# Low temperature acid fuel cells Past Present & Future

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# Fuel cell
# Our mission

- **To develop totally indigenous fuel cell for Indian armed forces & commercial use**
- **All necessary subsystems like fuel processor, startup systems etc.**
- **Spin off benefits**

# content

- Attention areas of PAFC and PEMFCs
- Improvement options tried by NMRL
- Balance of plant developed at NMRL
  - Hydrogen provision
  - Control system
  - Accessories
- New product range from NMRL

# Our Choices ...

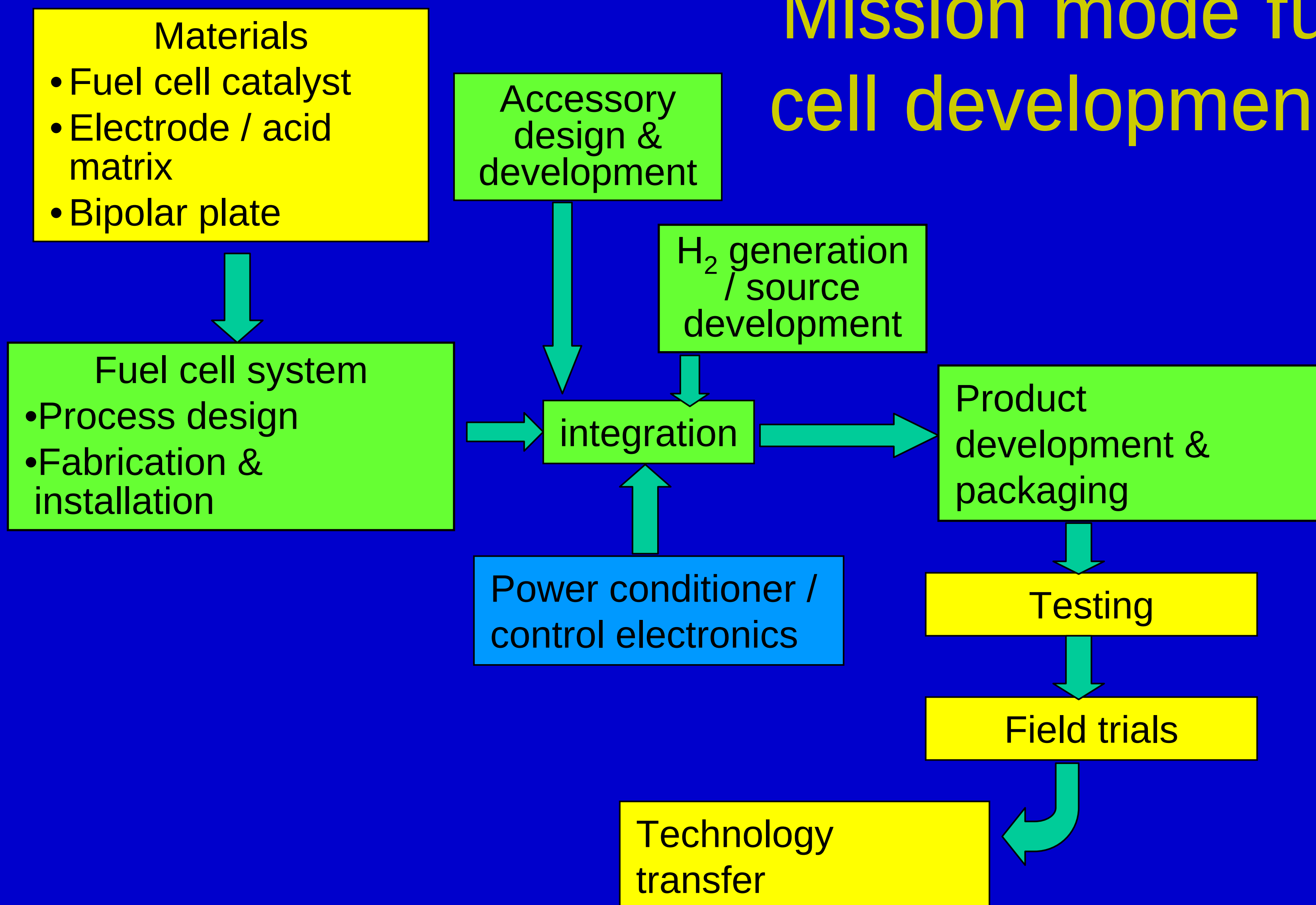
Mission mode systems

- Phosphoric acid fuel cell (PAFC)
  - The main workhorse
- Polymer electrolyte fuel cell (PEMFC)
  - Mobile and small systems
- Direct borohydride fuel cells with integrated fuel bank
  - Handheld systems
  - UAVs
  - Soldier as a system

R&D systems

- Solid oxide fuel cell (SOFC)
  - Material / component stage
- Direct carbon fuel cell (DCFC)

# Mission mode fuel cell development...



# Achievements so far in fuel cell systems…

## PAFC

- Catalyst
- Carbon paper
- Electrode
- Acid holder matrix
- Low cost Graphite gas distributor plate materials

- Acid management systems
- Humidifiers
- Thermal systems
- Power conditioners

- Online hydrogen generation devices
- Novel hydrogen storage materials

Status :- Limited production for army – Through industry – upto 10kW complete power packs

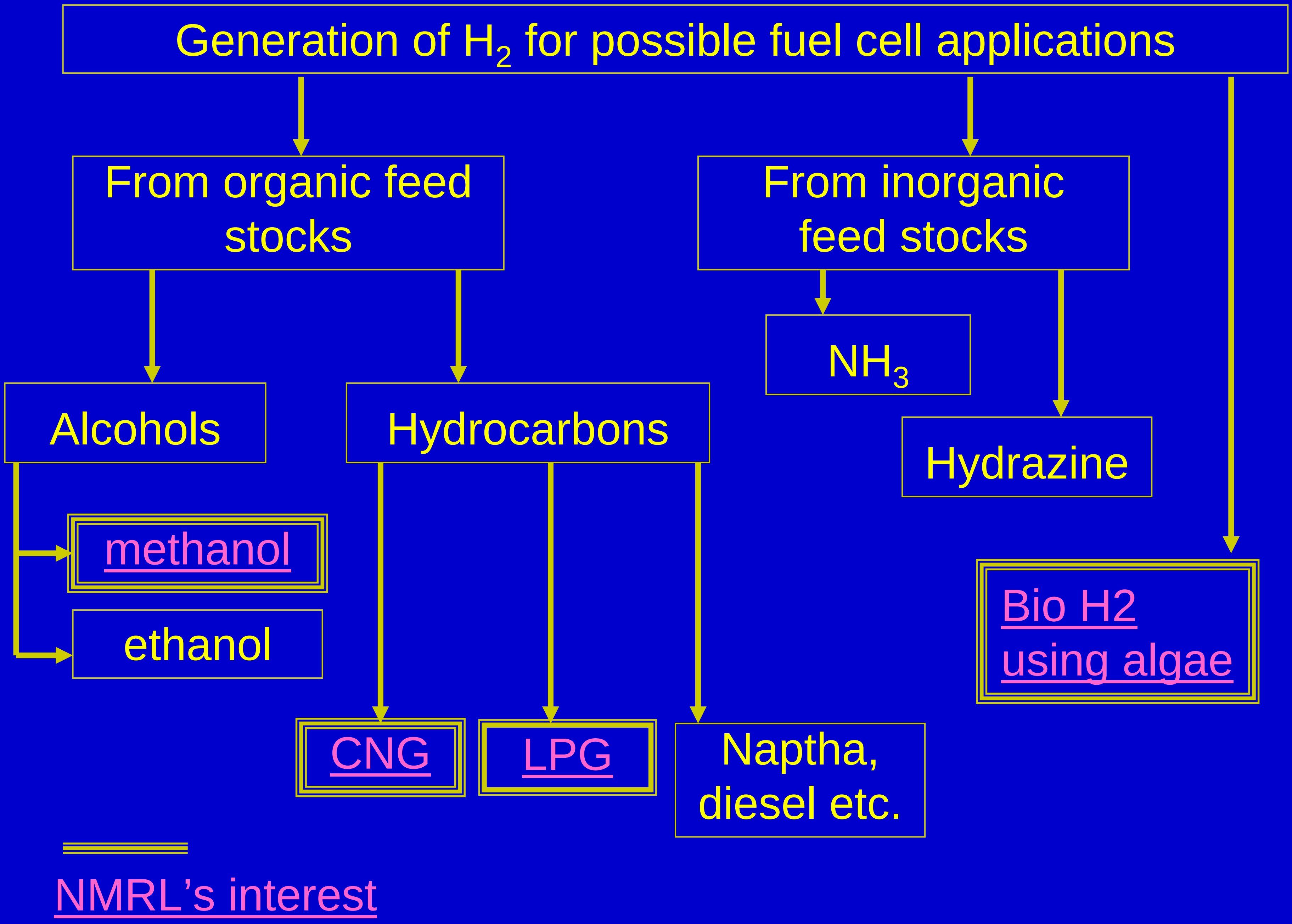
# Achievements so far in fuel cell systems…

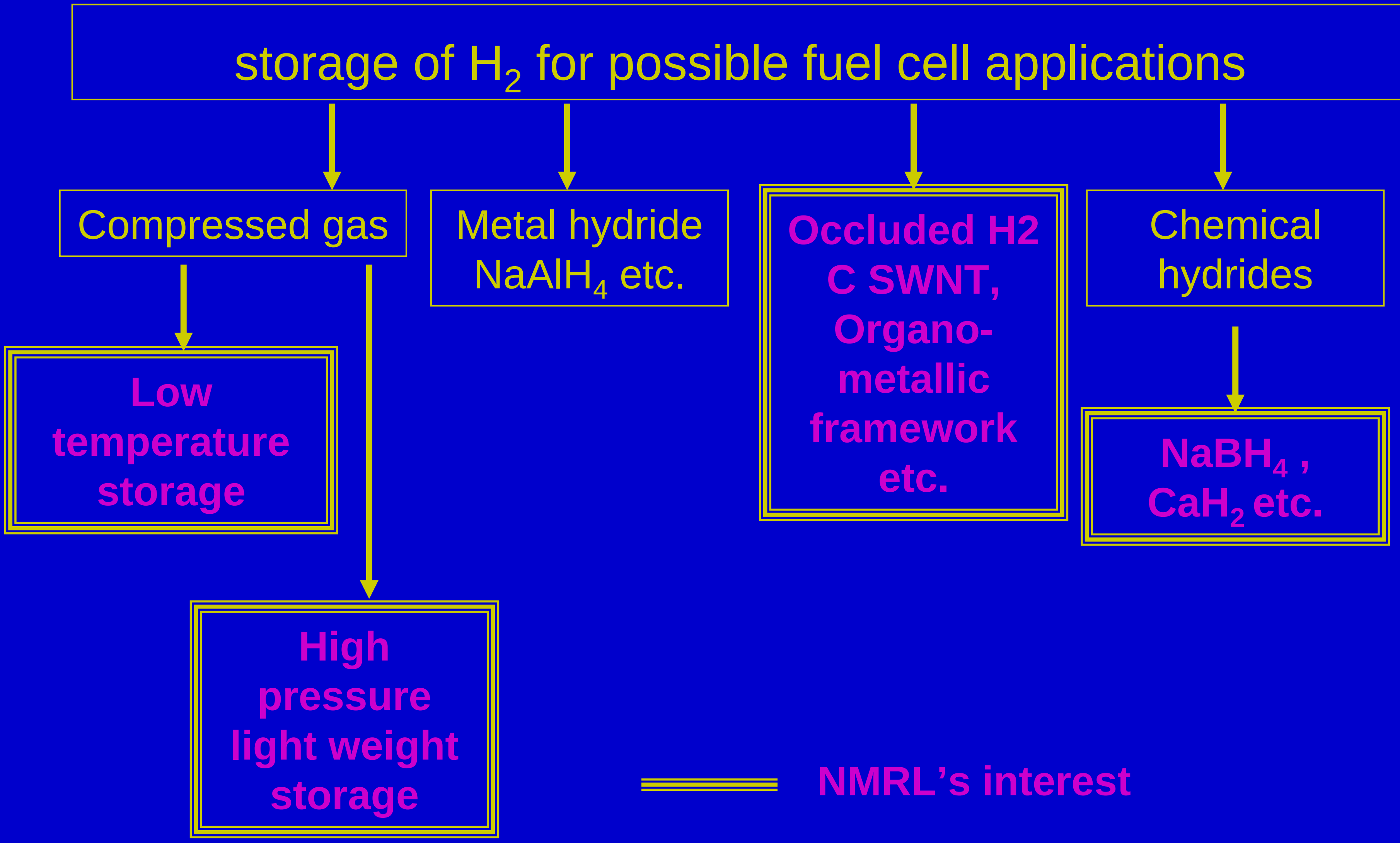
## PEMFC /DMFC

- **Alloy Catalyst (PEMFC,DMFC)**
- **Carbon paper**
- **Electrode, (PEMFC/DMFC)**
- **Novel low cost membrane as Nafion substitute**
- **MEAs & CCMs (PEMFC)**
- **Graphite gas distributor plate (PEMFC/DMFC)**

- **Humidifiers internal & external**
- **Thermal systems & Power conditioners**

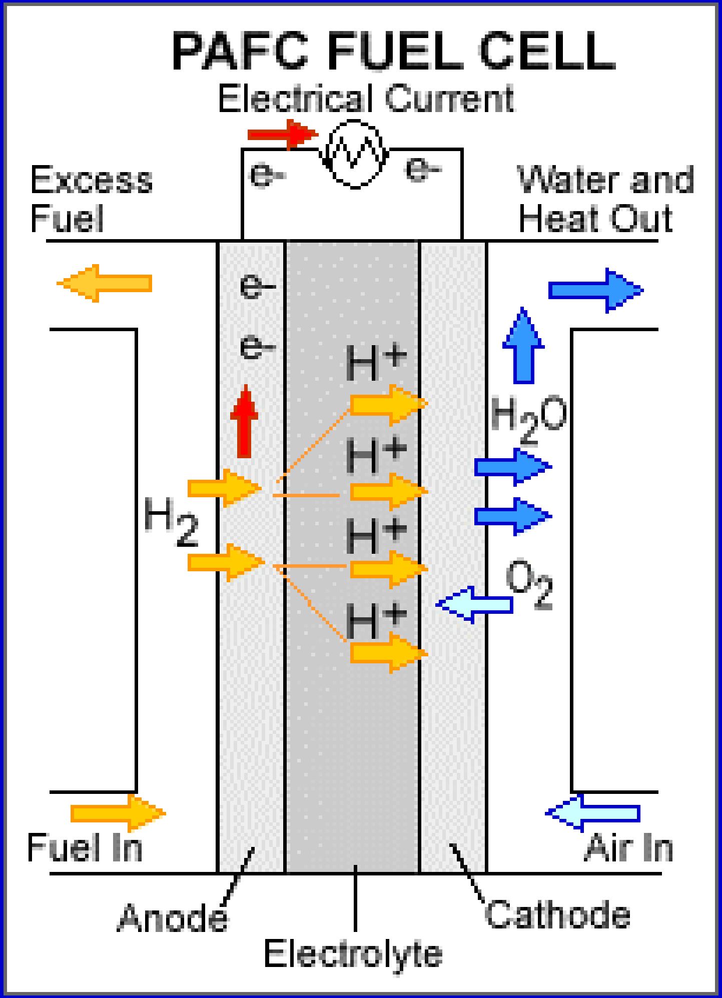
Status :- Prototypes with all accessories upto 100w – Beta models (PEMFC)


Generation of H2 for possible fuel cell applications
From organic feed stocks
From inorganic feed stocks
NH3
Alcohols
Hydrocarbons
Hydrazine
methanol
ethanol
Bio H2 using algae
CNG
LPG
Naptha, diesel etc.
NMRL's interest


storage of $H_2$ for possible fuel cell applications
Compressed gas
Metal hydride $NaAlH_4$ etc.
Occluded H2 C SWNT, Organo-metallic framework etc.
Chemical hydrides
Low temperature storage
High pressure light weight storage
$NaBH_4$ , $CaH_2$ etc.
NMRL's interest

# Phosphoric Acid Fuel Cells (PAFC)

| | |
|---|---|
| Electrolyte | Phosphoric Acid |
| Operating temperature | 160°C-200°C |
| Charge carrier | $H^+$ |
| Prime cell components | Graphite based |
| Catalyst | Platinum |
| Product water management | Evaporative |
| Product heat management | Process gas + Independent cooling medium |



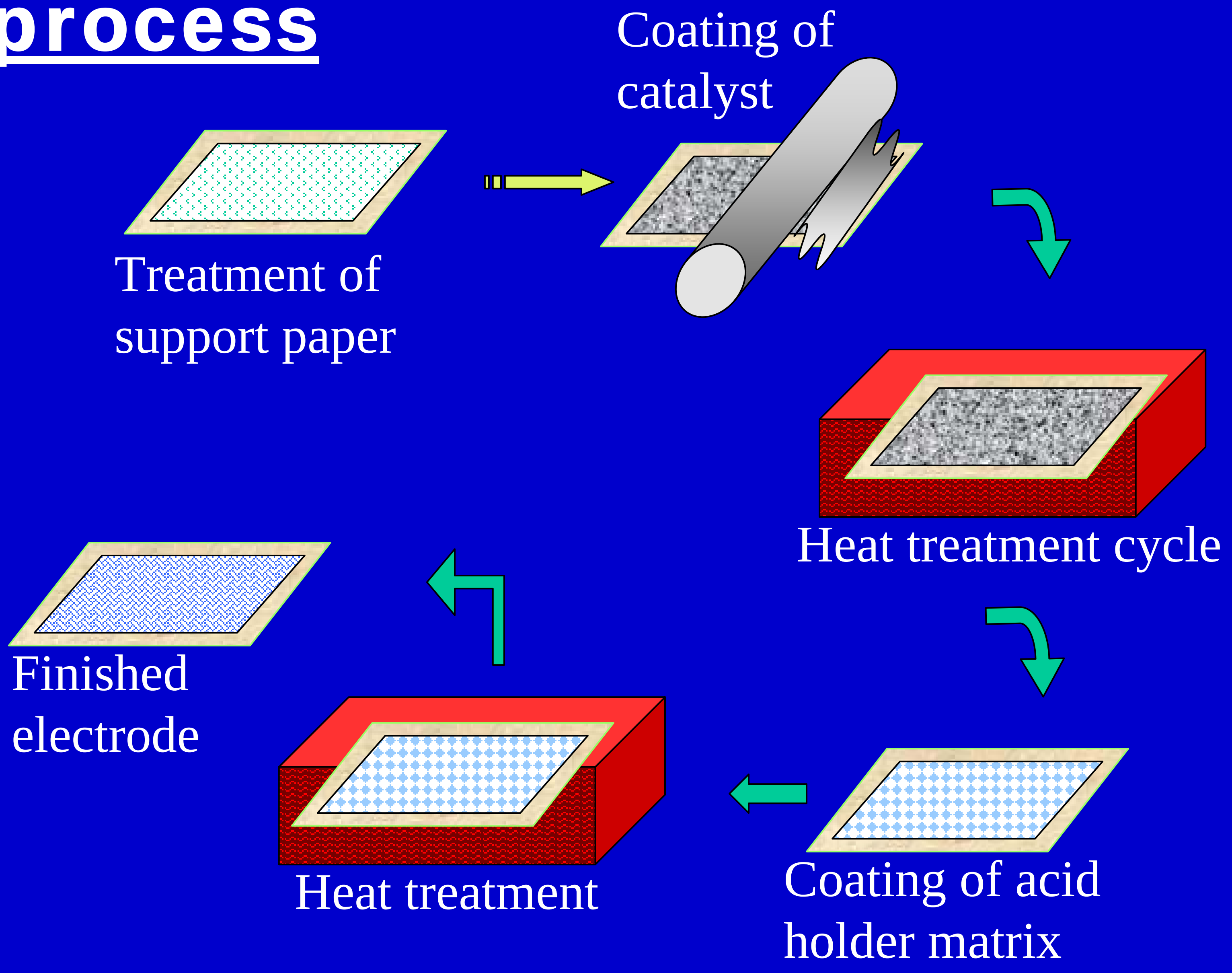

- **Moderate power density**

# PAFC Materials

| Component | ca. 1965 | ca. 1975 | Current Status |
|---|---|---|---|
| **Anode** | PTFE-bonded Pt black | PTFE-bonded Pt/C | PTFE-bonded Pt/C |
| | | Vulcan XC-72[a] | Vulcan XC-72[a] |
| | 9 mg/cm$^2$ | 0.25 mg Pt/cm$^2$ | 0.1 mg Pt/cm$^2$ |
| **Cathode** | PTFE-bonded Pt black | PTFE-bonded Pt/C | PTFE-bonded Pt/C |
| | | Vulcan XC-72[a] | Vulcan XC-72[a] |
| | 9 mg/cm$^2$ | 0.5 mg Pt/cm$^2$ | 0.5 mg Pt/cm$^2$ |
| **Electrode Support** | • Ta mesh screen | • Carbon paper | • Carbon paper |
| **Electrolyte Support** | • glass fiber paper | • PTFE-bonded SiC | • PTFE-bonded SiC |
| **Electrolyte** | • 85% $H_3PO_4$ | • 95% $H_3PO_4$ | • 100% $H_3PO_4$ |

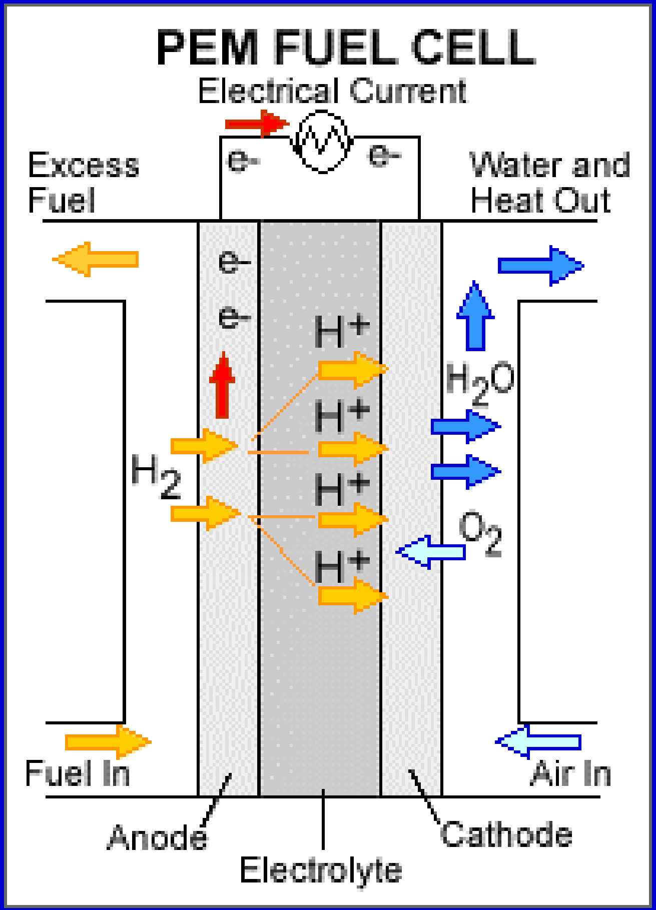
a - Conductive oil furnace black, product of Cabot Corp. Typical properties: 002 d-spacing of 3.6 Å by X-ray diffusion, surface area of 220 m$^2$/g by nitrogen adsorption, and average particle size of 30 μm by electron microscopy.

# Electrode preparation process



# Proton Exchange Membrane Fuel Cells (PEMFC)

| | |
|---|---|
| Electrolyte | Ion Exchange Membranes |
| Operating temperature | 80°C |
| Charge carrier | $H^+$ |
| Prime cell components | Carbon based |
| Catalyst | Platinum |
| Product water management | Evaporative |
| Product heat management | Process gas + independent cooling medium |



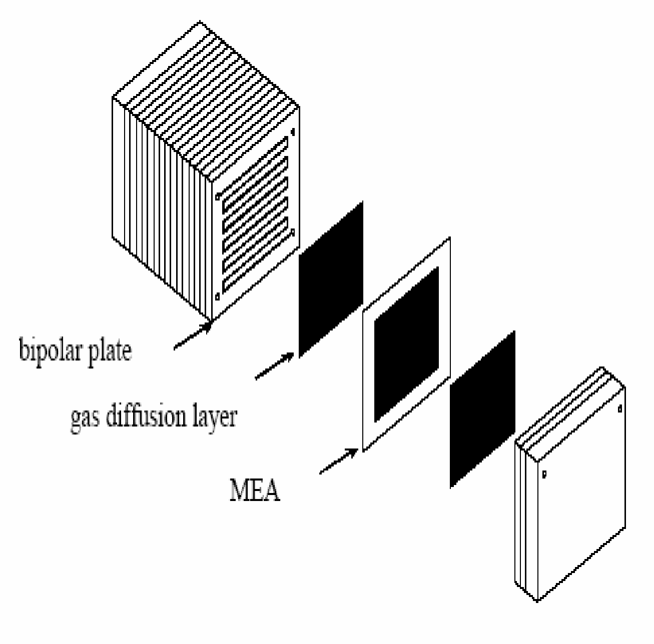

**Technology Scenario**

**At R & D stage in India**

- **Very sensitive to CO poisoning**

# PEMFC materials

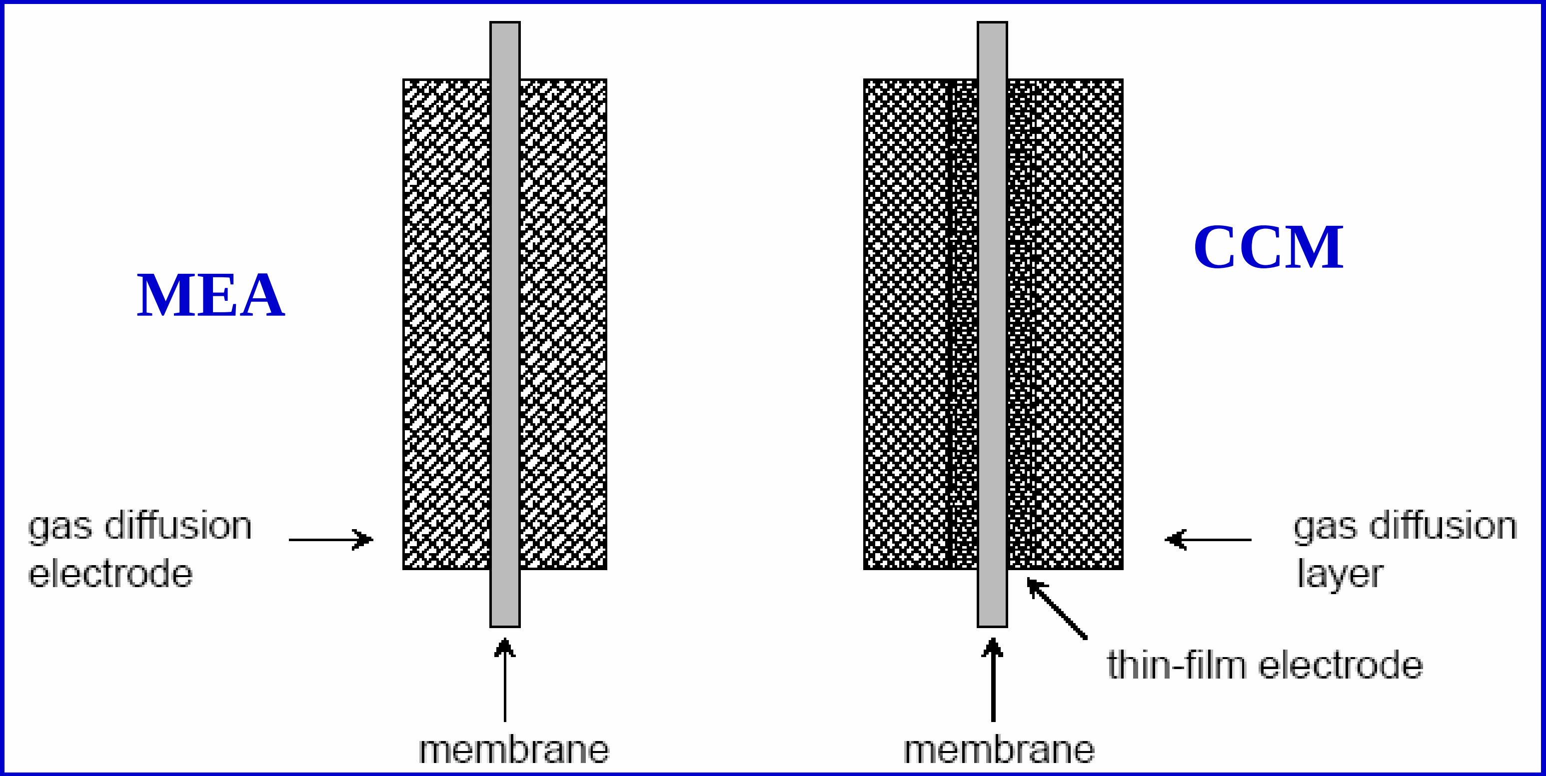
| | |
|---|---|
| anode | Pt on carbon (Vulcan XC72) typically 0.1-0.5mg/cm$^2$, bonded on carbon paper/cloth support with nafion binder for ionic bridge |
| cathode | Pt on carbon (Vulcan XC72) typically 5-0.5mg/cm$^2$, bonded on carbon paper/cloth support with nafion binder for ionic bridge |
| electrolyte | Fluro sulphonic acid based proton conducting polymer membrane like nafion, dow membrane etc. |



# PEMFC basic configuration

Catalyst layer thicker,
Pt/C ~20%
Hot pressed assy

Catalyst layer coated on
membrane, Pt/C 20-50%
Press contact assy



# Observations -
# the present systems

## Problems with PAFC are …

- Highly corrosive environment allows only graphite / carbon components
  - Enhances cost
  - Special manufacturing
- Higher operating temperature
  - High startup time
- Need to be run continuously
  - frequent stopping of hydrogen (start/stop) reduces life

## Advantages of PAFC are …

- Mature technology with proven very high availability (~85%)
- Higher operating temp allows high CO (<2%) allows direct reformer gas
- Multi fuel option
- Novel methods promises cost reduction
- Highly rugged with long proven life 10,000-50,000 hour

## Problems with PEMFC are …

- Low operating temperature limits CO tolerance (in ppm)
- High cost of membrane
- Fragile in nature & require comprehensive humidification
- Low membrane life in actual stack condition
- Local overheating melts membrane allowing direct crossover & failure

## Advantages of PEMFC are …

- Pressurized versions have high current density
- Relatively quicker startup
- Only pure $H_2O$ as output / spillage
- Multiple option for bipolar plate
- Suitable for small vehicle / portable power applications

anode: $H_2 \rightarrow 2H^+ + 2e^-$

cathode: $\frac{1}{2}O2 + 2e^- + 2H^+ \rightarrow H_2O$

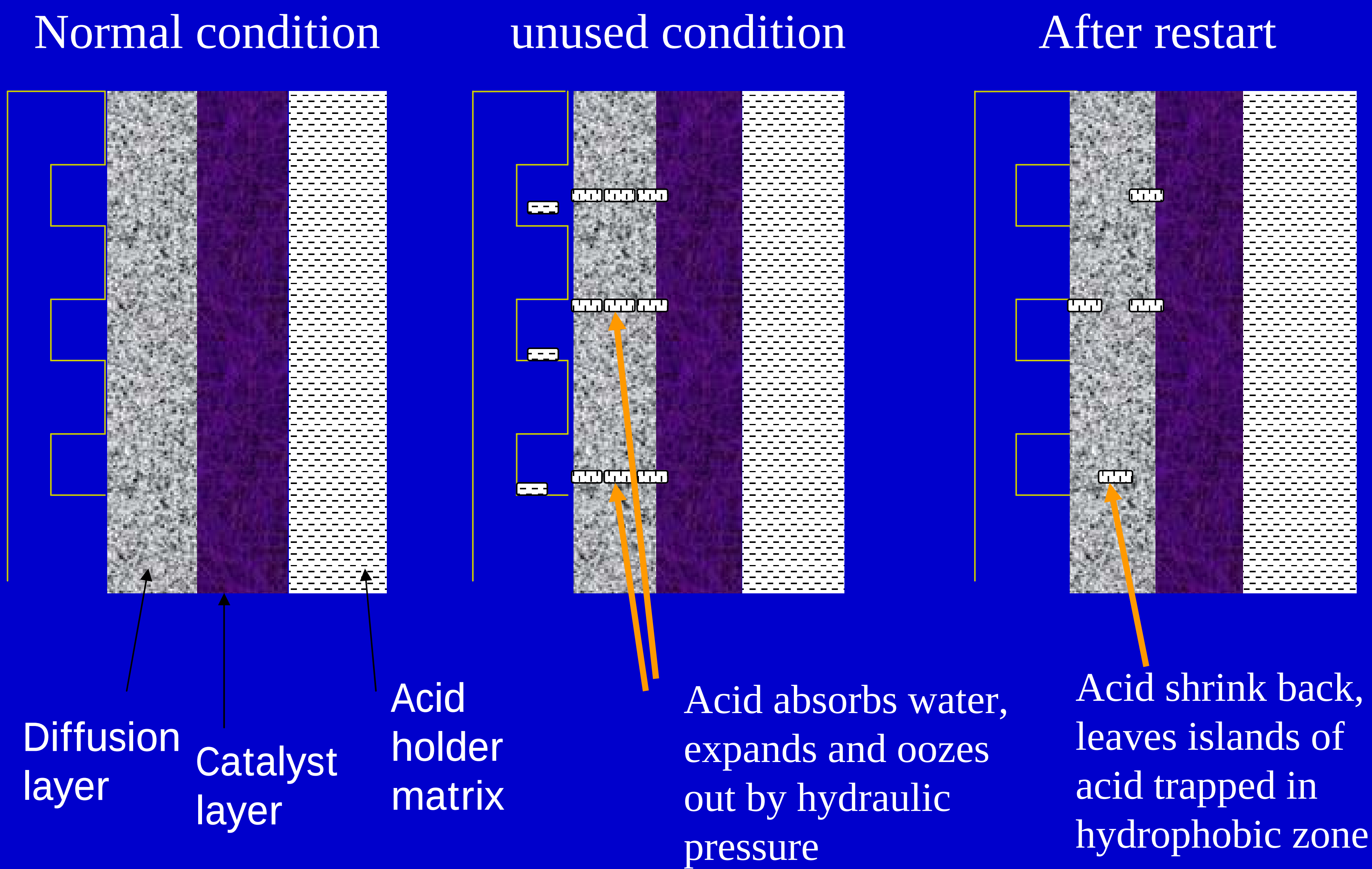
Cell : $\frac{1}{2}O_2 + H_2 \rightarrow H_2O$



**Nexa®**

| | | |
|---|---|---|
| **Performance** | Rated net power | 1200 watts[1] |
| | Rated current | 46 Amps[1] |
| | DC voltage range | 22 to 50 Volts |
| | Operating lifetime | 1500 hours |
| **Fuel** | Composition | 99.99% dry gaseous hydrogen |
| | Supply pressure | 0.7 - 17 bar (10 to 250 PSIG) |
| | Consumption | ≤ 18.5 SLPM[2] |

# Start/stop induced diffusion problem of PAFC



# Start/stop induced catalyst sintering in PAFC

- Under operation, inorganic groups of the catalyst support ...
  - Reduces at cathode
  - Oxidised at anode
  - Cause readjustment of acid in the catlalyst layer
- After $H_2$ withdrawal
  - Reverse phenomena occurs
- Repeatation of this cause
  - Loosening of Pt particles
  - Dissolution and sintering
- Combined effect
  - Loss of about 3-5mV per stop without necessary precautions

# The peroxide problem for PEMFC

## Cathode kinetics of acid fuel cells

$O_2 + 4H^+ + 4e \Rightarrow 2H_2O$ $\qquad E^0 = 1.229$

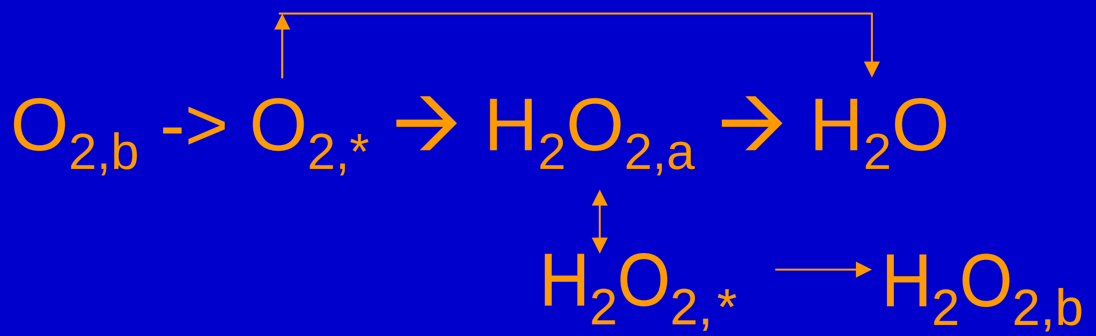
The peroxide route:-

$O_2 + 2H^+ + 2e \Rightarrow 2H_2O_2$ $\qquad E^0 = 0.67$

$H_2O_2 + 2H^+ + 2e \Rightarrow 2H_2O$ $\qquad E^0 = 1.7$

$2H_2O_2 \Rightarrow 2H_2O + O_2$

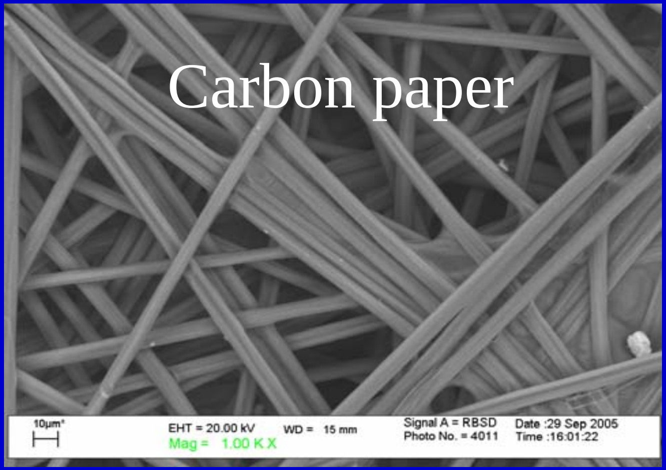
Zurilla et al. model :-

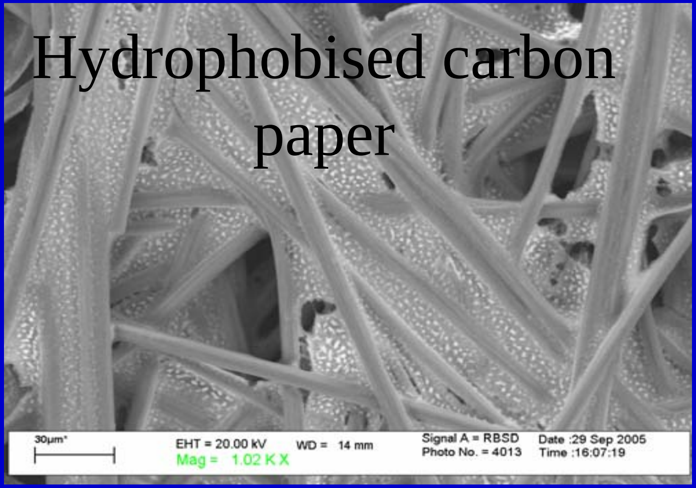


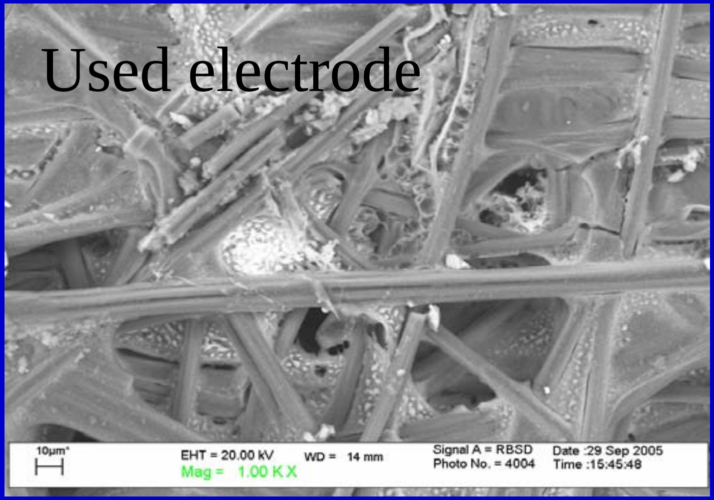
# Membrane degradation of PEMFC

- The peroxide generated at cathode attacks and oxidises membrane network
  - Cleavage of $SO_3H^-$ chains from the main backbone
  - Also oxidises the ionizing polymer in the cathode
  - Resulted in low membrane life

# Diffusion layer corrosion of PAFC/PEMFC



# The new wave of development

# The PEMFC membrane development

Target 1

- To make more CO tolerant
- Long life
- High temperature composite membrane

- $H_3PO_4$ doped PBI, PBSH etc.

Target 2

- To use pure hydrogen with simple subsystem
- Long life
- High performance

- Chemically stabilized membranes

# Issues for acid doped high temperature membranes

- Will face similar component problems like PAFC
- Low conductivity of the electrolyte
- Higher temperature reduces reactant solubility
- Combined effect
  - Low performance
  - High cost

# The electrolyte conductivities

Jens et al. Source .. internet

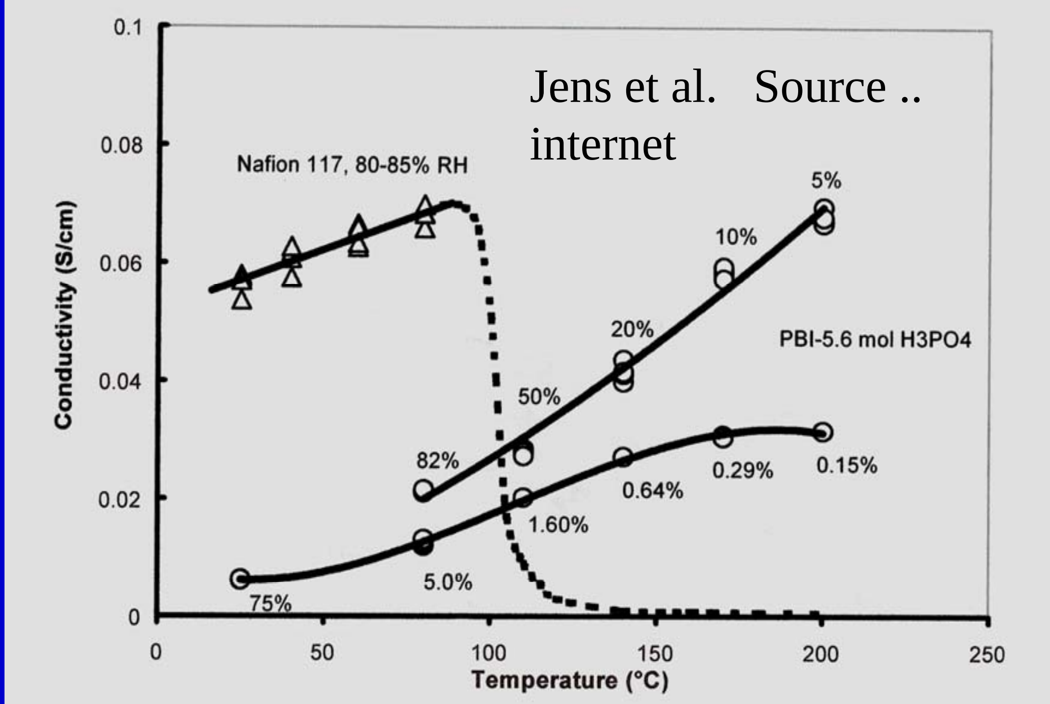
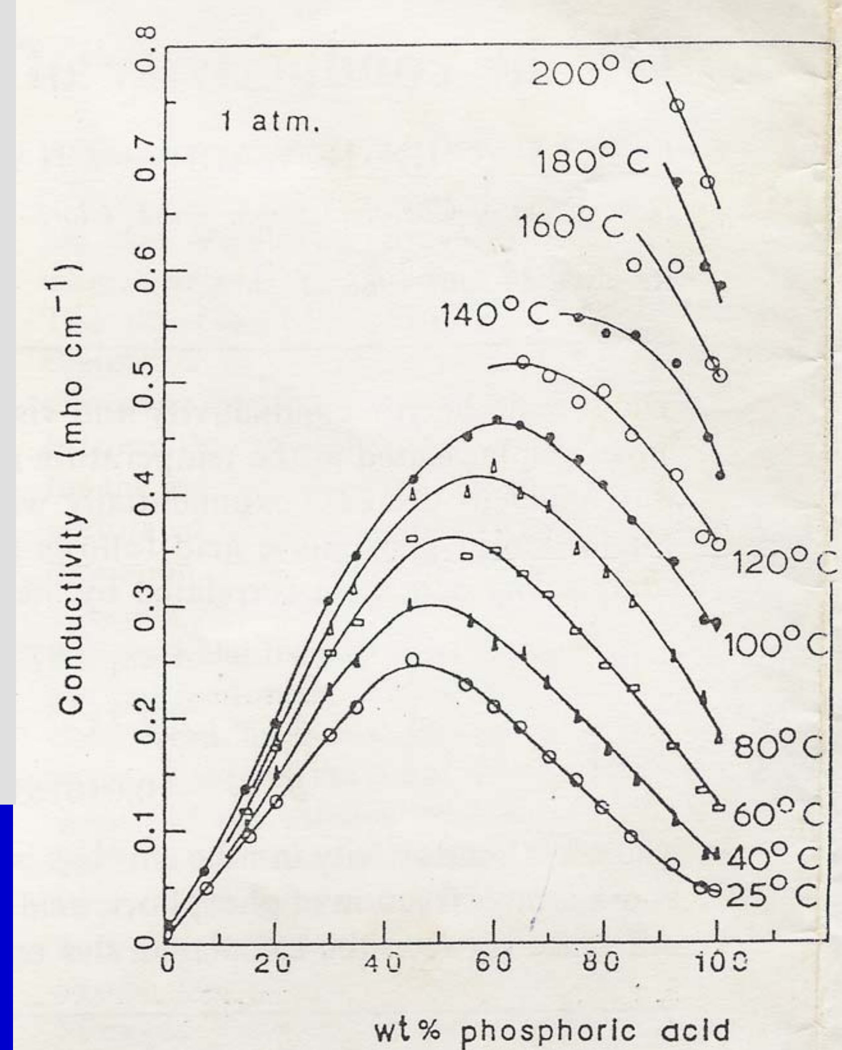


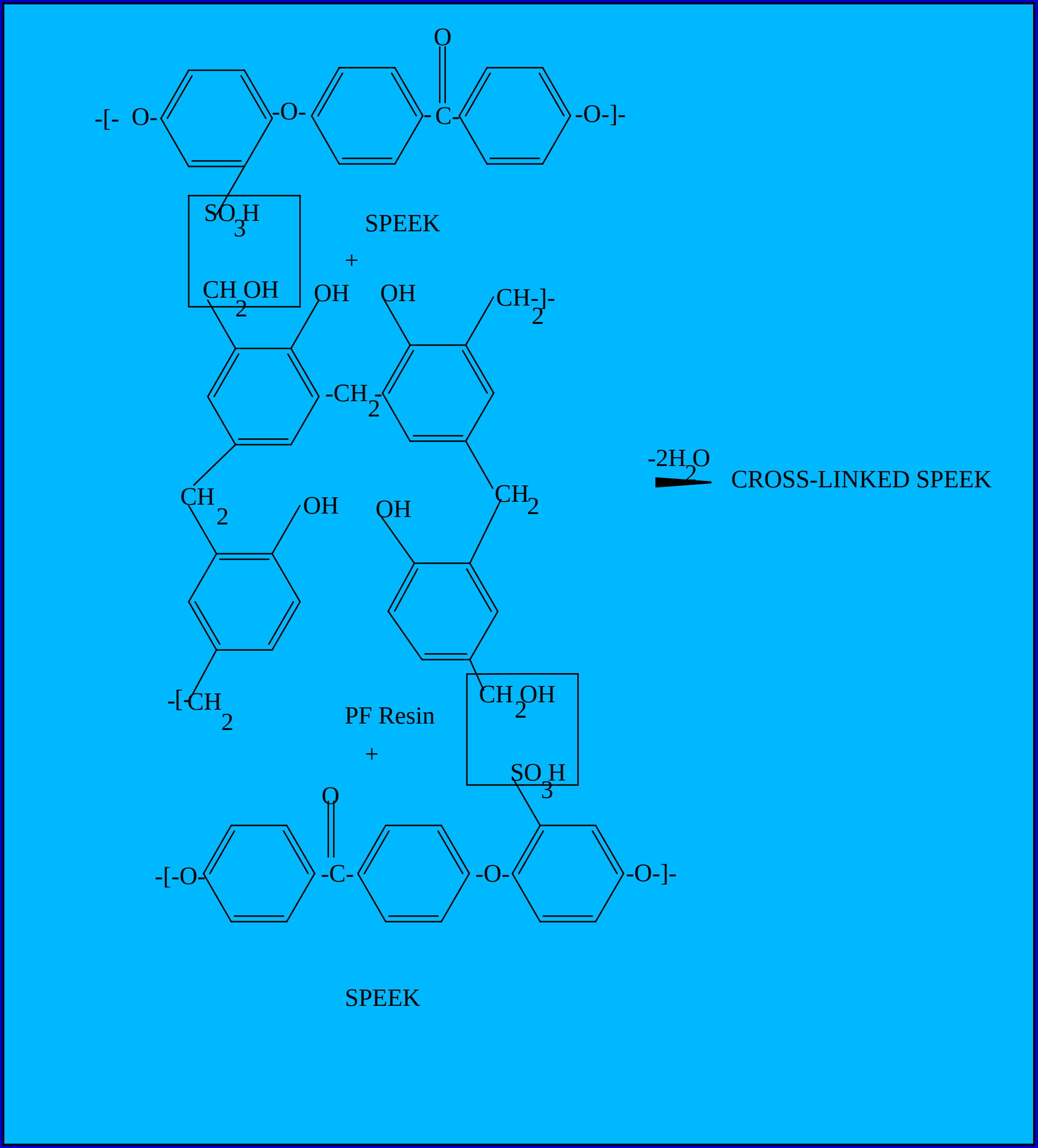

**Figure 2.** Conductivity of PBI doped with 5.6 % phosphoric acid. The percentages along the curves states the relative humidity. Measurements for Nafion 117 are added for comparison [10].



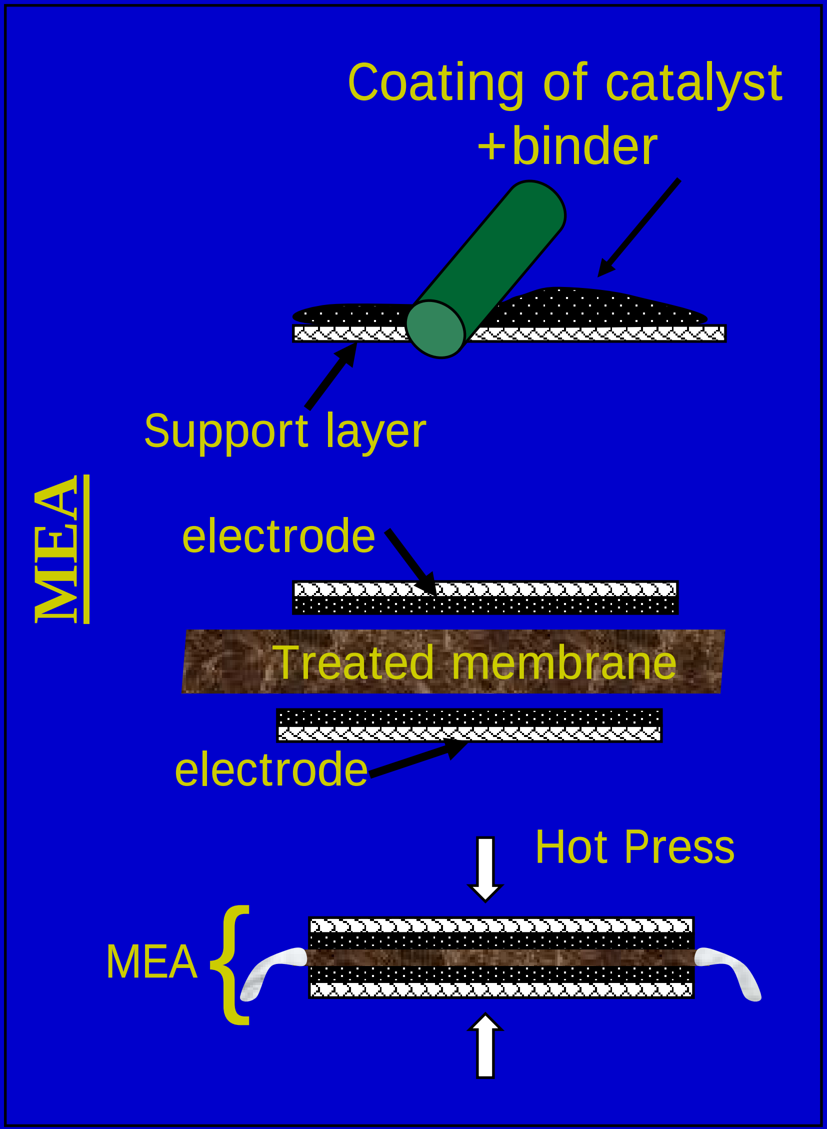
# NMRL tries low temperature chemical stabilized membranes with pure $H_2$ generation systems

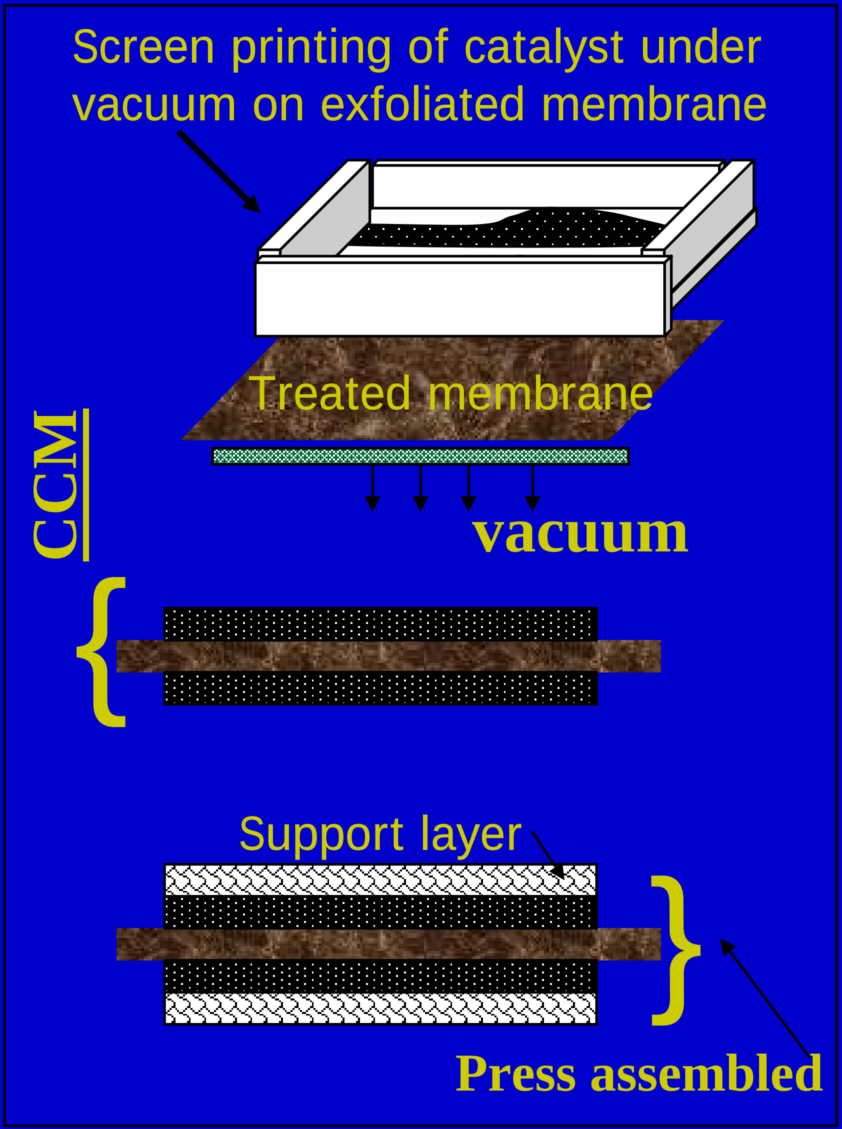
- Control
  - PEMFC stacks based on Nafion – 117 membranes with nafion in the electrode
- SPEEK membranes with Nafion and SPEEK in the electrode
- SPEEK membranes chemically stabilized with modified phenolic resin network and Nafion in the electrode

# Stabilization of SPEEK

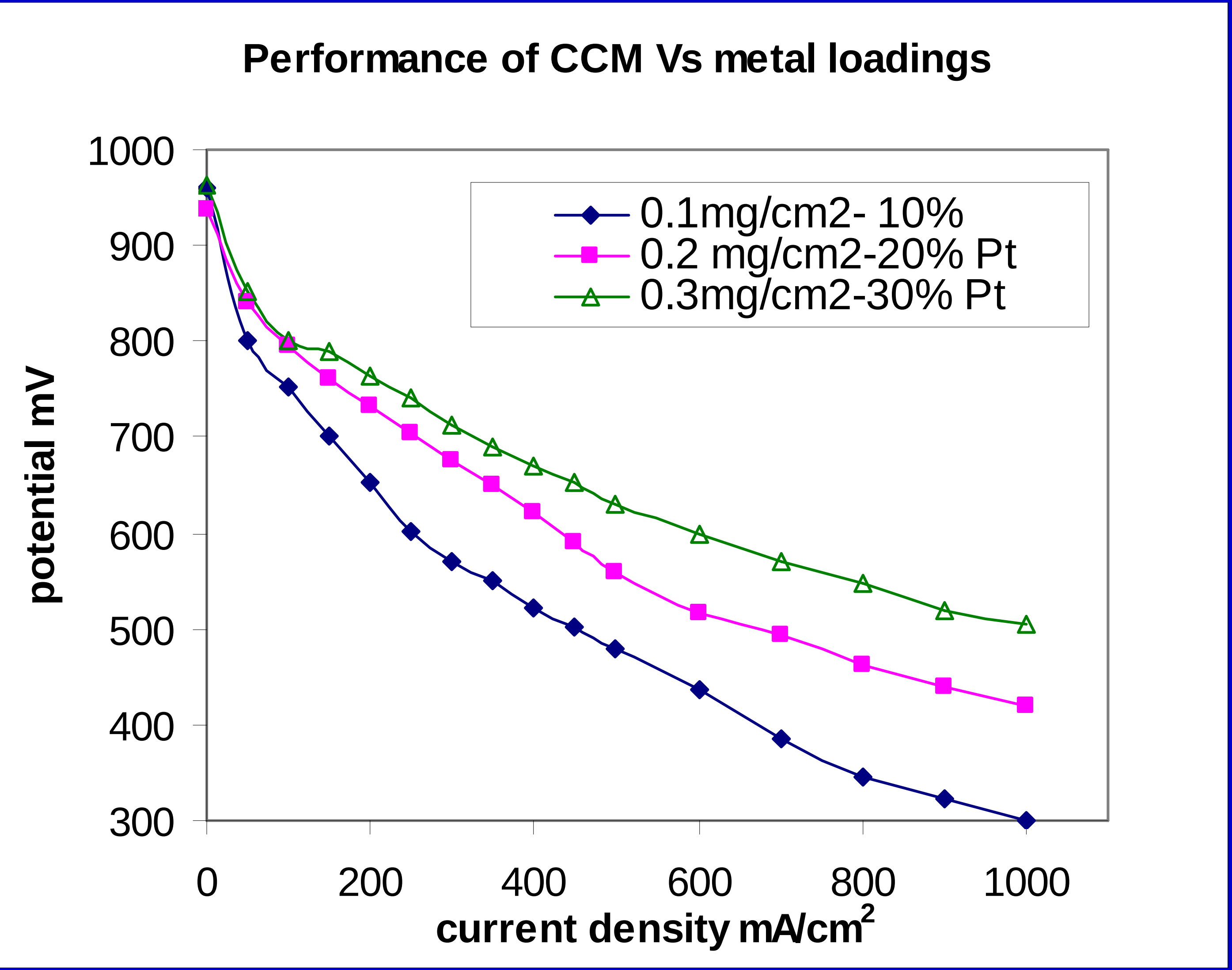


# Development of Membrane electrode assembly (MEA) & catalyst coated membrane (CCM)

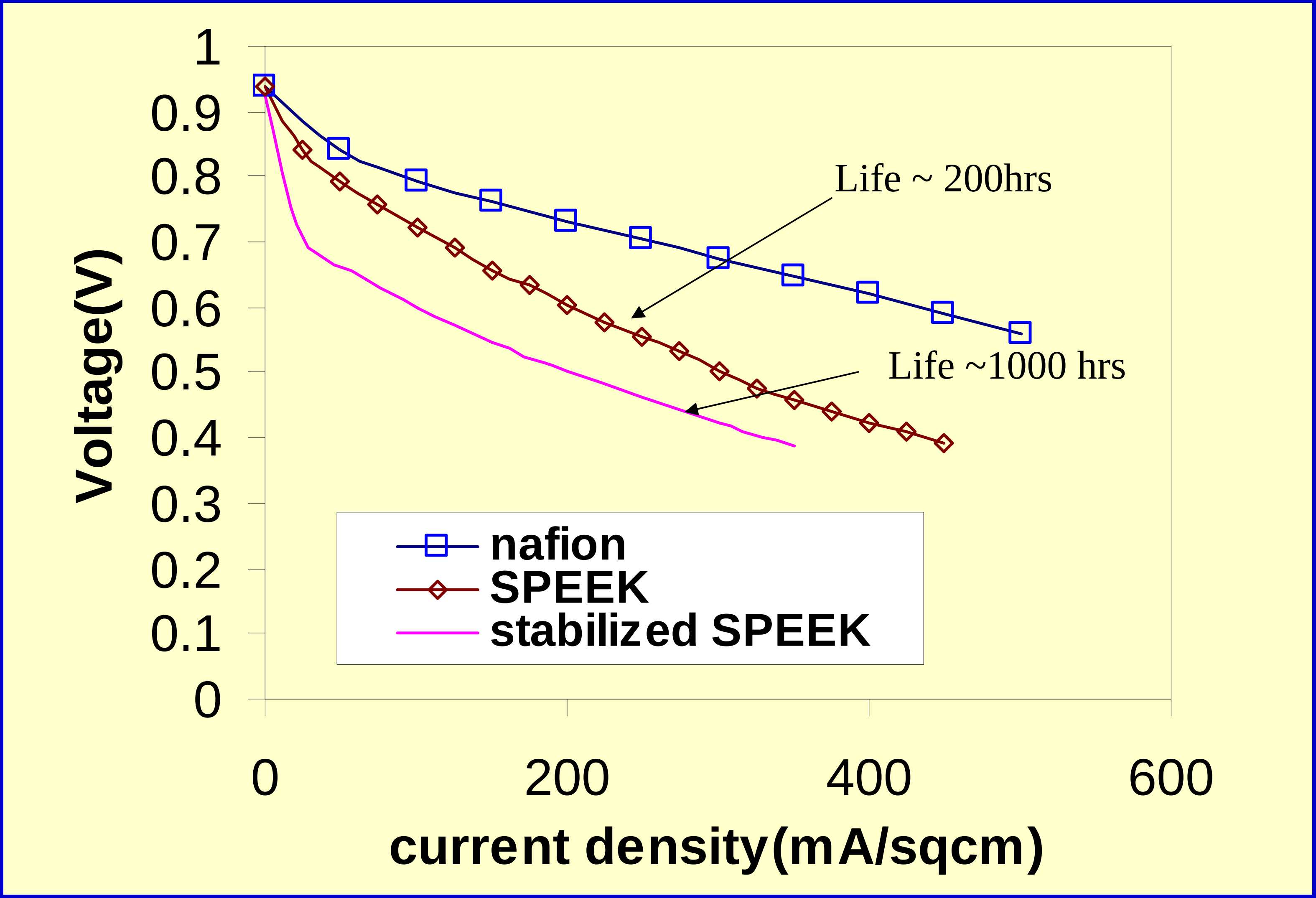


# Performance of PEMFC stack (Nafion), at $70^0C$, $80^0C$ humidification



# SPEEK performance



# Start / stop tolerant PAFC

## $H_3PO_4$ absorbed Siloxane based microporous gel

- Objective
  - To develop a gel material that can be coated on PAFC matrix to reduce crossover / enhance water retention
  - To use as an alternative to membrane for PEMFC
- Tested in unit cell/s & stacks
  - As such like a membrane
  - Applied over SiC matrix – operated in PAFC mode

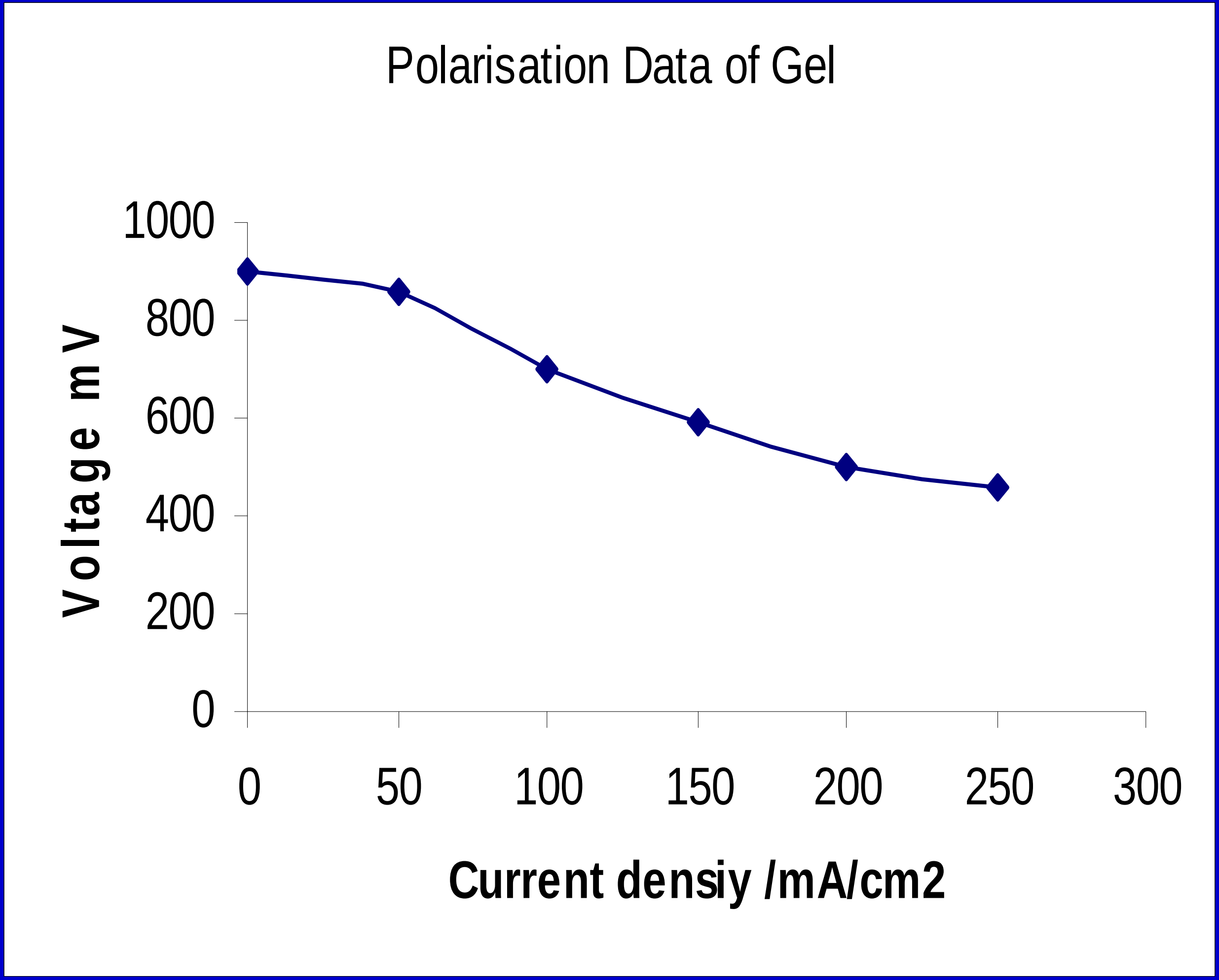
# The process

- Raw materials
  - $H_3PO_4$ and organic siloxane

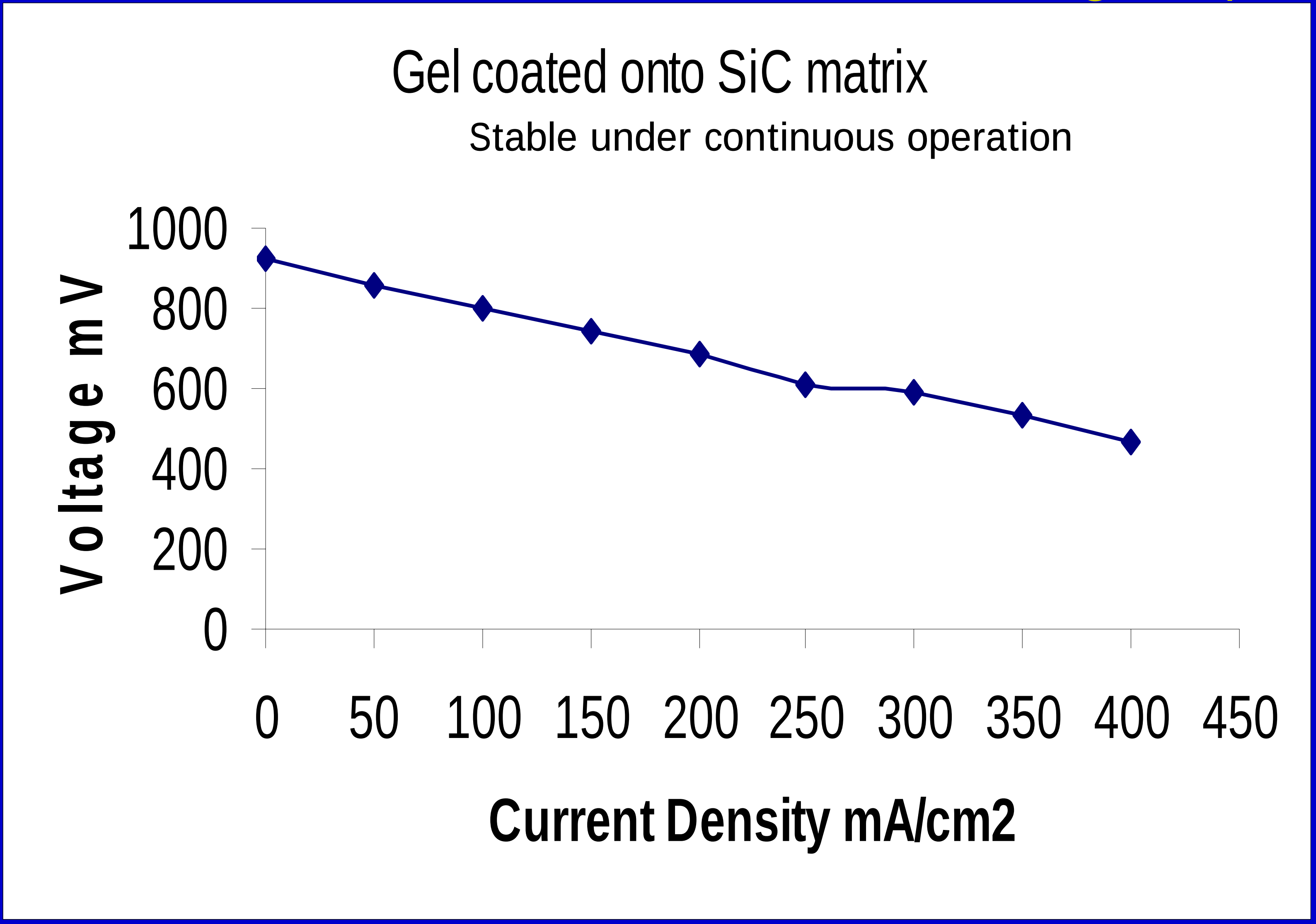
- $PO(OH)_2$-O-Si $(OH)_3$

- Followed by the condensation of OH groups and $H_2O$ elimination
  - resulting in the formation of 3-D network connected with bridging oxygen atoms (e.g.,P-O-Si ,Si-O-Si, P-O-P)

# Polarization data for gel with std PAFC electrode at 80$^0$C, no humidification



# Polarization data at 150$^0$C, no humidification, excess $H_3PO_4$



# Properties of Gel

- This gel material containing a large no. micropores and mesopores as revealed by SEM pictures, filled with" liquid " for fast protonation.
- The gel material shows high thermal stability and lower Humidity dependence.
- The thermal stability was determined by TG-DTA at heating rate of 10 $^{0}$C/min in air shows two endothermic peak at about 123 $^{0}$C and 212 $^{0}$Cdue to the removal of water from mesopores and dehydration of H3PO4.

# Balance of plant

Hydrogen provision system

# $H_2$ Content & requirement

| Material | $H_2$ evolution wt % | $H_2$ evolution lit/lit @NTP |
|---|---|---|
| $CH_3OH$ | 18.75 | 5250 |
| CNG | 50.00 | 8 |
| $CaH_2$ | 9.52 | 2133** |
| $NaBH_4$ | 21.05 | 4715** |
| Comp $H_2$ @200atm | 100.00 | 200 |
| ** considering powder density=1 | | |

| 1 kWatt power | $H_2$ consumption (lpm @ NTP) |
|---|---|
| At 100 % efficiency | ~6 |
| At ~65% efficiency (~0.6V cell pot) | ~10 |
| At ~65% efficiency (~0.6V cell pot) With 70% utilization | ~15 (with non faradic loss ~18) |

Pilot methanol reformer – 8-10 lpm hydrogen output for process design and scale up studies (1997)

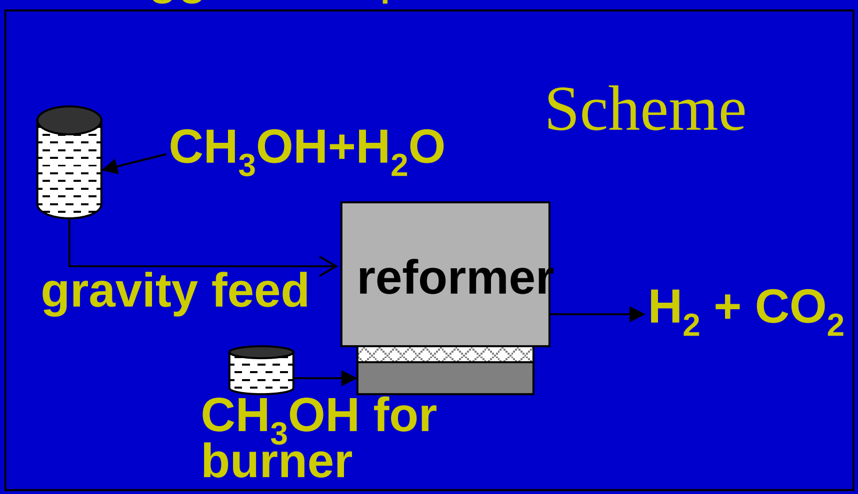
Compact reformer 1999
(80 lpm hydrogen)

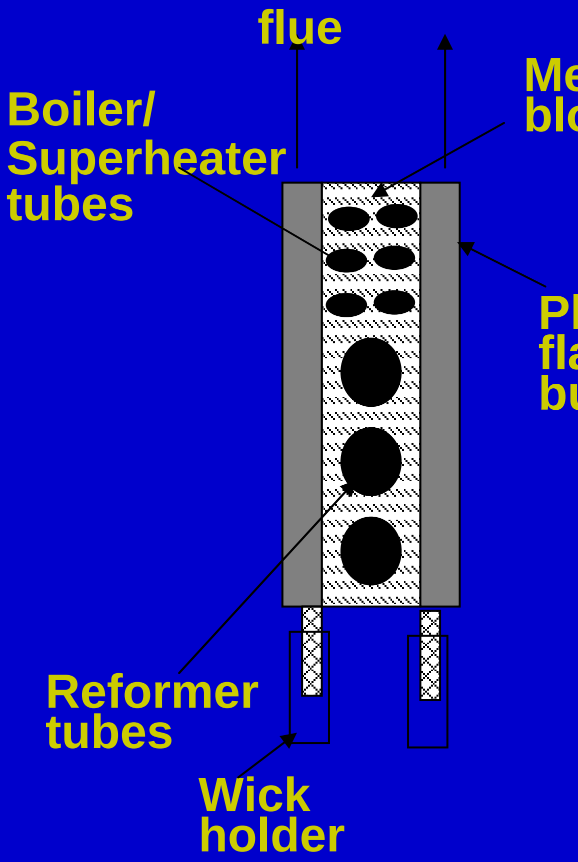
**Evolution of methanol reformer at NMRL**

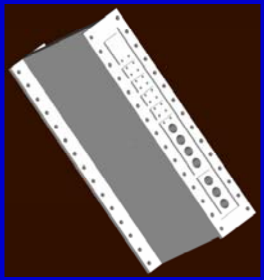
# Portable methanol reformer

## Requirements

- $H_2$ provision for PAFC operation (3 lpm)
- Compact carry pack
- No/low power consumption
- Rugged, simple



## Characteristics

- $H_2$ output – 5 lpm (max);
- Weight = 6 kg;
- Carriable in a shoulder bag

Evolution of methanol reformer at NMRL

High capacity methanol reformer , $50nM^3/hr$ –2003 hydrogen, suitable to ~60kW PAFC power pack

Process design of reformer – NMRL

Detail engineering, control systems and installation – Xytel India

Commissioning - NMRL

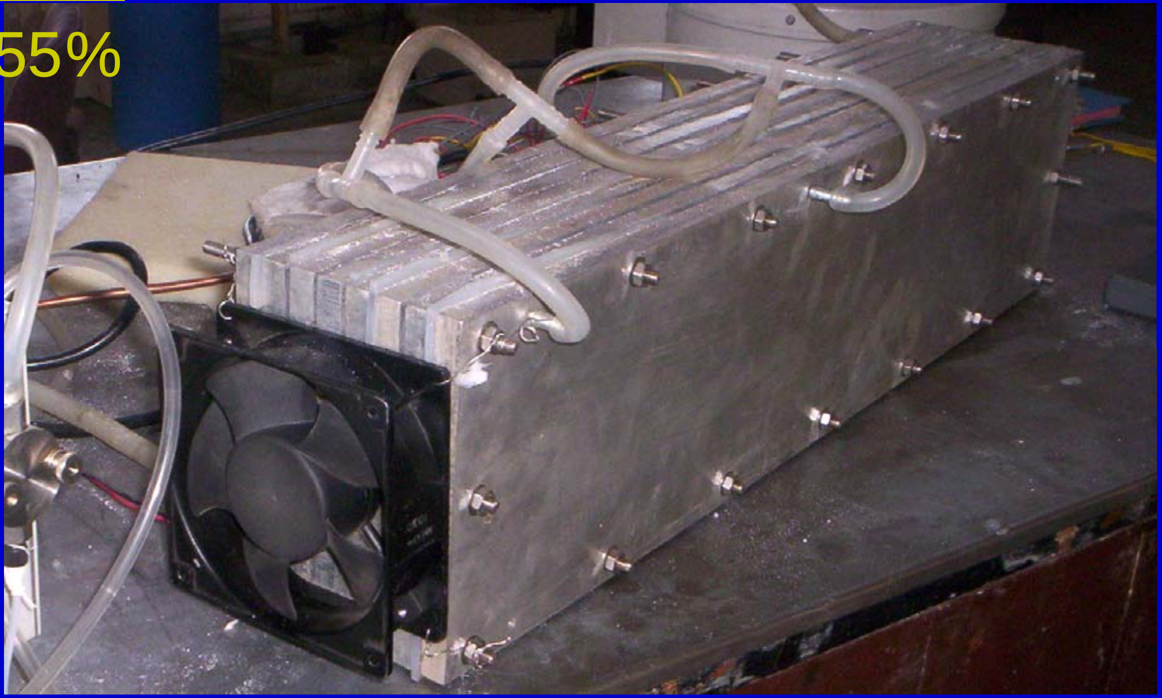
Evolution of methanol reformer at NMRL

# Planar reformer for mobile platform

Features

- $H_2$ for PAFC operation 1-10kw
- Compact
- Low power requirement
- Burner efficiency ~55% (without flue heat recovery)

Evolution of methanol reformer at NMRL



# Hydrogen generator for small fuel cells

**$NaBH_4$ cracker/s**

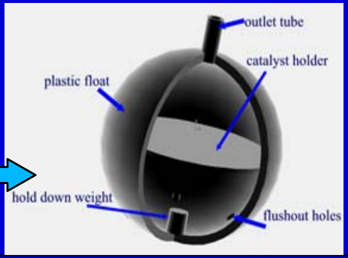
**Based on catalytic cracking of alkaline $NaBH_4$**

100W (~3lpm $H_2$)

- On demand $H_2$

5W (~150cc/min $H_2$)

- Pocket size
- Orientation free




$CaH_2$ based, one shot cartridge

- Capacity 50-150 watt
- Controlled water hydrolysis

# humidifiers

## Membrane humidifier with tail-hydrogen burner

- 65$^{0}$C saturation of H2
  - high humidification heat (~150W / kW)
- Uses tail H2 from PAFC
- No mist carryover
- Fast response

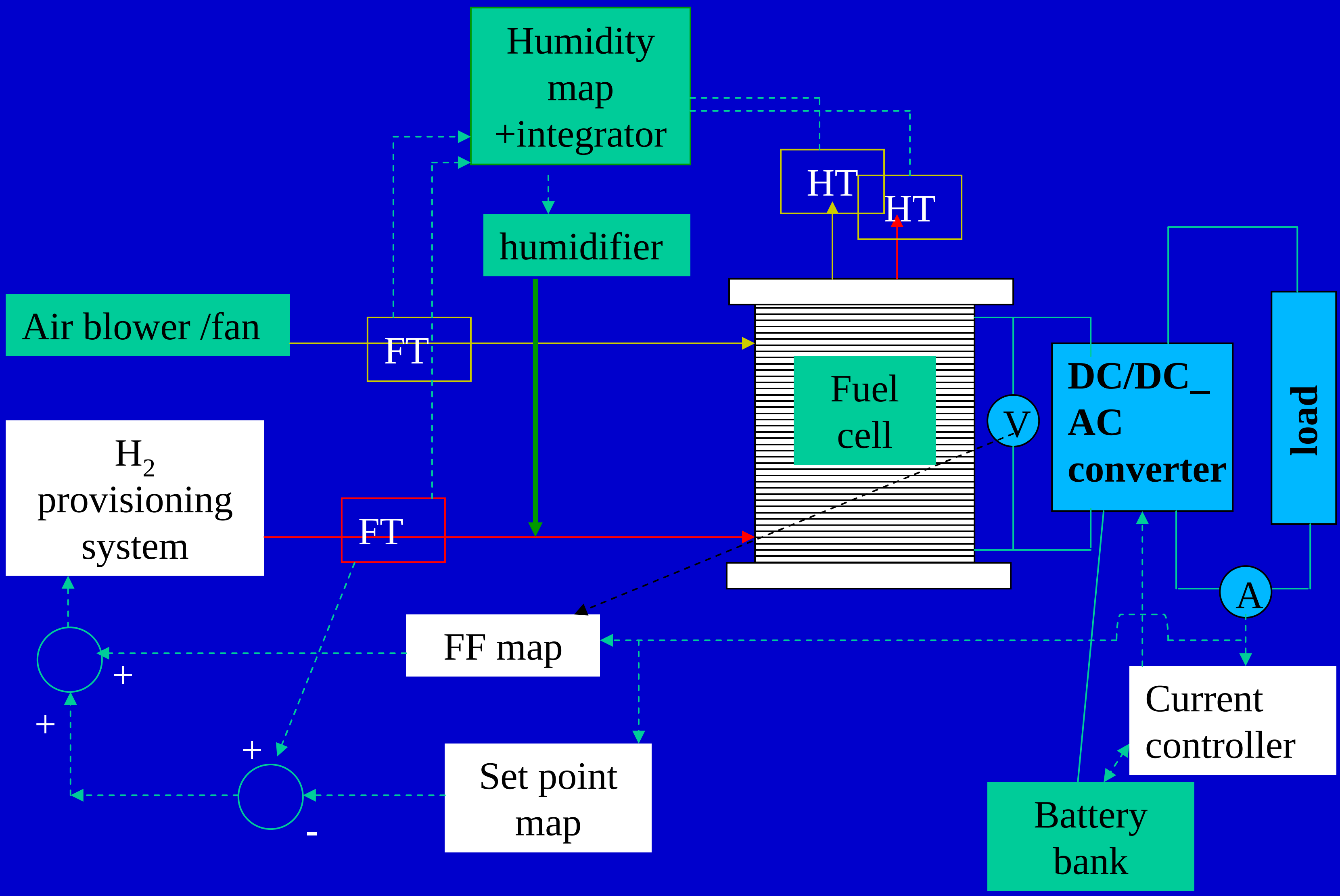
- Bayonet type moisture generator
  - ✓Converts part of the inlet $H_2$ to moisture
  - ✓Can be used as stack heater
  - ✓Insertable

# Control philosophy and control elements

# Control requirements

- Adjustment of $H_2$& oxidant (air) wrt load change
- Adjustment of humidity
- Power throttling – through power electronics

# Control scheme – 10kw decoupled mode



Start Up

Procedure

Pre Heating Timer ON

Heating ON by solenoid powering

Start $H_2$ if temp reached/manual

Fan ON

Load On if V>10V

# Micro PLC system for 1kW

Over Temperature
Over Load
Under Voltage
Over Voltage

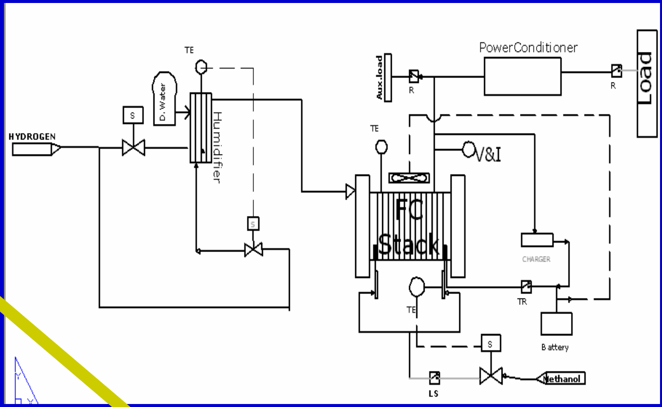
H2 Inlet Solenoid Off

Fan Relay Off

Load Off

Aux Load On

Alarm O/P (individual)




# **Micro Controller Based Control and Display Unit for 2-3 kW PAFC Generator**

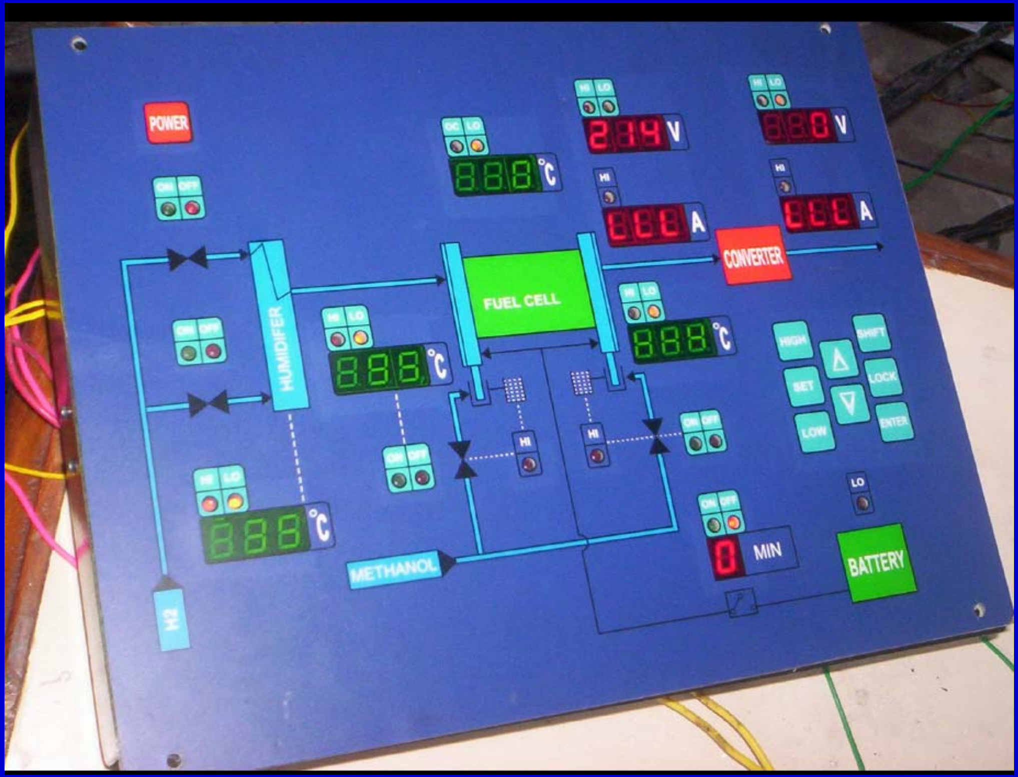
**Controls**

**I.**Temperature : 1.Stack

2.Humidifier

**II.**Pre heating time

**III.**$H_2$ Inlet solenoid On/Off




**Display**

**I.**Temperature (Status)

**II.**Voltage (Stack and Converter)

**III.**Current(Stack and Converter)

**Parameter Setting** : Through

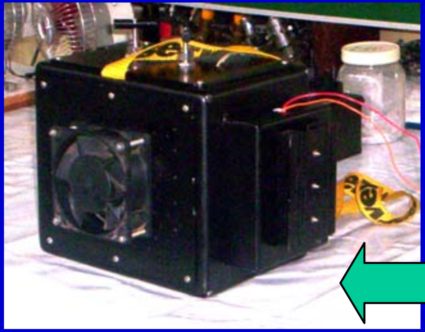
Panel keys

# Products developed at NMRL

# Products from NMRL's stable

**700-1000 watt PAFC based UPS / generator with built in compact methanol reformer**

- Delivers 220V AC, 700-1000VA



**100 watt universal power pack (engineered)**

- Output :- 12+0.05 V DC upto 100 watt (max)
- Hydrogen source by hydride cracking or

by compact catalytic burner based reformer

# 8 KW Phosphoric Acid Fuel Cell (PAFC) based power pack

- ❑ Power output
  - o 8kW, 220V, 1$\phi$, ac
- ❑ PAFC stack
  - o $H_2$/ref gas – air
  - o 6x1.5KW stacks

# DRDO – REVA fuel cell vehicle

An electric vehicle that runs on combined power of fuel cell and battery

The fuel cell charges the battery during idle time and share the load with battery while the vehicle is in operation

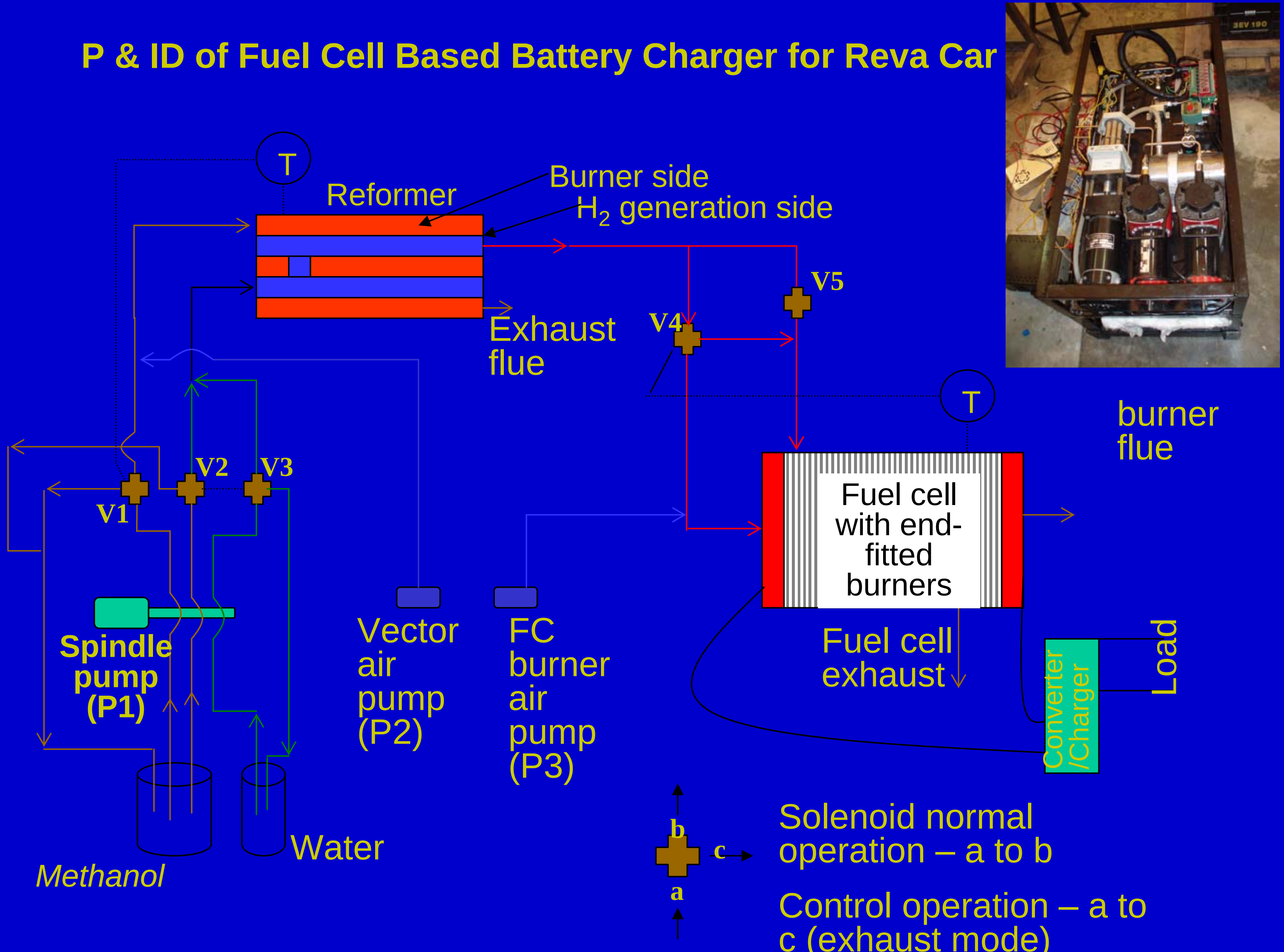

Range
Battery mode: 80km
Hybrid mode: 120km

- **Speed (max)- ~65kmph**
- **Mileage: - 20km per lit of methyl alcohol**
- **Operation mode – continuous**
- **Other advantages: - silent and very little emissions**

**Application areas**

- **Patrolling at sensitive areas**
- **Silent personnel transport**
- **High efficiency very low emission SUV – commercial**

# P & ID of Fuel Cell Based Battery Charger for Reva Car



**10kW fuel cell based mobile generator car**

# SHy-Power generator car


**Primary fuel methyl alcohol – no need to carry hydrogen cylinder !!**

The system

Power is generated by a novel electrochemical power device known as fuel cell

A fuel cell stack (a battery of fuel cells) produces DC power directly by reacting hydrogen gas with oxygen in the air.

The hydrogen is generated online by reforming methyl alcohol ($CH_3OH + H_2O = CO_2 + 3H_2$)

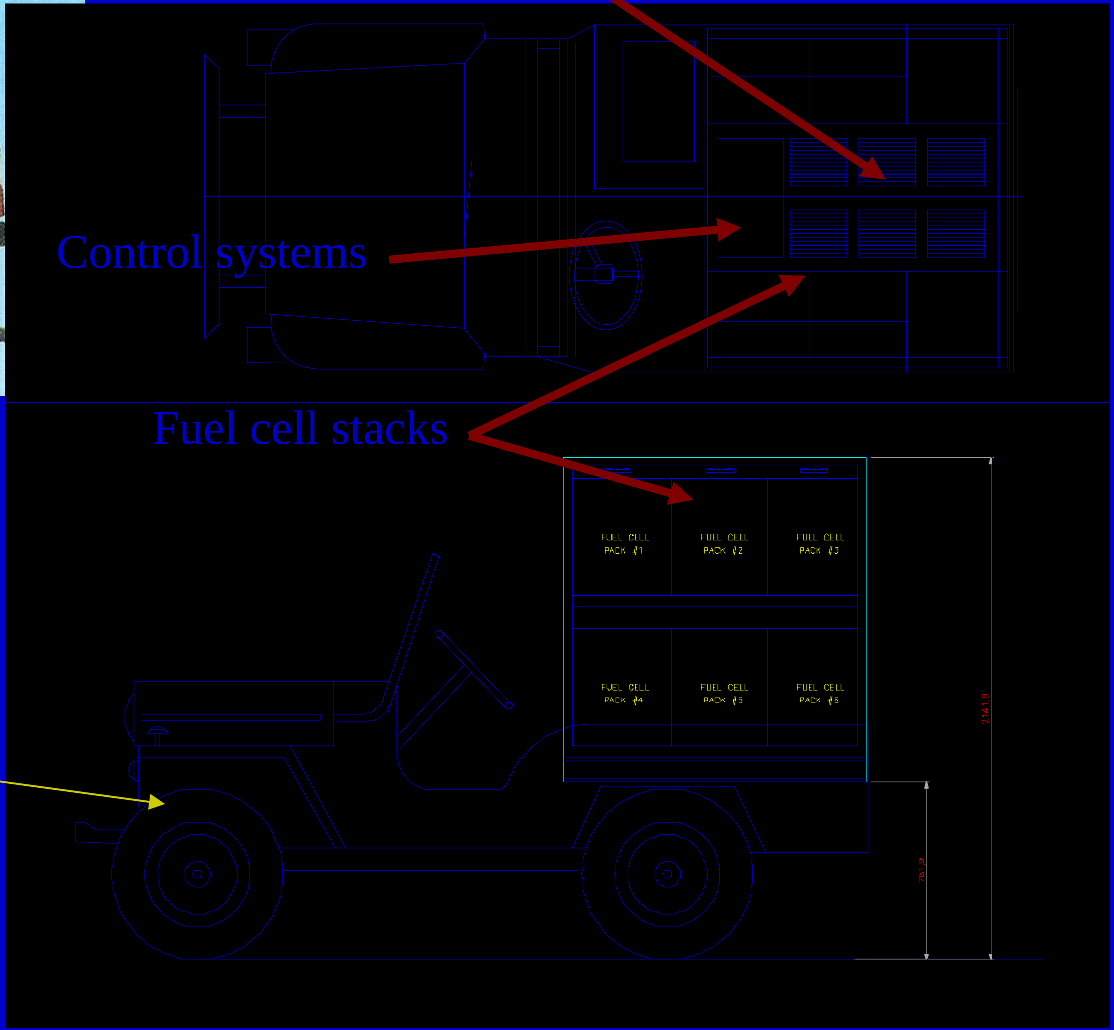
## Salient Features

- Mobile Power
- Stable & reliable
- Silent & Emission free
- Highly efficient
- Duty – Continuous

## Application areas

- "Drive in" remote, continuous power for land based troops
- Power generation at sensitive areas
- Distributed, green power – commercial application

# 10kW skid mount power pack




The platform:-
Infantry tactical vehicle
from, VRDE

## Trolley mounted version of Shy Power generator

## Capacity 10kw continuous

Application areas

- Remote onsite power generation
- Can be towed easily by a small vehicle
- Methanol as primary fuel

# New approaches

# System simplification

- Hydrogen carrying conduit
  - Borone hydride based systems
  - $NaBH_4$ regeneration for cost reduction
  - Dimethyl ether based carrier
    - Simple Reformer
    - Can be used like LPG directly in engines
    - Has high calorific value
    - low toxicity

Achievement summary

Our fuel cells operate at the top of the world !!