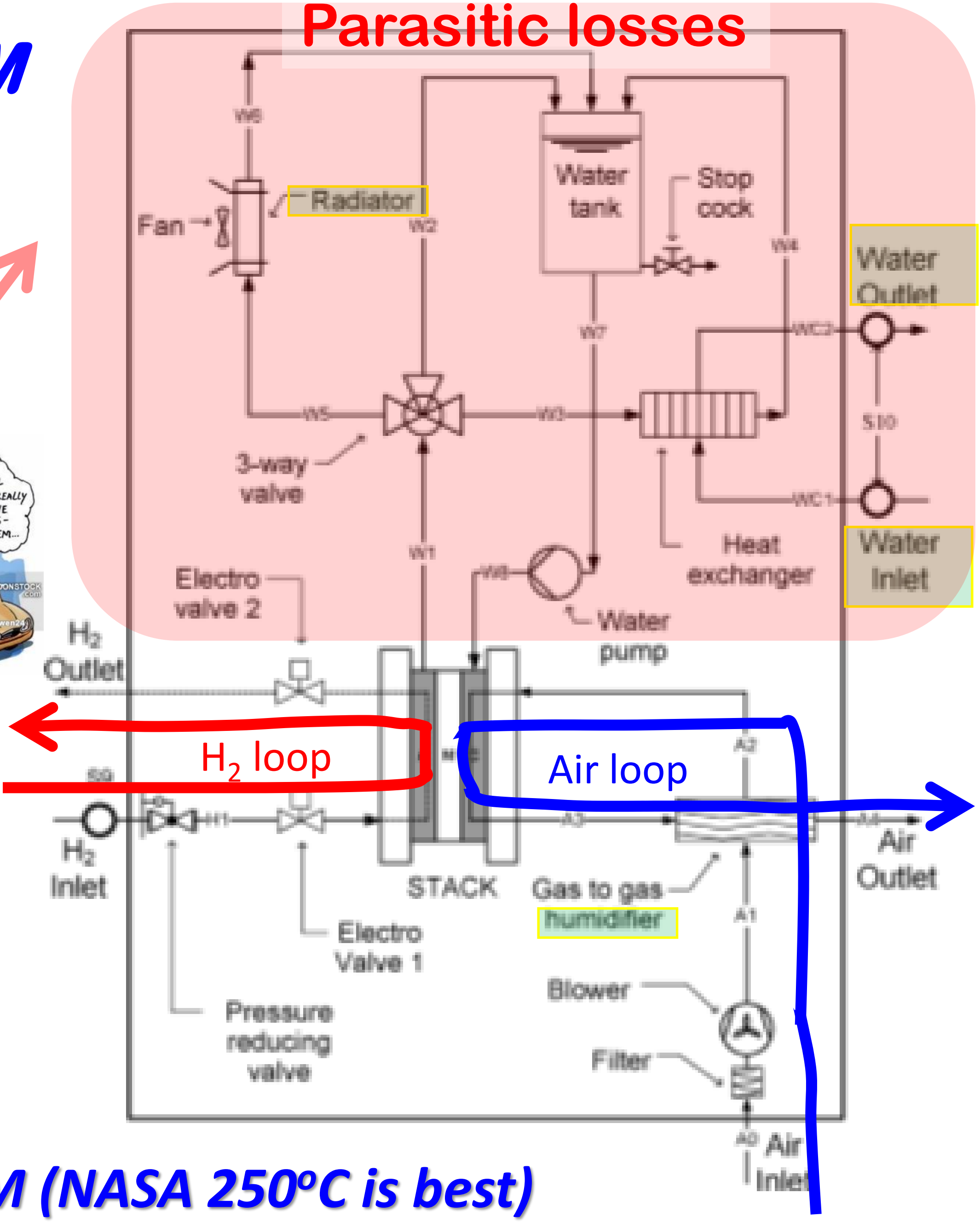
A fuel cell ***POWER SOURCE*** is a ***SYSTEM***

For low temperature PEM fuel cell (LT-PEM FC) system

- there is a need for humidifier to keep ion exchange membrane ionized and conductive.
- A very large radiator is needed for rejecting waste heat from low temperature fuel cell to the ambient

For high temperature PEM fuel cell (HT-PEM FC) system

- higher temperature fuel cells tolerate CO in hydrogen from natural gas can be used instead of purified hydrogen.
- heat management simplified and minimized
- water management is simplified or eliminated
- electrode reaction kinetics are faster at higher temperatures (higher power) which opens door to higher power and cheaper (less) catalyst material



System considerations lead to HT PEM (NASA 250°C is best)

BIG QUESTION: Is there a suitable ionomer membranes for a HT PEM fuel cell?

Summary of advantages of HT PEM Technology

- Lower temperature operation for HT PEM FC (170°C) than turbine (> 800ºC) or solid oxide fuel cell (> 800ºC)
- Smaller and lighter than room temperature fuel cell: small radiator, no humidifier
- Quieter, more efficient and lower thermal signature than internal combustion engine
- Lower cost fuel cell membrane (hydrocarbon) than room temperature fuel cell membrane (fluorocarbon)
- *Higher system efficiency* due to good thermal integration to fuel source (e.g., hydrocarbon reformer)
- *Higher system efficiency* due to one-phase (gas) fluidics
- Shock and vibration tolerant, made with plastics and metals not brittle ceramics
- Faster startup time to full power than solid oxide fuel cell… even low temperature PEM
- Simplified system design (no membrane humidification, low working pressures)

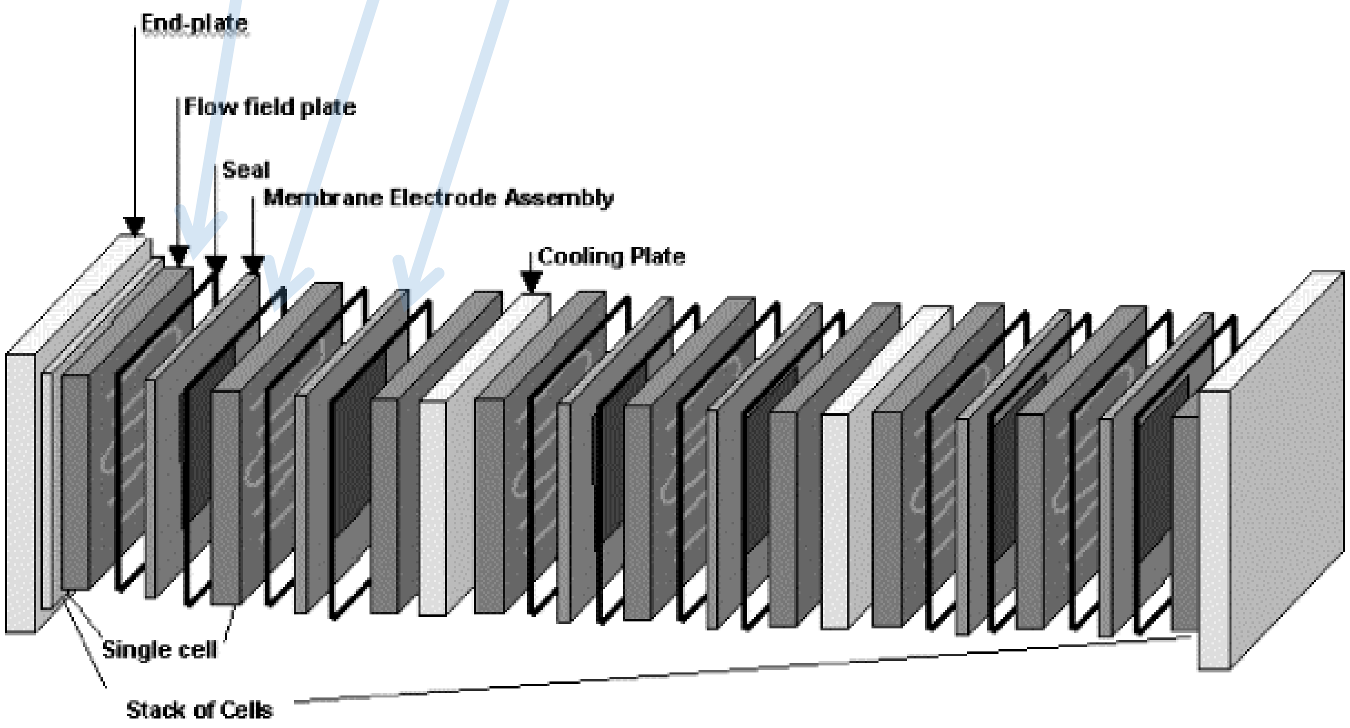
Summary of possible disadvantages of HT PEM Technology

Operating at elevated temperatures is not solely beneficial however, because higher temperatures can result in more rapid component degradation, including

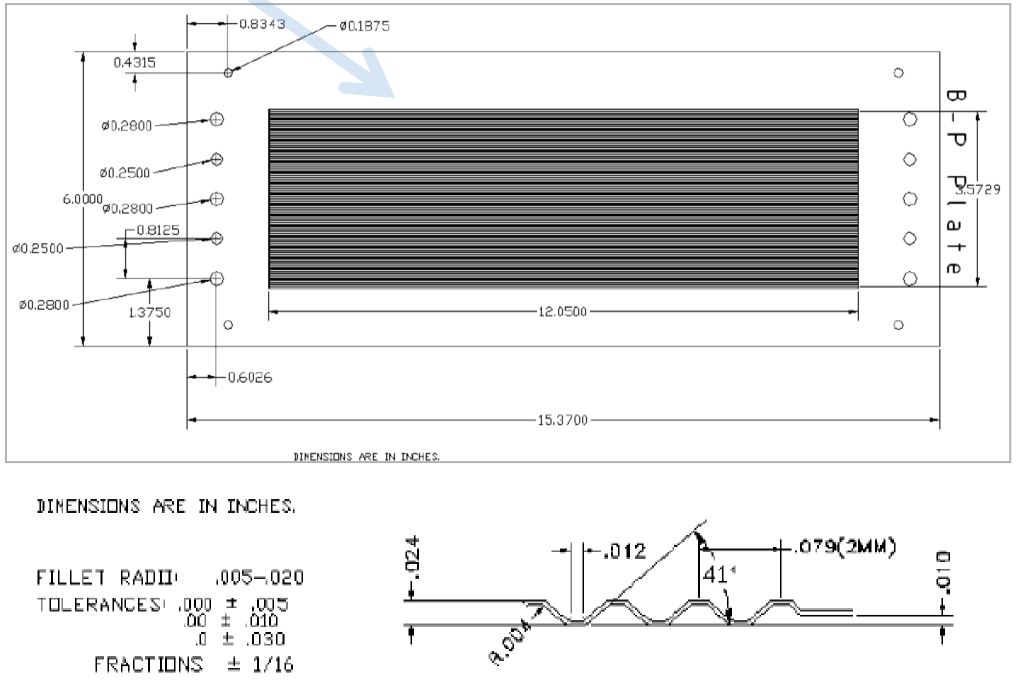
- corrosion of bipolar plates *
- catalyst support,*
- degradation of seals, *
- degradation of membranes**

Other Components for PEM Fuel Cell Stack Assembly

- **Fuel cell stack has several hundred layers of thin materials with its own dimensional tolerances and assembly and material cycling tolerances can result in poor sealing and stack failures.**
- **To address these issues, novel developments include:**
  1. **metal bipolar plates with parallel flow field**
  2. **stable gaskets with asymmetric design to prevent parabolic flow**
  3. **membrane electrode assemblies (MEAs) which need no water for proton conduction.**

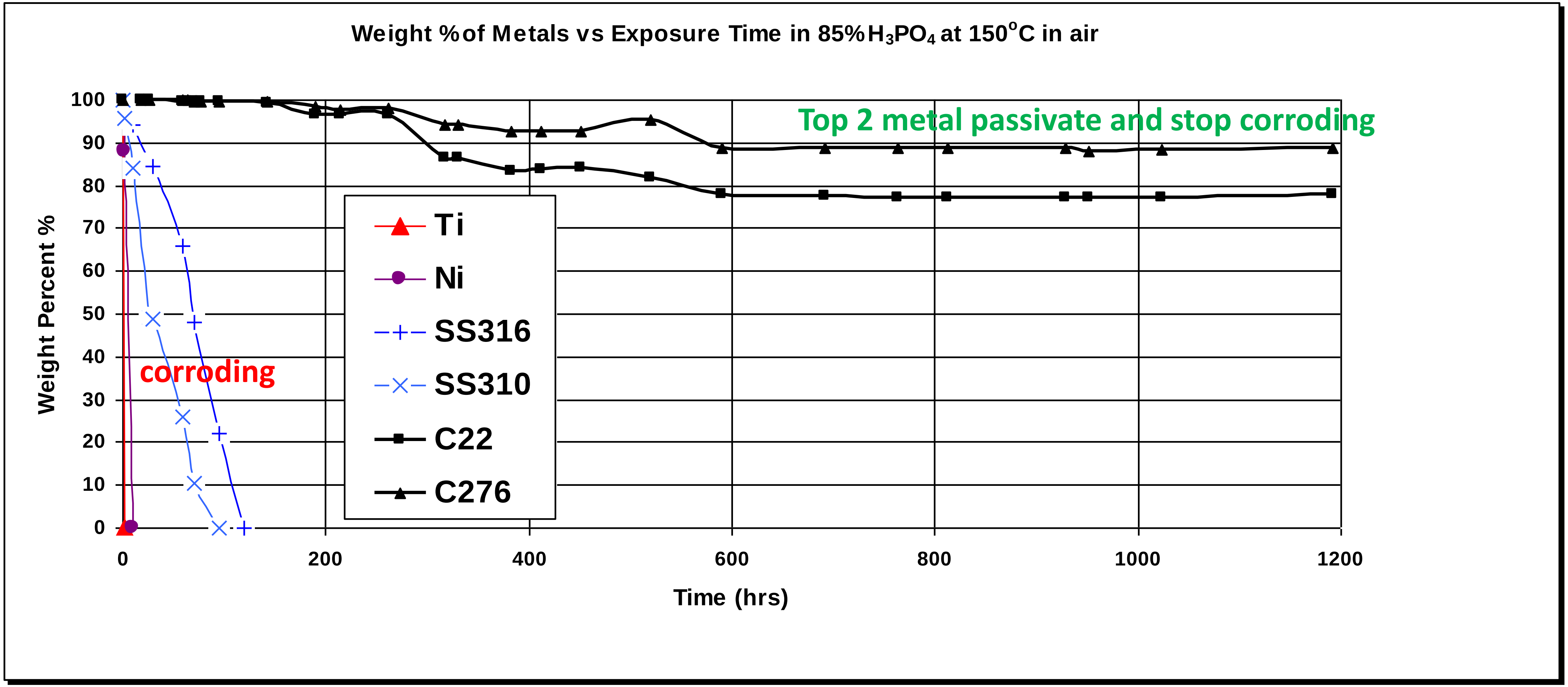


PEM stack with conventional milled graphite BPP



One metal BPP geometry

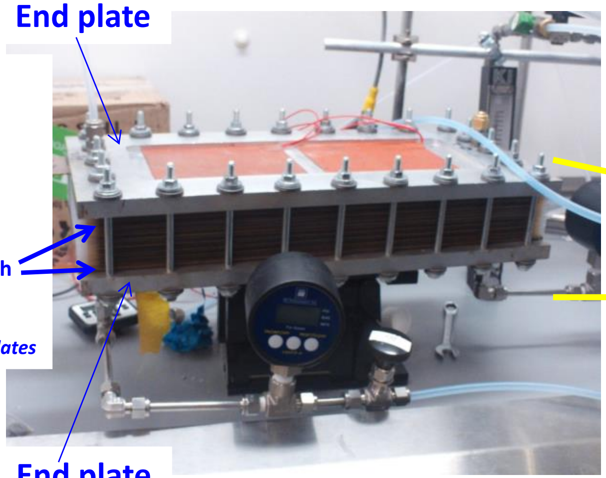
Corrosion testing of *metallic bipolar plate* material



- C276 Alloy selected from corrosion data
- C276 bipolar plates are conductive and stable with 50 nanometer of gold plate
  - *Resistance only 0.6 Ohms as measured on a 1 x 2 x 0.1 cm plate with probes 1 cm apart*

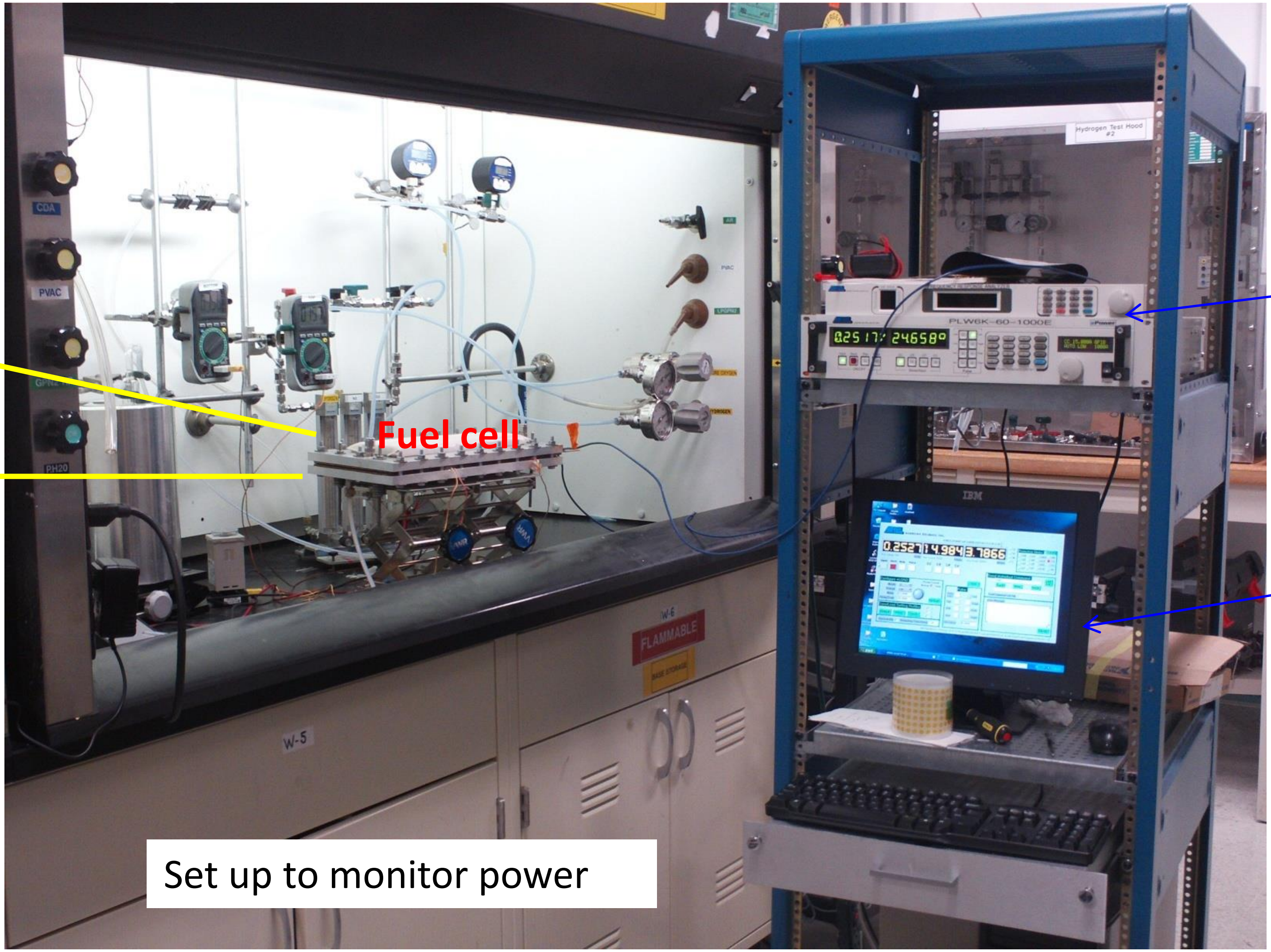
Test station for HT PEM *Fuel Cell Stack* with Metal Bipolar Plate

End plate



20 cells with
- metal BPPs
- seals
- *no cooling plates*

End plate

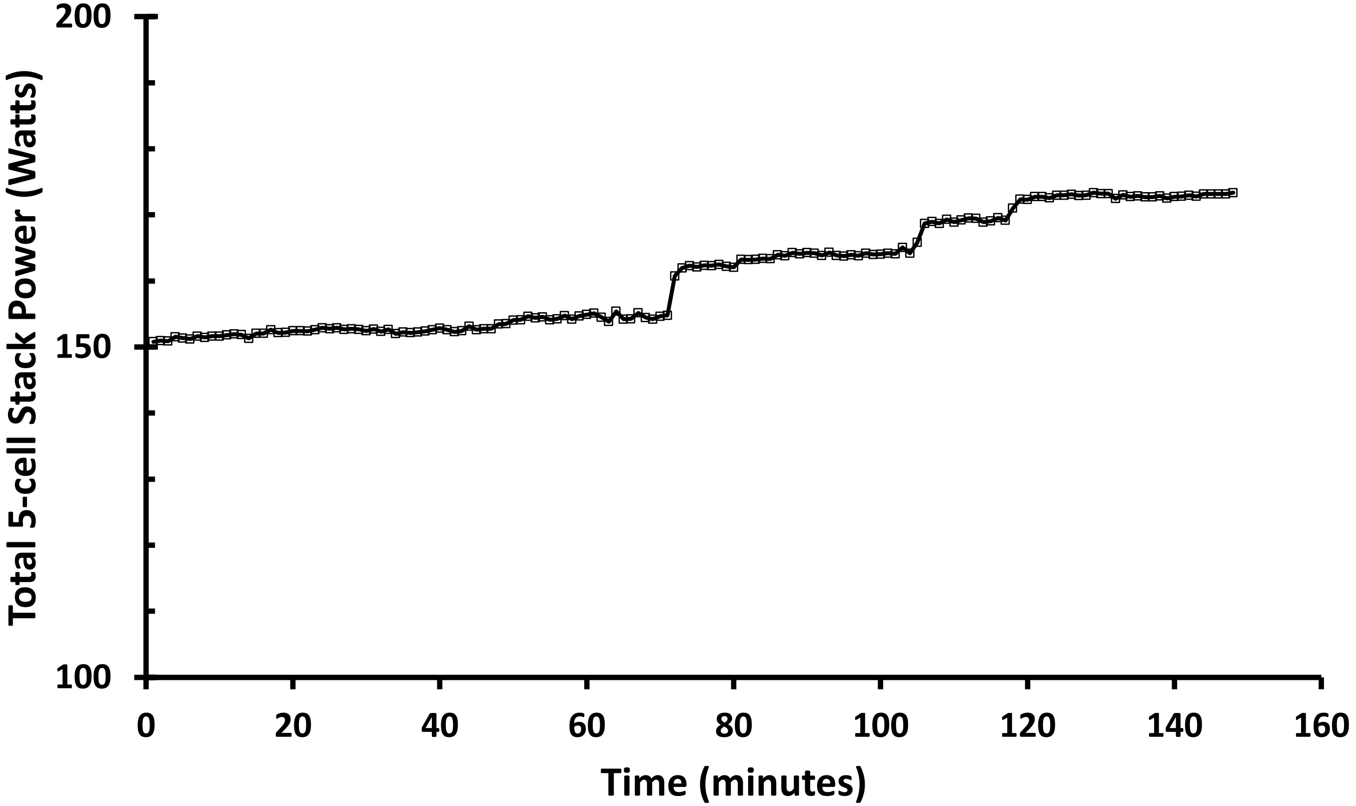


AMREL Electronic Load

Control and Recording Computer

Start up power for a passively cooled 5-cell HT PEM stack

- phosphoric acid (H_3PO_4) loaded polybenzimidazole (PA PBI) housed in metallic bipolar plates with PFA gaskets at 172°C.



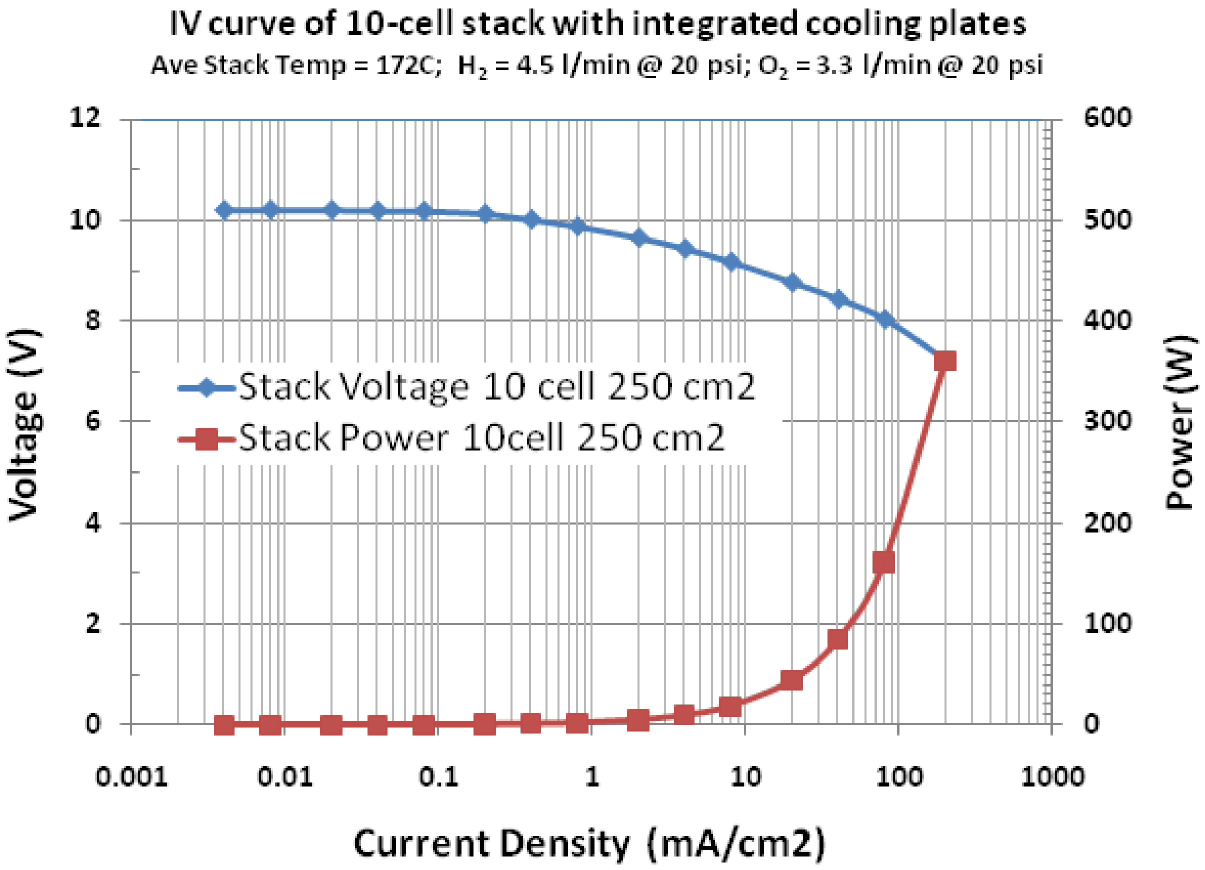
Decent stack performance with PA PBI membrane … but H_3PO_4

- can wash out of PBI membrane giving:
  - voltage drop from resistive losses
  - voltage loss due to short circuiting
- limit temperature: 210°C > T > 140°C
  - too low water wash
  - too high H_3PO_4 condensation

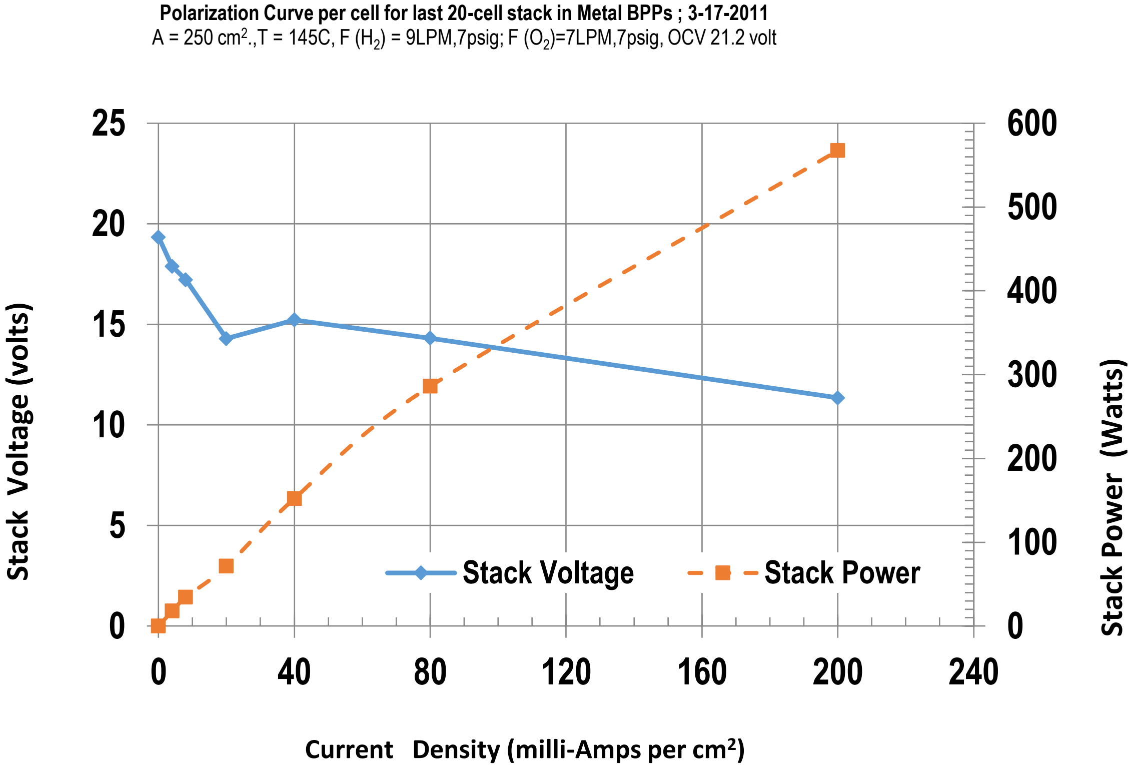
MEA is BASF C3 phosphoric-acid-loaded polybenzimidazole (PA PBI) with porous graphite gas-fed electrodes with 0.5 mg Pt/cm^2
Area per cell = 250 cm^2, Stack voltage 3 volt. Total current =58A. Gas feeds: 3.6 LPM hydrogen 1.8 LPM oxygen. P =30psig.
Cell voltage 0.6 volt. Current density = 235 mA/cm^2. Raw P^{density} per cell = 140 mW/cm^2 (not IR corrected). T = 172°C.

Scale up of fuel-cell stacks house in metal bipolar plates

10 cell - cooled



20 cell – NOT cooled



passively-cooled with metal fins; produced > 350 Watts $P^{density}$/cell = 0.2 A/cm^2.

produced almost 700 Watts.

Need an actively-cooled stack using a flowing liquid in a metal BPP

Can be done by laminating 1 extra metal foil to each bipolar plate to allow rapid thermostatting for:

- heating stack (by burning some H_2 and O_2) for rapid start-up (less than 1 minute) of fuel cell power-source system
- cooling stack to keep MEA and cell temperature even to stop (uneven “thermal run-away”) for safe high-power operation of the stack.

What’s next?

Design of 1. *thermostatted metallic bipolar plate* with 2. *PFA gasket*

Using metal instead of graphite can:

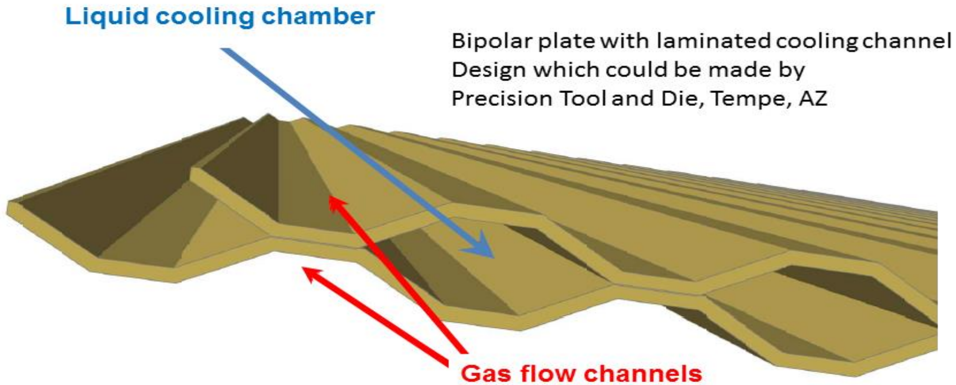
- Lower cost from $100 to $1 per plate
- Lower weight and volume leading to higher specific and volumetric power densities as shown in Table

Using Perfluoroalkoxy (PFA) sheet in an asymmetric gasket :

- evenly spreads gas with low pressure drop in parallel flow field
- gives a stable and tight seal to 350^{o}C

1.Thermo-statted metallic bipolar plate (BPP)

- with brazed internal cooling channels (or 3-D metal printing)

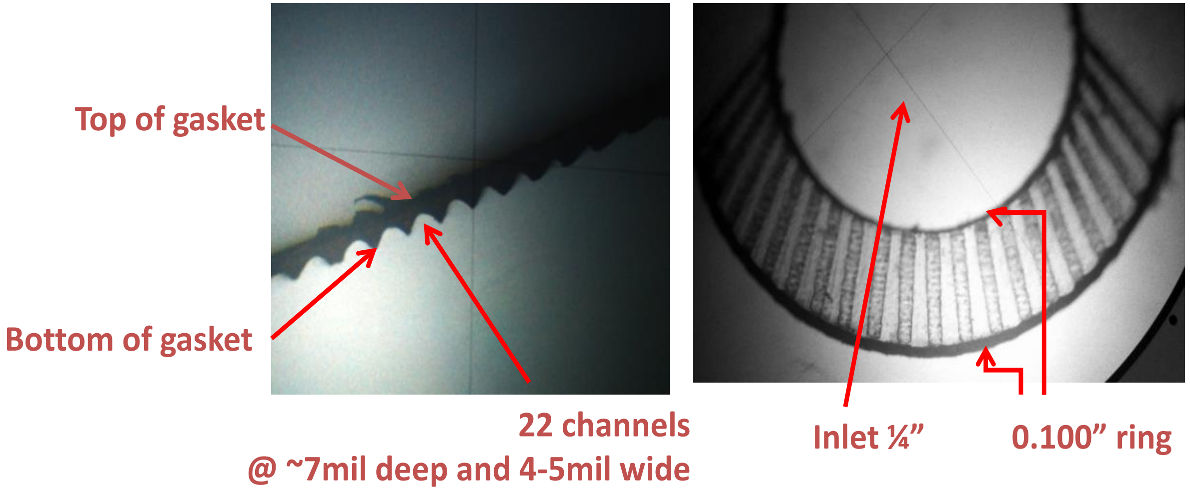


4 mil thick metal stamped and brazed, for thin light BPP.

<u>Specific and Volumetric power densities with metal versus graphite bipolar plates.</u>

	Metallic	Graphite
Specific Power (Watts / kg)	365	169
Power Density (Watts/liter)	691	396

2.PFA gasket with radial rib design



Ribbed gasket pattern (alternating land and channel) for mechanical support and low pressure drop from gas inlets to outlets

Tested with CDA@4-5psi, Flow @ inlet= 98sccm, Flow @ outlet= 92sccm

Summary of status of HT PEM Technology

Operating at elevated temperatures is not always beneficial, because higher temperatures can result in more rapid component degradation, including:

- corrosion of bipolar plates Metal bipolar plates
- catalyst support, graphite and metal oxide supports
- degradation of seals, stable PFA Teflon seals have been demonstrated
- degradation of membranes …polymer electrolyte membrane (PEM) is key to HT PEM FC system development

Durability of HT-PEM is a primary focus for HT PEM fuel cell

Alternative High temperature PEM membranes

Question – Anything better than phosphoric acid loaded PBI?

Answer -Yes …protic salt membranes!

HT- PEM membrane electrode assemblies (MEAs)is the the heart of the fuel cell system

phosphoric-acid-loaded polybenzimidazole MEA operates at 140 TO 190°C

EXIT BASF

BASF recently announced exiting its high-temperature proton exchange membrane fuel cell business
BASF was vendor of phosphoric-acid-loaded polybenzimidazole (PA loaded PBI) membranes

ENTER ADVENT

- US-based Advent Technologies (East Hartford, Connecticut) novel membrane technology for HT-PEMFC.
- Advent claims a *proprietary membrane material* for its HT-PEMFC based upon phosphoric acid loaded *pyridine with cross-linking for* greater mechanical strength versus PA loaded PBI.
- Advent claims two advantages
    1. operation at higher temperatures than PBI-based HT-PEMFC MEA, in some cases above 200°C and with greater stability.
    2. Pressures inside the MEA can also approach those used in PAFC – a well-proven fuel cell type

Clearly, electrolyte membranes will make or break a fuel cell system

*see: Fuel Cells Today, 28 Aug 2013; http://www.fuelcelltoday.com/analysis/analyst-views/2013/13-08-28-a-turning-point-for-high-temperature-pem-fuel-cells

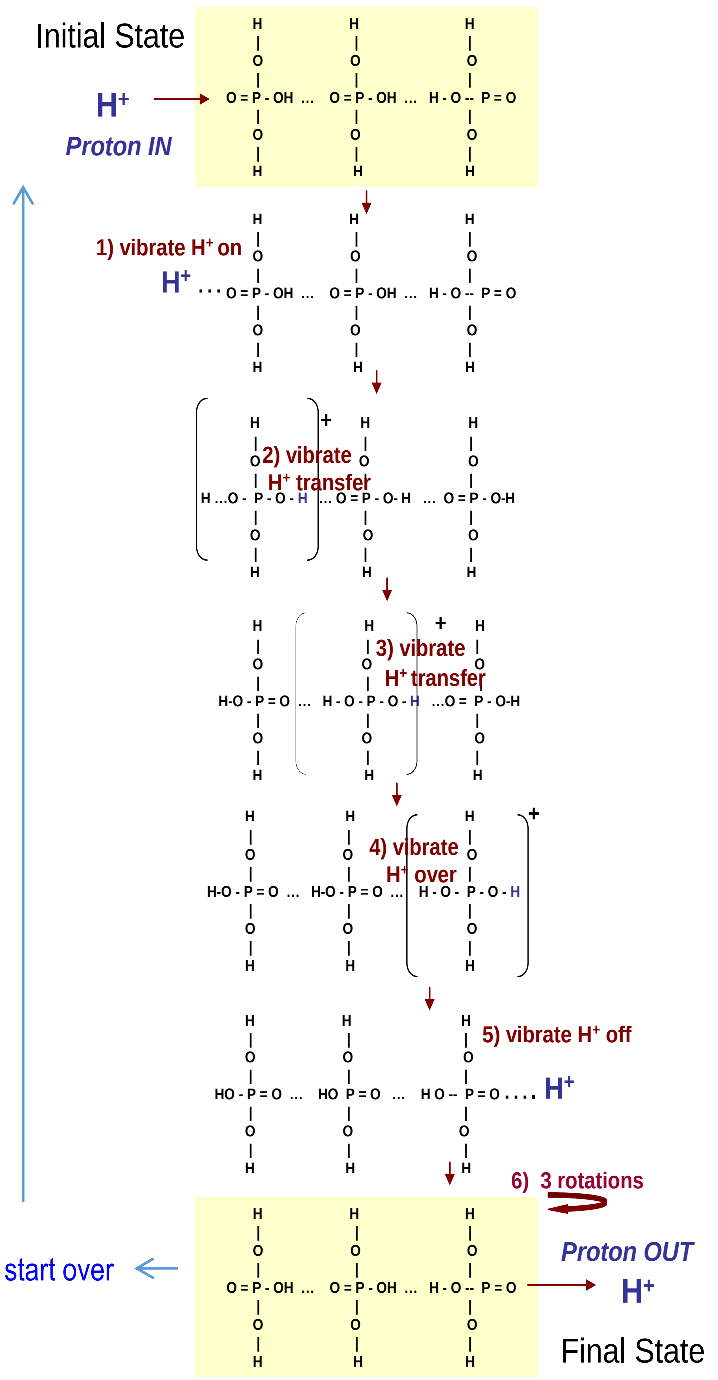
Old and New Proton-conducting Electrolytes

Old - Phosphoric acid

- ❑ Anhydrous phosphoric acid suggests how to synthesize an electrolyte that conducts proton with no water.
- ❑ Phosphoric acid self-ionizes and proton transfers between phosphoric acid, H_3PO_4 **(acceptor base)**, and its ionic forms, such as, phosphonium ion, $H_4PO_4^+$ **(donor acid).**
- ❑ **H^+ transfer by rotational and vibration motions, because H_3PO_4 and $H_4PO_4^+$ have suitable energy separation** (proper ΔpK) **and symmetry.**

New - Protic salt

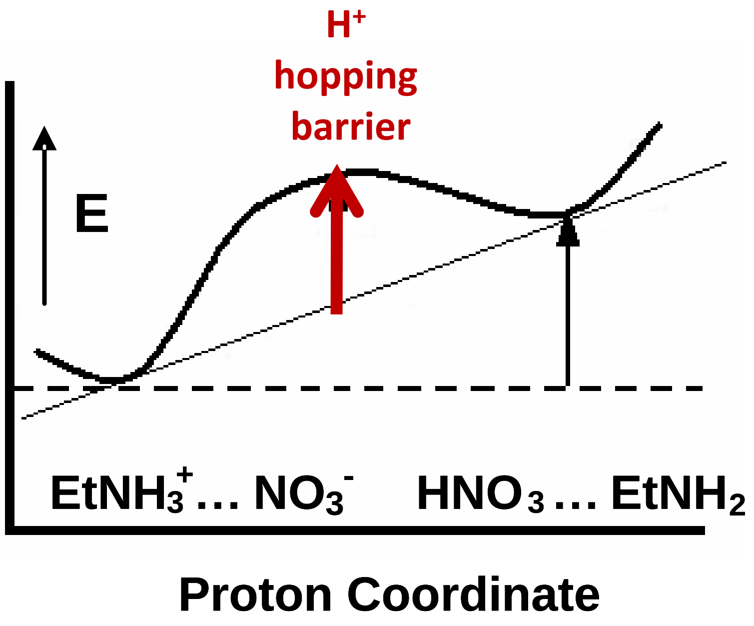
- ❑ A new class of proton-conducting salt electrolytes was conceived. These are called: protic ionic liquids **(pILs)** when in liquid form, and protic ionic membranes **(pIMs)** when in polymeric form.
- ❑ A neat **protic salt electrolyte forms by transfer of proton from a Bronsted acid to a Bronsted base.**
- ❑ pIL electrolytes, or a crystalline solid *or polymeric* versions, have **high proton-conductivities** (e.g., σ[25°C] > 10 mS/cm), which follow Arrhenius behavior temperature **when the constituent acid and base have:**
    - **an optimal difference in pKa (~14) and**
    - **ions that are highly symmetrical** (rotationally free)**.**



PROTIC IONIC LIQUID (pIL) proton-conducting Electrolyte *CONCEPTS*

pILs are a new class of solvent-free proton-conducting electrolyte. These are stable salts made when a acid transfers proton to a base. These “dry” proton conductors that can function at very high temperatures.

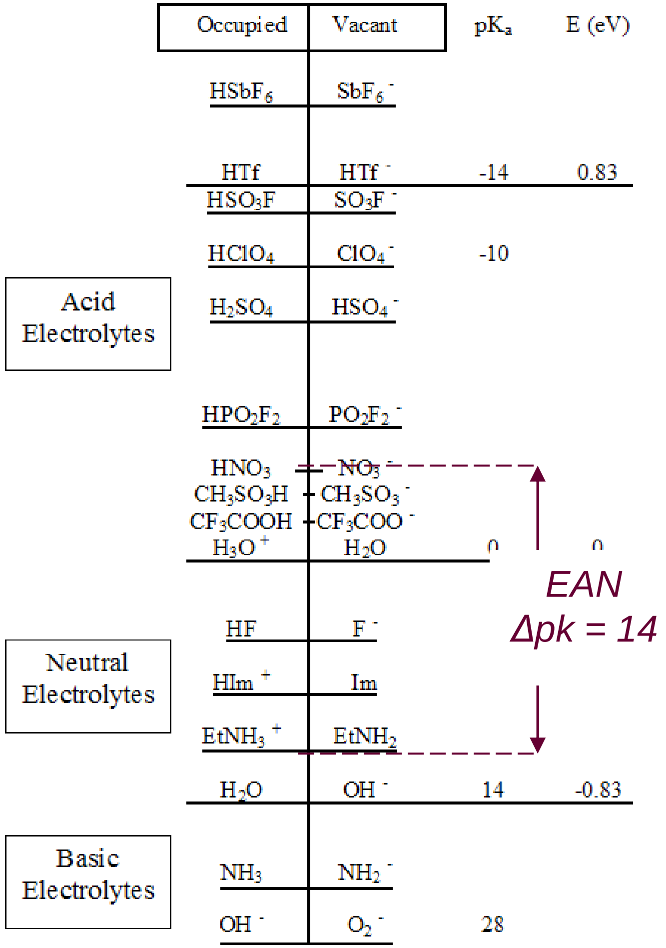
A protic ionic liquid (pIL) is made by transferring a proton from an acid to a base.



Energy Diagram for the EAN (ethyl ammonium nitrate) pIL with:

- proton transferred (Left)

- not transferred (Right),



Gurney proton energy level diagram.

- for any pair of levels, the stable entities are upper right and lower left.

Advantages of anhydrous proton-conducting pILs in HT PEM

- **pILs eliminate humidifier and drastic size reduction of radiator**
- **Other advantage …catalysis (next slide)**

Catalytic Oxygen Reduction in anhydrous pIL vs. Aqueous Electrolytes

Cyclic voltammogram of Pt surface in:

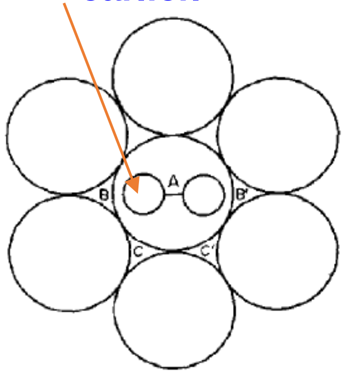
- **aqueous sulfuric acid electrolyte (solid black line)**
- **versus protic salt (dotted blue line).**

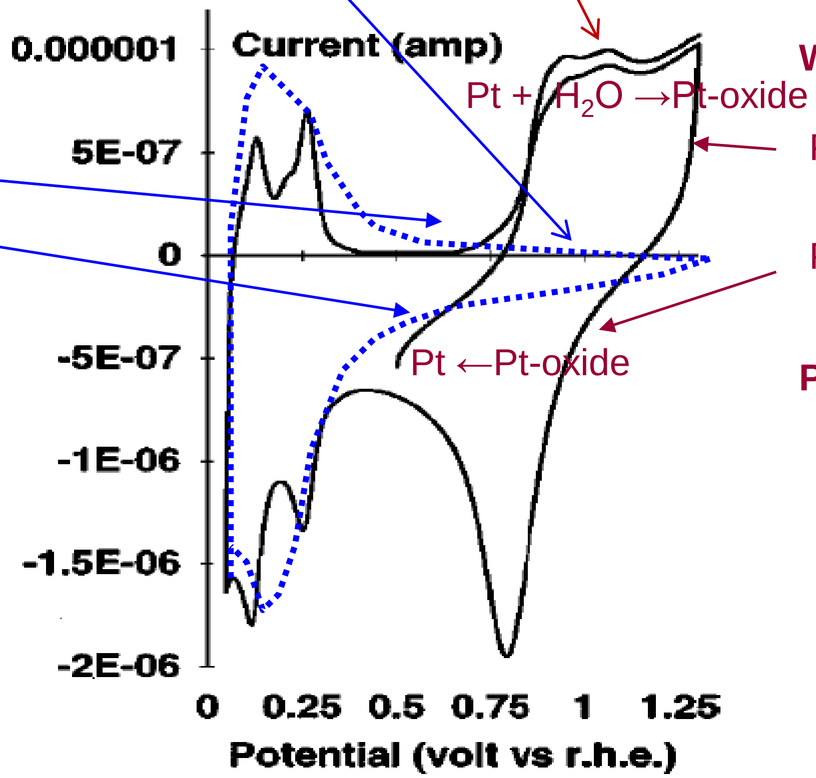
With protic salt electrolyte

There is

- no Pt-oxide formation
- nor oxide reduction

O_2 access to Pt is unimpeded and O_2 reduction occurs earlier.





Voltammetry of Pt in aqueous and ionic liquids. Initial potential was 0.5 V vs RHE. Scan rate: 50 mV/s. Ar atmosphere. Temperature: 30 °C.

With aqueous electrolyte

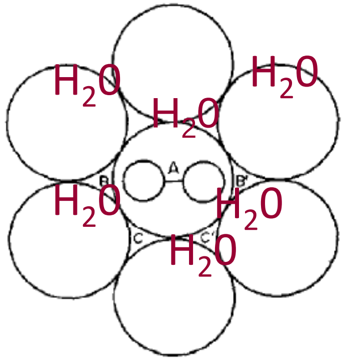
Pt-oxide formation

$Pt + H_2O \rightarrow Pt\text{-}OH + H^+ + e^-$

Pt-oxide reduction

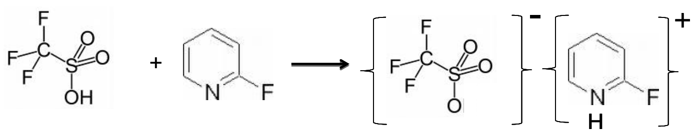
$Pt\text{-}OH + H^+ + e^- \rightarrow Pt + H_2O$

Pt-oxide blocks adsorption sites delaying O_2 reduction.



Consequence of this difference? … see next slide

Oxygen reduction on Pt in pIL versus Aqueous Electrolyte

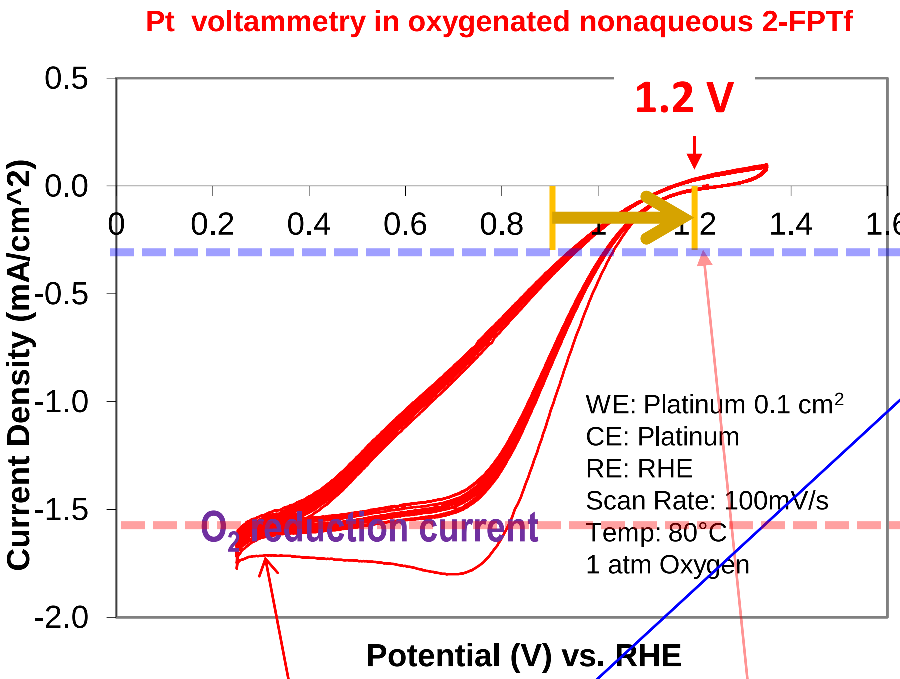


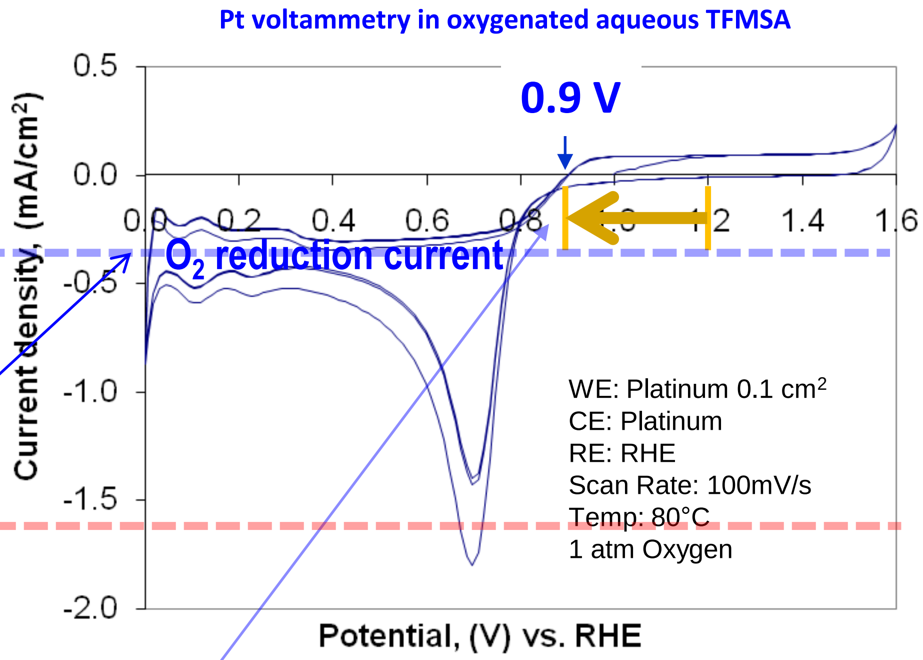
Trifluoromethane sulfonic acid (TFMSA)

2-Fluoropyridine

2-Fluoropyridinium Triflate (2-FPTf) Protic Ionic Liquid m.p. 85°C

$CF_3SO_3H + xs\ H_2O \rightarrow CF_3SO_3^- + H_3O^+ + xs\ H_2O$

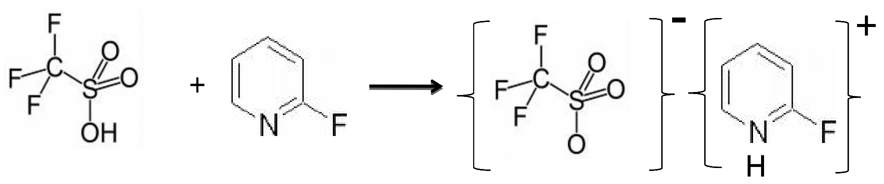




- Oxygen reduction *faster* on Pt in 2-FPTf and starts at 1.18V at 80°C, the *thermodynamic limit* for the ORR, 100% efficient
- Oxygen reduction *slower* on Pt in aqueous triflic acid starts at 0.9 V, *0.3 V below the thermodynamic limit, 75% efficient*

H_2/O_2 fuel cell Performance in Fluoro-pyridinium triflate (2-FPf) pIL vs PA

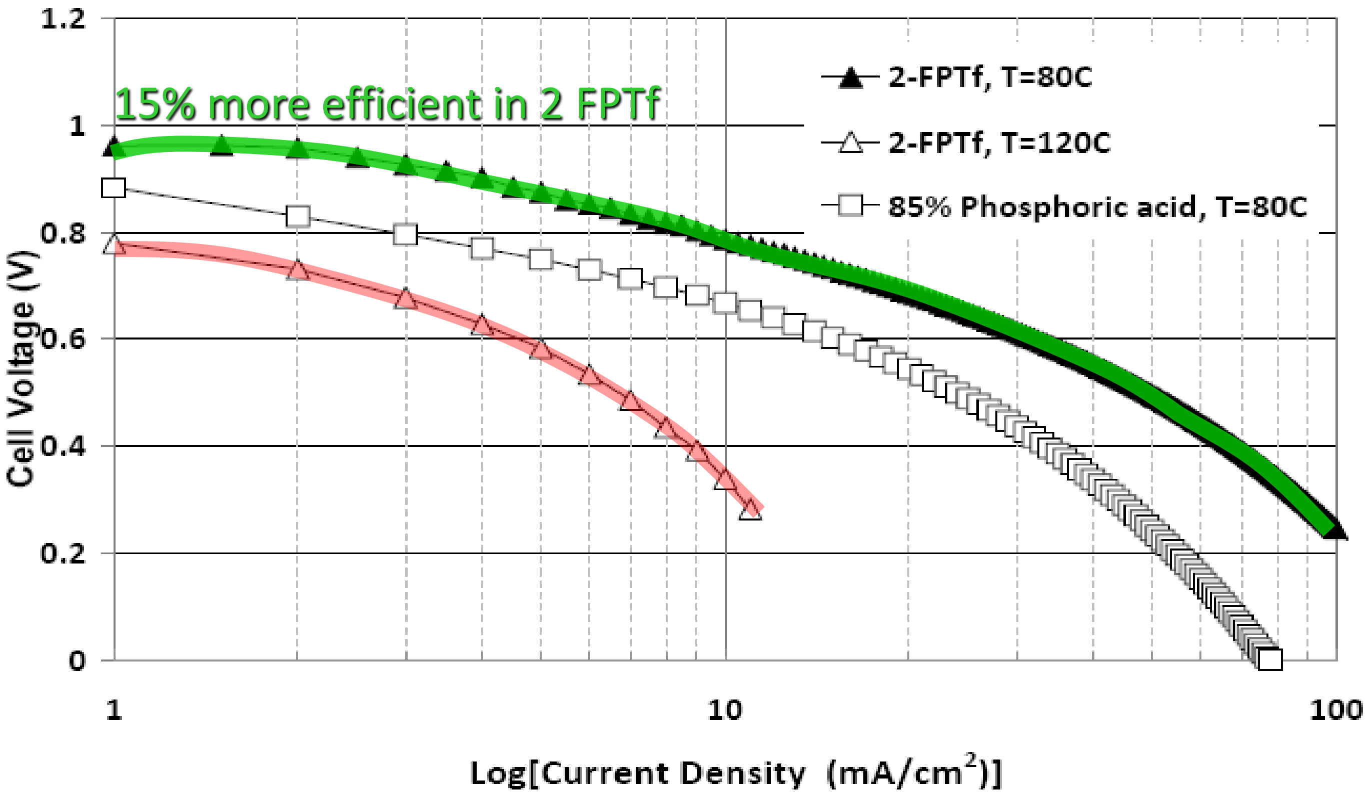
- the first synthetic liquid electrolyte that out performs phosphoric acid



Trifluoromethane sulfonic acid (TFMSA)

2-Fluoropyridine

2-Fluoropyridinium Triflate (2-FPTf) Protic Ionic Liquid m.p. 85°C



<u>2-FPTf is made by mixing</u>

- 1 part triflic acid (TFMSA) and
- 1 part 2-fluoropyridine

<u>Why does 2-FPTf work better?</u>

2-FPTf is a "water-free" electrolyte so platinum-oxide does NOT form and the oxygen electrode is NOT polarized.

This increases the cell voltage, efficiency and power density.

I/V curves for H_2 and O_2 fed to Pt-catalyzed porous electrodes in 2-FPTf electrolyte at 80°C and 120C and 85% phosphoric acid electrolyte at 80°C. σ(2-FPTf) = 4×10^{-3} Scm^{-1} , A = 0.5 cm^2, thickness^{electrolyte} = 0.3 cm.

Solid electrolytes (PEM) only

Liquid Electrolyte Fuel Cell vs Solid PEM Fuel Cell

Issues making *liquid fuel cells unacceptable* especially for portable applications

- liquids leak
- liquid can seep between electrodes causing short circuits
- liquids soften materials accelerating mechanical failure

All of these issues are corrected by using a solid polymer electrolyte

Only solid polymer electrolyte membrane (PEM) fuel cell is acceptable !

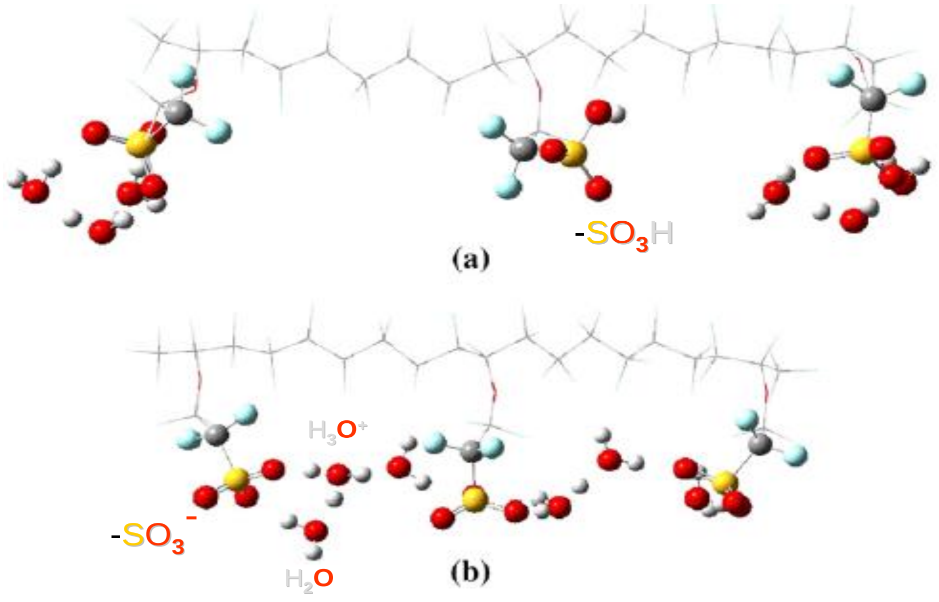
But not all solid electrolytes are equally good

- Solid oxide fuel cell (SOFC ceramicmembrane) is not shock and vibration tolerant, nor suitable for automotive
- Water solvated membranes (like Nafion) are vibration tolerant BUT have large radiators and need inefficient *humidifiers*
- *pIL addresses both issues*

The “Nafion Problem” **Nafion was first solid polymer electrolyte membrane…but**

Nafion has an equivalent weight is 1100 g per -SO_3H group, so with too little water, there is no proton conduction,

- pendant sulfonic acid groups are neither all ionized nor bridged by water molecules, as is shown in Fig. a.
- with 3 waters per -SO_3H group, proton conducts, water bridges ionized acid groups, as shown in Fig. b.



a) Non-conducting
Low water form

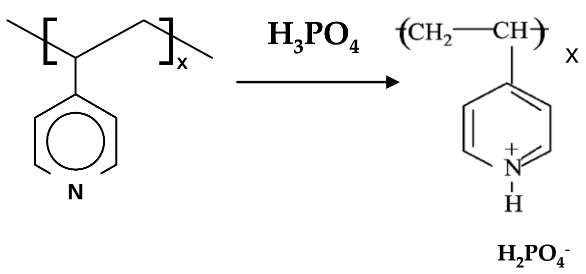
b) Conducting
High water form

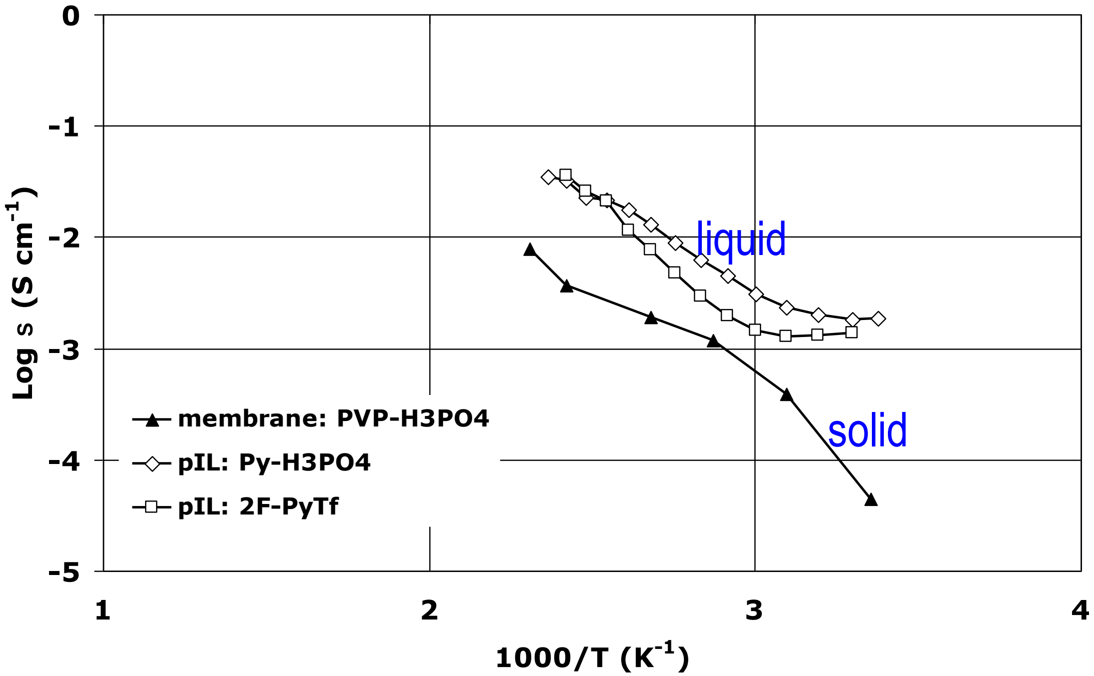
- ***BUT***… 3 waters or more per acid means ***bulk-like water*** is in the membrane.
  - so operating temperature must be ≤ 80°C at atmospheric pressure;
  - need to humidify feed gases to retain solvent water;
  - large radiators are needed to reject waste heat from 80°C to room temperature
  - the performance of platinum catalyzed cathodes is poor (Pt-oxide),
    - E cathode < 0.9V or lower, and fuel-cell efficiency no higher than ~60%

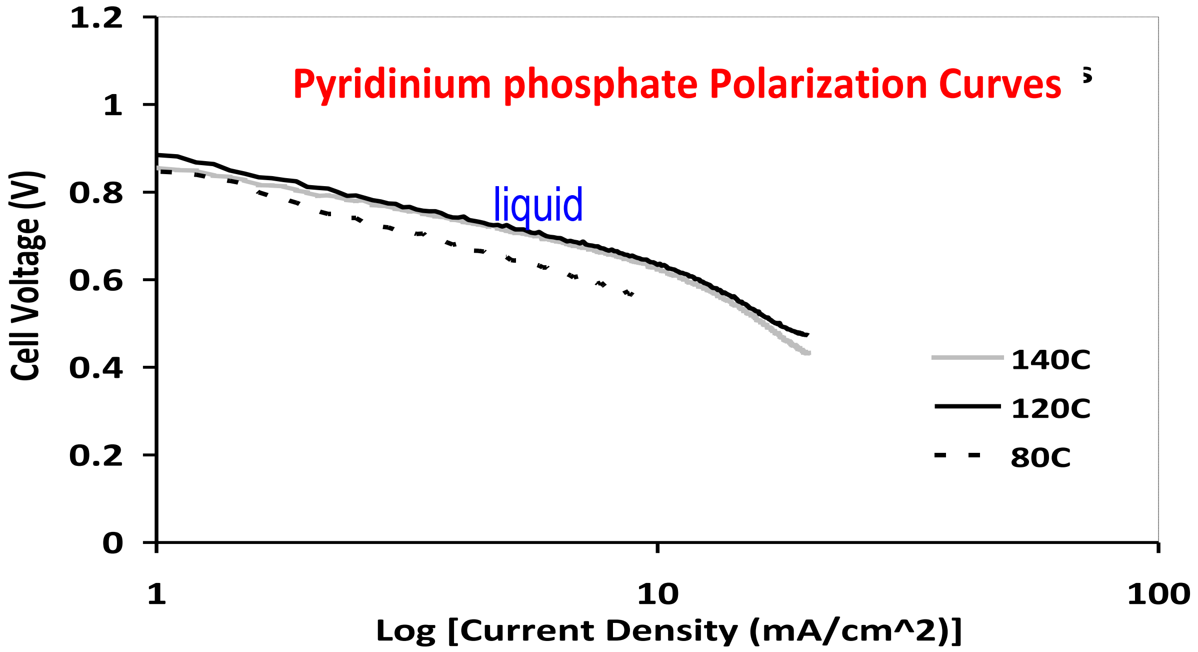
What to do? … solution … go to a non-aqueous proton conductor

Non-aqueous proton conductors

- liquid pyridinium phosphate
- versus solid polyvinyl pyridinium phosphate membrane





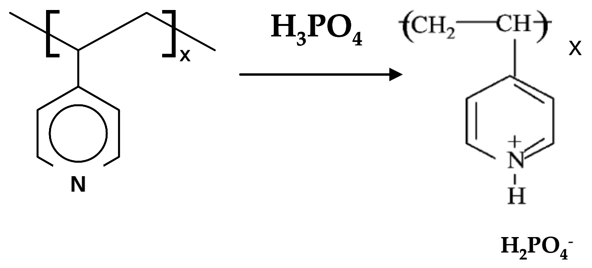


Conductivity for 3 electrolyte samples as a function of temperature. Solid triangle: Solid poly vinyl pyridinium phosphate (PVP-H3PO4) membrane, Open diamond: Liquid pyridinium phosphate pIL (P-H3PO4), Open square: Liquid 2-fluoro pyridinium triflate (2-FPyTf). Electrodes E-Tek Pt/C (0.5mg/cm^2) fed dry: H_2 gas. T=25 to 150^{o}C

Unoptimized fuel cells polarizations with hydrogen anode and oxygen cathode using a non-fluorinated liquid pyridinium phosphate salt (PP) .

Solid polyvinylpyridinium phosphate (PVPP) membrane

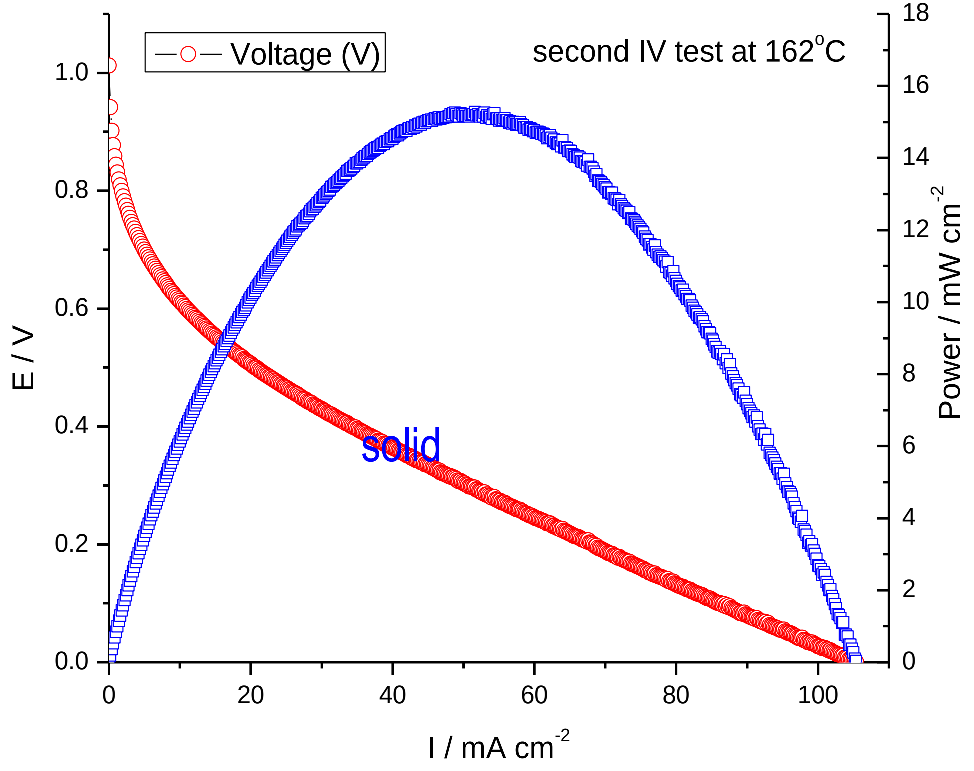
***The solution*, PVPP, a non-aqueous protic salt membrane, a“proton wire” that uses no water and leaches no ions**



PVPP made by reacting each pyridine in polyvinylpyridine polymer with 1 phosphoric acid

A H_2/O_2 fuel cell with PVPP was run overnight under constant load of 30 mA/cm2 and the polarization (I/V test performance) did not change.

This overnight stability is strong evidence that the proton only is hopping through this solid membrane which has no leachable ions or solvents.



I/V curve for H_2/O_2 fuel-cell with poly vinyl pyridine fully neutralized with phosphoric acid. Temp. = 162°C; σ =0.005 S/cm.

This kind of advanced HT-PEM fuel cell will be very reliable in practical use.

This sparingly soluble PVPP membrane is a crude form of Advent insoluble crosslinked “proprietary membrane material”.

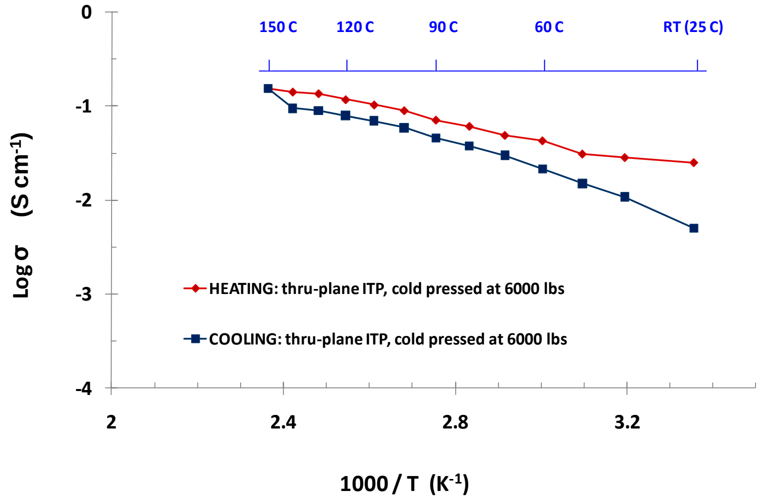
Composites of inorganic and organic polymers

- inorganic polymers , indium tin pyrophosphate (ITP)

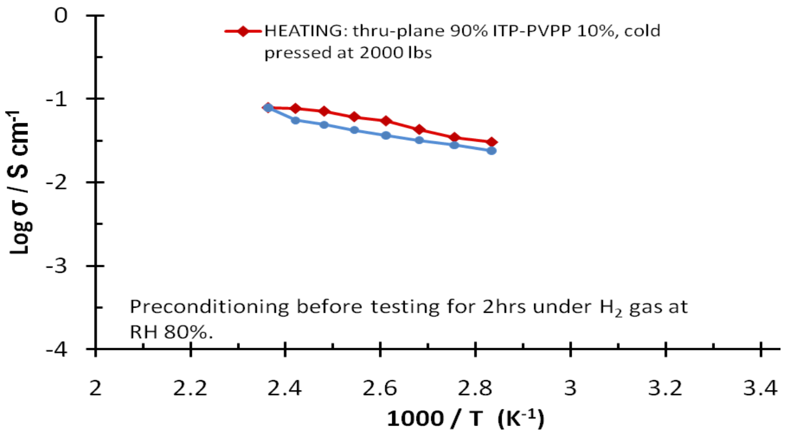
- organic polymer, polyvinyl pyridinium phosphate (PVPP)

Inorganic and organic composition polymer electrolyte membrane (PEM)

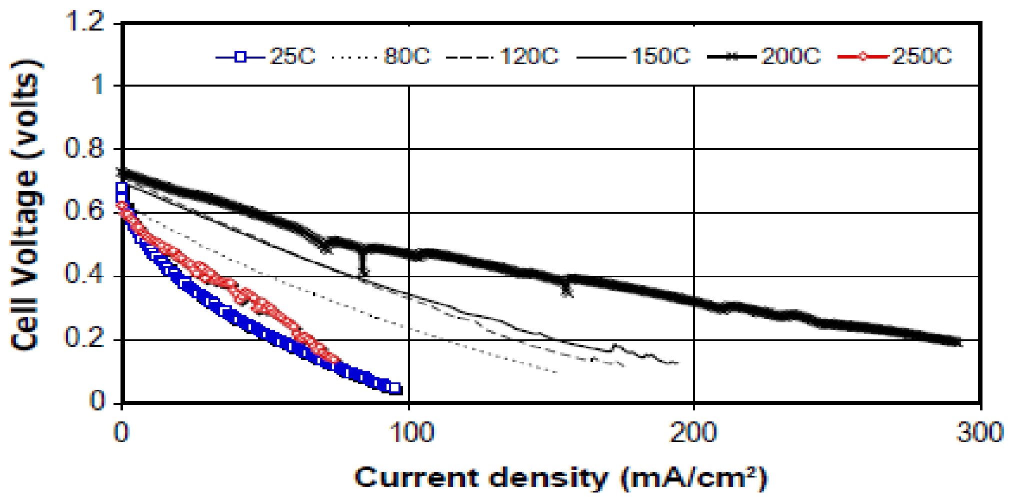
ITP

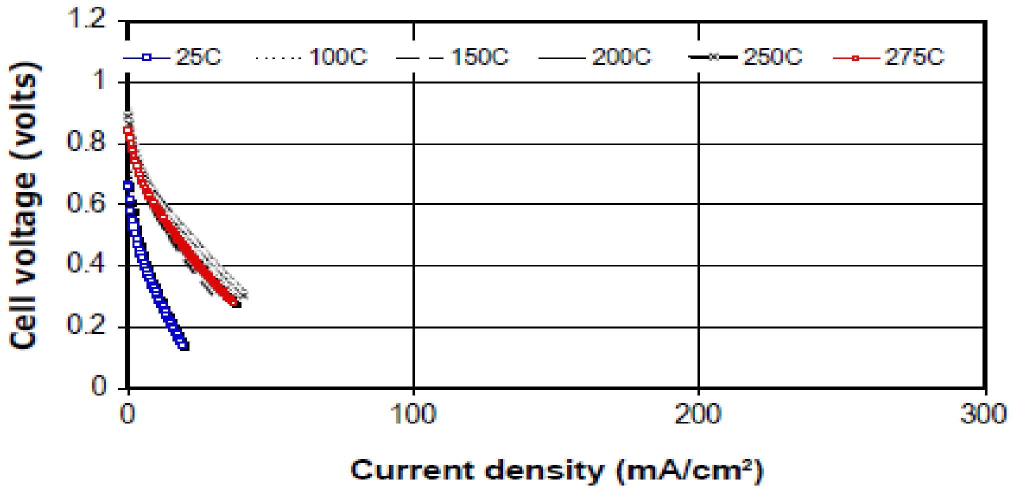


ITP/PVPP



Through-plane conductivity of a pure ITP (top) and 90%ITP/10%PVPP (bottom) membrane with electrodes under dry hydrogen atmosphere. Membrane thickness = 1.65mm, and area = 0.484 cm^2. Frequency range: 50 kHz to 10 Hz. AC amplitude: 50mV. Thickness of sputtered Pt el= 20nm. ETEK electrodes (0.5 mg of Pt per cm^2) used as gas diffusion layer. Pt screen current collectors. J4 ITP membrane.



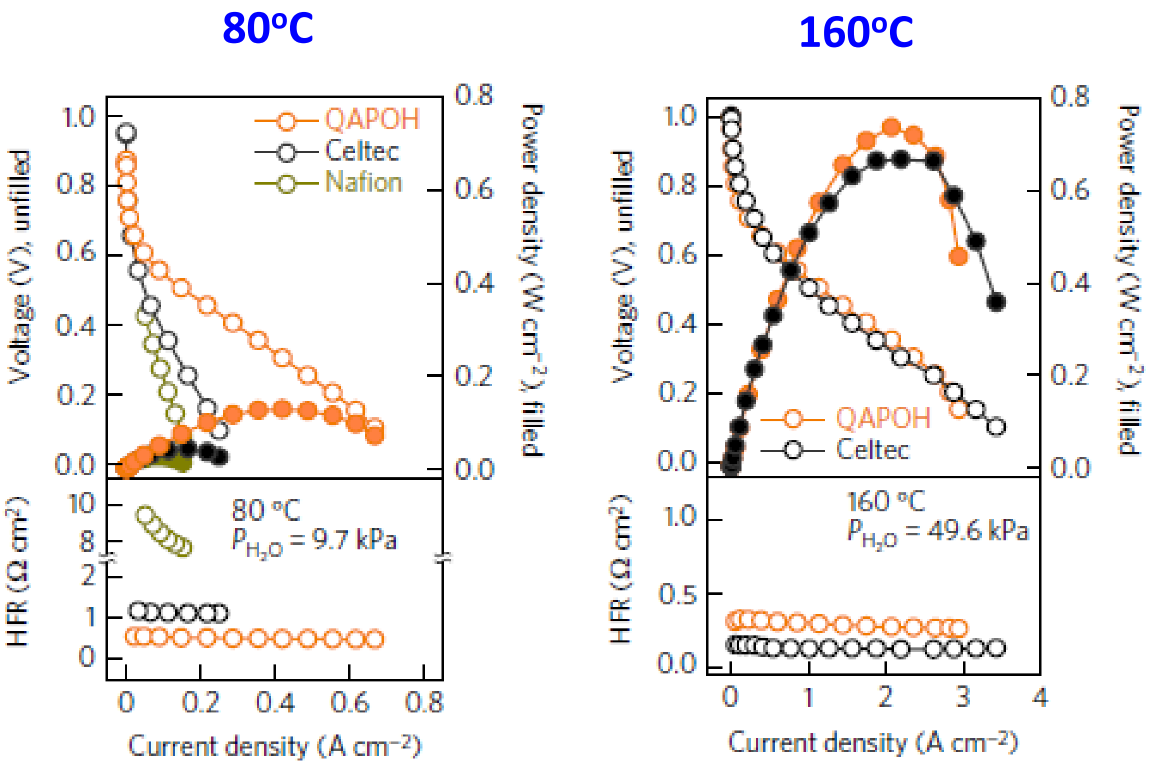


H2 / O2 Fuel cells made with a pure ITP membrane (top) and a membrane with an 90% ITP/ 10% PVPP blend (bottom). ETEK electrodes (0.5 mg of Pt per cm^2) used as gas diffusion layer. Pt screen current collectors.

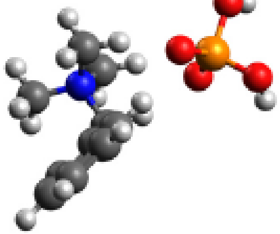
New organic polymers

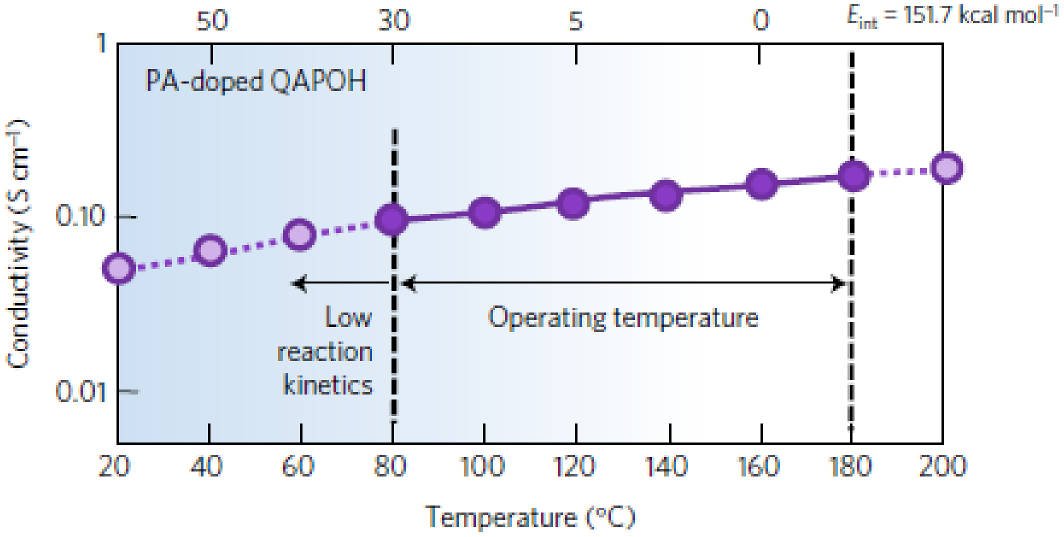
HT PEM Fuel cell based on quaternary ammonium-biphosphate ion pairs

Cy Fujimoto (Sandia National Lab) and Yu Seung Kim (LosAlamos National Lab)



Fuel cell performance





Proton Conductivity of PA-doped QAPOH PEM fuel membrane

- Unlike phosphoric acid (PA) loaded PBI, authors claimed the phosphoric acid does come NOT come out in presence of liquid water, with PA loaded benzyl trimethyl ammonium (BTMA) groups on polyphenylene backbone membrane.
- Claimed a new class of stable PEM fuel cell that can operate at low and high temperatures and retain phosphate even when water wet.
- Has high conductivity and fuel cell performance at high temperatures to 180°C.

But low temperature performance suffered due to water leaching phosphoric acid (PA)

Is all lost?

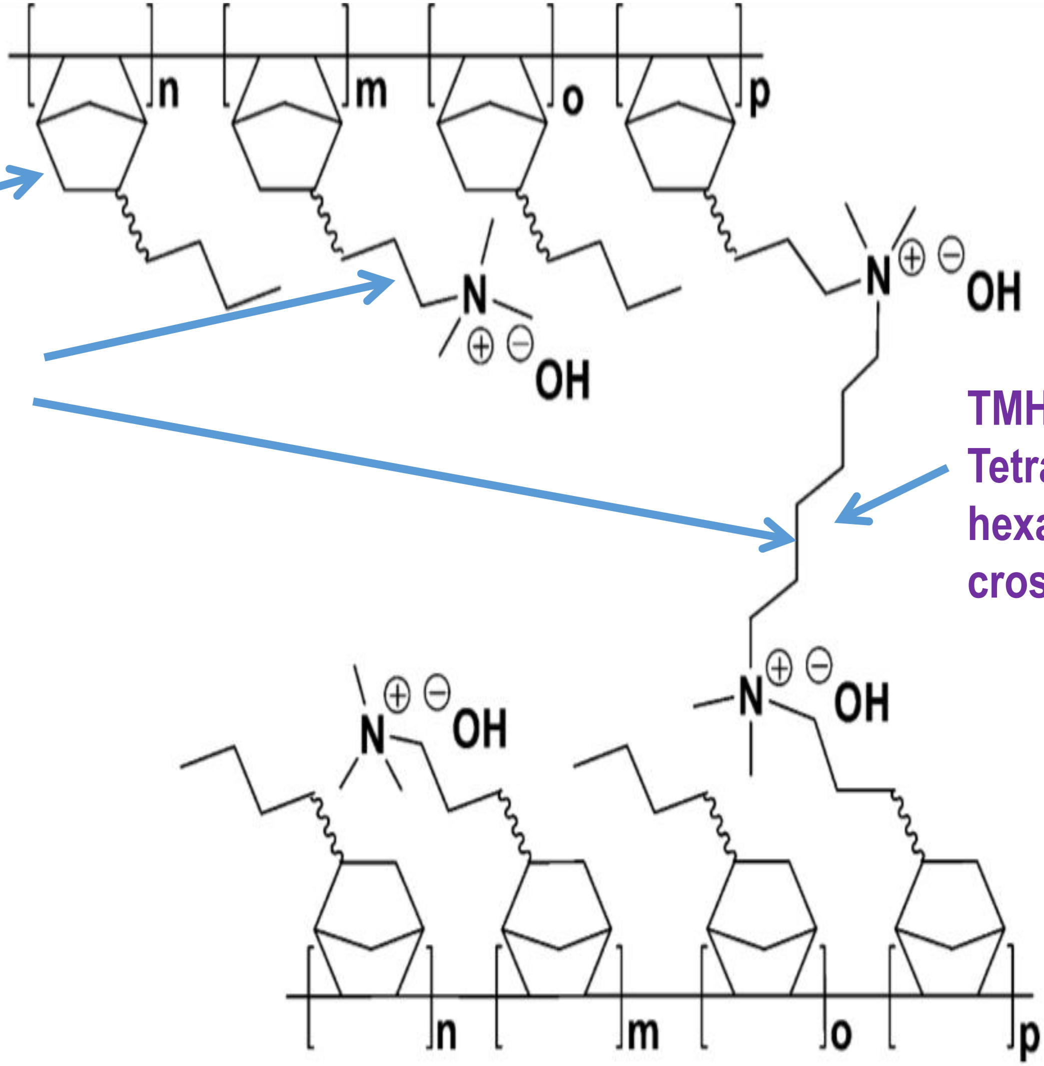
No

Stable conductive ammonium hydroxide polymer**
… precursor to HTPEM

*Stable AEMs under realistic operating conditions (e.g., 80 °C and 1 M KOH) have been synthesized by combining

- all-hydrocarbon backbone
- with tethered cations on long alkyl chains

Tetrablock copolymer, PNB-X34-Y66



TMHDA (N,N,N',N'-Tetramethyl-1,6 hexane diamine cross-linking agent

* Lee, W. H.; Mohanty, A. D.; Bae, C. Fluorene-Based Hydroxide Ion Conducting Polymers for Chemically Stable Anion Exchange Membrane Fuel Cells. ACS Macro Lett. 2015, 4, 453−457.

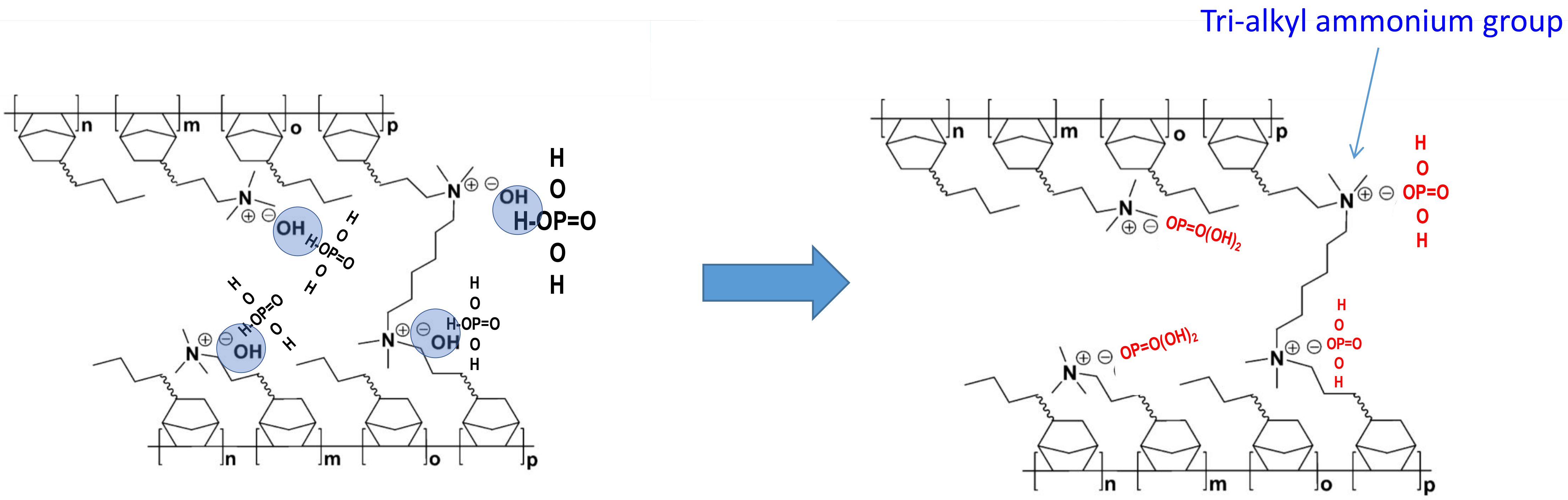
* Ono, H.; Kimura, T.; Takano, A.; Asazawa, K.; Miyake, J.; Inukai, J.; Miyatake, K. Robust anion conductive polymers containing perfluoroalkylene and pendant ammonium groups for high performance fuel cells. J. Mater. Chem. A 2017, 5, 24804−24812.

* Lee, W. H.; Kim, Y. S.; Bae, C. Robust Hydroxide Ion Conducting Poly(biphenyl alylene)s for Alkaline Fuel Cell Membranes. ACS Macro Lett. 2015, 4, 814−818.

** Mandal, M., Huang, G., and Kohl, P. A., "Highly Conducting Anion Exchange Membranes Based on Cross-linked Poly(norbornene): Vinyl Addition Polymerization", ACS Journal of Applied Energy and Materials, 2, 2447-2457 (2019).

From hydroxide conductor to high temp proton conductor

- by adding an acid (here, phosphoric acid) to hydroxide adduct of ammonium polymer



H_3PO_4 + X-linked block copolymer PNB-X34-Y66 $\longrightarrow$ HT PEM

hydroxide conductor

high temp proton conductor

Benefits of new polymer for making a HTPEM fuel cell

- This new polymer offers a a new platform for stable proton conduction in a polymer electrolyte membrane (PEM) at high temperature ($T \leq 200^oC$)
- Conductivity of ammonium phosphate comparable to phosphoric acid, expect high conductivity in the polymer membrane (conductivity around 0.1 S/cm)
- Ionic groups are covalently and electrostatically immobilized so *TRULY WATER INSOLUBLE and NONLEACHABLE* for extending stable operation at both high and low temperatures ($-55^oC \leq T \leq 200^oC$) in the presence of liquid water.

Conclusions and Recommendations for future research

Evolution of fuel cells is system optimization by

- reducing components to decreasing size, weight and parasitic losses
- increase fuel cell power density with catalysts (Pt) to decrease size and weight
- using polymer electrolyte membrane (PEM) is preferred electrolyte affording better system designs
- catalyst and electrolyte are intimately related for improving fuel cell

Insoluble protic salt polymers with a high density of covalently attached protic salt groups allow proton to be conducted without water at elevated temperatures following Arrhennius behavior.

- Protoic salts membranes :
    - are Bronsted salts which contain a proton and whose acid and base moieties are covalently and electrostacically attached to polymer
    - have pK separated by more than 4 units and less than 14. Here amines and phosphates
    - but other combinations possible

These developments give a promising path toward stable water-free proton conducting membranes for stable, compact and efficient fuel cell systems with low levels of Pt catalysts and possibly non-platinum catalyst for the hydrogen and oxygen fuel cell for fuel cell in the 100kilowatt range for automotive and distributed power applications

Main terrestrial markets suiting HT-PEMFC technology:

1. micro-CHP (emergency and off-grid residential electricity and heat)
2. power production (distributed generation)
3. portable power (automotive)
4. hydrogen separation (electrolysis of water and hydrogen compression)
5. electrical power *inside* airplanes
6. remote communications stations and battery chargers
7. Storage and use of renewables, like solar during sundown, wind during calm, etc.

Acknowledgements

Army Research Office,
ARO Project No. W911-NF-04-1-0060
Dr. Robert Mantz, Project Monitor

NASA-Glen
NASA Project No. NC04GB06G
Dr. James Kinder, Project Monitor

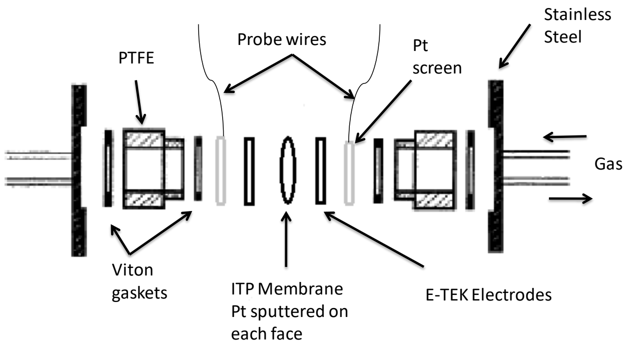
U. S. Department of Energy
DoE Project No. DE-FG36-06G016029
Drs. Kathi Epping, Gregory Kleen Project Managers

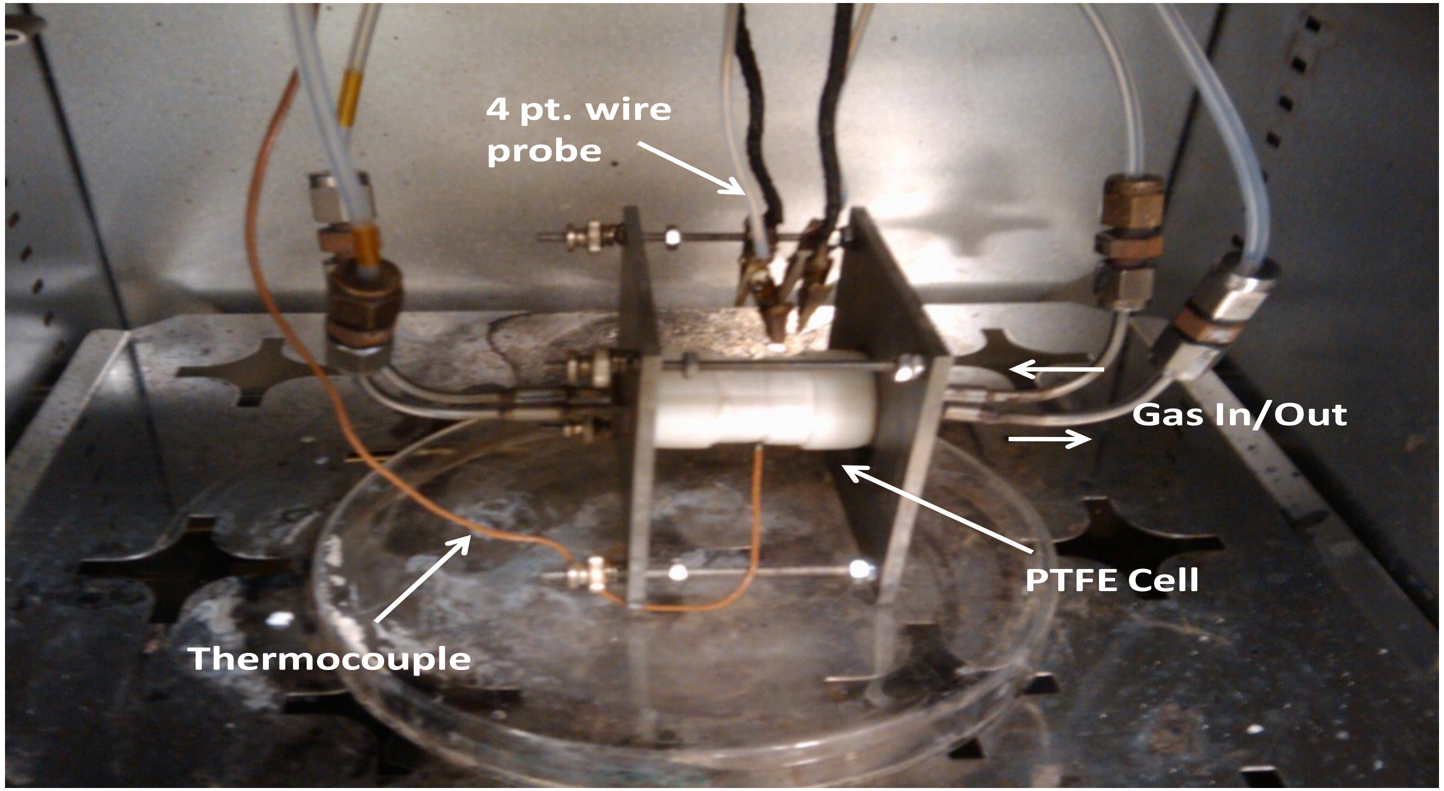
BOEING *and* SCIENCE foundation ARIZONA Innovation at Work

Drs. Joanna Moore, James Kinder and Jean-Phillipe Belieres
Project Monitors

EXTRA SLIDES

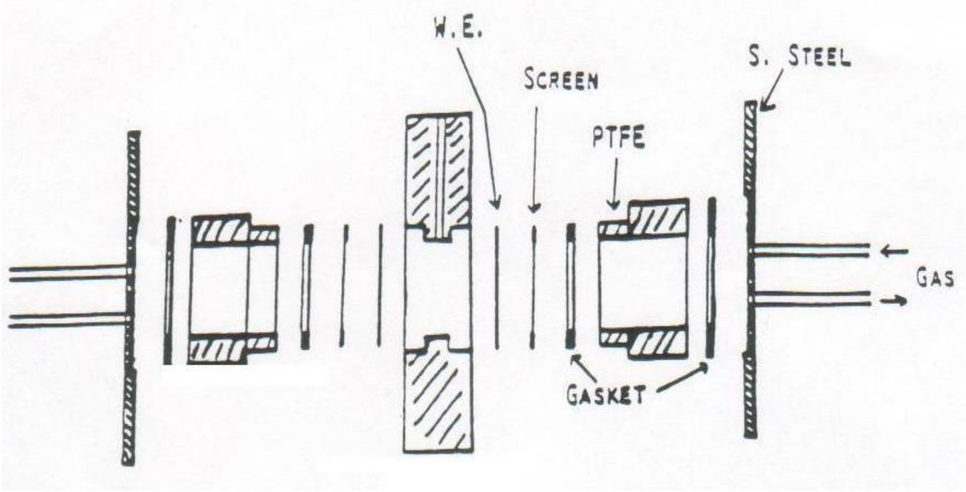
Solid Electrolyte Test Fuel Cell

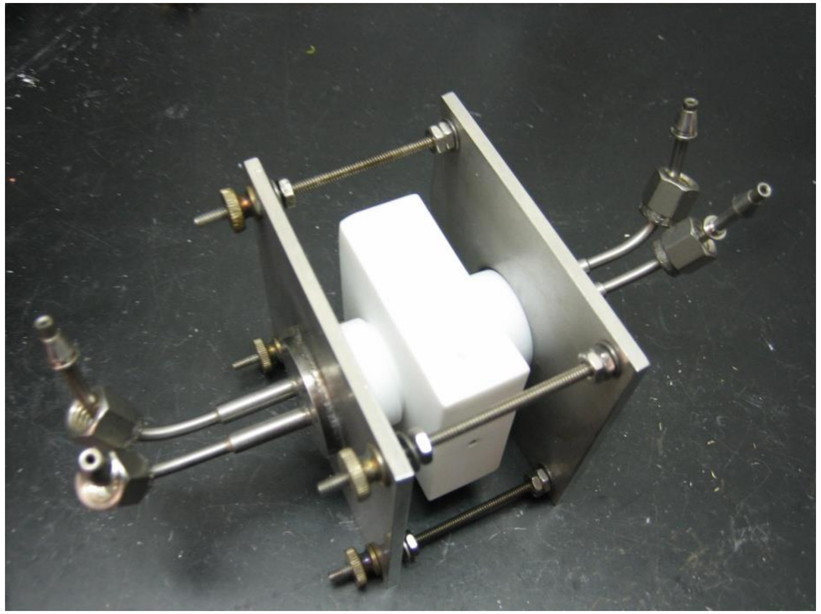




Schematic diagram (top) and real hardware (bottom) for accepting solid electrolyte membrane electrode assembly and feeding oxygen to one side and hydrogen to the other to produce fuel cell measurements inside isothermal oven.

Liquid Electrolyte Fuel Cell Test Hardware



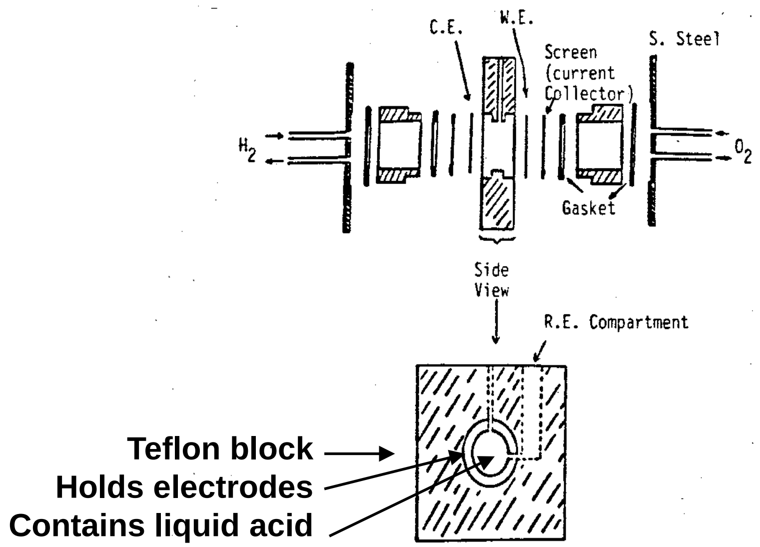


- ➢E-TEK ELAT V3 electrodes (Pt loading 0.5 mg/cm^2) compression sealed around Ionic Liquid contained in Teflon (PTFE) cell body.

- ➢Liquids tend to leak and cause shorts in the fuel cell, not suitable for commercial use.

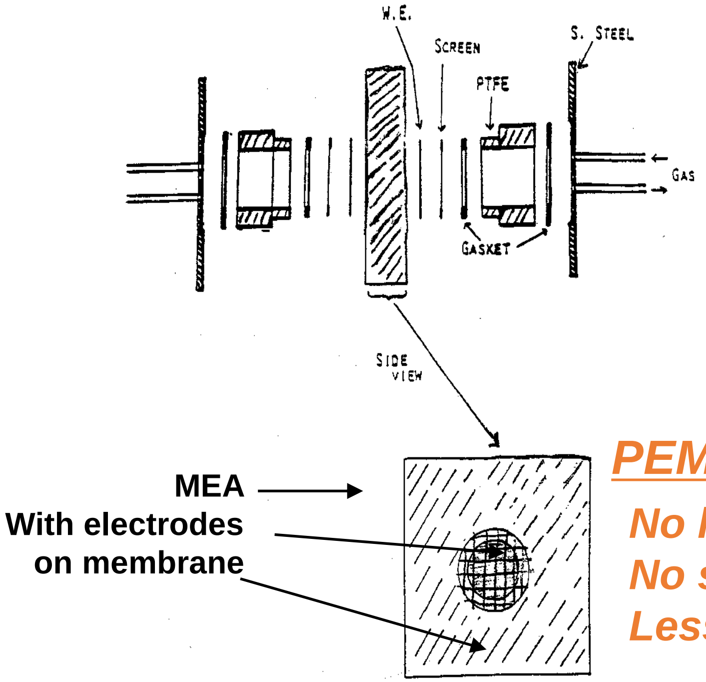
Liquid vs. Polymer Electrolyte Membrane (PEM) Fuel Cell

Liquid Fuel Cell



Schematic representation of PTFE micro fuel cell with Gas Fed Electrodes and liquid electrolyte, like phosphoric acid.

Solid PEM Fuel Cell



PEM Preferred

No leaks
No shorts
Less Corrosion

Schematic representation of a micro fuel cell with Gas Fed Electrodes and PEM electrolyte, like Nafion.