Challenges in Material Development for PEMFC

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Presented by

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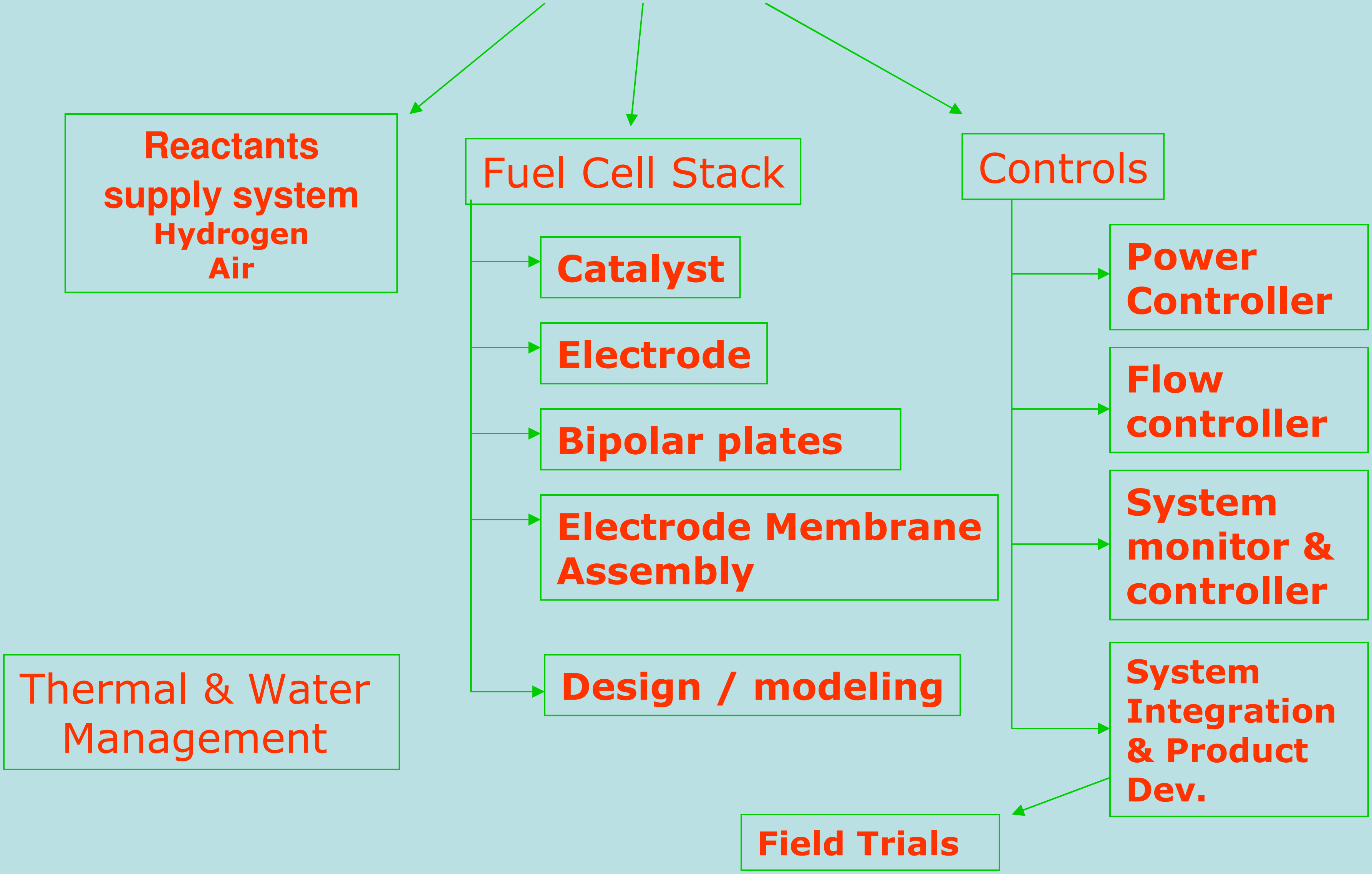
at the
National Seminar on Challenges in Fuel Cell Technology: India's Perspective
Dec. 1- 2,2006, New Delhi, India

Fuel Cell System

CFCT-ARCI



Reactants supply system
Hydrogen
Air

Fuel Cell Stack

- **Catalyst**
- **Electrode**
- **Bipolar plates**
- **Electrode Membrane Assembly**
- **Design / modeling**

Controls

- **Power Controller**
- **Flow controller**
- **System monitor & controller**
- **System Integration & Product Dev.**
  - **Field Trials**

Thermal & Water Management

Fuel Cells and stacks

Major Components of Fuel cell stack

1. Electrodes (anode and cathode)
   - Electro-Catalyst, Gas diffusion media
2. Electrolyte
   - Proton Exchange Membrane or immobilised phosphoric acid
3. Bipolar Plates
4. Gaskets and sealants

ARC-I is presently working on PEM fuel cell development for use in

- ➢UPS Systems
- ➢Transportation application
- ➢Decentralized Power Generation

Materials Issues in PEM Fuel Cell Technology Development

- **Bipolar Plates (cost & performance)**
  - Issues: Presently used graphite requires expensive extensive machining, permeability of gases a serious issue, ~60% of fuel cell stack cost is for the bipolar plates; ~65% of weight is from these plates
  - Solution: Develop low cost carbon composites, use exfoliated materials, coating of conducting carbon polymer or metal substrates, light weight components fro transportation and portable applications
- **Electro Catalysts (cost & performance)**
  - Issues: High cost, limited performance, poisoning by CO, reduce qty.
  - Solution: New catalysts, better distribution of catalyst on support - novel support materials, non-noble metal catalysts
- **Membrane (cost & performance)**
  - Issues: Single supplier (Dupont), high cost, depends on high water content for ion conduction, operation below 100 C, high methanol permeability
  - Solution: New membranes based on high temperature materials, new strategies for developing composite polymers using commercial resins

ARC-I is addressing some of these material issues:

1. **Development of low cost and low weight bipolar plates**
2. **Development of Non Noble Metal catalysts**
3. **Low cost membrane**

Tungsten carbide(WC) for PEMFC

1. WC has catalytic properties similar to Platinum-like noble metals.
2. Pt-like behavior was due to donation of e^- from carbon to the 5d band of W, resulting in an electronic structure similar to that of Pt.
3. WC plays an important role as an anode catalyst when reformate H_2 fuel is used.

The differences in catalytic activities of tungsten carbide result from the differences in

surface properties,
particle morphology and
chemical composition of the surface layer than that of the bulk.

Particle morphology has a strong influence on electrocatalytic properties of tungsten carbide catalysts.

Adjusting the particle morphology is an efficacious way to control its catalytic activity

Extensive attention is required to prepare tungsten carbide catalysts.

Different methods of synthesis

1, **Intermittent Microwave Heating** --- relatively simple and rapid --- But no electrocatalytic activity ---- only composite tungsten carbide nanocrystal promoted Platinum on carbon is active

2. **Chemically reduced mechanical alloying** of tungsten oxide, magnesium and carbon by ball milling for 2 days, involves many steps like removal of by product, washing, rinsing and drying.
The method is time consuming and energy intensive and not suitable for scaling up.

3. **Hydrocarbon cracking of oxide powders** at 600-1400C for 2h. The final product contains pure tungsten in addition to the carbide, which requires additional carbon and carburisation. Hence this process is inefficient and not amenable for large scale production.

For high surface area samples the following parameters need to be optimized

- the space velocity of the synthesis gas,
- the precursors,
- the ratio of the composite in the mixture gas,
- pressure and temperature.

CFCT/ARCI Objective is

- to develop a simple cost effective process to synthesize nano WC powders.
- to replace the expensive Pt by the non noble metals in PEMFC
- to identify the exact composition of tungsten carbide for improved catalytic activity.

Advantages of present method developed at ARCI

1. An improved two step process from precursors which are readily soluble in water and cost effective.

2. The composition of Nano WC can be controlled by varying the ratio of precursors

3. The sample is free of oxides

4. Particle morphology can be controlled from 60 – 80 nm.

5. Catalytic activity of the nanotungsten carbide can be improved by engineering the composition of nano WC.

The Tungsten carbide powders developed at ARCI have been successfully used as anode catalyst in PEM Fuel cell.

Use of tungsten carbide as catalyst support is also being investigated

Studies on ORR with tungsten carbide is under progress..

Organic-Inorganic Composite polymeric membrane for fuel cell humidification

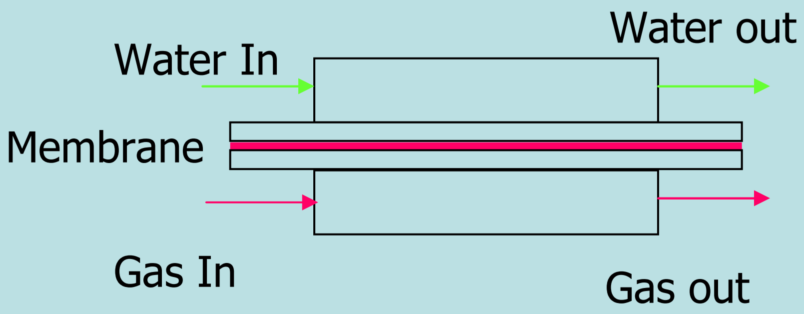
PEMFC performance is strongly governed by conductance of the membrane electrolyte.

- Membrane (Nafion)conductance is strongly dependent on its hydration state (Higher the hydration state – better is the conductivity)

Reactant gases have to be humidified to prevent membrane from drying out.

One of the methods of humidification is through the use of membranes

Principle of membrane humidifier



Water or gas rich in moisture is passed on one phase of the membrane and the inlet gas to be humidified is passed on the other phase of the membrane.

Water diffuses across the hydrophilic membrane and is evaporated into the gas stream thus humidifying it.

Membranes used for humidification

Polymeric materials satisfying the following properties can be used for membrane humidification

- High water transport property across the membrane

-All ion exchange and hydrophilic polymers satisfy this condition

- Sufficient strength to withstand the pressure across the membrane due to water/ gas rich in moisture and gas to be humidified on the other side.

Most commonly used materials include

1. Nafion or other perfluorosulphonic acid membrane. Cost of these materials are prohibiting

2.Composite materials in which polymer is filled with hydrophilic materials- High loadings of the hydrophilic filler

ARCI I (CFCT) HAS DEVELOPED A LOW COST MEMBARNE & A HUMIDIFIER

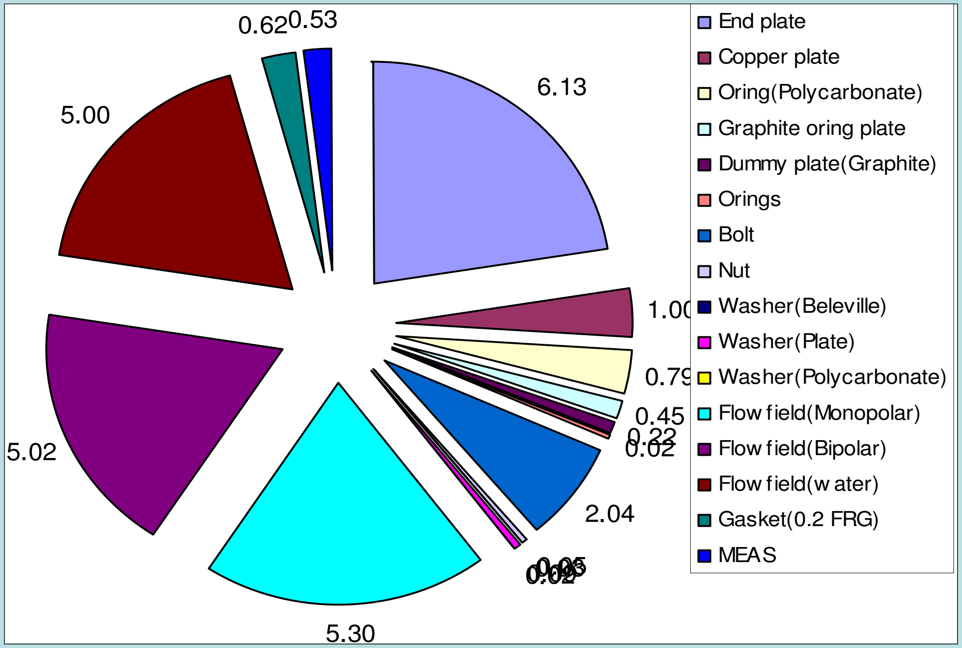
The process and the design have been patented.

Advantages of the CFCT-ARCI membrane humidifier

1. Parasitic power losses(power required for heating water, evaporation etc.) are reduced .
2. These humidifiers can be integrated into the fuel cell stack so that the temperature of the stack and the humidifier are the same.
3. It does not lead to flooding of the gases.

Bipolar plates
Present Status

Total weight of the 1 KW stack ~26 kgs
Weight of bipolar plates ~ 16 kgs .



Bipolar plates

Bipolar plate ----- the electrode plate that separates individual cells in a stack
--- high density graphite with machined flow channels.

----Both material and machining costs are high

Development efforts are needed to replace graphite

The bipolar plate requirements

- low-cost materials and processing - goal of <$10/kW
- light weight, thin <3mm
- sufficient mechanical integrity
- high surface and bulk electronic conductivity
- low permeability between fuel and oxidant and
- corrosion resistance <16 μA/cm2

Bipolar plates

Choice of material is important to the performance and lifetime of the PEM fuel cell stack.

A range of bipolar plate materials exist including

- **Composites (carbon-Carbon, carbon-polymer),**
- **Titanium and TiN**
- **Aluminum, and**
- **Stainless Steel**

The material of choice will depend upon the driving constraints of the application, e.g.
Mass market, military, space, stationary power

Bipolar plates

Metals:

Although the metals especially bipolar plates with SS can be made at low cost as plate forming techniques are well established,
the corrosion and membrane poisoning , Formation of insulating oxides are major issues
Bipolar plates with Ti and TiN are expensive
Corrosion protection coating techniques for Aluminum still not developed

Carbon – Polymer composites

<u>Advantages:</u>
Potentially low cost for high volume manufacturing

<u>Disadvantages:</u>
Higher electrical and thermal resistance
Process depends on the type of polymer
Higher anisotrophy

Issues in Carbon –Polymer Composite bipolar plates

Polymer	Advantages	Disadvantages
Fluoropolymers	Chem stability	Expensive,
PVDF	Hydrophobicity	high viscosity
Liquid crystal polymer	High Thermal stability	Expensive low viscosity
Polyphenilidenesulfide	High thermal stability	Low viscosity expensive
Polyphenelene	High thermal stability	
Phenolic resin	Low price	Post curing necessary
Vinyl ester	Fast processing	Limited thermal stability
Polypropylene	Low price, processability	Longer molding time

ARC-I has developed a technology for making Exfoliated Graphite (EFG) and the technology has been transferred

Gasket materials made from EFG are already used in many applications e.g., gaskets

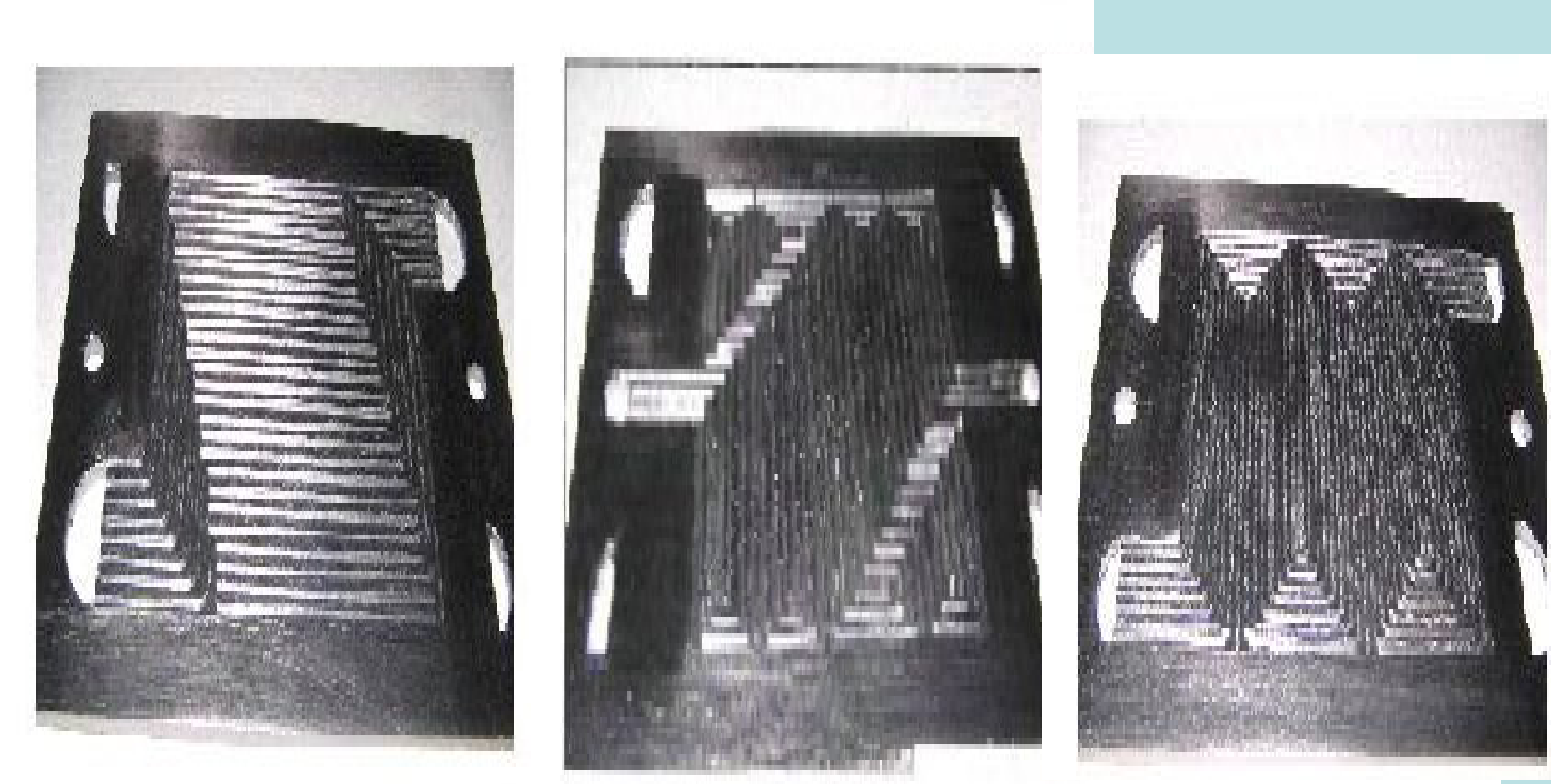
EFG can be used to make bipolar plates suitable for Fuel cells

ARCI (CFCT) has developed a technology for making bipolar plates (various designs) using EFG which have been successfully used in developing fuel cell stacks of various capacities

The process has been patented

Advantages of using Exfoliated Graphite (EFG) plates

- Light weight
- No machining required
- Easy Manufacturability
- Amenable for Large scale production
- Time conserving
- Easy to assemble and disassemble in a stack
- Flow field designs can be embossed
- No cutting to the desired siz- No loss of material
- Die size determine the area of the plate



Low Cost bipolar plat

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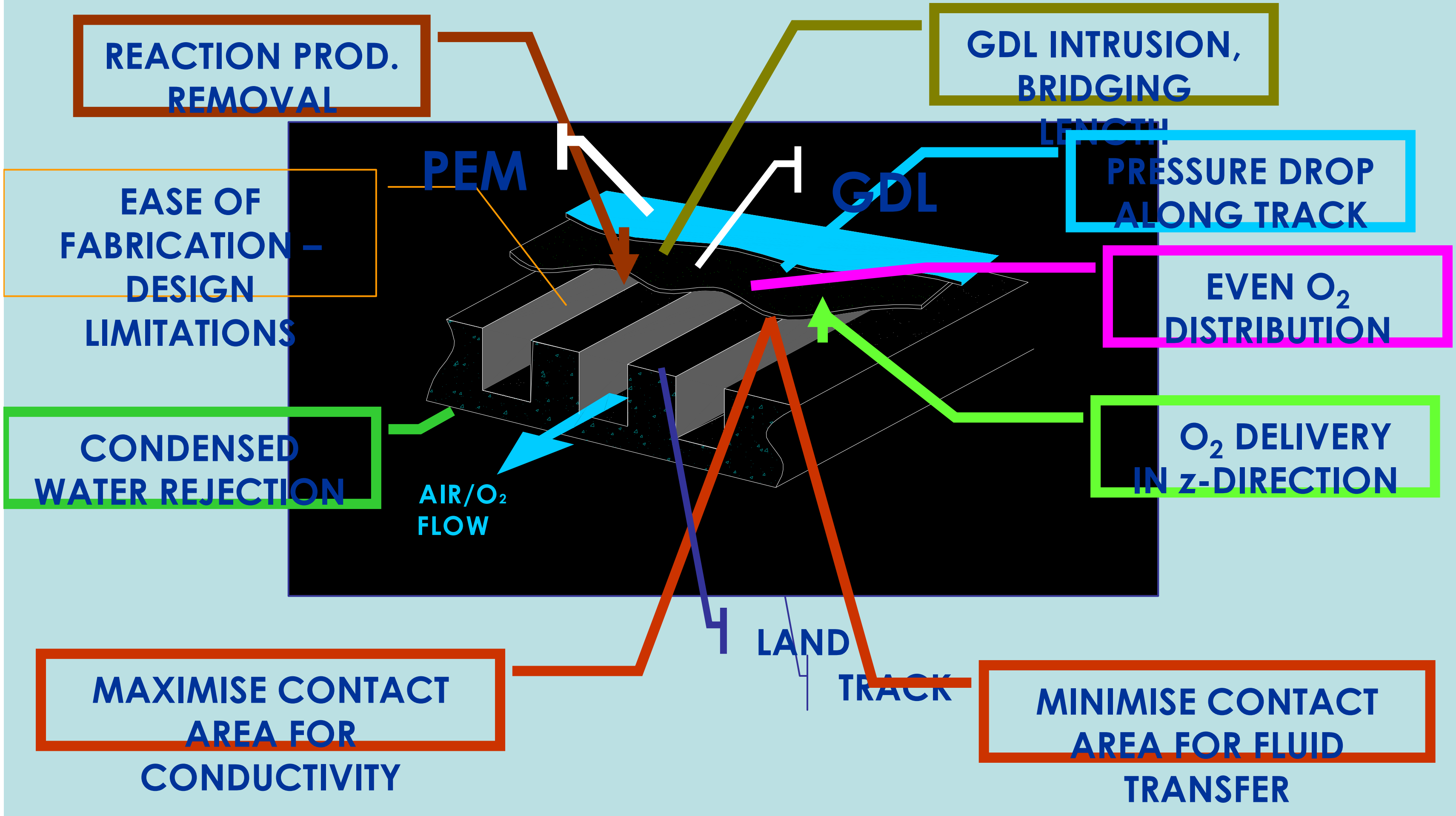
Factors Influencing PEMFC Performance



REACTION PROD. REMOVAL

GDL INTRUSION, BRIDGING LENGTH

PRESSURE DROP ALONG TRACK

EASE OF FABRICATION – DESIGN LIMITATIONS

EVEN O_2 DISTRIBUTION

CONDENSED WATER REJECTION

O_2 DELIVERY IN z-DIRECTION

MAXIMISE CONTACT AREA FOR CONDUCTIVITY

MINIMISE CONTACT AREA FOR FLUID TRANSFER

- FC systems are complex entities.

- The complexity is hidden in the microscopic details , mostly inaccessible to the experimental “eye”.

- More specifically , FC operation entails circulation of protons, electrons, reactants and water , with the processes in the structural elements of the cell coupled strongly and non linearly to each other.

- The fundamental difficulties associated with FC design stem from this non linear coupling.

Herein lies a Challenge!

Catalyst Support

High surface area carbon
(Increased Catalyst utilization)

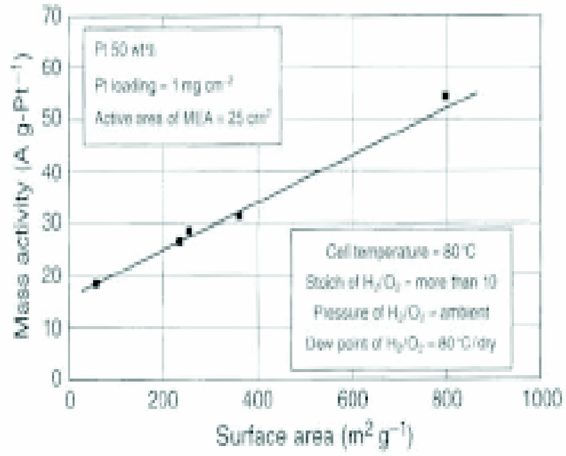
Vs

Fast Carbon Corrosion

Highly-dispersed platinum on carbon black (furnace black) has normally been used for the PAFC. Experience shows that in this type of cell the carbon cathode is subject to degradation and loss of carbon by an electrochemical oxidation mechanism .

The degradation of PEMFC cathodes has not, until recently, been such a concern because of the relatively low operating temperature. As developers seek to raise the operating temperature, however, cathode degradation could become more important.

Effect of carbon support on the Mass activity of Pt



Mass activity of 0.9V of Pt catalysts versus surface area of carbon support.

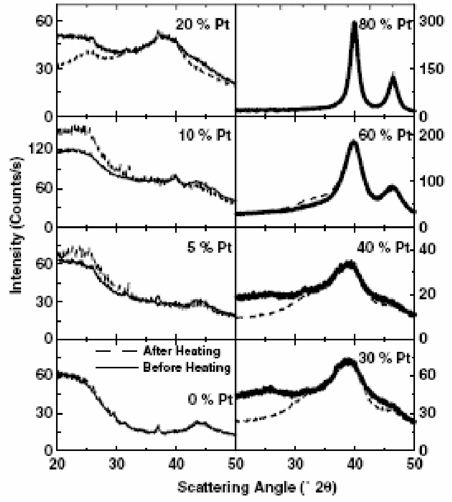


Fig. 11. X-ray diffraction profiles for samples before and after extended oven exposure at 195°C. The platinum loading for each sample is indicated on each panel. Solid line—before heating; dashed line—after heating.

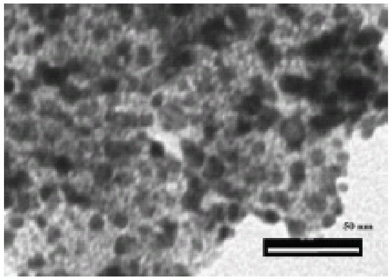


Fig. 12. TEM image of the sample with 80wt% platinum as received. The scale bar on the figure indicates 50nm.

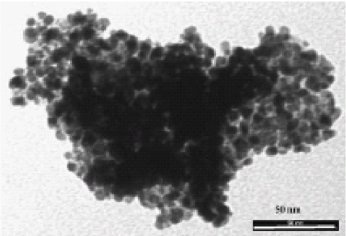


Fig. 13. TEM image of the sample with 80 wt% platinum after long-term exposure to air at 175°C. The scale bar on the figure indicates 50nm.

•Thermal studies (heating from 125 to 195 C) on samples comprising Pt (5–80 wt.%) on BP 2000 carbon of high surface area(~1350sq.m/g) show significant weight loss presumably from the catalysed combustion of carbon with oxygen.

•With the base carbon heated in air at 195 C, no weight loss was detected even after 3000h

•This weight loss increased as the temperature was raised from 125 to 195 C and also as the Pt loading was increased

•TEM images indicate that the weight loss was primarily from the carbon and that the Pt particles did not sinter or agglomerate during exposure to air at high temperatures.

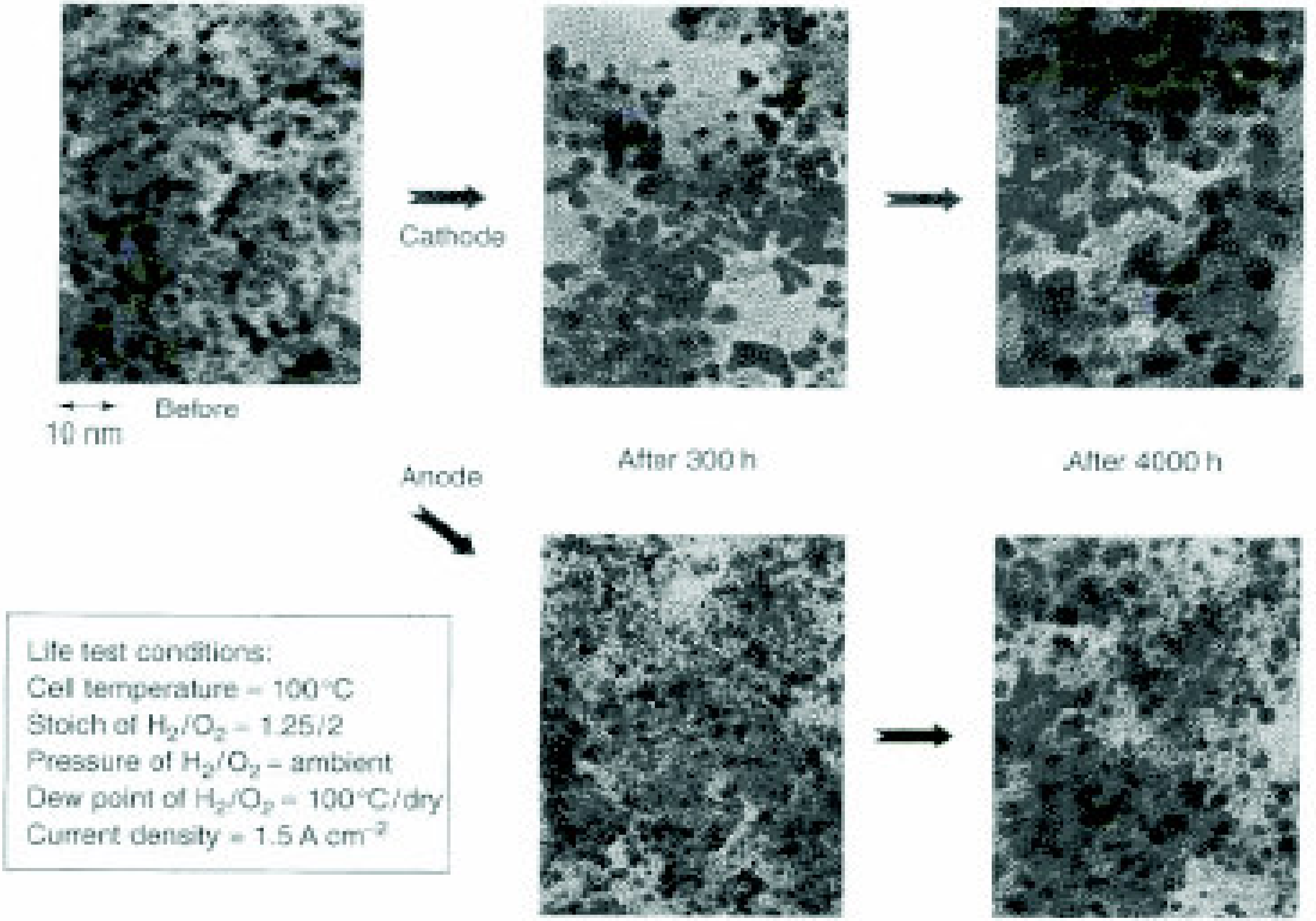
Source : Stevens and Dahn, Carbon 2005, p189

Catalyst

Nano catalysts have high surface area and perform better

The question is the how to translate the good performance showed by the nano catalysts in electrochemical studies (half cell) into single cell and eventually to the stack.
The issue here is how to retain the activity of the catalyst with out its sintering

TEM micrographs of catalyst particle growth after FC opera



Life test conditions:
Cell temperature = 100°C
Stoich of H_2/O_2 = 1.25/2
Pressure of H_2/O_2 – ambient
Dew point of H_2/O_2 = 100°C/dry
Current density = 1.5 A cm^{-2}

Test conditions: 100C, H2/.O2 1.25/5,Pressure ambient,
Dew point 100C, CD 1.5 A/sq cm

The Catalyst layer

At the catalyst layer, the following reactions occur

- **Reactant diffusion,**
  - **Electron and proton migration, and**
    - **Charge-transfer kinetics**
    - **The presence of liquid water complicates further.**
- **Thickness, composition and pore-space morphology control the transport and reaction.**
  - **The size distributions and wetting properties of pores control water and heat exchange**
    - **Hydrophilic micropores are good for evaporation**
      - **Hydrophobic mesopores are good for gas transport.**

For optimal catalyst utilization, water management and the overall successful performance of the cell, understanding the rules of this competition is difficult

Role of Catalyst Layers

- Local capillary equilibrium between the liquid and gas phase should exist in the micropores (1–10 nm) favouring large evaporation rates
  - Mesopores (10–40 nm) should be open for gaseous transport of reactants and products.
    - The two major functions – evaporation and gaseous transport are controlled by Part of Micro- and Mesopores, and their respective wetting properties,

The issues of Catalyst/catalyst layers

Pt activity in conventional CLs reaches at most 10–20 % of its full potential

- Most of the expensive Pt is utilized ineffectively
  - CLs need to be made much better and much cheaper.
    - Composition and thickness need to be readily adjusted

Getting 100% utilisation, requires more innovative fabrication procedures – electrochemical deposition of Pt at this boundary.

Difficult to estimate how much effort should be invested in such procedures, but their prospects for optimized catalyst utilization are clear.

Two key measures of CL performance:

- **catalyst utilization**
- **catalyst effectiveness.**

Catalyst utilisation in ideal three-phase composites:

- **Catalyst particles at the intersections of the Pt/C phase,**
- **Gas pores - connected with the GDL and**
- **Ionomer phase - connected with the membrane**

Catalyst effectiveness is ,

- **varying concentrations and**
- **reaction rates with performance.**

Role of Catalyst Layers

- CL’s are the best the source of any water management problems in FCs.
  - PEFCs need a medium that converts huge amounts of liquid water arriving in the CL into vapour.
    - Once liquid water arrives in GDLs or FFs, they are unable to handle it.
      - The CL is the PEFC’s favourite water exchanger.
        - High rates of evaporation effectively convert the waste heat of the reaction into latent heat of vapour
        - Effective operation of CLs in terms of FC water balance is closely linked to their porous structure.

Catalyst & Catalyst layers

The thrust in R&D has been towards reducing the catalyst amount and developing CO tolerant catalysts. The progress is impressive
Binary and ternary catalysts have been tested especially for DMFC

But

For performance improvement equal if not more thrust should have been on developing high performance cathode catalysts (and catalyst layer) as its function determines the oxygen reduction kinetics which in turn determines the cell performance.
Pt-Co/Cr/Sn have been reported to improve the ORR

The challenge is to develop low cost highly stable oxygen reduction catalysts

The Fuel Cell Electrode

The electrode is a complex subject with a number of simultaneous reactions taking place in its structure.

The electrode structure among other things determines the the percentage utilization of the catalyst which is a major issue

Understanding the rules of this competition is crucial for optimal catalyst utilization, water management and the overall successful performance of the cell.

The Fuel Cell Electrode

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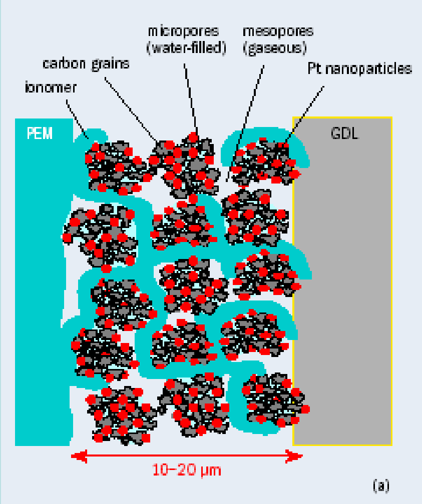
Methods for fabricating electrodes are:
silk screening, brushing, spraying and rolling

In these methods catalyst layers are present as a three phase composites. There are several inactive sites .

Even the best electrode can give at best 10-20% utilization which means the knowledge of the structural details is incomplete



Three phase composite stucture of conventioanl CL .Pt catalyst(1-10 nm) deposited on high-surface-area carbon.

CL in the present form is not highly effective. It is essential to enlarge the effective surface area by diminishing the size catalyst particles and to distribute the catalyst only on the surface of the electrode for a thin nanostructured catalyst film. More innovative fabrication procedures are required.

Alternative catalyst layer

Site selective Electro deposition of Pt on a substrate at the boundary should form the electronically conductive phase

- **make CLs of extremely thin two-phase composites (~100–200 nm thick) with the catalyst deposited site specifically**

The remaining volume filled with liquid water as the medium for proton and reactant transport.

Since impregnation with ionomer is not used in this method

- **the protonic contact resistance at the PEM/CL interface can be mitigated**
- **CL insensitive to the type of PEM.**
- **This could result in 100% Pt utilization**

While making such an electrode on a small scale may be possible, large scale production would be a challenge

Nanostructured MEA

In the conventional method, it is very difficult to control the nanostructure due to conc. catalyst ink and heat press process.

ARCI is looking at developing Electrophoretic deposition and pulsed electro-depostion techniques which offer many advantages

Membrane Electrolyte

Present status of commercial Membranes

- Dupont has been supplying Nafion series of membranes for over two decades
- Initially used thicker membrane was slowly changed to thinner membranes with improved performance
- Durability and degradation have become big issue and Dupont supplies only a chemically stabilised membrane which is yet to be tested in full scale.
- This new development is going to affect the progress in developing PEMFC especially in labs where Dupont membrane is used in the absence of other suppliers

Membrane Electrolyte

PROTON-CONDUCTING FUEL CELL MEMBRANES

HYDROGEN FUEL CELL

Main Challenges

1. Stability of membrane above 80°C
2. Water retention above 80°C
2. Cost of existing membrane materials

DIRECT METHANOL FUEL CELL

Main Challenges

1. Reduction of methanol crossover while maintaining high proton conduction
2. Stability of membrane above 100°C
3. Produce an appropriate membrane at moderate cost

"For practical use," it is crucial to develop PEMs of high conductivity under low humidity (0–50%) at high temperatures (100–200ºC)."

Two key approaches are being investigated in this regard.

1. To increase the water-holding ability of the Nafion (or similar) membrane at temperatures greater than 100 ºC by doping the membrane with inorganic materials.
2. Replace Nafion-like membranes and to exploit alternative chemical species for proton conduction.

Until now, scientists have had some limited success pursuing the Nafion-replacement strategy with systems such as PBI-H_3PO_4 and imidazole where H_3PO_4 and imidazole are the respective proton conductors.

On the plus side, these systems enable Fuel Cells to operate at temperatures above 100 ºC.

The downside is the propensity of small molecules like H_3PO_4 to leak out with water, and the poor conductivity and electrochemical stability of imidazole.

Membrane Electrode Assembly

The membrane and the catalyst layers are bonded together to form the MEAs. – zero gap assembly

The present fabrication procedures hardly reveal any degree of precision and there is considerable scope for improvement

The major challenge is to develop methods which are suitable for bulk production

Bipolar plates

Bipolar plate ----- the electrode plate that separates individual cells in a stack
--- high density graphite with machined flow channels.

----Both material and machining costs are high

Continuous R&D has resulted in developing bipolar plates which most of the following requirements

- **light weight, thin <3mm**
- **sufficient mechanical integrity**
- **high surface and bulk electronic conductivity**
- **low permeability between fuel and oxidant and**
- **corrosion resistance <16 mA/cm2**

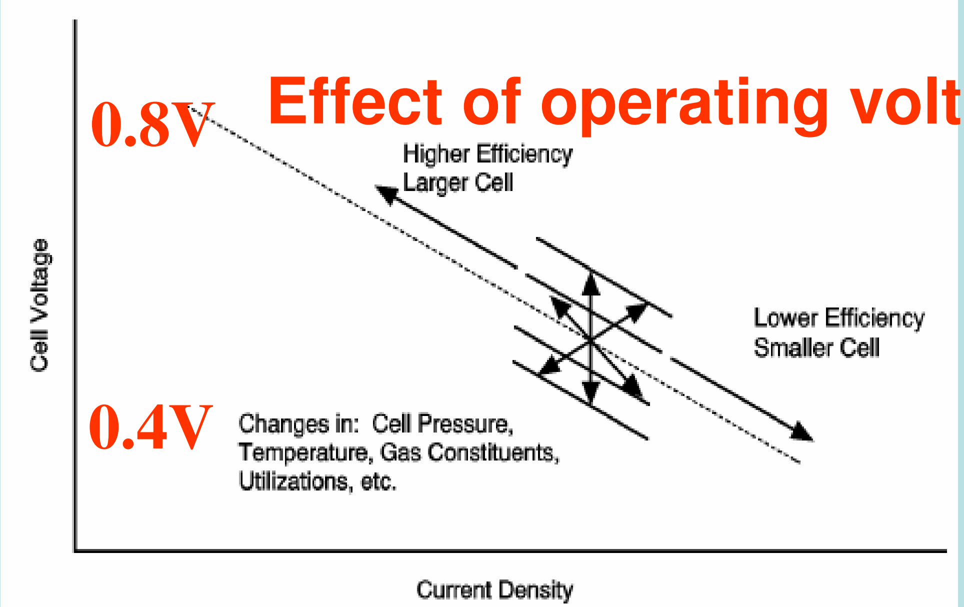
The Challenge is to covert this knowledge into manufacturing to reach the goal of <$10/kW

FC system must be designed as a whole, not as a collection of stand-alone parts . A FC is like a living organism : malfunctioning of one organ is likely to destroy the whole body

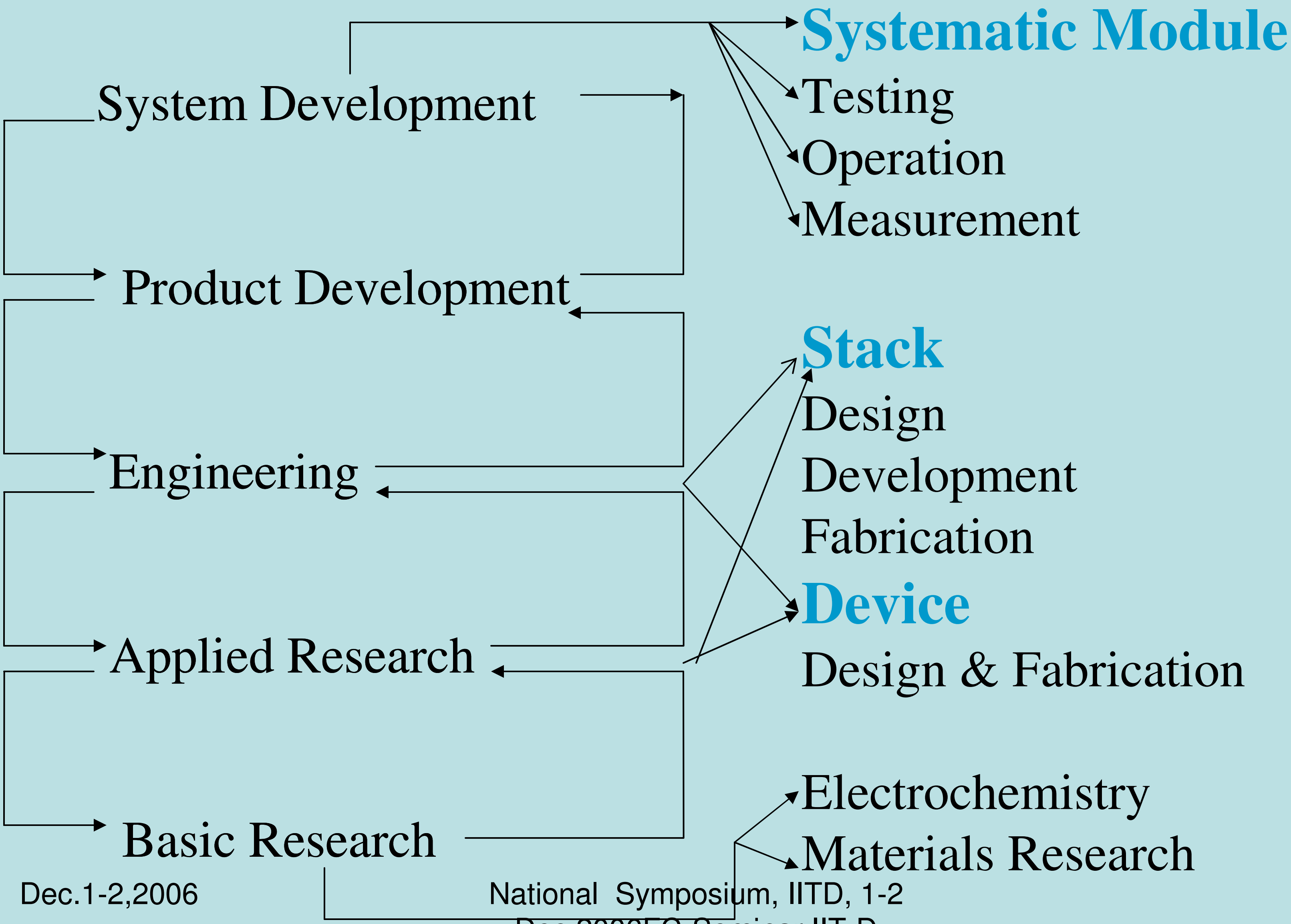
FC design can therefore be thought of as optimization problem . The merit function in this optimization process being the power density obtained at given cost, weight and life time.

This merit function is the focal point for the technology push

Effect of operating voltage



Need of the hour - Integrated R & D



System Development

Product Development

Engineering

Applied Research

Basic Research

Systematic Module

Testing

Operation

Measurement

Stack

Design

Development

Fabrication

Device

Design & Fabrication

Electrochemistry

Materials Research

Standards

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Rating of Improvements in Fuel Cell technology

- Some commonly agreed measures for system efficiency are
power density, dynamic behavior, durability

This requires a harmonized testing procedures both for entire Fuel Cell systems and for system components under a variety of boundary conditions

e.g. Different applications
Different stack concepts
Type of fuels and quality

Till recently no standardized test procedures for Fuel Cells, stacks, and systems existed.

The same applies for their assessment against user requirements in the stationary, transport and portable applications.

In practice, many laboratories and manufacturers have developed their own test protocols to meet their needs and those of their customers showing clearly the need for harmonisation of testing procedures and measurement methods to ensure a smooth introduction of the technology and to provide equal opportunities of the market operators and a decent and confident comparison basis for the customers.

US Fuel cell council has announced a trial protocol for testing single cells and stacks
FTSTEP is another attempt in EU