PEM Fuel Cells: Overview

Workshop on PEMFC Systems

Arun K Tangirala

Department of Chemical Engineering
Indian Institute of Technology Madras

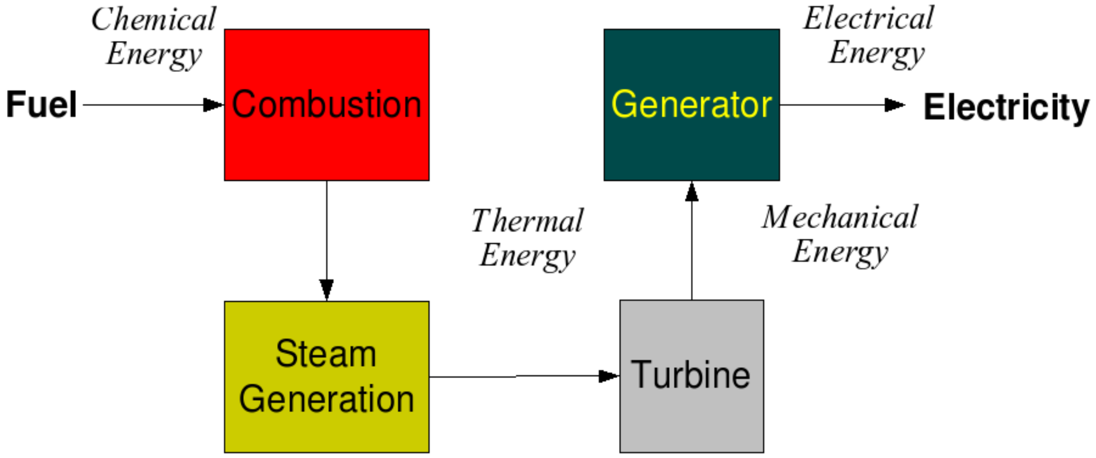
PEMFC Workshop, Singapore

Outline

What is a fuel cell?

An electrochemical device that converts chemical energy (of a fuel) directly into DC electricity.

A typical conversion of chemical energy into electricity energy has involved

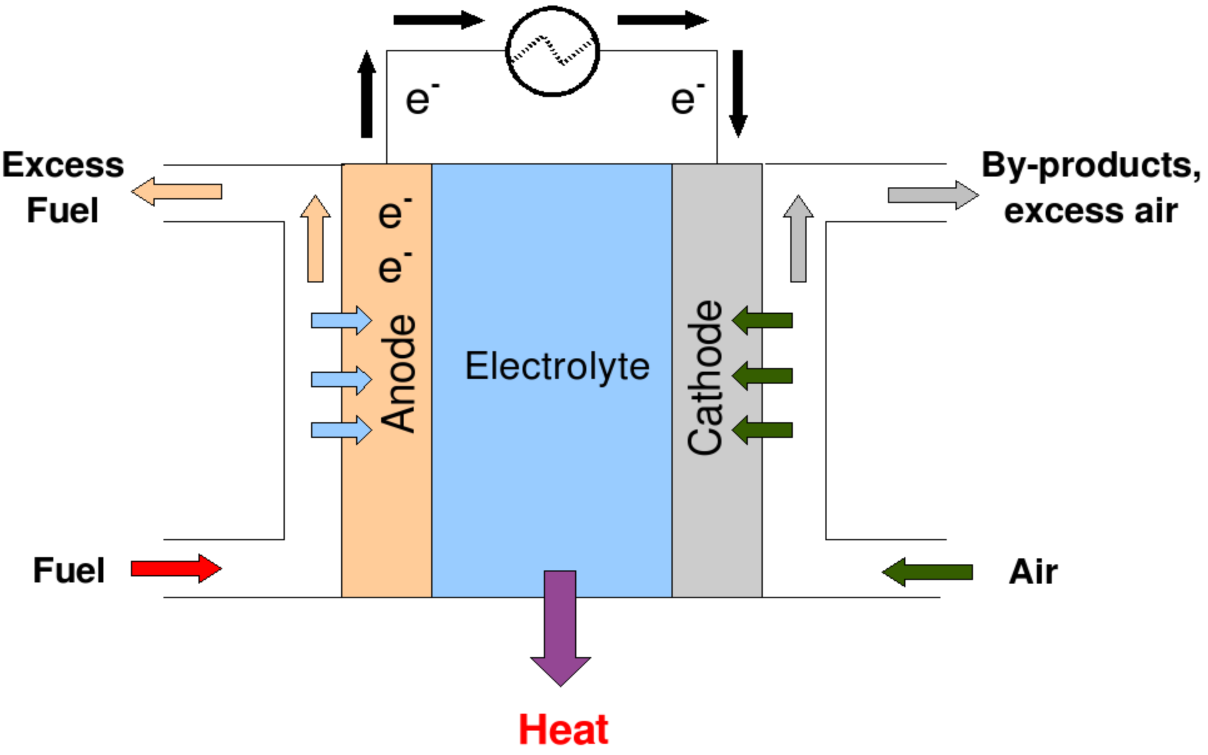


Fuel
Chemical Energy
Combustion
Thermal Energy
Steam Generation
Turbine
Mechanical Energy
Generator
Electrical Energy
Electricity

A fuel cell circumvents this conversion and therefore is expected to be

- Simpler and (hence) less expensive
- More efficient than the conventional processes

Schematic diagram of a typical fuel cell



A fuel cell directly converts the [chemical] energy of a fuel into electrical energy by means of an electrochemical reaction. The primary by-products are heat and water.

Motivation

Efficiency:	Fuel cells, in principle, operate at much higher efficiencies than the existing means.
Clean environment:	They produce low or zero emissions; this is indeed a strong factor!
Energy security:	Since these devices use hydrogen as a fuel, dependence on fossil fuels can be reduced significantly.
Simplicity:	Fuel cells contain no moving parts and in general have repetitive components. Hence, there is a potential to produce them in bulk in a cost-effective manner.

Motivation contd ...

Modular:	These devices can be added in modules to generate more power. Useful in enhancing productivity and reducing the burden on initial planning.
Minimal noise:	Due to the absence of moving parts, fuel cells are inherently quiet. Noise levels in the transportation sector can be significantly reduced. Also, useful in military/security applications.
Size and weight:	Size and weight are design parameters, which can be optimized particularly for technology in powering electronic devices.

Fuel cell materials are at present expensive due to the cost of catalyst and membrane. The commercial viablity of fuel cells is yet to be proven. Demonstrations / pilot-scale experimentations have been successful. A strong focus is needed on the search for materials and development of techniques that can bring down the overall manufacturing cost.

History of Fuel Cells

1839	Grove-H_2, O_2 fuel cell
1855	Becquerel-Carbon fuel/fused nitrate/Pt, O_2
1877	Jablackoff-Carbon fuel/fused nitrate/cast iron, oxidant
1889	Mond and Lange: H_2, O_2 cell similar to modern fuel cells
1897	Jacques modified the fused salt cell, replacing nitrate with NaOH; cell developed 1 V and delivered 150 mA
1910	Taitebaum advocated the use of a porous diaphragm separator
1911	Beutner used platinum tube electrodes containing H_2 and O_2
1913	Siegel improved upon the Mond-Lange cell. Since then several molten slat systems have been tried
1911-1913	Biochemical fuel cells were strongly advocated and readvocated
1960s	Germini and Apollo spacecraft
1980s	Space Shuttle
1989	Perry Energy Systems with Ballard Power Systems successfully demonstrated a PEM fuel cell-powered submarine engine.
1990	California Air Resources Board announced zero emission vehicle mandate

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History of fuel cells contd ...

1993	George-town Bus demonstrated, with phosphoric acid fuel cell and onboard methanol reformer
1993	Partnership for a New Generation of Vehicles (PNGV) announced, a government / industry partnership aimed at producing cars with three times the fuel economy of current vehicles. Big Three US automakers begin studies of options, including fuel cells
1993	Ballard Power Systems demonstrated first hydrogen fuelled PEM fuel cell bus
1995	Daimler-Benz demonstrated the NECAR 1, an experimental PEM fuel cell van with hydrogen storage
1995-2000	Several European, American and Asian big automobile companies and other companies took initiatives for collaborative efforts and carried out experimental demonstrations of fuel cell-based vehicles.
2002	Honda (FCX4) Toyota (FCHV-BUS2) Nissan (X-Trail FCV) launched
2002	EPRI's Fuel cell program - 5 kW PEM and SOFC tests
2004	Honda delivered hydrogen powered fuel cell vehicles to the Mayor of San Francisco

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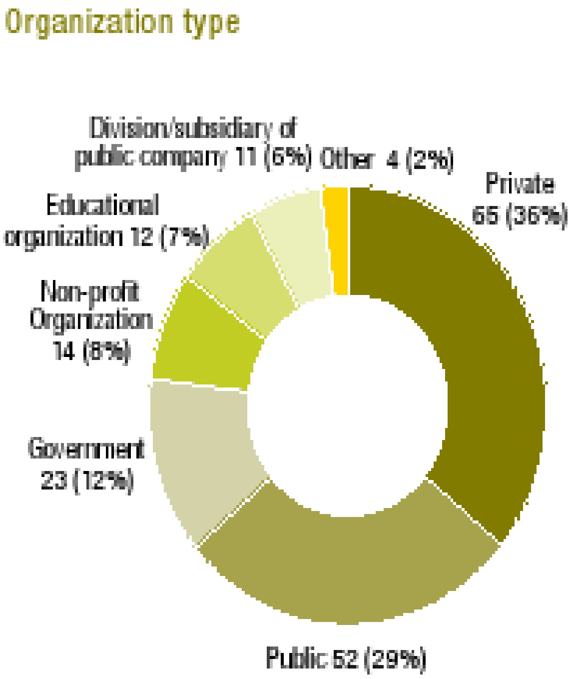
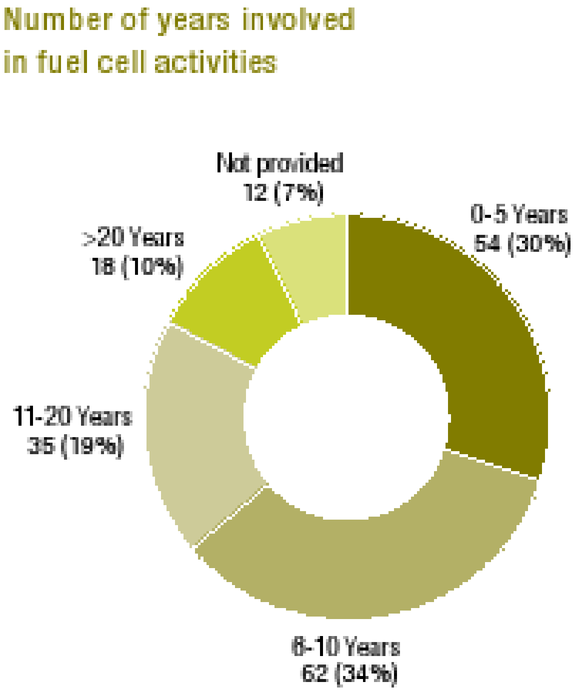
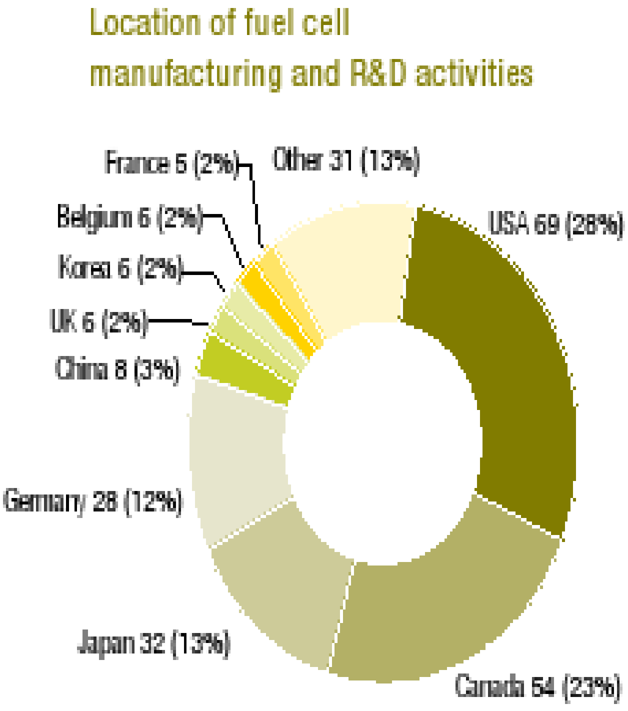
Market Survey

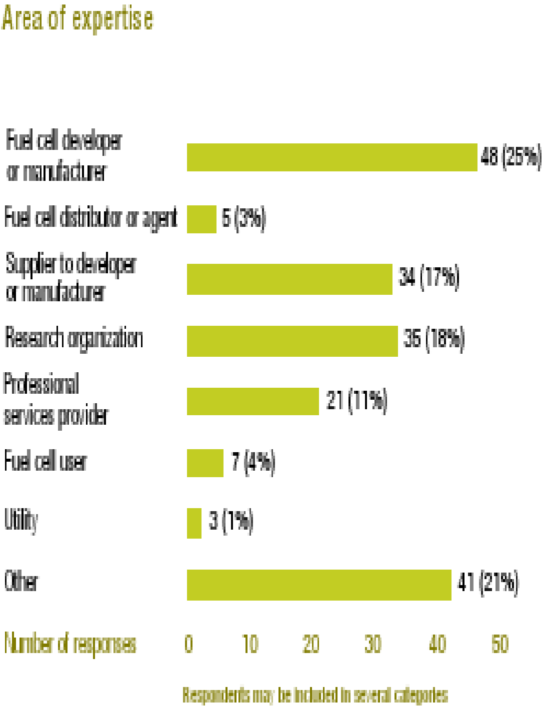
A market survey was conducted for the year 2005 by leading fuel cell industry associations in a worldwide industrial fuel cell survey:



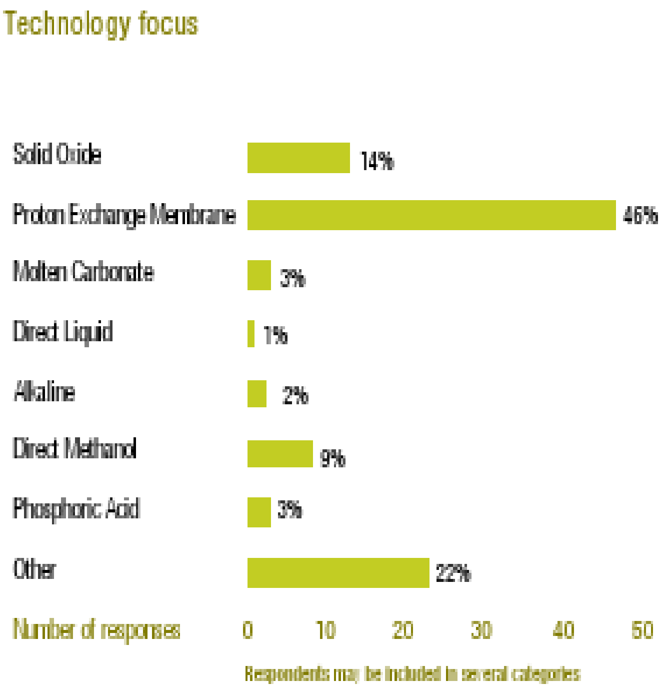


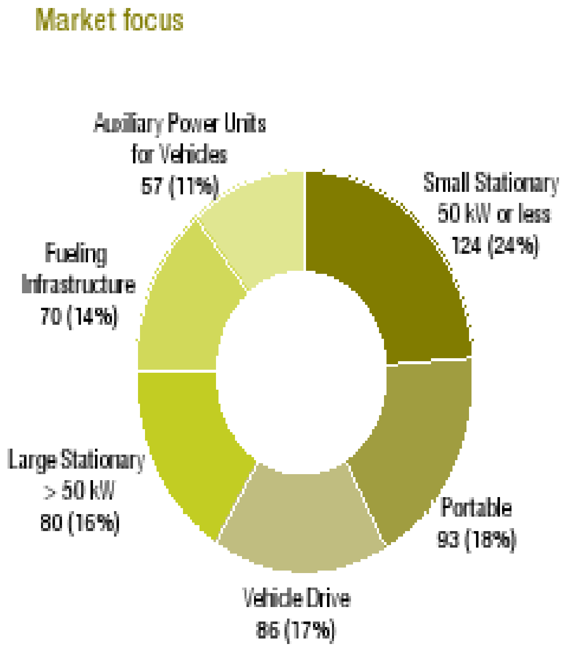
Activity Centres and Expertize



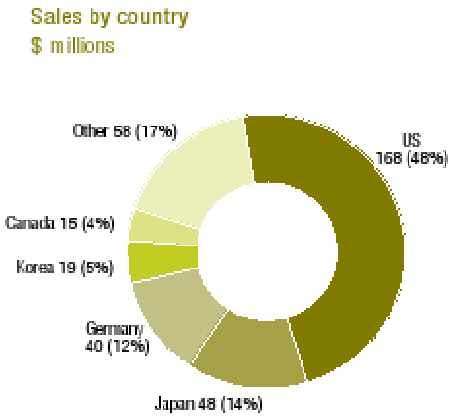


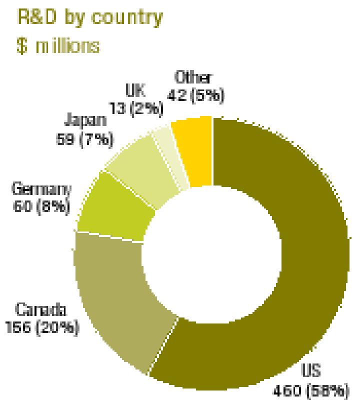
Focus: Technology and Market

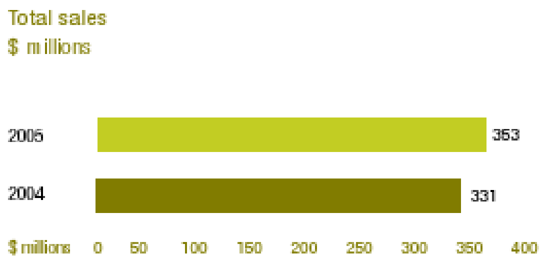


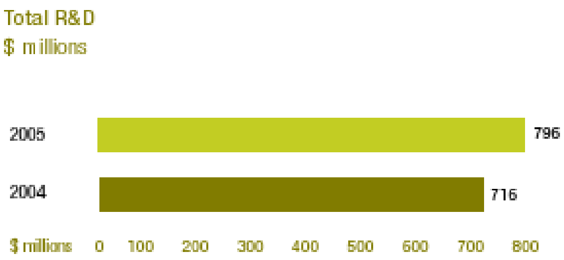


Money invested in R & D

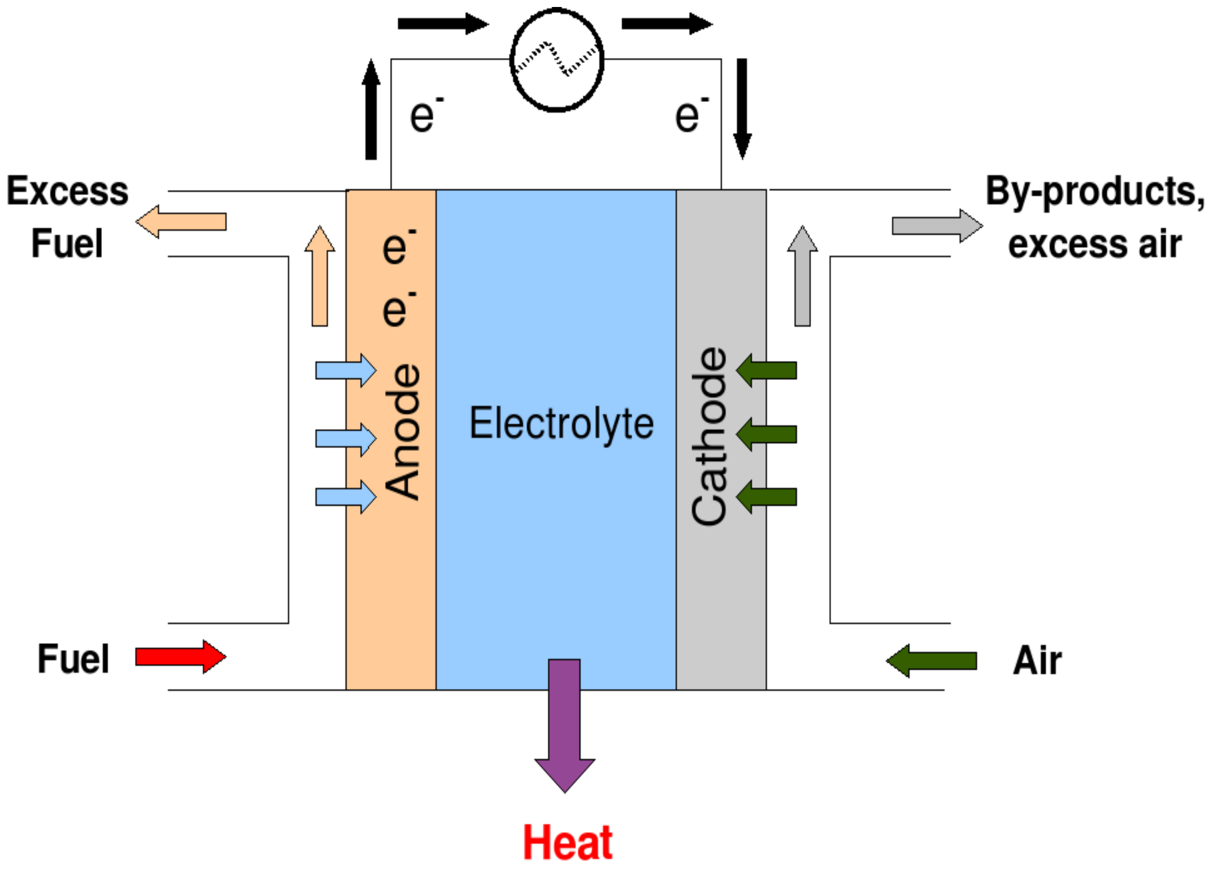








Schematic diagram of a typical fuel cell



Fuel Cell vs. Battery

- Similar to a battery (has two electrodes and an electrolyte) and generates DC electricity through electrochemical reactions
- FC requires a constant supply of fuel and oxidant.
- It is a energy-conversion device whereas battery is truly an energy-storage device.
- Electrodes in a fuel cell do not undergo chemical changes (in principle).
- FC generates two key by-products: heat and water. Therefore, an additional management system is required (unlike in the battery).
- Unlike in batteries, there are hardly any disposal issues in fuel cells.

Role of electrodes in a fuel cell

- They provide the necessary sites where ionization and deionization reactions can take place.
- They facilitate the ion transport away from or into the three-phase interface once it is formed.
- They provide a physical barrier that separates the bulk gas phase and the electrolyte.

In order to carry out all these functions the electrode material should be both catalytically active and should be a conductive material, simultaneously porous and also should be in solid form. The porous nature should be such that it is permeable to both the electrolyte and the gases.

Role of the electrolyte

- It must permit only the appropriate ions to pass between the anode and cathode. Passage of free electrons through the electrolyte results in a short-circuit and disrupts the reaction.
- The electrolyte should possess good ionic conductivity. It is not a molecular sieve as in the osmosis process!
- The type of fuel and the operating conditions also depends on the electrolyte.
    - The celebrated Nafion is a thirsty membrane! (requires good water management)
    - Nafion begins to lose mechanical strength beyond 80°C
    - MCFC require high temperatures to keep the electrolyte "molten".

Types of fuel cells

Fuel cells are generally grouped by the electrolyte that is used.

Electrolyte	**Fuel Cell Type**
Polymeric Ion Exchange Membrane	Polymer Electrolyte Membrane Fuel Cell (PEMFC)
Immobilised alkaline salt solution	Alkaline Fuel Cell (AFC)
Immobilised liquid phosphoric acid	Phosphoric Acid Fuel Cell (PAFC)
Immobilised liquid molten carbonate	Molten Carbonate Fuel Cell (MCFC)
Ceramic	Solid Oxide Fuel Cell (SOFC)

Another common type of cell known as Direct Methanol Fuel CEll (DMFC) exists, but can be treated as a variant of PEMFC with a different fuel.

Characteristics and features of fuel cells

Fuel cell Type	PEMFC	AFC	PAFC	MCFC	SOFC
Characteristics					
Operating temperatures	303-353 (K)	353-373 (K)	373-493 (K)	923-1123 (K)	973-1273 (K)
Current Density	high	high	moderate	moderate	high
Likely applications	Electrical utility, transportation	Military & space, residential plants	Electric utility and transportation	Electric utility	Electric utility
Power Output (W)	1 - 100k	500 - 10k	10k - 1M	100k - 10M+	1k - 10M+

Note: *DMFCs are not included in the comparison chart since they differ mainly in terms of the fuel, which is an alcohol unlike the traditional hydrogen.*

Characteristics of fuel cells contd ...

Fuel Cell	**Anode Reaction**	**Cathode Reaction**
PEMFC	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2}O_2 + 2e^- + 2H^+ \rightarrow H_2O$
AFC	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$\frac{1}{2}O_2 + 2e^- + H_2O \rightarrow 2OH^-$
PAFC	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2}O_2 + 2e^- + 2H^+ \rightarrow H_2O$
MCFC	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$\frac{1}{2}O_2 + CO_2 + 2e^- + \rightarrow CO_3^{2-}$
SOFC	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$

Fuel Cell	**Electrode**	**Charge carrier**	**Water management**
PEMFC	Pt	H^+	Evaporate
AFC	Ni/Ag metal oxides, noble metals	OH^-	
PAFC	Pt	H^+	evaporate
MCFC	Ni anode, NiO cathode	CO_3^{2-}	gaseous products
SOFC	Co-ZrO$_2$ Ni-ZrO$_2$ anode, Sr-LaMnO$_3$ cathode, Y$_2$O$_3$- stabilized ZrO$_2$ electrolyte	O^{2-}	gaseous products

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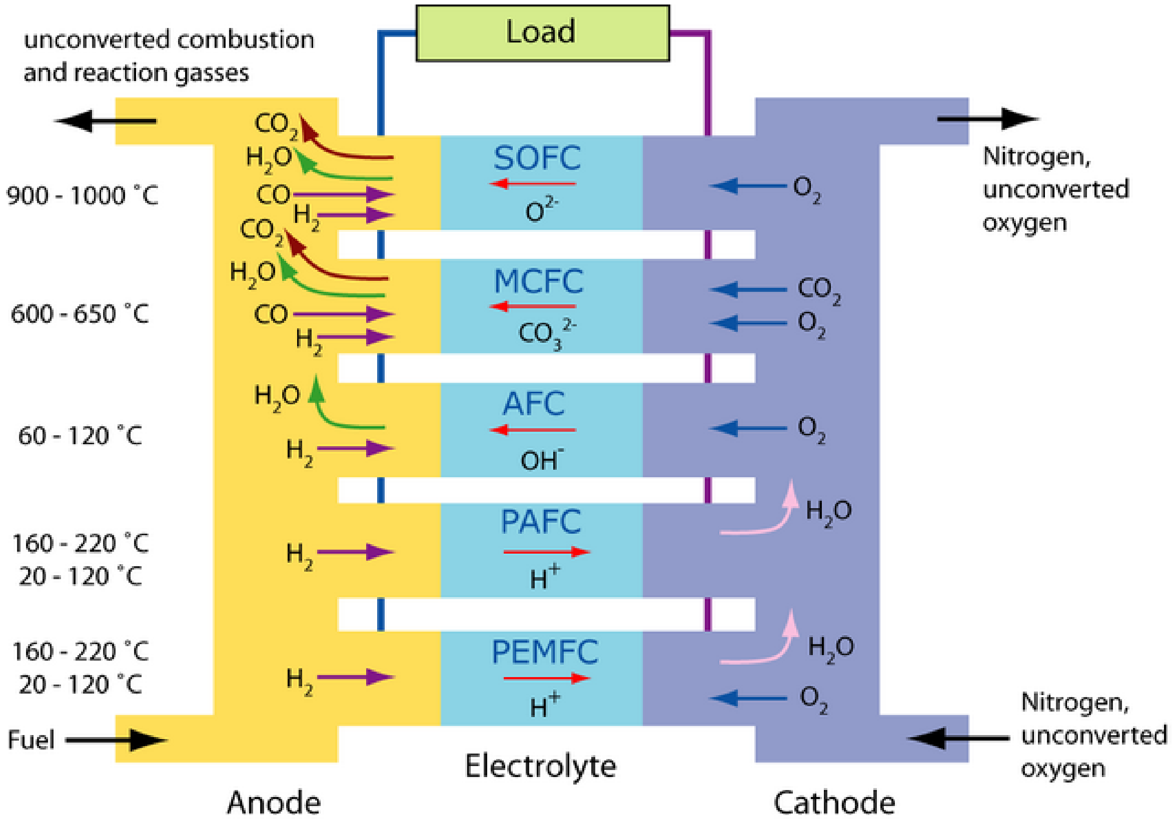
Pictorial view: Classification of fuel cells



Source: `http://www.msm.cam.ac.uk/doitpoms/tlplib/fuel-cells/figures/fuelcell_types_sml.png`

Advantages vs. Disadvantages

- **PEMFC**: Low temperature, quick start up, solid electrolyte reduced corrosion and management problems
  Sensitive to fuel impurities (minimal CO), water management
- **AFC**: High performance, simple design
  Expensive removal of CO_2 from fuel/air supplies
- **PAFC**: High efficiency for cogeneration, can tolerate impure hydrogen fuel
  Low current/power, large size/weight, leakage problem
- **MCFC**: High efficiency, flexibility of fuel types, internal reforming possible, CO/CO2 tolerant
  High temperature enhances corrosion, breakdown of cell components, longer start-up, start-stop cycle creates problem of thermal fatigue and cracking of parts
- **SOFC**: High efficiency, flexibility of fuels, solid electrolyte reduces corrosion and management problems, internal reforming possible
  High temperature enhances corrosion, breakdown of cell components, longer startupstart- stop cycle creates problem of thermal fatigue and cracking of parts

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Choice of fuels

- In theory, any chemical substance that can undergo oxidation and any oxidant that can be reduced (galvanostatically) can be used in a fuel cell.

- Hydrogen is used for the following reasons:
  - It is highly reactive when suitable catalysts are used
  - It could be produced from hydrocarbons.
  - It possesses high energy density
  - It can be stored cryogenically for closed-environment applications.
- Other fuels that indirectly or directly supply hydrogen can also be used. Methanol is one of the most popular choice. Methanol can be electro-oxidized at a fuel cell anode either directly or indirectly.
- Oxygen is preferred as an oxidant since it is readily and economically available from air, and it can be stored for closed applications.

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Fuel properties: A comparison

Fuel	$\triangle G^0$ (kcal/mol)	E^0_{theor} (V)	E^0_{max} (V)	Energy Density (kWh/kg)
Hydrogen	-56.69	1.23	1.15	32.67
Methanol	-166.80	1.21	0.98	6.13
Ammonia	-80.80	1.17	0.62	5.52
Hydrazine	-143.90	1.56	1.28	5.22
Formaldehyde	-124.70	1.35	1.15	4.82
Carbon monoxide	-61.60	1.33	1.22	2.04
Formic Acid	-68.20	1.48	1.14	1.72
Methane	-195.50	1.06	0.58	–
Propane	-503.20	1.08	0.65	–

Sources of hydrogen

- Pure hydrogen certainly provides the maximum efficiency; however, availablilty of pure hydrogen is difficult. It is often available in combination with other elements in nature.
- A great deal of pressure and volume is necessary to store pure hydrogen in order to reap the energy-to-weight efficiencies.

- **Reformation of hydrocarbons**: An attractive choice, but has certain limitations. Results in production of CO - a pollutant for the catalyst in [low temperature] fuel cells. Holds strong potential in large power plants.
- **Oxidation of methanol**: Methanol can be electro-oxidized at the anode either directly or indirectly. Fuel cells that directly take methanol as a fuel have received wide attention.
- **Renewable means**: Solar energy can be used to electrolyze water to produce hydrogen. Such a scheme provides a truly zero-emission fuel cell system.

A fuel cell stack

A single cell produces voltage < 1 V. In general, higher power outputs are realized by connecting several cells together in series - known as stacks. A supporting system for the stack is very much essential.

The role of the supporting system is to:

- Handle the supply of reactant gases and their exhaust, including the products
- Manage the heat (maintain the stack temperature) and water output (humidification, flooding).
- Regulate and condition the power output
- Monitor the operation and performance of stack
- Control the start-up, operation and shutdown of the stack and system components

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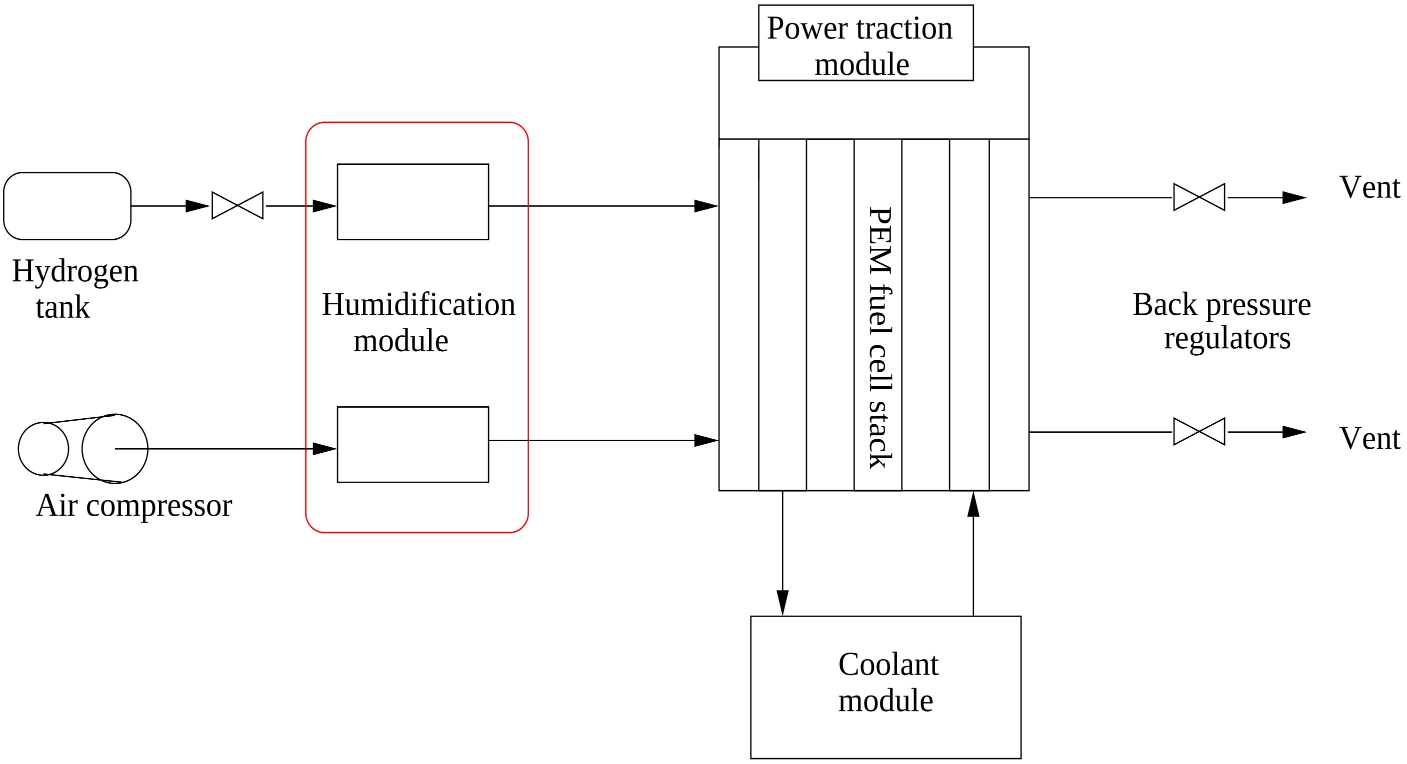
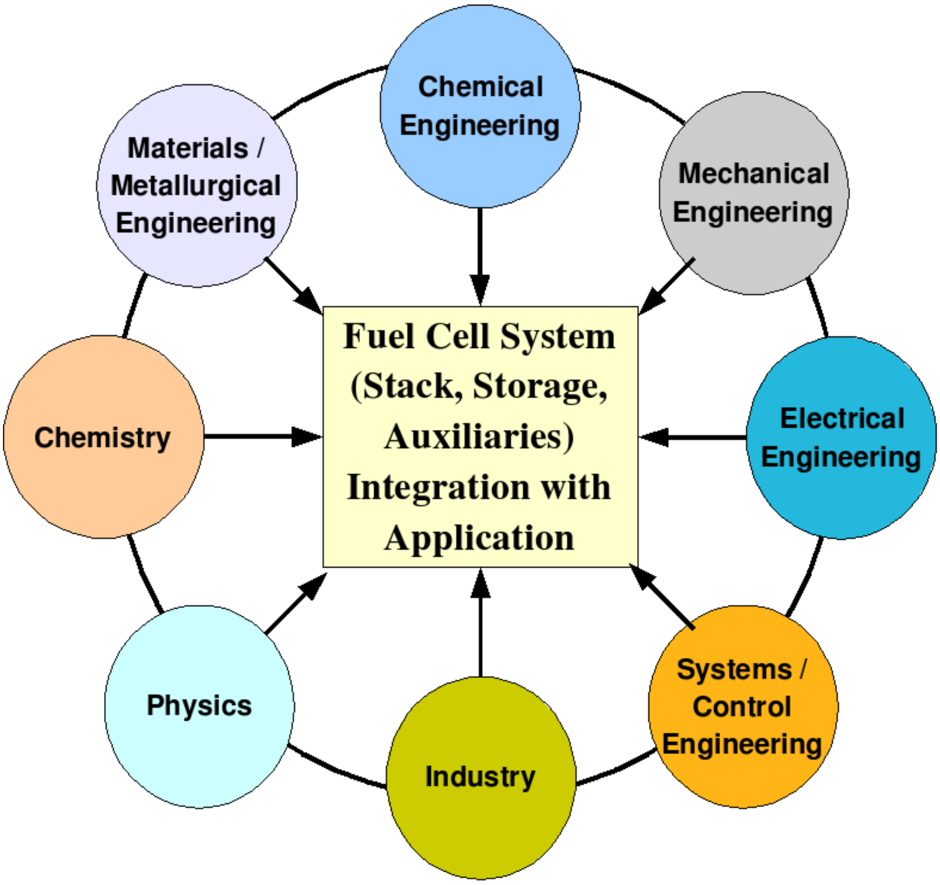
Schematic diagram of PEM fuel cell stack system



Focus of this workshop

- Exclusive focus on PEM Fuel Cells
- PEM fuel cells have received widespread attention:
  - Ability to operate at low (room) temperatures
  - Their viability
  - The ability to response quickly to varying loads
  - Low manufacturing costs (relatively)
  - Solid electrolyte (much easier to handle than the liquid electrolyte)
  - High power density
  - Low weight and volume compared to other fuel cells
- Aim of this course is to provide a system-level treatment with emphasis on system-level modelling, control and identification.

Requires expertize from various disciplines



Fuel Cell System (Stack, Storage, Auxiliaries) Integration with Application

Chemical Engineering

Mechanical Engineering

Electrical Engineering

Systems / Control Engineering

Industry

Physics

Chemistry

Materials / Metallurgical Engineering

Acknowledgements / Credits

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- Mr. Vasu Gollangi, Ph.D. candidate, Dept. of Chemical Engineering
- Various other sources and organizations

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Introduction to PEM Fuel Cells

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Arun K Tangirala

Department of Chemical Engineering
Indian Institute of Technology Madras

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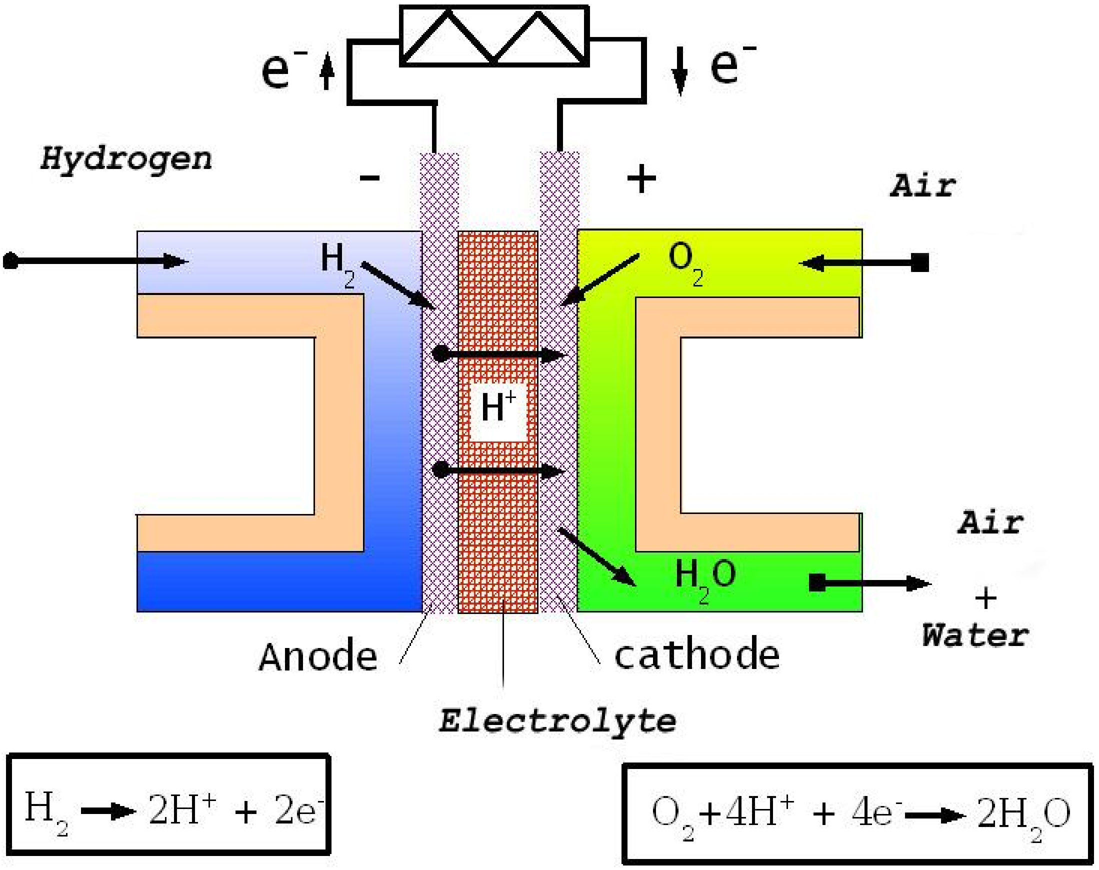
Outline

A PEM fuel cell

PEM fuel cell stands for Polymer Electrolyte Membrane Fuel Cell or a Proton Exchange Membrane Fuel Cell. The underlying technology is simple, viable and has a quick start-up.

- Hydrogen is the fuel, while oxygen (air) is the oxidant
- The catalyst is either Pt or Pt-alloy, which facilitates the dissociation of hydrogen at the anode.
- It operates at relatively low temperature (≈ 80°C)
- The noble metal catalyst is extremely sensitive to the presence of CO!
- Each cell produces around 0.7 V, about enough power to run a light bulb
- PEMFC systems are particularly well-suited for transportation and stationary applications.

Schematic diagram of PEM fuel cell



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

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Inside the PEM fuel cell

The key components are electrodes and the electrolyte (membrane) - known as the Membrane Electrode Assembly (MEA). Several phenomena occur within a cell.

- Gas flows through the channels (convective flow) and through the porous media
- Electrochemical reactions
- Proton transport through the polymer-electrolyte and water transport through the membrane
- Electron passage through the conducting material (external circuit / load)
- Water transport through porous catalyst and gas diffusion layers
- Two-phase flow of unused gas at the cathode
- Heat transfer (through conduction and convection)

Basic reactions

Anode:

$$H_2 \longrightarrow 2H^+ + 2e^-$$

Anode:

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O$$

Overall:

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

Some intermediate reactions occur, but the above reactions accurately describe the phenomena.

Heat of Reaction

The overall heat of reaction is equal to the heat generated by the combustion of hydrogen (combustion is exothermic)

The heat generated can be computed as

$$\triangle H = (h_f)_{H_2O} - (h_f)_{H_2} - \frac{1}{2}(h_f)_{O_2}$$

Heat of formation of *liquid* water is -286 kJ mol^{-1} while for a pure element, it is zero.

Therefore, a fuel cell should ideally yield 286 kJ mol^{-1} of energy (at 25°C). The reaction is written as:

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O(l) + 286 \text{ kJ/mol}$$

The energy generated above is also known as the heating value of hydrogen

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Heating value of hydrogen

HHV

The amount of heat generated by complete combustion of 1 mol of hydrogen. If 1 mol of H_2 is ignited, fully combusted and allowed to cool down (in a calorimetric bomb) to 25°C, the products are liquid water and heat equal to 286 kJ.

Lower Heating Value (LHV): The heat generated when hydrogen is combusted with excess of oxygen and allowed to cool down at 25°C. Product is water in vapour form mixed with unburnt oxygen and/or nitrogen. The heat generated is then 241 kJ mol^{-1}

HHV - LHV = heat of evaporation of water = 286 - 241 = 45 kJ mol^{-1}

The hydrogen heating value is a measure of energy that is input into a fuel cell, since it represents the maximum amount of [thermal] energy that can be extracted from H_2

How much energy can fuel cell yield?

Since every reaction is associated with generation of entropy, the entire heating value of hydrogen cannot be converted into electricity. The actual energy available is in fact the **Gibb's free energy**.given by

$$\triangle G = \triangle H - T\triangle S$$

The term $\triangle S$ represents the irreversible losses.and can be written as

$$\triangle S = (s_f)_{H_2O} - (s_f)_{H_2} - \frac{1}{2}(s_f)_{O_2}$$

The unit of s_f is energy mol^{-1} K^{-1}.
From thermodynamics, $\triangle S$ is computed as 48.68 kJ mol^{-1} at 25°C.
Therefore, the actual energy available for conversion is 237.34 kJ mol^{-1}.

Theoretical Fuel Cell Potential

The electrical work is computed by $W_{el} = qE$, where q is the amount of charge transferred and E is the potential difference.
The total charge transferred is given by $q = nN_{avg}Fq_{el}$ where

n = no. of electrons per molecule of H_2 = 2
N_{avg}= no. of molecules per mole (Avogadro's number) = 6.022×10^{23} molecules / mol.
q_{el} = charge of 1 electron = 1.602×10^{-19} Coulombs / electron

The product $N_{avg}q_{el}$ is known as 1 Faraday = 96,485 Coulombs / electron-mol
Assuming that the maximum amount of work available, which is $-\triangle G$ is fully converted into electrical work, the theoretical potential at 25°C is:

$$E = \frac{-\triangle G}{nF} = \frac{237340}{2 \times 96485}\frac{\text{J mol}^{-1}}{\text{Coulombs mol}^{-1}} = 1.23 \text{ Volts}$$

Effect of temperature

The basic equation describing the effect of temperature on the cell potential is:

$$E = \left(\frac{\triangle H}{nF} - \frac{T \triangle S}{nF} \right)$$

Clearly, the cell potential is expected to decrease as the temperature increases.(note that both $\triangle H$ and $\triangle S$ are functions of temperature)

$T(K)$	$\triangle H$	$\triangle G$	$\triangle S$	$E_{theor}(V)$
298.15	-286.02	-237.34	-0.16328	1.23
333.15	-284.85	-231.63	-0.15975	1.2
353.15	-284.18	-228.42	-0.15791	1.184
373.15	-283.52	-225.24	-0.15617	1.167

Effect of temperature in practice

In practice, the operating cell potential increases with increase in temperature! The cell losses are lower at higher temperatures and compensate substantially for the decrease in the theoretical cell potential. There are different kinds of voltage losses:

- Losses due to activation polarization
- Crossover losses (due to internal currents)
- Ohmic losses (due to internal resistance)
- Concentration polarization losses (due to rapid consumption of reactant)

These losses will be discussed at a later stage

Theoretical Efficiency of a Fuel Cell

Efficiency of any conversion device is defined as the ratio of energy output to the the energy available in the input.

For a fuel cell, the maximum possible efficiency is:

$$\eta = \frac{\triangle G}{\triangle H} = \frac{237.34}{286.02} = 83\%$$

- Hydrogen's HHV has been used to compute the efficiency. If LHV is used, then a higher value results (94.5 %). But use of lower heating value can be confusing!
- HHV is more appropriate since it accounts for all the energy available, while LHV does not account for the heat of condensation
- Carnot efficiency does not apply to a fuel cell since it is not a heat engine! There is no combustion but an electrochemical reaction in a cell

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Effect of pressure

A fuel cell is typically operated at higher pressures to ensure proper flow channelization of reactants at the electrodes.

Using the familiar Nernst equation (assuming gaseous products and reactants),

$$\triangle G = \triangle G_0 + RT \ln \left(\frac{P_{H_2O}}{P_{H_2} P_{O_2}^{0.5}} \right) \implies \triangle E = \triangle E_0 + \frac{RT}{nF} \ln \left(\frac{P_{H_2} P_{O_2}^{0.5}}{P_{H_2O}} \right)$$

- At higher reactant pressures, the cell potential is higher
- Pure reactants yield higher potential. In fact, the theoretical loss in using air vs. pure oxygen is

  $$\triangle E = E_{O_2} - E_{air} = \frac{RT}{nF} \ln \left(\frac{1}{0.21} \right)^{0.5}$$

  and equal to 0.012 V at 80°C.
- In practice, there is a higher loss associated with using dilute reactants

Electrode Kinetics

- **Exchange Current Density**: Denoted by i_0, it is analogous to the rate constant in chemical reactions. It is a measure of an electrode's readiness to proceed with the electrochemical reaction. In a fuel cell, $i_{0,anode} > i_{0,cathode}$ (several orders higher)

  For a redox reaction, the popular Butler-Volmer equation gives

$$i = i_0 \left\{ \exp\left(\frac{-\alpha_{Rd} F(E - E_r)}{RT} \right) - \exp\left(\frac{-\alpha_{Ox} F(E - E_r)}{RT} \right) \right\}$$

- **Overpotential**: The additional potential required above the equilibrium potential to force the electrode to proceed to a certain reaction rate. Overpotential is inversely associated with the exchange current density of the electrode. The overpotential losses are higher at the cathode in a fuel cell.
  - The hydrogen oxidation reaction has a much lower overpotential than the oxygen reduction (the former proceeds more readily than the latter)

Voltage Losses

- In absence of loads, the fuel cell would be expected to yield the theoretical potential. However, in practice, it is observed that the potential < 1 V. This implies that losses occur even under zero current conditions!
- Under closed circuit conditions, the losses are bound to be even higher!
- The various losses are associated to:
  - Kinetics of the electrochemical reactions
  - Internal electrical and ionic resistance
  - Energy spent in getting the reactants to the sites
  - Internal (stray) currents
  - Crossover of reactants

Activation Polarization Losses

- These losses occur due to the sluggishness of the electrodes (previously referred to as the overpotential). The exchange current density is both a qualitative and quantitative measure of the loss.
- The losses occur both at the cathode and the anode, but the oxygen reduction reaction requires more energy and therefore the loss is higher at the cathode.
- The famous Tafel equation gives a simplified (but a very reasonable) expression:

$$\triangle V_{act} = a + b \log i \quad \text{where} \quad a = -2.3\frac{RT}{\alpha F}\log i_0 \; ; \quad b = 2.3\frac{RT}{\alpha F}$$

  The quantity α is the "transfer coefficient". When $\alpha = 1$, the Tafel slope is -60 mV per decade at 60°C.
- The Tafel equation neglects the anode polarization losses.

Internal currents and crossover losses

- Some amount of hydrogen (reactant) diffuses from anode to cathode despite the impermeability of the electrolyte (membrane). Therefore, some amount of "short-circuit" occurs in a cell.
- Each molecule of H_2 cross- over reduces the electron supply by 2.
- These losses may be negligible in a fuel cell operation as such (the loss is much lower than the total current being generated). But, they become significant during open-circuit or at low current densities
- From earlier discussion,

$$E_{cell} = E_r - \frac{RT}{\alpha F}\ln\left(\frac{i}{i_0}\right) = E_r - \frac{RT}{\alpha F}\ln\left(\frac{i_{ext} + i_{loss}}{i_0}\right)$$

  meaning losses occur even when $i_{ext} = 0$! The OCV of hydrogen / air FC is about 0.94 to 0.97 V

Some remarks

- Although hydrogen cross-over and internal current losses may be equivalent, there is a difference.
- While loss of electrons has the same effect on the anode and cathode activation polarization, the hydrogen permeation lowers the cell potential of the cathode alone due to the formation of water.
- The hydrogen cross-over depends on membrane permeability, membrane thickness and the partial pressure of hydrogen.
- Typically a very low OCV is indicative of a hydrogen leak or short-circuit.
- Oxygen permeation can also occur, but is much smaller than that of hydrogen.
- The losses due to fuel crossover in PEM FCs are negligible since hydrogen is consumed almost immediately at the catalyst site.

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Ohmic Losses

- These losses occur due to resistance to the flow of ions through the membrane and to the flow of electrons in the conducting lement
- Such losses can be expressed using Ohm's law: $\triangle V_{ohm} = iR_i$ where i is current density and $R_i = R_{ionic} + R_{i,electronic} + R_{i,contact}$ is the total resistance.
- While electronic resistances are negligible, ionic and contact resistance are almost of the same order. Typical values of R lie between 0.1 and 0.2 Ωcm^2.

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Concentration Polarization Losses

- These losses occur at the electrode due to the concentration gradients that arise during the reduction / oxidation reactions.
- The expression is given by $\triangle V = \frac{RT}{nF} \ln \left(\frac{C_B}{C_S} \right)$, where C_B is the bulk concentration and C_S is the surface concentration.
- Using Fick's law, it can be shown that

$$\triangle V_{conc} = \frac{RT}{nF} \ln \left(\frac{i_L}{i_L - i} \right)$$

where i_L is the so-called limiting current density.

- One expects to see a sharp drop level of cell as $i \rightarrow i_L$, in practice, the drop is smoother due to the onset of significant activation polarization losses
- An empirical equation can be used to describe these losses

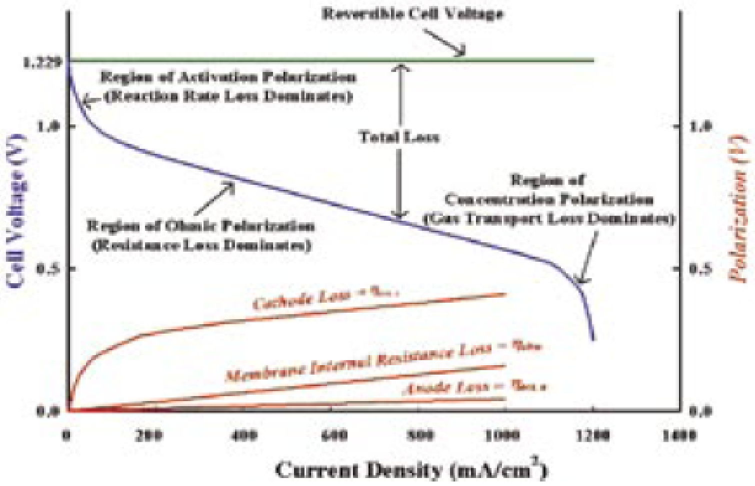
$$\triangle V_{conc} = c \ \exp \left(\frac{i}{d} \right)$$

Polarization curve

The plot between the voltage vs. current density is known as the polarization curve. It is one of the key performance curves and shows the functioning of the "heart" of the FCS.

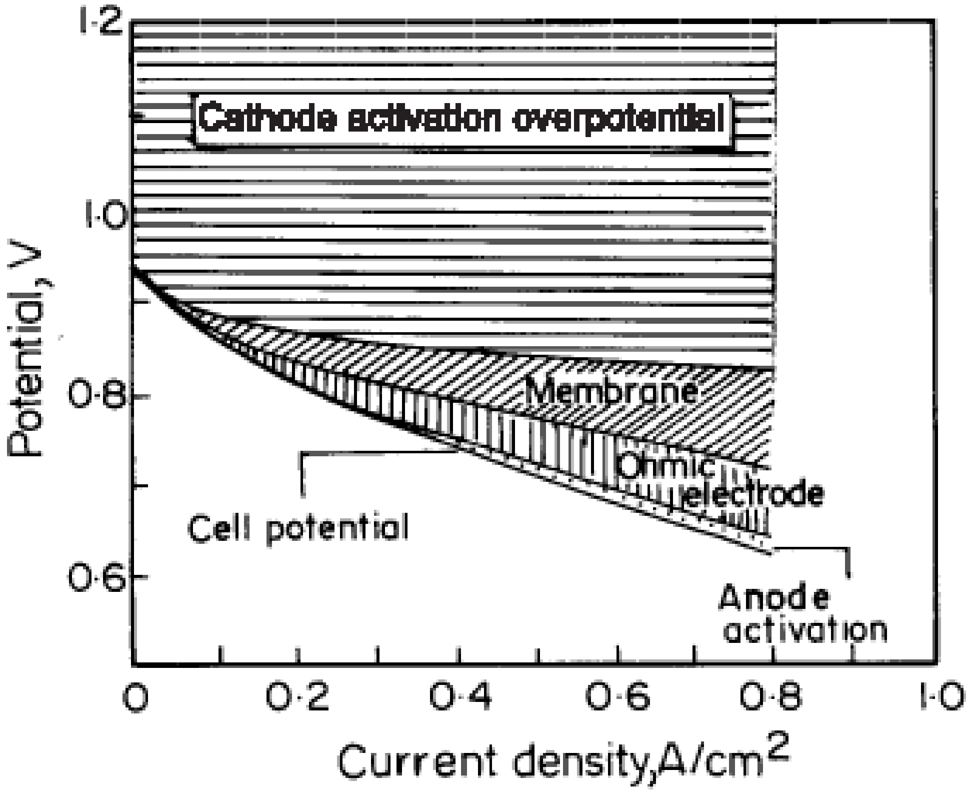
- Approximating all the above losses, the actual cell potential can be written as:

$$E_{cell} = E_r - \frac{RT}{\alpha F} \ln \left(\frac{i}{i_0} \right) - \frac{RT}{nF} \ln \left(\frac{i_L}{i_L - i} \right) - iR_i$$



Source: http://www.electrochem.org

Polarization curve for a typical PEMFC



Source: Fuel Cells: Principles and Applications by *B. Viswanathan and M. Aulice Scibioh*

Parameters affecting the polarization curve

- **Transfer coefficient:** This parameter has a strong effect on the fuel cell performance.
- **Exchange current density:** For each order of i_0 higher, the curve is shifted upwards by the value of Tafel slope
- **Crossover/Internal losses:** This effect is predominant only at low current densities
- **Internal Resistance:** These losses become significant as the current density increases.
- **Limiting current density:** The effect is only predominant at very high current densities
- **Operating pressure:** Higher pressures yield higher or elevated performance. A pressure increase from 1 atm to 200 kPa results in a gain of 34 mV.
- **Purity of oxygen:** Pure oxygen yields higher performance than with air. The gain is roughly 56 mV. Further, pure O_2 eliminates concentration polarization.
- **Temperature:** In general, the observation has been that higher voltage is obtained at higher temperatures. The mechanical strength of the membrane is also important, however.

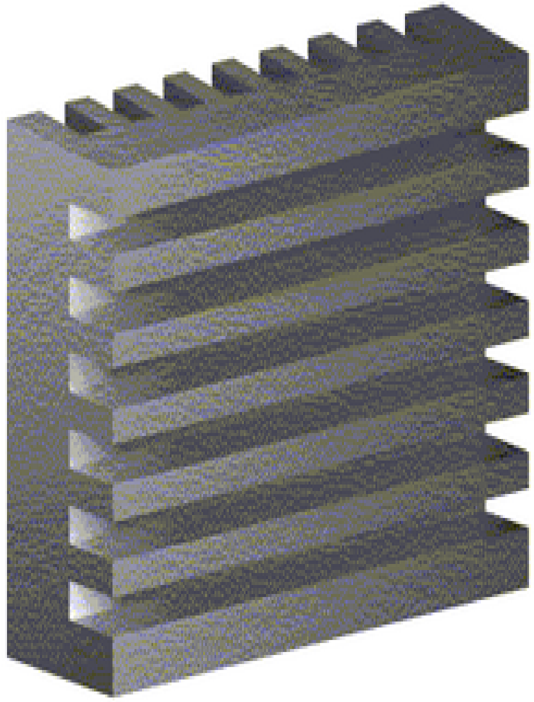
Uses of polarization curve

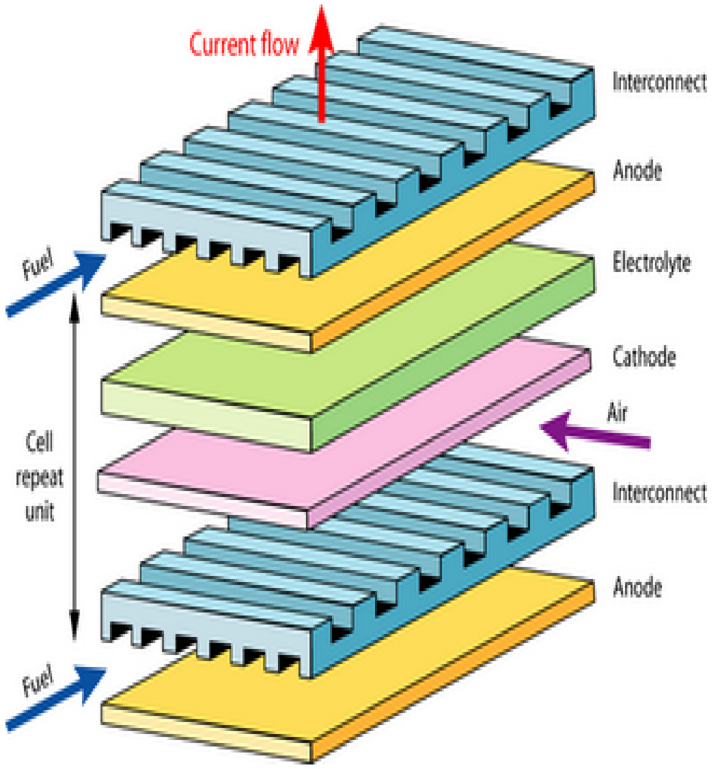
- It is the most important performance curve of the cell / stack. It is the “EEG” of the stack.
- It is widely used for (i) sizing of the stack (ii) control of a fuel cell and as a (iii) diagnostic tool
- A plot of cell potential vs. power density (W/cm^2)is very useful in determining the cell efficiencies and the operating point as well
- Almost all engineering models of the fuel cell contain a model of the polarization curve, since it represents the performance of the cell. A linear approximation can be used for a range of operating conditions.

Key components of a fuel cell

Membrane:	The heart of the cell, this is a key component that separates the reactants as well as promotes ionic conductivity
Electrodes:	The electrodes sit on both sides of the membrane and have to be porous to allow the reactants to reach the reaction sites.
Catalyst:	Another key component, present on both electrodes. The catalyst can also be a part of the membrane depending on the manufacturing process. In PEM cells, this is typically Pt.
MEA:	Known as the Membrane Electrode Assembly, it consists of the membrane sandwiched between two electrodes. The MEA sits in between what are known as collector / separator / bipolar plates.

A bipolar plate and stack assembly





Source: http://www.msm.cam.ac.uk/doitpoms/tlplib/fuel-cells/

Membrane

- Several membranes have been tried out over the past four decades. The most widely used membrane today is Nafion, which is a perfluorosulfonic acid (PFSA) membrane

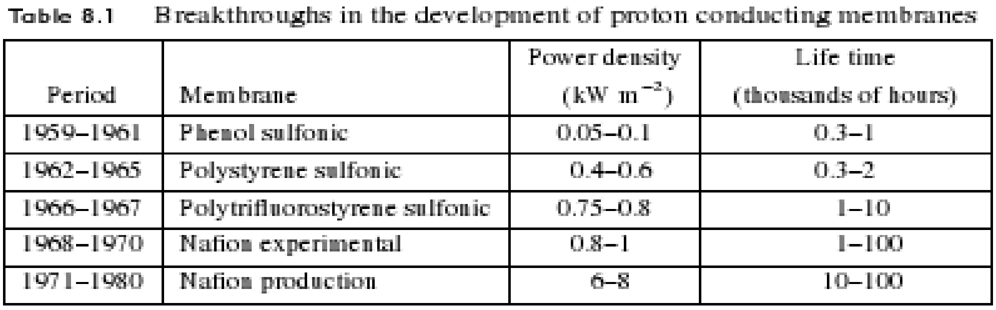
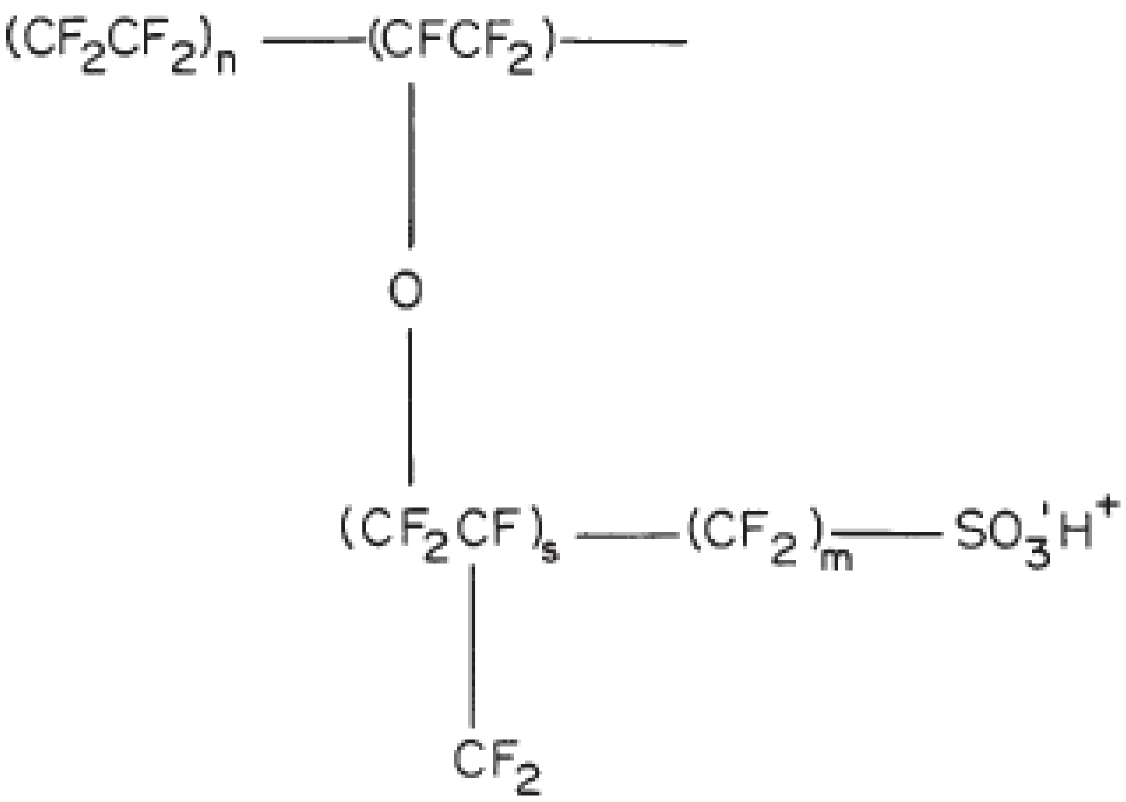


Table 8.1 Breakthroughs in the development of proton conducting membranes

Period	Membrane	Power density ($kW\ m^{-2}$)	Life time (thousands of hours)
1959–1961	Phenol sulfonic	0.05–0.1	0.3–1
1962–1965	Polystyrene sulfonic	0.4–0.6	0.3–2
1966–1967	Polytrifluorostyrene sulfonic	0.75–0.8	1–10
1968–1970	Nafion experimental	0.8–1	1–100
1971–1980	Nafion production	6–8	10–100

- PFSA consists of three regions: (1) a polytetrafluoroethylene (PTFE, DuPont's Teflon), which acts as a backbone, (2) side chains of -O-CF_2-CF-O-CF_2-CF_2- which connect the molecular backbone to the third region, and (3) ion clusters consisting of sulfonic acid ions.

Nafion structure



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Membrane

- When the membrane becomes hydrated, the hydrogen ions in the third region become mobile by bonding to the water molecules and moving between sulfonic acid sites.
- The PFSA membrane provides (and their variants) two advantages: (1) strength and stability in oxidation and reduction reactions, and (2) high protonic conductivities
- Disadvantages / Limitations
  - High costs $\approx$ US \$700 m^{-2}
  - Safety concerns arise from toxic and corrosive gases liberated at temperatures above 423 K.
  - Extensive supporting equipment requirements for use with PFSA membranes (humidification for example)
  - PFSA membrane properties degrade at elevated temperatures. Hydration forces the temperatures to be below the boiling point of water.

Alternative membranes

- The most promising membranes synthesized so far are based on: (1) sulfonated trifluorostyrene, (2) sulfonated copolymers based on α, β, β-trifluorostyrene monomer, and (3) radiation grafted membranes.
- Among the non-fluorinated membranes, the following have been proposed: (1) sulfonated poly(phenylquinoxalines), poly(2,6-diphenil-4-phenylene oxide), poly(arylether sulphone) or poly(2,6-diphenylnol)-based membranes; (2) acid doped polybenimidazole; (3) sulfonated polymide membranes; (4) styrene/ethylene-butadiene/styrene triblock copolymers; (5) partially sulfonated poly(arylene ether sulphone); (6) partially sulfonated polyether ether ketone (PEEK); (7) poly(benzyl sulfonic acid) siloxane (PBSS) based membranes; and (8) protonic electrolytes based on hydrogels.

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Electrodes

- The electrode is a thin catalyst layer pressed between the ionomer membrane and a porous, electrically conductive substrate (gas-diffusion layer (GDL)).
- The reactions take place on the catalyst surface where all the three kinds of species namely, gases, electrons and protons have access.
- Most common catalyst for both electrodes is Platinum (Pt)
- The surface area is important and not the “amount” or weight
- Catalyst surface active area is greatly increased if ionomer is included in the catalyst layer
- MEAs are prepared in two ways: (1) Deposit the catalyst layer on to the GDL and hot-press it to the membrane or (2) Applying the catalyst layer directly to the membrane, forming a catalyzed membrane

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Gas Diffusion Layer

This layer is present between the catalyst and the bipolar plates

- It provides a pathway for reactant gases
- Provides a pathway for the product water
- Electrically connects the catalyst layer to the bipolar plate
- Serves to conduct heat generated in the reaction
- Provides mechanical support to the MEA
- The most important properties are: (i) porosity (ii) electrical conductivity (iii) compressibility and (iv) permeability

Usually the carbon fiber-based materials such as carbon fiber papers and woven carbon fabric serve as good materials for the GDL.

The thickness can vary between 0.017 and 0.04 cm, while the porosity varies between 70% to 80%.

Bipolar plates

- In a single-cell configuration, there are no bipolar plates. They come into role for a stack-type configuration.
- They connect cells in series - therefore, electrical conductivity is required.
- They separate the gases in adjacent cells - requires impermeability (to gases)
- Provide structural support for the stack - demands adequate strength but not at the cost of weight!
- Conduct heat from active cells to cooling cells - requires good thermal conductivity
- Contain the flow channels - hence they must be conformable.

Materials for bipolar plates

- Graphite or metallic plates serve as a choice for the material. While graphite is brittle and has low electrical conductivity, it has excellent chemical stability (corrosion resistant).
- Metallic plates are on the other hand, light weight, structurally rigid and provide good conductivity, but require protective coating against corrosion within the cell environment.
- Ballard patented a sandwich of two embossed graphite foils with a thin metallic sheet in between those foils.
- Some amount of interfacial (contact) and bulk resistance is bound to be present in practice.
- The contact resistance is the more important one and depends strongly on the claming force.
- Surface characteristics and the effective conductivities of the contact surface also affect the interfacial contact resistance.

Fuel Cell Operating Conditions

The operating conditions of the fuel cell are determined by

- Pressure: Higher pressure yields higher potential, but the additional effort of pressurizing the gases has to be taken into account!
- Temperature: Higher temperatures yields higher temperature, but there is an optimal temperature for every design. The parasitic power losses and the heat management should be taken into account here.
  - The temperature inside the cell may not be uniform
  - Typically, the temperature of the exit air is a good measure of the temperature of the cell
  - Since heat is a by-product, a control system is necessary to maintain the desired temperature
  - If coolant is used, the coolant temperature in general provides a good measurement of the operating temperature

Operating parameters

- Reactant flow rates: These flow rates must be equal to or higher than the rate at which they are consumed
- The stoichiometric ratios must be kept in mind
- In practice, both reactants are fed in excess of requirements.
- Hydrogen (oxygen) can be supplied in three modes
  - Dead-end mode: No control is required. Reactant is being supplied as it is consumed.
  - Flow-through mode: Supply is slightly in excess to account for cross over losses
  - Re-circulation mode: Unused reactant is recycled back for consumption at the inlet
- In general, the excess supply for hydrogen is smaller when compared to oxygen (or air)

Reactant flow rates

- At the cathode side if air is used, the excess ratio is typically 2, while for oxygen, it is between 1.2 and 1.5
- Higher flow rates improve the efficiency, but parasitic losses (compressor / blower power) may be higher
- Excess air flow rate is good because
  - Higher flow rate helps remove product water from the cell (avoids flooding)
  - Higher flow rates keep oxygen concentration high
  - Purging is important to remove unused reactants from the pores

Reactant Humidity

- The membrane requires water for good protonic conductivity. Hence, both reactant gasss have to be humidifed before they enter the cell
- In general, the anode side humidity requirements are higher than that on the cathode side for good performance
- Relative Humidity (RH) is simply the amount of water vapour present in the gas to the maximum amount that the gas can hold at that temperature
- Although there is enough water generated at the cathode side, air humidification is needed to prevent drying of the portion of the membrane near the air inlet.
- At low temperatures, product water is more than sufficient
- At higher flow rates, more water is required.
- Mass balance and energy balance can be written to compute the water and heat generated in a cell stack

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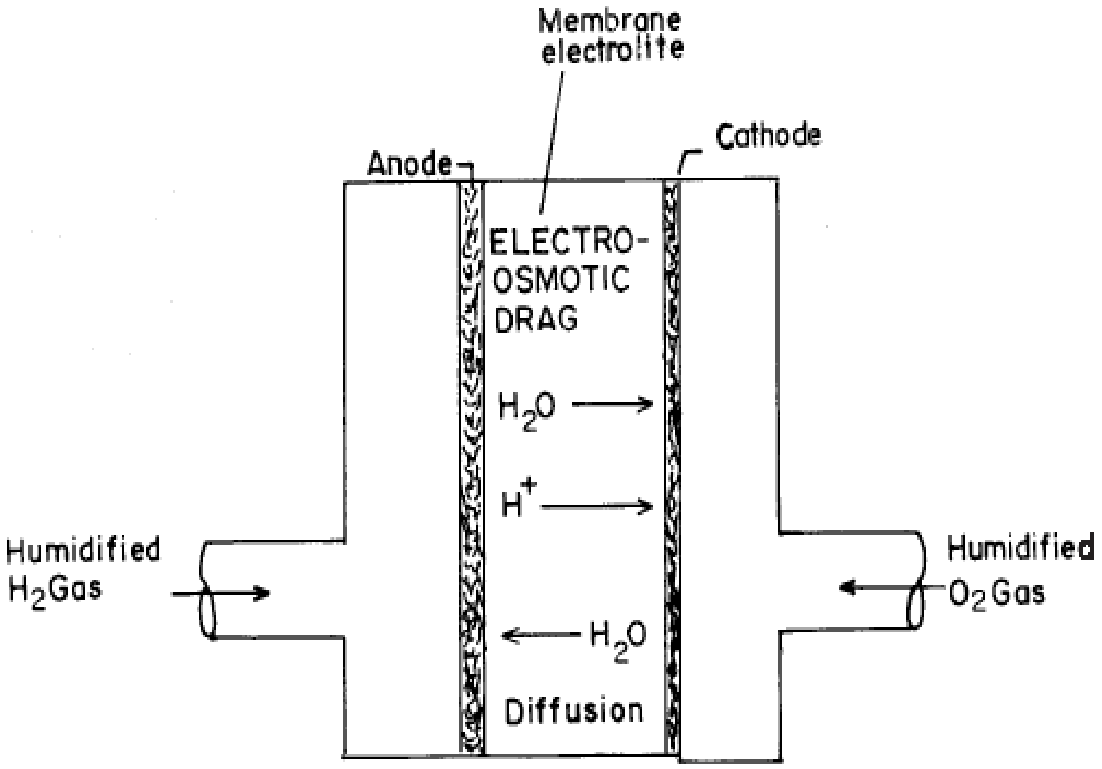
Transportation of water within a cell



Source: Fuel Cells: Principles and Applications by *B. Viswanathan and M. Aulice Scibioh*

Stack Design

The stack design is to-date a challenging area since there are many conflicting requirements. The optimal design depends on the application. Some of the key aspects are:

- Uniform distribution of reactants to each cell
- Uniform distribution of reactants inside each cell (flow channelization)
- Maintenance of required temperature in each cell (control and monitoring)
- Minimum resistive losses (choice of materials, configuration, uniform contact pressure)
- No leak of reactant gases (internal or external)
- Mechanical sturdiness (internal pressure, including thermal expansion, external forces during handling and operation, etc)
- Weight-to-volume ratio

Applications of PEMFCs

1. Around 1960s: PEMFCs in NASA's Gemini space flights
2. After 1960s: Use of AFCs in place of PEMFCs by NASA
3. Around 1980s: Improved PEMFC technology makes it preferred choice over AFCs
4. 1990s: Automobiles / buses using PEMFC technology appeared on the road

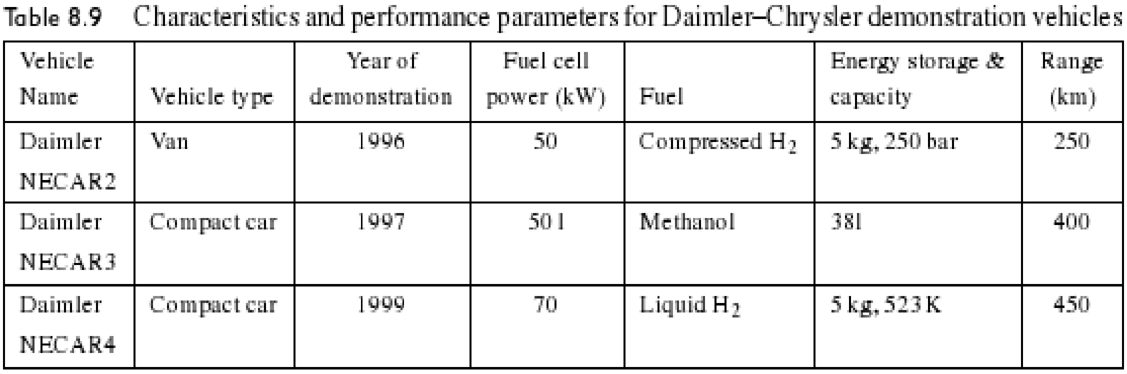


Table 8.9 Characteristics and performance parameters for Daimler–Chrysler demonstration vehicles

Vehicle Name	Vehicle type	Year of demonstration	Fuel cell power (kW)	Fuel	Energy storage & capacity	Range (km)
Daimler NECAR2	Van	1996	50	Compressed H_2	5 kg, 250 bar	250
Daimler NECAR3	Compact car	1997	50 l	Methanol	38l	400
Daimler NECAR4	Compact car	1999	70	Liquid H_2	5 kg, 523 K	450

5. Potential for military and civilian applications as portable power sources
6. Power generation systems - residential and commercial buildings

Scientific challenges

- Finding anodic electrocatalysts tolerant to CO at levels of 100 ppm (with low loading of noble metals)
- Inventing a cathodic electrocatalyst that can reduce the overpotential for the reduction reaction
- Finding alternative proton conducting membranes with lower cost but about the same proton conductivity of the state-of-the-art perfluorosulfonic acid membranes
- Developing new proton conducting membranes not depending on water for high temperature operations
- (DMFCs) Discovering new materials for electrocatalysts and proton conducting membranes in order to (i) significantly increase the exchange current density for methanol oxidation, (ii) inhibit poisoning of the anode electrocatalyst by intermediates formed during methanol oxidation and (iii) minimize crossover of methanol from the anode to the cathode.

Introduction to Modelling and Control

Workshop on PEMFC Systems

Arun K Tangirala

Department of Chemical Engineering
Indian Institute of Technology Madras

PEMFC Workshop, Singapore

Outline

Challenges

Interaction

Dynamic models that quantify the inter-relationships of various physical quantities of a fuel cell system hold the key to the successful control & monitoring of a fuel cell system. FCS poses challenges in several aspects

Interaction: The changes in the control parameters of an FCS are not independent. For e.g., stack temperature also affects the humidity of the air and hydrogen inside the stack, since the vapour saturation pressure is strongly dependent on the temperature. Interactions dictate the pairing in control schemes and can limit the performance of a control system.

Challenges

Non-linearities

Non-lineariities The relationships between the variables can be extremely non-linear depending on the variations in the operating conditions. For e.g., the magnitude and sign of the gain of power density w.r.t power density and current density changes with the operating conditions.

A linearized model is typically a starting point for the control analysis of fuel cell systems. Non-linearities can limit the predictability of such models

Challenges

Multiscale phenomena

Multiscale phenomena: Different phenomena occur in a fuel cell system at different timescales. In an automotive propulsion-sized PEM fuel cell.

- Electrochemistry O(10^{-19} sec)
- Hydrogen and air manifolds O(10^{-1} sec)
- Flow control/supercharging devices O(10^{0} sec)
- Cell and stack temperature O(10^{2} sec)

Multiscale analysis of the fuel cell system may be necessary to enhance the understanding of the process behaviour as well as to design the control system.

Challenges

Spatial and Temporal Variations

Distributed Parameter System: The parameters (physical quantities) of a fuel cell system not only vary temporally but also spatially. The temperature, hydration, reactant pressure can vary significantly across the space between the electrodes. Thus, lumped parameter system based analysis of these systems can be of limited use when a precise operation is required.

Coupled PDEs may have to be solved.

Analytical Models

- Analytical models are only approximate and do not include an actual mode of transport process with in the cell, they are useful for quick calculations of simple systems.
- F. Standaert et al. [1998] developed an analytical model with many simplified assumptions to predict cell voltage analytically for various current densities for isothermal and non-isothermal conditions. This model also predicts the water management requirements.

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Semi-empirical & Mechanistic Models

- Semi empirical models combine theoretically derived differential and algebraic equations with empirically determined relationships.
- In mechanistic models differential and algebraic are derived based on the physics and electro-chemistry governing the phenomena internal to the cell.

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PEMFC model categorization

Semi-Empirical Models

Features / Authors	Polarization	Transport Phenomena	Thermal effects	Water Management	Concentration effects	CO Kinetics	Flow field effects	Membrane conductivity
Springer et al. (1991)	■							■
Amphlett et al. [1995]	■							
Lee et al. [1998]	■							
Ronald et al. [2000]	■							
Maggio et al. [2001]	■				■			
Ronald et al. [2002]	■							■
Pisani et al. [2002]	■							
Chan et al [2003]	■				■			
Maxoulis et al [2004]	■							
Yu et al. [2005]	■		■	■				

PEMFC model categorization

Mechanistic Models

Features / Authors	Dim.	Polarization	Transport Phenomena	Thermal effects	Water Management	Conc. effects	CO Kinetics	Flow field effects	Membrane conductivity
Bernardi & Verbrugge [1992]	1	■							■
Fuller et al. [1993]	2	■							
Gurau et al. [1998]	2	■							
Ticainelli et al. [1998]	3	■							
Um et al. [2000]	3	■				■			
Nguyen et al. [2000]	3	■							■
Baschuk & Li [2000]	1	■							
Dutta et al. [2001]	3	■				■			
Berning et al. [2002]	3	■							
Wang et al. [2003]	3	■		■	■				

PEMFC model categorization

Control-oriented Models

Features / Authors	Lumped Model	Distributed Parameter Model	Controlled Variables			
			Air Flow	H_2 Flow	Temp.	Power
Pukrushpan et al . [2004]	■		■			
Golbert and Lewin [2004]		■				■
Ardalan et al. [2005]			■			
Caux et al . [2005]	■		■	■		■
Li et al. [2006]					■	
Chengbow et al.	■		■	■		

Pukrushpan et al (2004) model

- Reactions at electrode/catalyst surface are instantaneous.
- Temperature of stack is maintained constant (80 °C)
- Relative humidity(RH) of gas(fuel/air) is 100%.
- Hydrogen supply from high pressure tank considered to be static due to its fast dynamics (a proportional controller is in place).
- Flooding does not occur at the cathode or anode side.
- Membrane is completely hydrated.
- Activity of the catalyst is constant over a long period of time.
- Control: Focus on air flow control by manipulating compressor motor voltage.

Modelling Basics

Process Modelling

Understanding and representing system behaviour

Models can be of various types depending on:

- Do we wish to model the steady-state behaviour or the transient (dynamic) behaviour?
- Are the important process variables dependent on process directions other than time? (e.g., is the concentration in a reactor varying with the location or can be assumed to be uniform?)
- Is there a random behaviour exhibited by the process?
- What kind of relationships do we wish to extract among the variables of interest? (e.g., linear, non-linear, time-varying, *etc.*)
- Also, what is the final use of the model? In this context, we encounter models such as control-relevant models, fault detection oriented models, soft sensors (focus on prediction), etc.

Points to remember: Model's end-use is important!

Application Area	Use	Required Properties
Process Control	Controller Design; Testing	Accurate s/s gain, stability; Good approximation of transient behaviour
Process Monitoring	Detect faults; Root-cause diagnosis	Capture features of normal operation; Accurately capture interrelationships between variables (s/s & dynamic)
Plant Design	Predict equipment operation; Economic Decisions	Accurate prediction of s/s behaviour; Mostly concentrate on s/s effects (sometimes short-term effects)

Points to remember contd ...

Application Area	Use	Required Properties
Operator Training	Predict process and control system behaviour	Good representation of process dynamic behaviour
Operations Optimization	Develop product change strategies; optimal operation	Accurate transient behaviour; Accurate economic information and s/s behaviour
Operations scheduling	Predict long-term process behaviour; Resource allocation	Accurate economics; Good s/s prediction
Environmental	Weather forecast; Predict pollution levels; Facilities Design	Accurate dynamics; Incorporates safety levels

Where do we stop model building?

- This is a key step that has to be addressed both before and after model validation.
- Termination of a modelling procedure is usually determined by the accuracy requirements of the model. The accurary requirements are in turn determined by the end use of the model.
- For example, if the model is to be used in a control loop, modelling errors are permissive since feedback is forgiving. But for an improved performance of the loop, model-plant mismatch has to be minimized accordingly.
- If a model for the orbit of a rocket has to be developed, the accuracy requirements are very high. Small errors can lead to disasters!

Remember: No model can accurately match the process behaviour. Uncertainty is inevitable, however, may be kept minimal with a certain confidence.

Classification of Models

First-principles models

- First-principles: Models that are developed from fundamentals using basic laws and constitutive relationships.
  - Give rise to causal, continuous, non-linear differential-algebraic equations
  - Very effective and reliable models $\longrightarrow$ closely resemble process behaviour
  - Require good numerical ODE and algebraic solvers.
  - Can be an extremely difficult task for several systems.
  - Widely used in commerical simulators.
  - Useful models for performing root-cause diagnosis.
  - Models may not exhibit robustness with respect to changing process conditions.

Classification of Models

Data-Driven Models

- Empirical: Models that are developed from sampled measurements (data))of variables.
  - Identified models are discrete.
  - Model structures have to be assumed/known *a priori*.
  - Model quality is strongly dependent on data quality.
  - Model building is relatively less time-consuming.
  - Popular in process industry due to easy availability of data.
  - Large amount of freedom in choosing the model.
  - Difficult to relate to physical parameters of the process.
  - Models can be adapted according to the application, e.g., control-oriented, monitoring-oriented.
  - Arriving at continuous-time models is a non-trivial task.

Non-linear (NL) vs. linear models

- Virtually every process behaves in a non-linear fashion. Therefore, non-linear models can be expected to emulate a process much better than a linear model.
- Fortunately, for "small" changes in the operating conditions, the behaviour of many processes can be given a linear approximation.
- Linear models are simple to work with and easy to comprehend. NL models can get very cumbersome and can reduce the transparency of analysis.
- Analytical solutions can be easily provided for responses of linear systems. Such privilege is seldom enjoyed by NL descriptions.
- Other issues exist, which encourage us to use linear models as a starting point.

Linearized models

- The actual description of the system (if available) is a mix of non-linear differential-algebraic system. Or the true system will behave like one. How do we obtain a linear approximation of this system?
  1. If mathematical description is available, then use Taylor's series expansion of the non-linear terms and find the linear approximation.
  2. If it is too cumbersome for a Taylor's series expansion, then simulate the NL model and use numerical perturbation techniques.
  3. If the description is unavailable, then carry out experimental analysis by giving small changes in the inputs to fit a linear model.

  In all cases, since the original non-linear description or system is being approximated, the resulting models are called linearized models.

Empirical Modelling (System Identification)

- System always consists of a mixture of deterministic and stochastic processes.
- *"Identification is an art. The creativity of the user combined with the richness of data results in a model that can beautifully emulate the underlying phenomena.?*
- Iterative procedure - seldom a one-round effort.
- Demands perseverance, good process knowledge, skill and an intuitive understanding.
- Final model should be [somewhat] physically meaningful.
- Always involves a trade-off between bias (accuracy/quality) and variance [of parameters] (complexity/cost of modelling). Keep the model simple, flexible and close-to-accurate.
- Simple models with good structures can work better than complex models with complicated structures.

Terminology

1. Inputs:
   - Quantities that affect process operation.
   - Manipulated variables in the control context.
   - Model inputs need not be process inputs.
2. Outputs (Process responses):
   - Quantities which are a result of process operation.
   - Controlled variables in control loops.
3. States:
   - Quantities "inherent" to the process that are representative of the condition of the process. (E.g.: Height of a tank, quality of steam)
   - **Model states need not correspond to any physical quantity**!
4. Parameter:
   - A physical/chemical property that characterizes a process.
   - Most often, needs to be specified/known
   - An adjustable parameter in process design.
   - **In empirical modelling, this quantity is more often estimated.**

Procedure to develop a First-Principles Model

1. **Problem Definition**: Define
   - Objectives and Usage.
   - System Boundaries.
   - Fundamental quantities.
   - Assumptions.
   - Process outputs/inputs and measurements.
2. **Develop equations**: Write
   - Material/Mass/Momentum Balance equations.
   - Constitutive relationships.
3. **Check for consistency**.
4. **Identify model parameters, states, inputs and outputs**.
5. **Obtain Numerical/Analytical solutions for specified conditions**.
6. **Model Validation/Verification**.

F.P. Modelling with Material Balance - Example 1

System: Conical Tank of height H and radius R with inlet and outlet flows (F_i and F_o).
Objective: To obtain a dynamic model between F_i and h.
Fundamental quantity of interest: Mass
Mass Balance equation:

$$\frac{dV\rho}{dt} = F_i\rho_i - F_o\rho_o$$

Assume:

1. Fluid is incompressible, *i.e.*, $\rho_i = \rho_o = \rho$.

Therefore, the mass balance yields,

$$\frac{dV}{dt} = F_i - F_o$$

Now, we need to express the LHS of the above equation in terms of h and some known parameters.

Example 1 $\cdots$ continued

For a conical tank,

$$\begin{aligned}\frac{h}{r} &= \frac{H}{R} = \alpha \text{ (constant)}\\ \Longrightarrow V &= \frac{\pi}{3}\pi r^2 h = \frac{\pi}{3\alpha^2}h^3\end{aligned}$$

Therefore, we can write the balance equation as:

$$\begin{aligned}\frac{\pi}{3\alpha^2}\frac{dh^3}{dt} = F_i - F_o \quad \Longrightarrow \quad h^2\frac{dh}{dt} &= \frac{\alpha^2}{\pi}(F_i - F_o)\\ \Longrightarrow \frac{dh}{dt} &= \frac{\alpha^2}{\pi h^2}(F_i - F_o)\end{aligned}$$

To arrive at a relationship between F_i and h, we make use of the
Constitutive relationship: $F_o = \beta\sqrt{h}$.
Finally, we arrive at the model:

$$\frac{dh}{dt} = \frac{\alpha^2}{h^2}(F_i - \beta\sqrt{h})$$

The above model has: Inputs: F_i, Outputs: h, States: h, Parameters, α, β

In order to solve the above ODE, we need to know how F_i varies with time and the initial condition $h(0)$.

Energy Balances

Total Energy (TE): $TE = U + PE + KE$, where $KE = \frac{1}{2}mv^2$ and $PE = mgh$.
Energy/mole: $\hat{TE} = \hat{U} + \hat{PE} + \hat{KE}$
Energy/mass: $\bar{TE} = \bar{U} + \bar{PE} + \bar{KE}$
For chemical processes, where thermal effects are large, the potential and kinetic energy terms can be usually neglected.
For flow systems, we define a new state known as **enthalpy**:

$$\begin{aligned} H &= U + pV \\ \hat{H} &= \hat{U} + p\hat{V} \\ \bar{H} &= \bar{U} + \frac{p}{\rho} \end{aligned}$$

The energy balance equation is written based on the law of conservation of total energy. For flow systems, it is meaningful to express the final equation in terms of enthalpy.

Material and Energy Balance: Example 2

System: Stirred Tank Heater of fluid volume V with inlet F_i and outlet F_o. Heat is supplied at a rate Q.

Objective: To obtain a model for variation of temperature with time.

Fundamental quantities of interest: Mass, Energy.

First, start with material balance.

Material Balance:

$$\frac{dV\rho}{dt} = F_i\rho_i - F_o\rho$$

Energy Balance:

$$\frac{d(TE)}{dt} = F_i\rho_i\bar{TE}_i - F_o\rho\bar{TE}_o + Q + W_T$$

Neglecting the PE and KE terms, we have

$$\frac{dU}{dt} = F_i\rho_i\bar{U}_i - F\rho\bar{U} + Q + W_T$$

STH Example ··· continued

Before we introduce the enthalpy term, it is useful to express the total work term as a combination of fixed work (shaft work) and flow work,

$$W_T = W_s + F_i p_i - Fp$$

Therefore,

$$\frac{dU}{dt} = F_i \rho_i \left(\bar{U}_i + \frac{p_i}{\rho_i} \right) - F\rho \left(\bar{U} + \frac{p}{\rho} \right) + Q + W_s$$

Enthalpy is defined as $H = U + pV$, therefore the energy balance equation takes the form:

$$\frac{dH}{dt} - \frac{d(pV)}{dt} = F_i \rho_i \bar{H}_i - F\rho \bar{H} + Q + W_s$$

Now, $\frac{d(pV)}{dt} = V\frac{dp}{dt} + p\frac{dV}{dt}$. If we assume that the pressure change is negligible (good assumption for liquids) and the volume is constant, we obtain:

$$\frac{dH}{dt} = F_i \rho_i \bar{H}_i - F\rho \bar{H} + Q + W_s$$

STH Example ··· continued

The total enthalpy term is $H = V\rho\bar{H}$.
Now, we need to express the specific enthalpy in terms of temperature. From thermodynamics, we know that:

$$\bar{H}(T) = \int_{T_{ref}}^{T} c_p \, dT$$

Assume constant heat capacity. Then, the energy balance equation can be written as

$$\frac{d}{dt}(V\rho c_p(T - T_{ref})) = F_i \rho_i c_p (T_i - T_{ref}) - F\rho c_p (T - T_{ref}) + Q + W_s$$

If we assume constant density (incompressible fluids), then $F_i = F$ (from mass balance)

$$\begin{aligned} V\rho c_p \frac{dT}{dt} &= F\rho c_p (T_i - T) + Q + W_s \\ \Longrightarrow \frac{dT}{dt} &= \frac{F}{V} c_p (T_i - T) + \frac{Q}{V\rho c_p} \end{aligned}$$

where we have neglected shaft work (reasonable for CSTH).

The above model has Inputs: F, T_i, Q, Outputs: T, States: T and Parameters V, ρ, c_p.

Initial condition $T(0)$ and the inputs need to be known to solve for the temperature profile.

State-space Models

A general state-space model is represented as:

$$\dot{\underline{x}} = \underline{f}(\underline{x}, \underline{u}, \underline{p}) \qquad \text{(State equation)}$$
$$\underline{y} = \underline{g}(\underline{x}, \underline{u}, \underline{p}) \qquad \text{(Output equation)}$$

where

$\underline{x}$:	States (Fictitious quantities, but usually observable through outputs other measurements
$\underline{u}$:	Inputs (inputs to the model)
$\underline{y}$:	Outputs (Outputs of the model)
$\underline{f}$ & $\underline{g}$:	Non-linear functions of the inputs, states and parameters

If the *state equation* allows us to solve for x so as to obtain $\underline{x} = \underline{h}(\underline{u}, \underline{p})$, then we can establish a direct relationship between the output and input as $\underline{y} = \underline{G}(\underline{u}, \underline{p})$. **This is the idea behind converting a state-space model to a transfer function representation.**

Linear State-Space Models

Linear state-space models are of the form:

$$\dot{\underline{x}} = A\underline{x} + B\underline{u} \qquad (\underline{f} \text{ is a linear function of } \underline{\mathrm{x}} \text{ and } \underline{\mathrm{u}})$$
$$\underline{y} = C\underline{x} + D\underline{u} \qquad (\underline{g} \text{ is a linear function of } \underline{\mathrm{x}} \text{ and } \underline{\mathrm{u}})$$

- Solutions to linear state-space models are easy to obtain.
- Matrix A is known as the **transition matrix** or the **Jacobian matrix**.
- The transition matrix carries useful information about the properties of the system such as stability, slowness/fastness of the system, etc.

$$\boxed{\underline{x}(t_2) = e^{A(t_2-t_1)}\underline{x}(t_1) + e^{At_2}\int_{t_1}^{t_2} e^{-A\tau}B\underline{u}(\tau)\,d\tau}$$

Linearization of a general state-space model

A general state-space model

$$\begin{aligned}\dot{\underline{x}} &= \underline{f}(\underline{x}, \underline{u}, \underline{p})\\ \underline{y} &= \underline{g}(\underline{x}, \underline{u}, \underline{p})\end{aligned}$$

can be linearized to yield a linear state-space model (locally linear):

$$\dot{\bar{\underline{x}}} = A\bar{\underline{x}} + B\bar{\underline{u}}$$
$$\bar{\underline{y}} = C\bar{\underline{x}} + D\bar{\underline{u}}$$

where each elements of the matrices A, B, C and D are calculated as:

$$a_{ij} = \left.\frac{\partial f_i}{\partial x_j}\right|_{x_s, u_s} \qquad b_{ij} = \left.\frac{\partial f_i}{\partial u_j}\right|_{x_s, u_s}$$
$$c_{ij} = \left.\frac{\partial g_i}{\partial x_j}\right|_{x_s, u_s} \qquad d_{ij} = \left.\frac{\partial g_i}{\partial u_j}\right|_{x_s, u_s}$$

Note that the **linearized models are always in terms of deviational quantities**. Here onwards, it is understood that a linear(ized) model is always in terms of deviational quantities and therefore we drop the bar notation for the quantities for convenience sake.

Transfer Function Models

We will henceforth denote the transfer function of a system as $G(s)$. To recall,

$$G(s) = \frac{\text{LT of the output}}{\text{LT of the input}} = \frac{Y(s)}{U(s)} = \frac{N(s)}{D(s)}$$

MATLAB: tf, tfdata, pole, zero

E.g.: gs = tf([1 0], [1 2 2]) = $\dfrac{s}{s^2+s+1}$

It is useful to note the following points:

- **Transfer function of a system is always obtained by setting initial conditions to zero.**
- Therefore, transfer function models are (almost) always expressed in deviation quantities.
- TF models always express the input-output relationship and therefore do not involve any states. However, TF models can be converted into SS models and vice versa.
- The roots of $N(s) = 0$ are known as the **zeros** of the system, while the roots of $D(s) = 0$ are known as the **poles** of the system. No. of poles = Order of the system.
- Transfer function definition given above is applicable only to Linear Time-Invariant (LTI) Systems (*i.e.*, systems with constant coefficient, linear ODEs).

A Simple Example: Tank System

Consider a tank setup with inlet flow rate F_i and outlet flow rate F_o. The outlet flow rate is related to the fluid level in the tank by a non-linear relationship $F_o = \beta\sqrt{h}$, where $h(t)$ is the height of the fluid in the tank at any time. Find the transfer function between the inlet flow rate and the height of the fluid in the tank. Assume constant density.

Solution:

Mass balance yields: $\boxed{\dfrac{dh}{dt} = \dfrac{F_i}{A_c} - \dfrac{\beta}{A_c}\sqrt{h}}$

Linearizing around $(h_s, F_{i,s}) \rightarrow$ $\boxed{\dfrac{d\bar{h}}{dt} = -\dfrac{\beta}{2A_c\sqrt{h_s}}\bar{h} + \dfrac{\bar{F}_i}{A_c}}$

The transfer function model is obtained by applying the Laplace transform to both sides of the linearized ODE to obtain,

$$s\bar{H}(s) - h(0) = -\frac{\beta}{2A_c\sqrt{h_s}}\bar{H}(s) + \frac{\bar{F}_i(s)}{A_c} \quad \Longrightarrow \quad (s + \frac{\beta}{2A_c\sqrt{h_s}})\bar{H}(s) = \frac{1}{A_c}\bar{F}_i(s)$$

Therefore, $\boxed{G(s) = \dfrac{\bar{H}(s)}{\bar{F}_i(s)} = \dfrac{\frac{1}{A_c}}{s + \frac{\beta}{2A_c\sqrt{h_s}}} = \dfrac{K_p}{\tau_p s + 1}}$ is the desired transfer function.

K_p is the process gain, while τ_p is the process time-constant.

State-space models to Transfer function models

Given a linear state-space model, $\boxed{\begin{aligned}\dot{x} &= Ax + Bu\\ y &= Cx + Du\end{aligned}}$ find the transfer function between the output $y(t)$ and $u(t)$.

Solution: First apply Laplace Transform to both sides of the state equation to obtain

$$sX(s) - x(0) = AX(s) + BU(s) \Longrightarrow (sI - A)X(s) = BU(s) \Longrightarrow X(s) = (sI - A)^{-1}$$

Then take the Laplace Transform of the *output equation* and substitute for $X(s)$

$$Y(s) \quad = \quad CX(s) + DU(s)$$

$$\boxed{Y(s) = [C(sI - A)^{-1}B + D]\, U(s)} \quad \Longrightarrow \quad \boxed{G(s) = \frac{Y(s)}{U(s)} = C(sI - A)^{-1}B + D}$$

Eigenvalues & Poles - the connection

We shall now make an interesting observation.

> **Eigenvalues obtained from a linear state-space model (A, B, C, D) are identical to the poles of the transfer function $G(s)$ relating the outputs and the inputs.**

Order of a system = No. of poles = No. of eigenvalues of the state-space model = No. of states in the state-space model.

Transfer function to State-Space models $\cdots$ contd.

Thus, we obtain the SS model,

$$
\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \vdots \\ \dot{x}_n \end{bmatrix}
=
\overbrace{\begin{bmatrix} 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \vdots & & \cdots & & \vdots \\ -a_n & -a_{n-1} & -a_{n-2} & \cdots & 1 \end{bmatrix}}^{A}
\begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{bmatrix}
+
\overbrace{\begin{bmatrix} 0 \\ 0 \\ \vdots \\ K \end{bmatrix}}^{B} u(t)
$$

$$
y = \underbrace{\begin{bmatrix} 1 & 0 & \cdots & 0 \end{bmatrix}}_{C}
\begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{bmatrix} + 0u
$$

MATLAB command: tf2ss. **Note: The conversion from SS to TF model is unique, whereas the conversion from TF to SS model is not unique.**. Therefore, for an LTI system, there can be only one input-output relationship but there can be several state-space representations.

Process Control Basics

Motivating factors

Safety:	Safe operation of the process is foremost for the well-being of the people and for the development of the plant. Certain quantities of interest such as temperature, pressure should be within limits.
Product specs:	Desired amount and quality of the products should be maintained.
Environmental:	Regulations according to laws should be satisfied. For example, pollutant levels from an industry should not exceed a limit or the emission of harmful gases should be controlled.
Constraints:	Operational constraints exist on various equipment. These should be satisfied throughout the process operation. For *e.g.*, tanks should not overflow or go dry, distillation columns should not be flooded.
Economics:	Operation of a plant must be optimal in order to adapt to market conditions.

Ensuring stability of process

- A process is stable if the associated physical quantities return to their normal values after the disturbance has ceased.
- A process is bounded input-output stable if the output stays within bounds for all inputs that are within bounds.
- Stable processes are also known as self-regulating processes.
- Unstable processes result in variables that do not return to their normal values or sometimes go out of bounds after disturbed by external influences. These require *stabilization*.
- Examples of unstable system: A bicycle, inverted pendulum, reactor at certain operating conditions.

Suppressing effects of disturbances

Suppressing the effects of external disturbances is one of the most common objectives of a controller in a plant.

- This is known as the regulatory problem.
- Disturbances effects should be minimized/eliminated within the shortest amount of time possible.
- Two kinds of disturbances exist - measured and unmeasured disturbances. The latter ones are difficult to handle.
- Unmeasured disturbances are modelled as random signals with some average properties (for e.g., zero mean).
- Disturbances can even move the process out of the operating regime temporarily.

Quality/Production demands and specifications

Meeting quality specifications and production targets are as important as the disturbance rejection problem

- This is known as the set-point tracking or the servo problem.
- Changes in set-points occur due to changing markets, shifts to new operating conditions, uncertainties in stock availabilities, *etc*.
- In advanced control systems, the set-points to the lower level (PID) loops come from the higher level loops (e.g., DMC).
- A controller that ensures good tracking need not necessarily provide good disturbance rejection.

Elements of controller design

- Control Objectives: What are the operational objectives that a control system is called upon to achieve? Usually the objectives are a mix of the regulatory , servo and/or performance optimization requirements.
- Select Measurements: What variables should be measured in order to monitor the performance of the process? Sometimes the lack of measurements can force one to modify the control objectives or search for alternative measurements.
  - If the measured variables are those which are being controlled, then they are *primary* measurements
  - If the measured variables are used to infer controlled variables, then they are *secondary* measurements.

Elements of controller design

- **Manipulated variables:** These are very important quantities to choose. The choice of manipulated variables depends on the degrees of freedom available and their relationship with the controlled/performance variables. The choice is important since it affects the performance of the control scheme.
- **Control Configuration:** It is the *information structure* through which the available measurements connect to the chosen manipulated variables (for *e.g.*, feedback or feedforward). The “best” control configuration has to be chosen.
- **Control Law:** How are the manipulated variables adjusted for changes in controlled variables or under external influences? The law or the technique determines the performance as well as limitations of the control scheme.

Control Configurations

1. **Feedback control:** The controlled variables are directly measured are used to adjust the manipulated variables. This configuration implements *compensatory* actions.
2. **Feedforward control:** The disturbances are directly measured (if possible) to adjust the manipulated variables. This configuration implements *anticipatory* actions.
3. **Inferential control:** Secondary measurements are used to estimate the unavailable / infrequent / missing measurements and the manipulated variables are adjusted accordingly.

Advanced control strategies

- Many classical control strategies work well for single-loop systems. However, several processes are multivariate in nature, which are difficult to handle with interaction (coupling) and time-delays.
- Classical control may not be effective / optimal in presence of constraints.
- Advanced control schemes (such as Model Predictive Control) make use of an explicit model of the process, take into account the constraints, minimize a cost criterion and move the input accordingly. Although the models that are employed are linear, the resulting controllers are non-linear in nature.
- The MPC type controllers require a very good working model as well as demand a maintenance of this model as the process changes itself.
- Usually these controllers determine the set-points for the lower level PID control loops such as those used in level control, flow control, pressure control.

Feedback Control

Feedback control is the most "common" type of control that is used everywhere since ancient times. It relies on a measurement of the output and adjusts the input by comparing the present output value with the target value (set point).

- The primary motivating factor for feedback control is uncertainty about the system. Compensatory action is taken after the input effects the output.
- Feedback control is also useful when the disturbances affecting the system are unmeasured.
- It is robust to parameter variations and modelling errors. Feedback is forgiving.
- Requires the measurement of quantities of interest.
- Controllers should be designed so that the closed-loop system is stable!

Design Issues

- What type of feedback controller should be used for a given process?
- How do we select the best values for the adjustable parameters of a feedback controller? - the *controller tuning problem*
- What performance criterion should be used for the selection and tuning of the controller?

  A variety of performance criteria are available: (i) Keep the maximum deviation (error) as small as possible, (ii) Achieve short settling times and (iii) Minimize the integral of absolute errors and so on.
  In general, criteria can be divided into (i) steady-state performance criteria and (ii) dynamic response performance criteria

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Characteristics of process responses

Gain K: This parameter quantifies the change in the output for a unit step change in the input at steady-state.

Time-constant (τ): This parameter quantifies the time taken for the system response to reach 63.2% of the steady-state value. It is also the residence time for flow systems. The settling time of the system is roughly 4-5 times τ. The smaller the time constant, the faster the dynamics of that system.

Time-delay t_d : The time taken for the change in the input to appear in the output for the first time. Makes the control problem challenging particularly for multivariate systems.

Damping ratio ζ: If $\zeta > 1$, the system is overdamped, $\zeta = 1$, critically damped and $\zeta < 1$, underdamped.

First-order and Second-order Systems

- The order of the system is indicative of the capacity of the process. For example a single tank can be treated of order-one process. Addition of every order increases the sluggishness of the response.
- A first-order-plus-time-delay (FOPTD) system is characterized by the parameters Gain (K), a time-constant (τ) and a time-delay (t_d). The step response of such a system is a sigmoidal (S)-shape with a delay.
- An overdamped second-order-plus-time-delay (SOPTD) is characterized similar to that of an FOPTD system except that it has two time-constants τ_1 and τ_2. The step response is similar to that of an FOPTD system with more sluggishness
- SOPTD with oscillatory modes (underdamped), is characterized by a time-constant τ and a damping ratio $\zeta < 1$.
- In general, an n^{th}-order system is characterized by n different time-constants.

Simple performance criteria

The most important steady-state criterion is that *the error at steady-state should be zero*.

The dynamic performance criteria are based on the characteristics of the closed-loop system such as:

- Overshoot
- Rise time (*i.e.*, Time needed for the response to reach the desired value for the first time)
- Settling time (*i.e.*, Time needed for the response to settle within 5% of the set point)
- Decay ratio (Ratio between two successive peaks of the closed-loop response)
- Frequency of oscillation of the transient

Satisfying all these criteria may result in conflicting objectives. A balance must be achieved.

Time-Integral performance criteria

1. Integral of the square error (ISE), where

$$\text{ISE} = \int_0^\infty e^2(t)\, dt$$

   Strongly suppresses large errors than IAE

2. Integral of the absolute value of the error (IAE), where

$$\text{IAE} = \int_0^\infty |e(t)|\, dt$$

   Strongly suppresses small errors than ISE

3. Integral of the square error (ITAE), where

$$\text{ITAE} = \int_0^\infty t|e(t)|\, dt$$

   Strongly suppresses errors that persist at long times

Remarks on time-integral criteria

- Different criteria lead to different designs.
- For the same criterion, different input changes lead to different designs.
- It is very tedious.
- They rely on models (transfer functions) of the process, sensor and the final control element which may not be known exactly.
- A proportional controller leads to a non-zero offset. Therefore, the value of criteria will be infinite and therefore cannot be used to tune a P controller.

PID control

One of the most popular classical feedback controllers is the Proportional + Integral + Derivative (PID) control due to its simplicity and efficiency.

Proportional: Moves the input proportional to the (present) error (difference between the set point and output). Characterized by a gain K_c. Used to stabilize systems and increase the speed of the closed-loop system. Results in offset in the output at steady-state.

Integral: Moves the input proportional to the integral of the error (looks at the past values of the error). Characterized by a reset time τ_I or an integral gain K_I. Eliminates the offset. Inevitably used in tracking set-points. Can result in sluggishness of the response.

Derivative: Moves the input proportional to the derivative (rate of change) of the input (anticipates the change in error). Characterized by a derivative constant τ_D. Useful to make sure there is no wind-up from the integral action. Also reduces the sluggishness of the integral action.

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Simple guidelines

A three-mode PID controller clearly offers the most flexibility in the controller design. At the same time, the complexity of the tuning procedure increases with the parameters. Therefore, there is a trade-off between the *desired response and the tuning difficulty*.

- *If possible, use simple proportional controller*. Simple P controller can be used if (i) offsets obtained are moderate and acceptable or (ii) the process has an integrating action for which the P control does not yield an offset. A P controller is used for e.g., in liquid-level control.

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Simple guidelines · · · contd.

- *If a simple P controller is unacceptable, then use a PI*. A PI should be used when P alone cannot provide sufficiently small steady-state errors. A PI control is used for e.g., in flow control. The PI can make the response sluggish.
- *Use a PID controller to increase the speed of the closed-loop response and retain robustness*. For a multicapacity process, the PI can add to the sluggishness of the system. In such cases, the D controller can be used to increase the quickness of the response as well as to give more robustness. For e.g., in temperature or composition control.

Feedforward control

Unlike feedback, feedforward relies on anticipatory strategies. It measures the load (disturbance) directly and moves the input accordingly so that the impact of the disturbance is minimized or eliminated.

- Since it takes anticipatory action, the effect is prevented rather than "cured" as in feedback control.
- Assumes that the disturbances can be measured. More often, this may not be true.
- Requires a precise knowledge of how the disturbance and the input affect the process.
- It is good for slow systems or systems with large dead-time.
- Does not introduce instability in the closed-loop response.
- Sensitive to modelling errors and parameter variations.

Design of feedforward controllers

- Requires a good knowledge of the effects of inputs and disturbances on the controlled quantities. Performance $\equiv$ model quality.
- Static feedforward controller: Makes use of steady-state gains of the disturbances and inputs on controlled quantities.
- Dynamic feedforward controller: Makes use of the transient relationships of the disturbances and inputs with the controlled quantities.
- The DFF controller involves the inverse of the process. Therefore, some complications arise. But they can be handled using appropriate modifications.
- The feedforward controller can never represent a conventional feedback controller.

Feedforward vs. Feedback

Feedforward	Feedback
Acts before the disturbance affects the system	Waits until the effect has appeared in the system.
Is good for slow systems or with large dead-times	Unsatisfactory for slow processes and with large delays
Requires identification of all possible disturbances and their measurement	Does not require so.
Sensitive to parametric uncertainties	Insensitive (robust) to uncertainties
Does not introduce instability in the system	Can render the closed-loop system unstable
Requires good knowledge of the process model	Robust to modelling errors
Cannot cope with unmeasured disturbances	Can handle unmeasured and unidentified disturbances quite well.

Adaptive control / Gain scheduling

Processes may drift in time, operating conditions may change depending on the product resulting in different regimes of the process. Thus one linearized model and/or one controller setting cannot handle the performance criteria

- Identify the different operating regimes and design the controller parameters accordingly.
- Program these tunings into the controller according to the schedule $\longrightarrow$ Gain scheduling
- Gain scheduling can be done in other ways (will be discussed).

Alternatively, the performance criteria can be evaluated on-line to design the controller parameters at regular intervals of time. This is *self-adaptive* control. Under this category two methods exist *model-reference adaptive control* and *self-tuning regulators*.

Model Predictive Control (MPC)

Motivation

- Natural way of handling multivariable processes
- Actuator limitations (constraints) can be taken into account
- Allows one to operate closer to constraints (unlike with conventional control)
- Relatively easy and intuitive tuning procedures

Several names denoting particular variants: DMC, EPSAC, GPC, QDMC, SOLO, PFC

Outputs of MPC loops are typically the set-points to lower level PID loops which operate at a faster rate.

Elements of MPC

- Model: Mathematical/Quantitative representation of relationships between process outputs and manipulated variables (inputs).
    - Typically step response models are used.
    - Should have good knowledge of disturbance characteristics.
- Prediction:
    - Prediction Horizon (NP): Predict the behaviour of the plant over a horizon. This is an important tuning parameter of the MPC algorithm.
    - Control Horizon (NC): The length of the horizon over which the control input is assumed to vary while making the prediction. Typically, NC $<$ NP and is set to 1. As NC increases, the aggressiveness of the controller increases.
- Optimization function: An objective function comprising deviations from set-points and suppression of input changes.
  Constraints on absolute values of inputs as well as input changes are imposed. Typically the first element of the input trajectory is implemented and the entire procedure is repeated subsequently.

Implementation of MPC

Terminology and hierarchy

- Reference trajectory: Different from set-point trajectory. This trajectory describes the path along which the output returns to the set-point after a disturbance has occurred.
- Disturbances: In practice, disturbances cause the predictions to deviate from actual output. The disturbances may be unmeasured. Estimate this disturbance as the difference between the predicted output and measured output. Assume it remains unchanged during the prediction horizon
- Stability: Stability is an issue when the APC controllers are being tuned on-line. One way of ensuring stability is to make the prediction horizon quite long. Another way is to impose a terminal constraint on the process state.

Tuning MPC algorithms

- Weights: Heavy weights on the control moves will suppress control action (conservative) while smaller weights will make the controller aggressive.
- Horizons: Choosing a higher NC makes the controller aggressive. Typically NC $= 1$. Choosing NP small can render the controller unstable or aggressive.
- Disturbance Model: The "model" of the disturbance should be included in the overall plant model in order to completely eliminate the disturbance effects. For example, a step-type (constant) disturbance can be accounted for by including an integrator in the disturbance model.
- Reference trajectory: One of the most common reference trajectories is the exponential one. The output reaches the set-point in an exponential fashion. Honeywell's RMPCT uses a straight line

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Modelling and Control of PEMFC Systems

Workshop on PEMFC Systems

Arun K Tangirala

Department of Chemical Engineering
Indian Institute of Technology Madras

PEMFC Workshop, Singapore

Outline

1. Model for the Fuel Cell System
   - A Lumped Parameter Model for Air flow rate control
   - Model for Thermal and Water Management
2. Control of Fuel Cells
   - Overview
   - Control of stack temperature and air flow rate
   - Continuous humidication and control of RH
   - Motivation

Lumped Parameter Model for Air Flow rate control

Pukrushpan et al (2004). Control of Fuel Cell Power Systems

Inputs

- Current - Load demand
- Compressor motor voltage

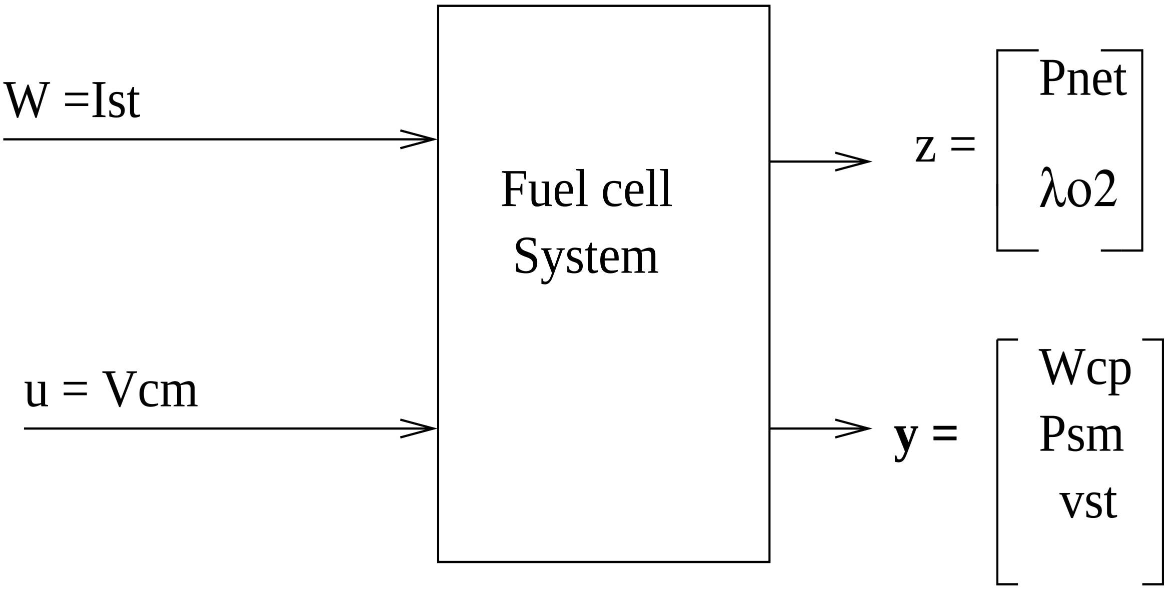
Performance outputs

- Net Power
- Oxygen excess ratio

Measured outputs

- Compressor flow
- Supply manifold pressure
- Stack voltage

Overview of control problem



W =Ist

u = Vcm

Fuel cell System

$$z = \begin{bmatrix} Pnet \\ \lambda o2 \end{bmatrix}$$

$$\mathbf{y} = \begin{bmatrix} Wcp \\ Psm \\ vst \end{bmatrix}$$

Control problem formulation

Assumptions of PEMFC stack model

- Reactions at electrode/catalyst surface are instantaneous.
- Temperature of stack is maintained constant (80 ^{o}C)
- Relative humidity(RH) of gas(fuel/air) is 100%.
- Hydrogen supply from high pressure tank considered to be static due to its fast dynamics (a proportional controller is in place).
- Flooding does not occur at the cathode or anode side.
- Membrane is completely hydrated.
- Activity of the catalyst is constant over a long period of time.

Compressor flow model

A dynamic model is assumed for the air flow from the compressor, which will be controlled by manipulating the compressor motor voltage supply given to the compressor motor.

Jensen & Kristensen method is used to obtain an empirical model of the compressor. The parameters are obtained for an Allied signal compressor data.

$$W_{cp} = \phi \rho_a \frac{\pi}{4} d_c^2 U_c \tag{1}$$

$$U_c = \frac{\pi}{60} d_c N_c \tag{2}$$

$$\phi = \phi_{max} \left[1 - exp \left(\beta \left(\frac{\phi}{\phi_{max}} - 1 \right) \right) \right] \tag{3}$$

Compressor flow model contd....

where ϕ_{max}, β and Ψ_{max} are polynomial functions of the Mach number M

$$M = \frac{U_c}{\sqrt{\gamma R_a T_{atm}}} \tag{4}$$

A lumped rotational parameter model with inertia is used to reperesent the dynamic behavior of the compressor speed.

$$J_{c}p\frac{d\omega_{cp}}{dt} = (\tau_{cm} - \tau_{cp}) \tag{5}$$

where

J_{cp} : Combined inertia of compressor and motor (kg.m^2)

ω_{cp} : Compressor speed (rad/s)

Compressor flow model contd...

τ_{cm} : Compressor motor torque input (N-m)

τ_{cp} : Torque required to drive the compressor (N-m)

The compressor motor torque is calculated using a static motor equation

$$\tau_{cm} = \eta_{cm}\frac{k_t}{R_{cm}}(V_{cm} - k_v\omega_{cp}) \tag{6}$$

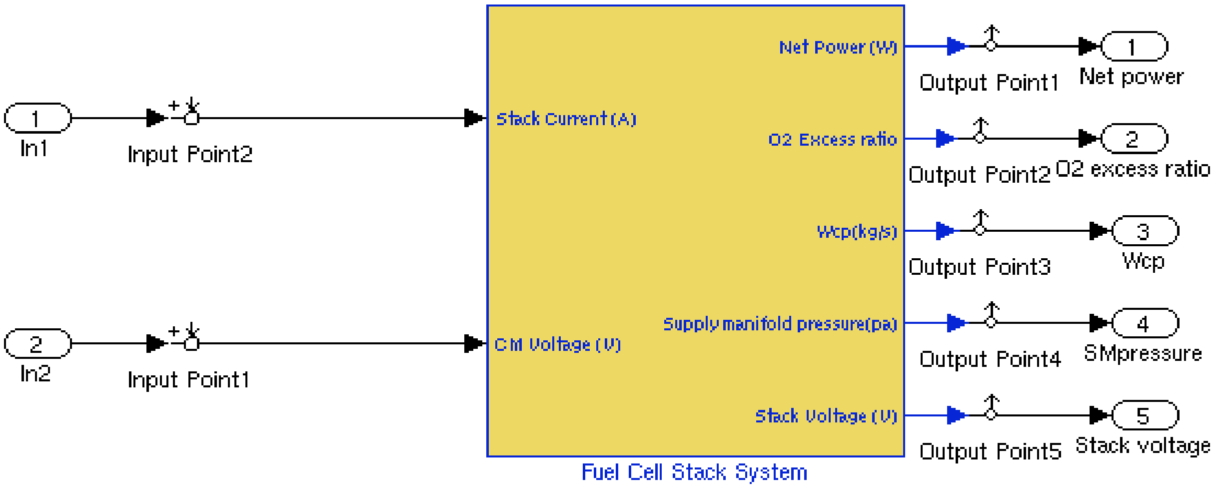
Torque required to drive the compressor is calculated using a thermodynamic equation

$$\tau_{cp} = \frac{C_p}{\omega_{cp}}\frac{T_{atm}}{\eta}\left[\left(\frac{P_{sm}}{P_{atm}}\right)^{\frac{\gamma-1}{\gamma}} - 1\right]W_{cp} \tag{7}$$

Features of model

- Lumped parameter model of reactants on anode cathode side
- Empirical model for polarization curve
- Static model H_2 tank
- Dynamic model for compressor flow
- Static model for humidifier

Simulation block diagram

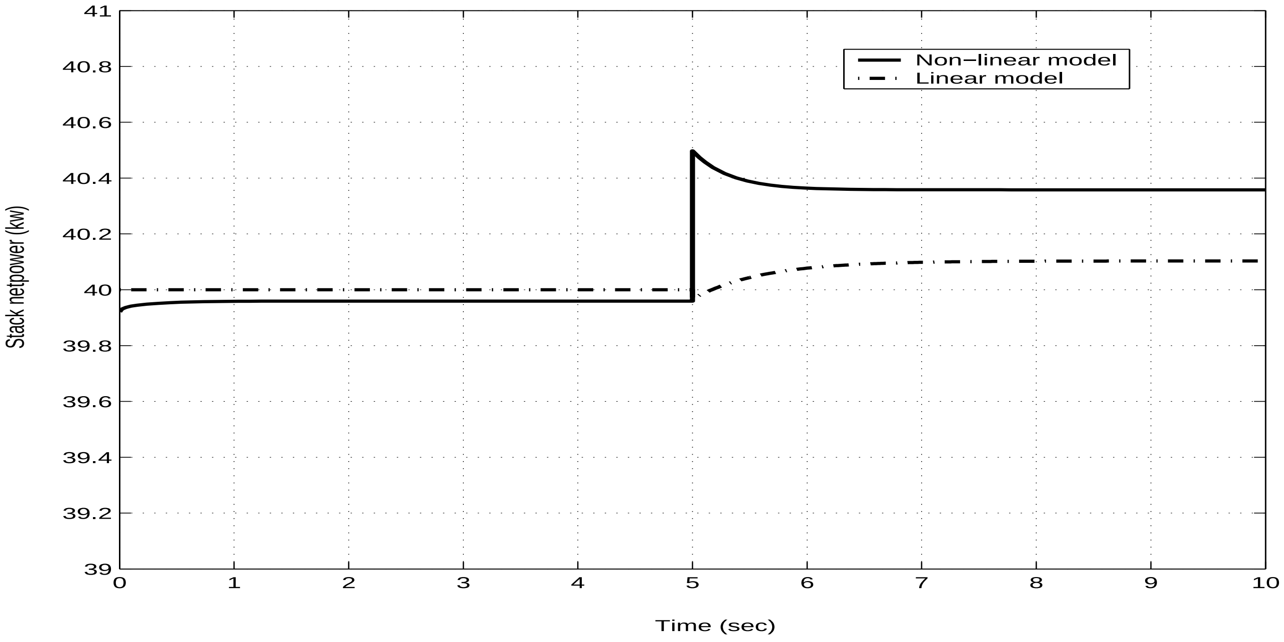


The model is documented in
"Control of Fuel Cell Power Systems: Principles, Modeling, Analysis, and Feedback Design,"
by Jay T. Pukrushpan, Anna G. Stefanopoulou, and Huei Peng, Springer Verlag,
London, UK, ISBN 1-85233-816-4

Linearized models are identified with and without the static feedforward in place.

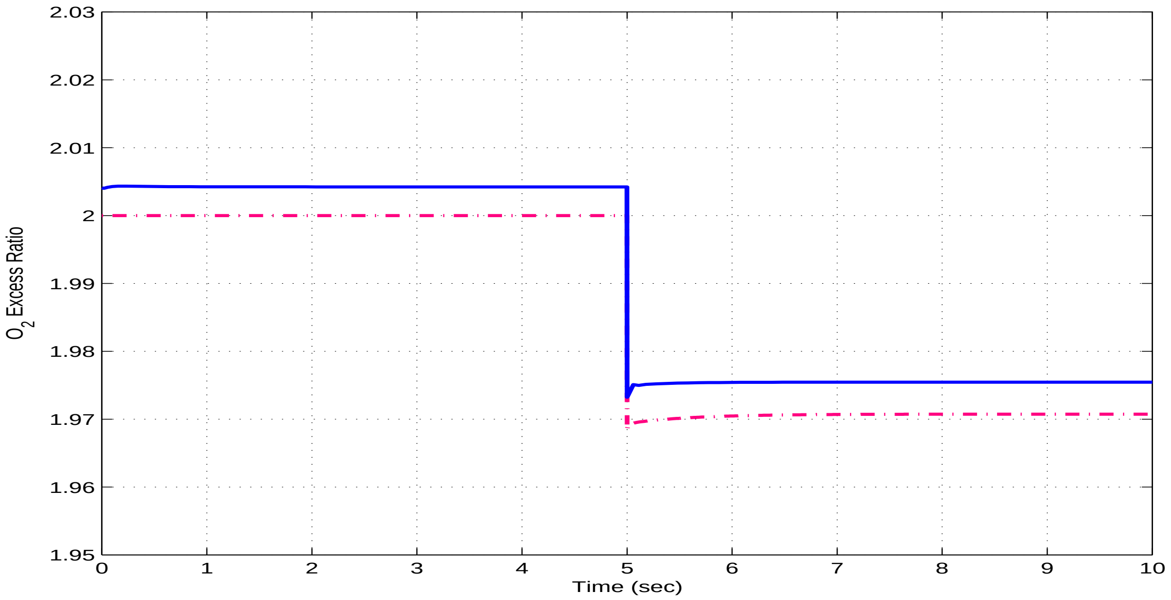
Comparing responses of non-linear & linearized models

A unit step change in current density was provided. The change in net power is shown.



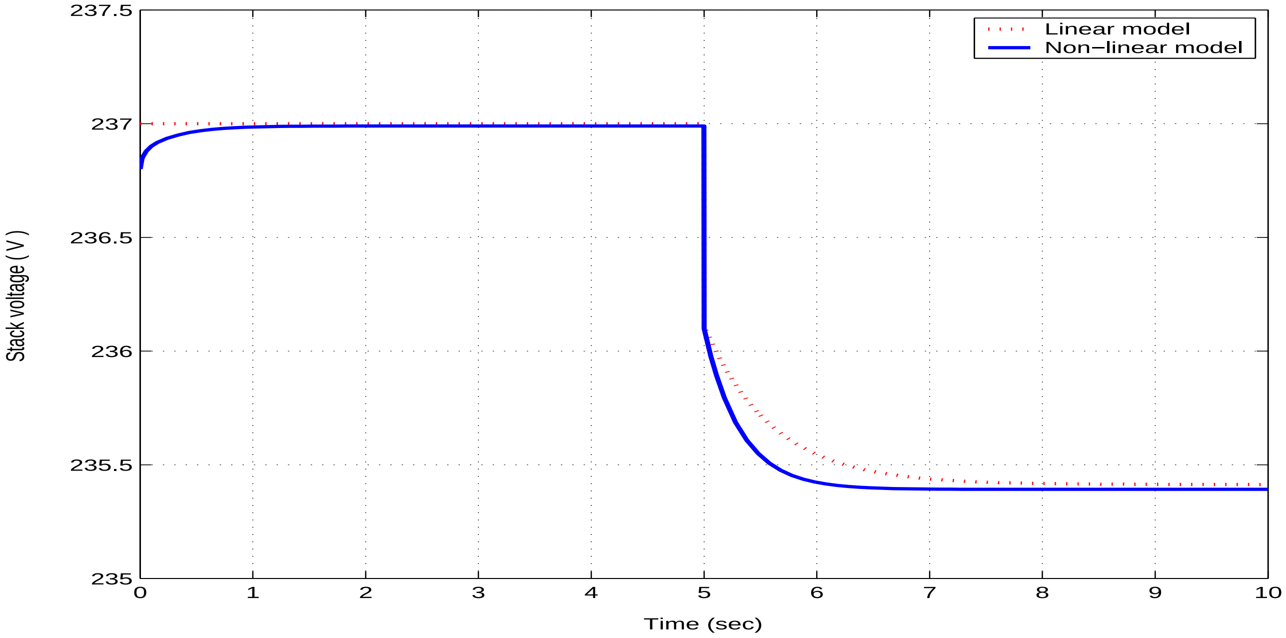
Comparing responses of non-linear and linearized models

A unit step change in current density was provided. The change in O_2 excess ratio is shown.



Comparing responses of non-linear and linearized models

A unit step change in current density was provided. The change in stack voltage is shown.



First-principles Modelling
Thermal and Water Management
Gollangi et al (2006)

Assumptions

- The product water generated at the cathode is assumed to be in liquid state
- The water vapour and liquid is assumed to be in equilibrium
- Ideal gas law was employed for gaseous species
- Stack temperature is uniform due to high thermal conductivity and sufficient no of cooling plates.
- The water transport across the membrane assumed to be in vapour phase.
- The liquid water at the surface of the channels assumed to be negligible.
- The H_2 gas entering into the stack on anode side is saturated.
- No liquid water at anode side

Fuel cell total energy balance

Based on fundamental energy balance for a fuel cell the lumped model has been developed as follows

$$\begin{aligned} Q_{theo} &= Q_{elec} + Q_{sens} + Q_{latent} + Q_{loss} \\ W_{out} &= W_{in} + W_{gen} \end{aligned}$$

where

Q_{theo}: Theoretical energy of the electrochemical reaction

Q_{elec}: Electrical energy generated from the stack ($V_{stack}I$)

Q_{sens} : Sensible heat of fuel and oxidant on anode and cathode side and coolant water

Q_{latent}: Energy due to phase phase change

Q_{loss} : Energy loss due to convection to the surroundings

Energy loss due to natural convection

$$Q_{loss} = hA(T_{stack} - T_{atm})$$

Thermal loss by convection to the surrounding is given as

$$\frac{hL}{K} = \left[0.825 + 0.387 \frac{Ra^{0.1333}}{[1 + \frac{0.492}{N_{pr}}^{0.56}]^{\frac{8}{27}}} \right]$$

where

h : Film heat transfer coefficient (W/m^2.K)

A : Area of perimeter (m^2)

L : Length of the stack(m)

Sensible heat

Sensible heat of cooling water:

$$Q_{sens,W} = N_W C_{p,W}(T_{Wout} - T_{Win})$$

Sensible heat at anode side:

$$\begin{aligned} Q_{sens,a} &= N_{H_2,a,out} C_{p,H_2}(T_{aout} - T_0) + N_{W,g,a,out} C_{p,H_2O,g}(T_{a,out} - T_0) \\ &\quad - N_{H_2,a,in} C_{p,H_2}(T_{a,in} - T_0) - N_{W,g,a,in} C_{pH_2O,g}(T_{a,in} - T_0) \end{aligned}$$

Sensible heat at cathode:

No liquid water enters at cathode inlet.

Sensible heat ...Contd

$$\begin{aligned} Q_{sens,c} &= N_{O_2,c,out}C_{p,O_2}(T_{cout}-T_0)+N_{W,g,c,out}C_{p,H_2O,g}(T_{c,out}-T_0) \\ &+ N_{W,l,c,out}C_{p,H_2O,l}(T_{c,out}-T_0)+N_{N_2,c,out}C_{p,N_2}(T_{cout}-T_0) \\ &- N_{O_2,c,in}C_{p,O_2}(T_{cout}-T_0)+N_{W,g,c,in}C_{p,H_2O,g}(T_{c,out}-T_0) \\ &+ N_{N_2,c,in}C_{p,N_2}(T_{cout}-T_0) \end{aligned}$$

Latent heat at cathode:

The amount latent heat on cathode side is depends on where the gas can be saturated due to formation of water on cathode side.

$$Q_{latent} = (N_{W,g,c,out} - N_{trans} - N_{W,g,c,in})H_{vapourisation}$$

Flow rates

$$\begin{aligned} N_{a,H_2,in} &= \frac{\alpha I \times N_{cells}}{2F} \\ N_{c,air,in} &= \frac{\beta I \times N_{cells}}{4F \times 0.21} \\ N_{W,g,a,in} &= N_{H_2,a,in}\frac{P^{sat}_{W,g,a,in}RH_{in}}{P_{a,in}-P^{sat}_{W,g,a,in}RH_{in}} \end{aligned}$$

Water transfer across the membrane is the sum of electro-osmatic drag, diffusion flux and convection flux

$$N_{trans} = N_{drag} + N_{diff} + N_{conv}$$

Temperatures of stack and outlet flows

From law of energy: Energy accumulation = Energy in - Energy out

$$\begin{aligned}
\frac{dT_{stack}}{dt} &= \frac{Q_{theo} - Q_{elec} - Q_{sens} - Q_{latent} - Q_{loss}}{M_{stack} C_{p,stack}} \\
T_{a,out} &= 2\left[T_{stack} - \frac{Q_{sens,a} + Q_{mass,a}}{(hA)_a}\right] \\
T_{c,out} &= 2\left[T_{stack} - \frac{Q_{sens,c} + Q_{latent,c} - Q_{mass,c}}{(hA)_c}\right] \\
T_{W,out} &= \frac{(2T_{stack} - T_w in)hA_w + 2N_W C_p T_{Win}}{hA_W + 2N_W C_p T}
\end{aligned}$$

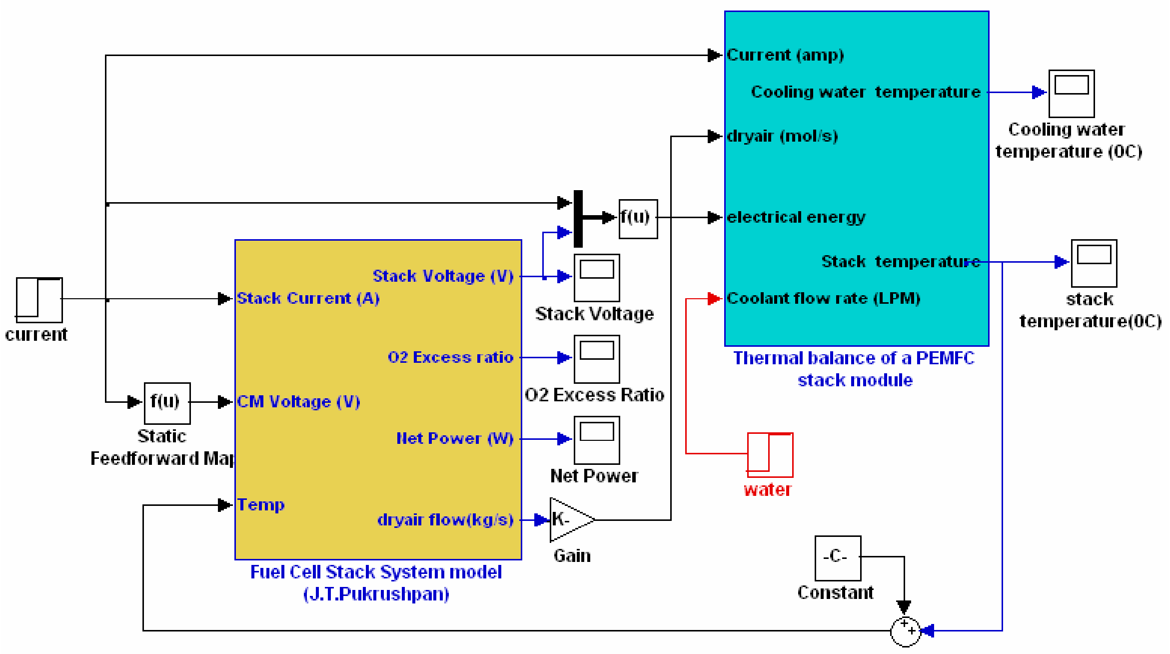
Temperatures of stack and outlet flows Contd..

where

$$\begin{aligned}
Q_{mass,a} &= N_{trans} C_{p,H_2O,g}(T_{stack} - T_0) + N_{H_2,con} C_{p,H_2,g}(T_{stack} - T_0) \\
Q_{mass,c} &= N_{trans} C_{p,H_2O,g}(T_{stack} - T_0) + N_{H_2,con} C_{p,H_2O,l}(T_{stack} - T_0) \\
&\quad - N_{O_2,con} C_{p,O_2,g}(T_{stack} - T_0) \\
Q_{sens} &= Q_{sens,a} + Q_{sens,c} + Q_{sens,W} \\
Q_{latent} &= Q_{latent,c}
\end{aligned}$$

Integrated Model

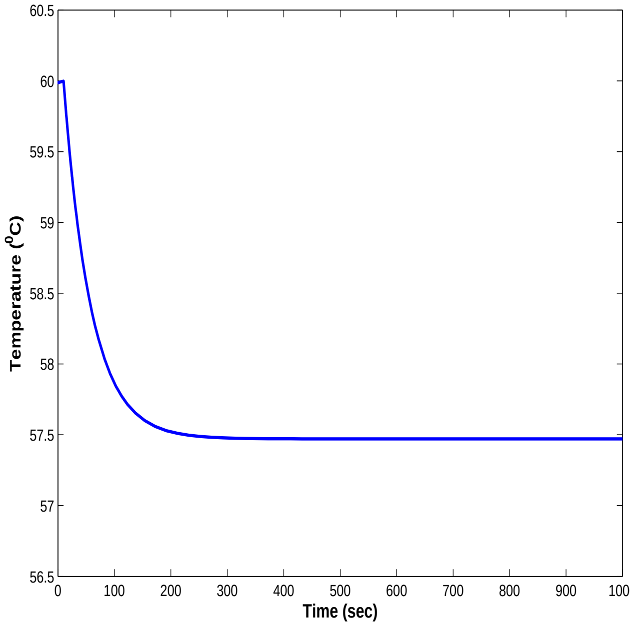
Temperature loop is open



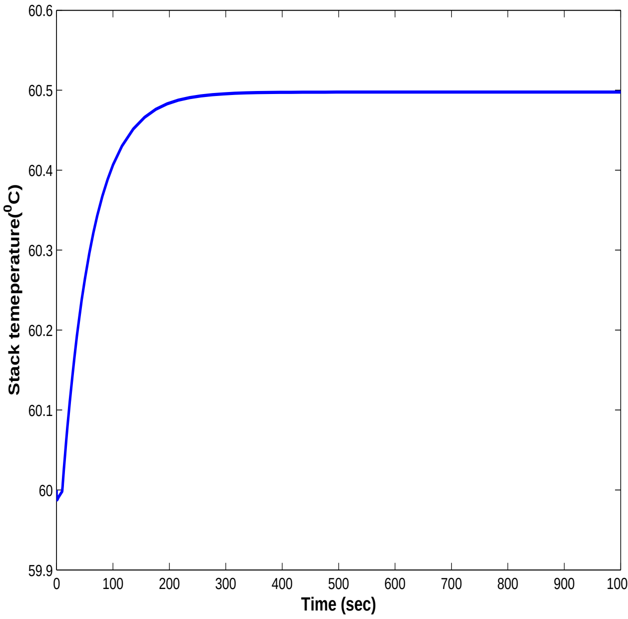
Open-loop simulation of integrated model

Unit step response to coolant flow & load change

Response to change in coolant flow



Response to a change in load



Performance of fuel cells

Fuel Cell Stack

A typical fuel cell system comprises a fuel cell stack integrated with several auxiliary components such as fuel and air supply systems, humidifiers, coolers, valves, *etc.*

Efficient fuel cell system power response depends on

- Air and hydrogen feed
- Flow and pressure regulation
- Heat and water management

Several auxiliary actuators such as valves, compressor motors, pumps, fan motors, expander vanes, humidifiers and condensers are involved in the control system

---

Control Issues

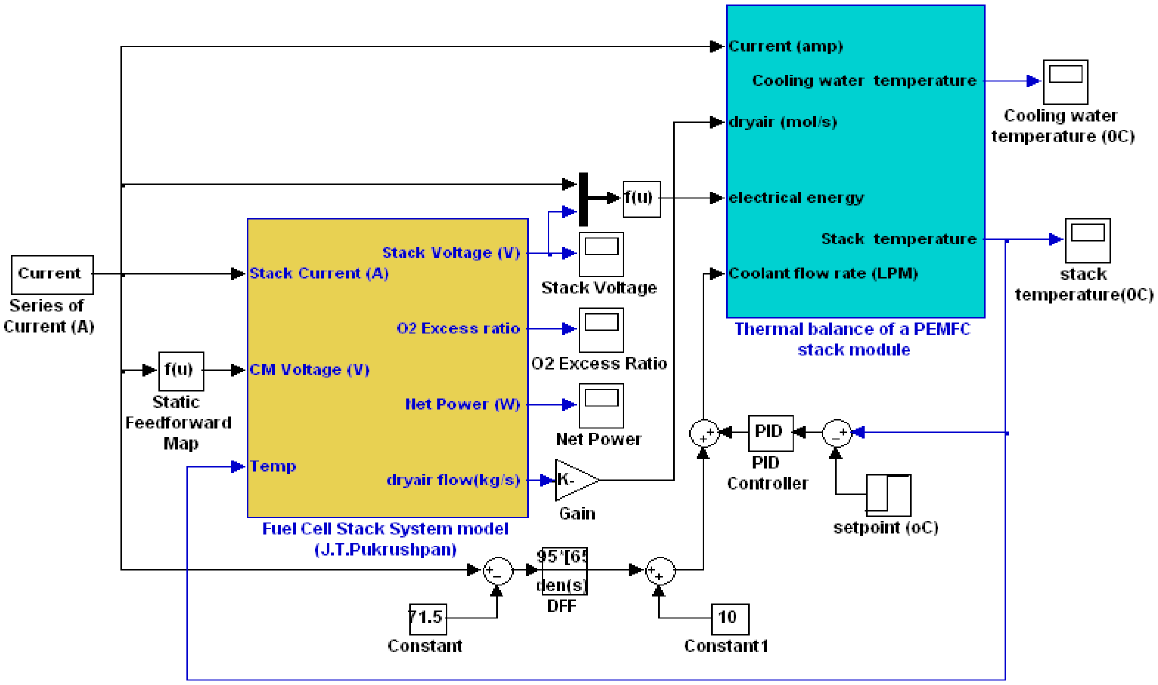
Parameters in the FCS

- Reactant flow rate control
- Maintenance of proper temperature
- Control of membrane hydration (to avoid membrane degradation and to prevent drying/flooding of the fuel cell)
- Control of total and partial pressures of the reactants across the membrane (to avoid detrimental degradation of the stack)
- Humidity of the air flow
- Power conditioner (to account for the significant variations in the fuel cell stack voltage) to condition the power supplied by the stack to the traction motors and auxiliary components.

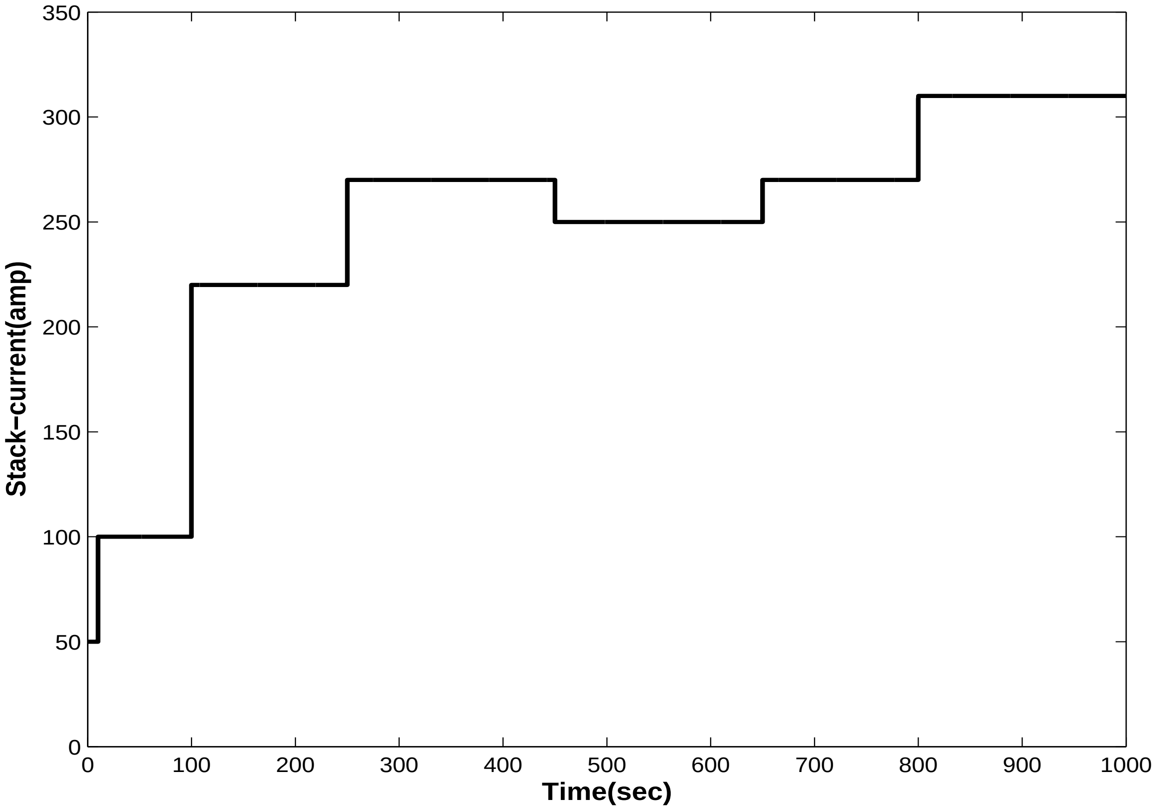
Univariate control:
Temperature control

Integrated Model

Temperature loop is closed

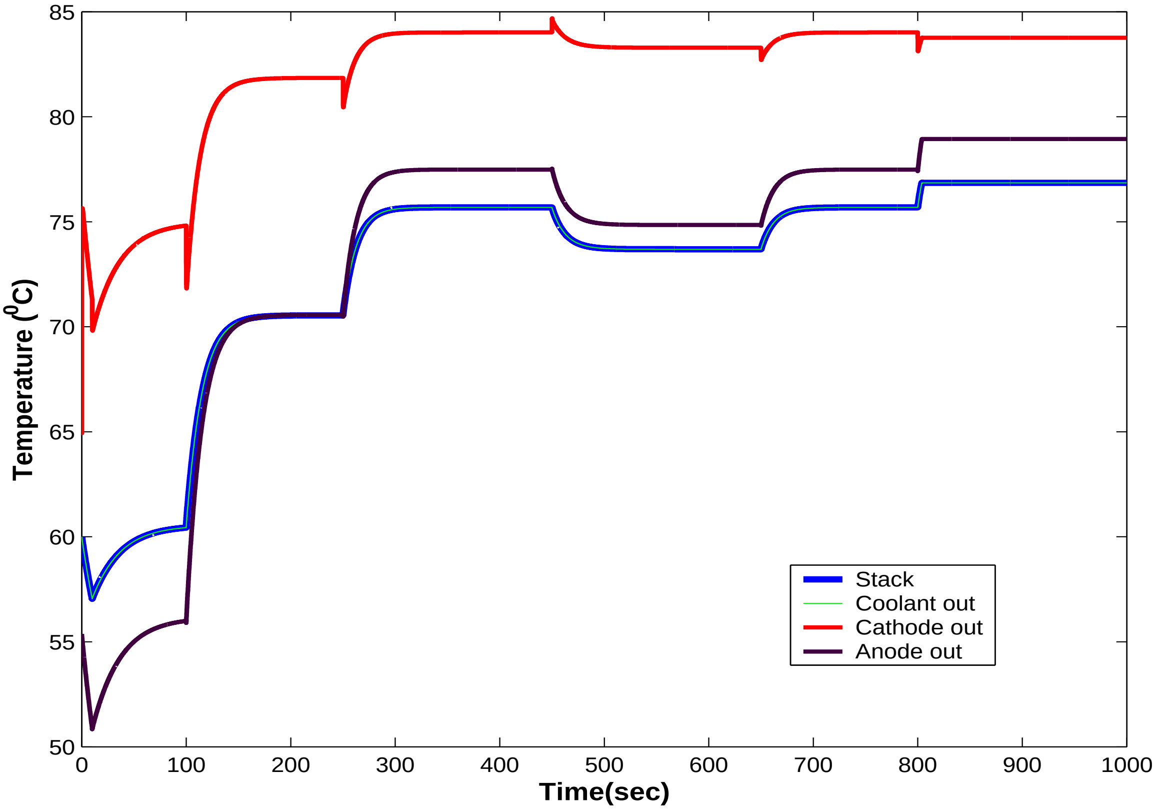


Load profile



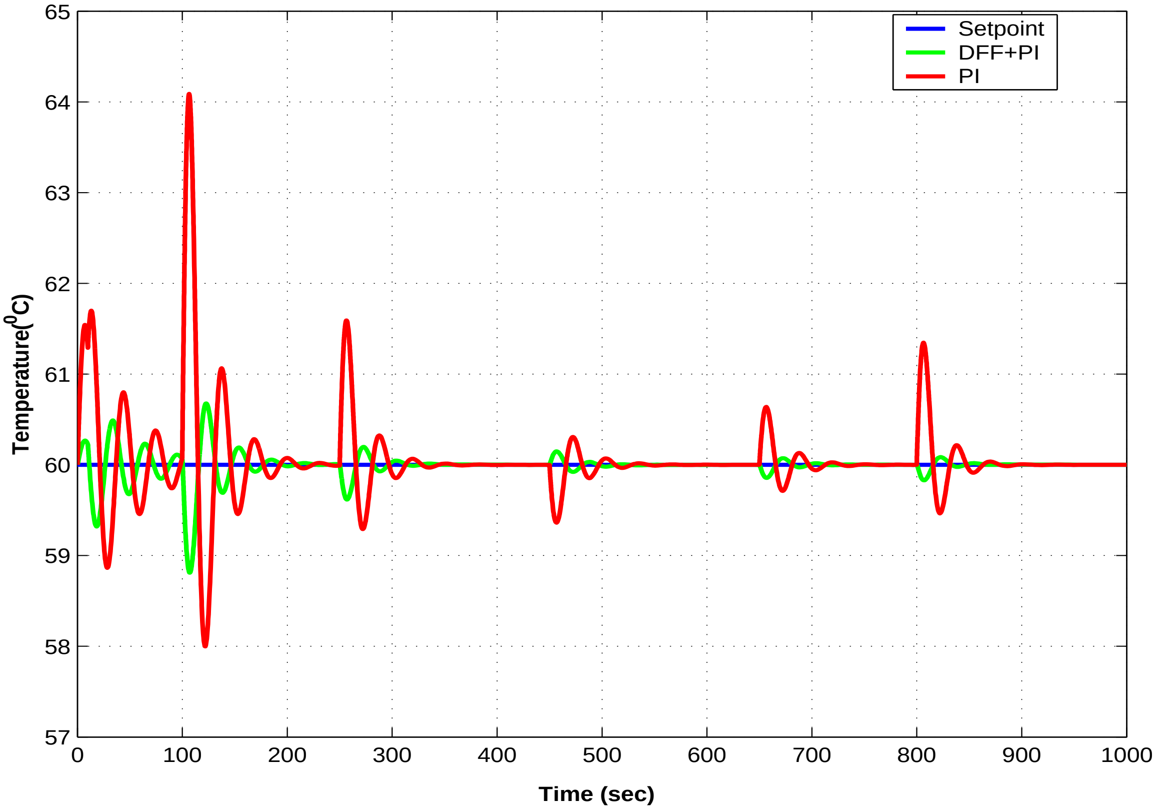
Temperature profiles

Response without controller



Stack temperature control

Comparison of control schemes



Non-linear control using exact linearization: Background

Exact linearization of non-linear systems

The exact linearization approach transforms the original nonlinear dynamic model into a linear model by a diffeomorphism mapping, and then transforms back to original nonlinear state space model(bijective mapping). Consider the following MIMO system

$$\frac{dx}{dt} = f(x) + \sum_{i=1}^{m} g_i(x)u_i \qquad (8)$$

$$\begin{bmatrix} y_1 \\ y_2 \\ y_p \end{bmatrix} = \begin{bmatrix} h_1(x) \\ h_2(x) \\ h_p(x) \end{bmatrix} \qquad (9)$$

where x $\in$ X $\subset$ R^n is the state, u $\in$ U $\subset$ R^m is the input or control vector and y $\in$ Y $\subset$ R^p output vector of the system.

Exact linearization of non-linear systems Contd..

- Relative degree is the important property of nonlinear system, it represents the number of times the output must be differentiated with respect to time so that the input can be expressed explicitly.
  for MIMO system.
- The problem of non-square can be solved by adding the additional states, the same are the outputs.

In case of MIMO system, the output (y_j) is to be differentiated untill the input shows up

$$y = h(x) \qquad \Longrightarrow h(f(x), g(x))$$

$$y_j^{!!} = L_f h_j + \sum_{i=1}^{m} (L_{g_i} h_j) u_i \qquad (10)$$

Exact linearization of non-linear systems contd...

$$
\begin{aligned}
y_j^{!!} &= L_f(L_f h_j) + \sum_{i=1}^{m} L_{g_i}(L_f h_j) u_i \\
y_j^{!!} &= L_f^2 h_j + \sum_{i=1}^{m} L_{g_i}(L_f h_j) u_i \\
y_j^{r} &= L_f^r h_j + \sum_{i=1}^{m} L_{g_i}(L_f^{r-1} h_j) u_i
\end{aligned}
$$

where L$_f$ and L$_g$ are the *Lie derivatives* of the smooth scalar function of $h(x)$ with respect to $g(x)$ and $f(x)$. If $L_g h_j(x) = 0$ for all i, then the y_j should be differentiated untill $L_{g_i} L_f^{r-1} h_j(x) \neq 0$

Exact linearization of non-linear systems Contd...

Performing the above procedure for each $y_{i=1 \cdots m}$, the obtained m equations can be written compactly as follows

$$
\begin{bmatrix} y_1^{r1} \\ y_2^{r2} \\ y_m^{r3} \end{bmatrix} = \begin{bmatrix} L_f^{r_1} h_1(x) \\ L_f^{r_2} h_2(x) \\ L_f^{r_m} h_m(x) \end{bmatrix} + E(x) \begin{bmatrix} u_1(x) \\ u_2(x) \\ u_p(x) \end{bmatrix} \tag{11}
$$

$$
E(x) = \begin{bmatrix} L_{g_1} L_f^{r-1} h_1 & L_{g_2} L_f^{r-1} h_1 & \dots & L_{g_m} L_f^{r-1} h_1 \\ L_{g_1} L_f^{r-1} h_2 & L_{g_2} L_f^{r-1} h_2 & \dots & L_{g_m} L_f^{r-1} h_2 \\ \dots & \dots & \dots & \dots \\ L_{g_1} L_f^{r-1} h_m & L_{g_2} L_f^{r-1} h_m & \dots & L_{g_m} L_f^{r-1} h_m \end{bmatrix} \tag{12}
$$

Exact linearization of non-linear systems contd...

The matrix $E(x)$ is decoupled matrix of size$(m \times m)$. If $E(x)$ is nonsingular, then the nonlinear state feedback control can be obtained as

$$U = -E^{-1}\begin{bmatrix} L_f^{r_1} h_1(x) \\ L_f^{r_2} h_2(x) \\ L_f^{r_m} h_m(x) \end{bmatrix} + E^{-1}\begin{bmatrix} y_1^{r1} \\ y_2^{r2} \\ y_m^{r3} \end{bmatrix} \qquad (13)$$

To track the setpoint, an integrator is augmented. In case of temperature control, the output (stack temperature) is state, the relative order is 1 (*i.e.*, the input appears explicitly in the first derivative of output with respect to time)

Non-linear model inversion for disturbance rejection

$$\frac{dT_{stack}}{dt} = \frac{Q_{theo} - Q_{elec} - Q_{sens} - Q_{latent} - Q_{loss}}{M_{stack} C_{p,stack}} \qquad (14)$$

In above equation the sensible heat of gases and latent heat are neglected due to uncertainity in the prediction. The resultant modified form is

$$Q_{sens,water} = Q_{theo} - Q_{elec} - Q_{latent} - Q_{loss} - M_{stack} C_{p,stack} \frac{dT_{stack}}{dt}$$

$$F_{water} = \frac{Q_{theo} - Q_{elec} - Q_{latent} - Q_{loss} - M_{stack} C_{p,stack} \frac{dT_{stack}}{dt}}{Cp_{H_2O}(T_{st} - T_{win})}$$

Non-linear model inversion + PI control

- The performance of PEMFC stack shows better performance on settling time of net power and O_2 excess ratio when the inversion model is being used.
- All the terms in non-linear model inversion are inferred from the available measurents of voltage, current and temperature.
- Temperature dynamics are much slower (of order two) when compared to that of other variables (voltage, current, reactant flow rates and pressure).

Non-linear model inversion + PI control Contd..

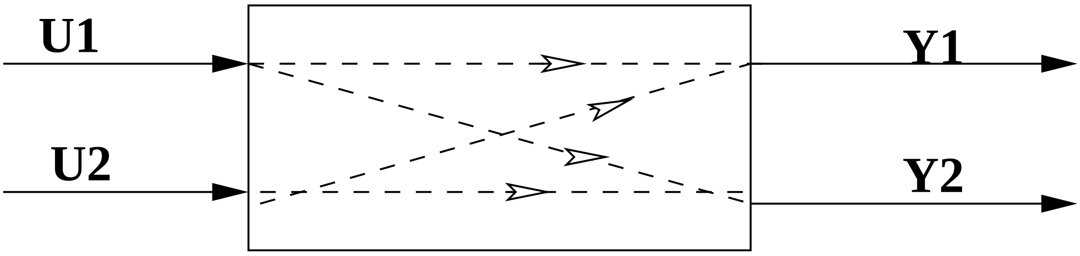
- Linear control can yield sub-optimal performance or even fail when the process exhibits fair amount of non-linearity and particularly over a wide range of operating conditions.
- The exact linearization technique uses linear control theory but still utilizes the non-linear model.
- The resulting controller is a feedforward + feedback type.
- Uncertainties in the model can lower the performance of the above scheme. Hence, a PI control is used in addition to the model inversion to handle the uncertanities.

Multivariable control:
Temperature and Air Flow control

Multivariate nature

- The four subsystems (i) reactant flow control (ii) heat management (iii) humidity control (water management) and (iv) power management control loops in general interact posing challenges.
- An increase in load can cause increase in stack temperature, which in turn affects the humidity requirements.
- The humidity control is also affected by the simultaneous increase in the reactants flow rate.
- There is a need to study the interactions present within the system.
- The steady-state interaction is provided by the Relative Gain Array (RGA) analysis.
- Dynamic interaction analysis is a more difficult task

Relative gain array



Relative gain array provides the best way among the possible $N!$ different ways to form the control loops between N inputs and N outputs. Consider a process of two inputs and two output:badboxes

- Introduce astep change in u_1 of magnitude $\triangle u_1$ keeping the u_2 at constant and record the new steady state value of output y_1. Let $\triangle y_1$ be the change from the previous steady state.

Relative gain array contd....

- The open loop static gain between y_1 and u_1 when u_2 kept constant is $(\frac{\triangle y_1}{\triangle u_1})_{u_2}$,
- In addition to static gain there is another open loop gain when u_2 varies to keep the output y_2 at constant value is $\triangle y_1$ when the change in input $\triangle u_1$.
- The ratio of the two open-loop gains is the relative gain between y_1 and u_1 as follows

$$\lambda_{11} = \frac{\left.\frac{\triangle y_1}{\triangle u_1}\right|_{u_2}}{\left.\frac{\triangle y_1}{\triangle u_1}\right|_{y_2}} \qquad (15)$$

if $lambda_{11} = 0$ then y_1 does depend on u_1, if $lambda11 = 1$ then u_2 does not affect y_1 and if $0 < \lambda_{11} < 1$ then interaction exists between u_2 and y_1.

Relative gain array contd....

Similar interpretations arise out of

$$\lambda_{12} = \frac{\left.\dfrac{\triangle y_1}{\triangle u_1}\right|_{u_1}}{\left.\dfrac{\triangle y_1}{\triangle u_1}\right|_{y_2}} \text{relative gain between } y_1 \text{ and } u_2$$

$$\lambda_{21} = \frac{\left.\dfrac{\triangle y_2}{\triangle u_1}\right|_{u_1}}{\left.\dfrac{\triangle y_2}{\triangle u_1}\right|_{y_1}} \text{relative gain between } y_2 \text{ and } u_1$$

$$\lambda_{22} = \frac{\left.\dfrac{\triangle y_2}{\triangle u_2}\right|_{u_1}}{\left.\dfrac{\triangle y_2}{\triangle u_2}\right|_{y_1}} \text{relative gain between } y_2 \text{ and } u_2$$

Steady-state interaction for the 2 × 2 system

In order to know the input-output pairing, interaction studies between the inputs (compressor voltage and coolant flow rate) and outputs(air flow rate and stack temperature) have been studied on non-linear simulink model. The resultant relative gain array analysis matrix is:

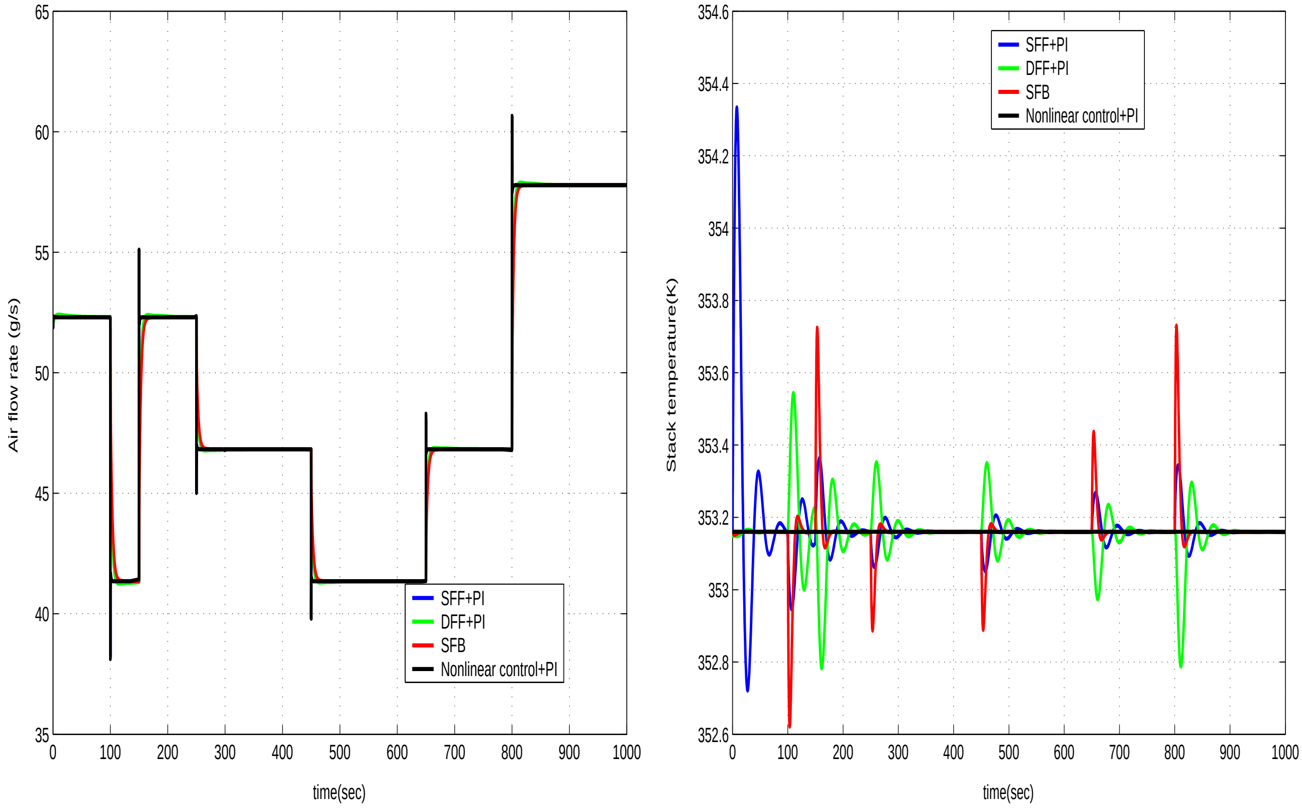
$$\text{RGA} = \begin{bmatrix} 1.0723 & -0.0713 \\ -0.074 & 1.0675 \end{bmatrix}$$

Compressor voltage-air flow rate and water flow rate-stack temperature are the best input-output pairs. The interactions between these pairings are quite weak.

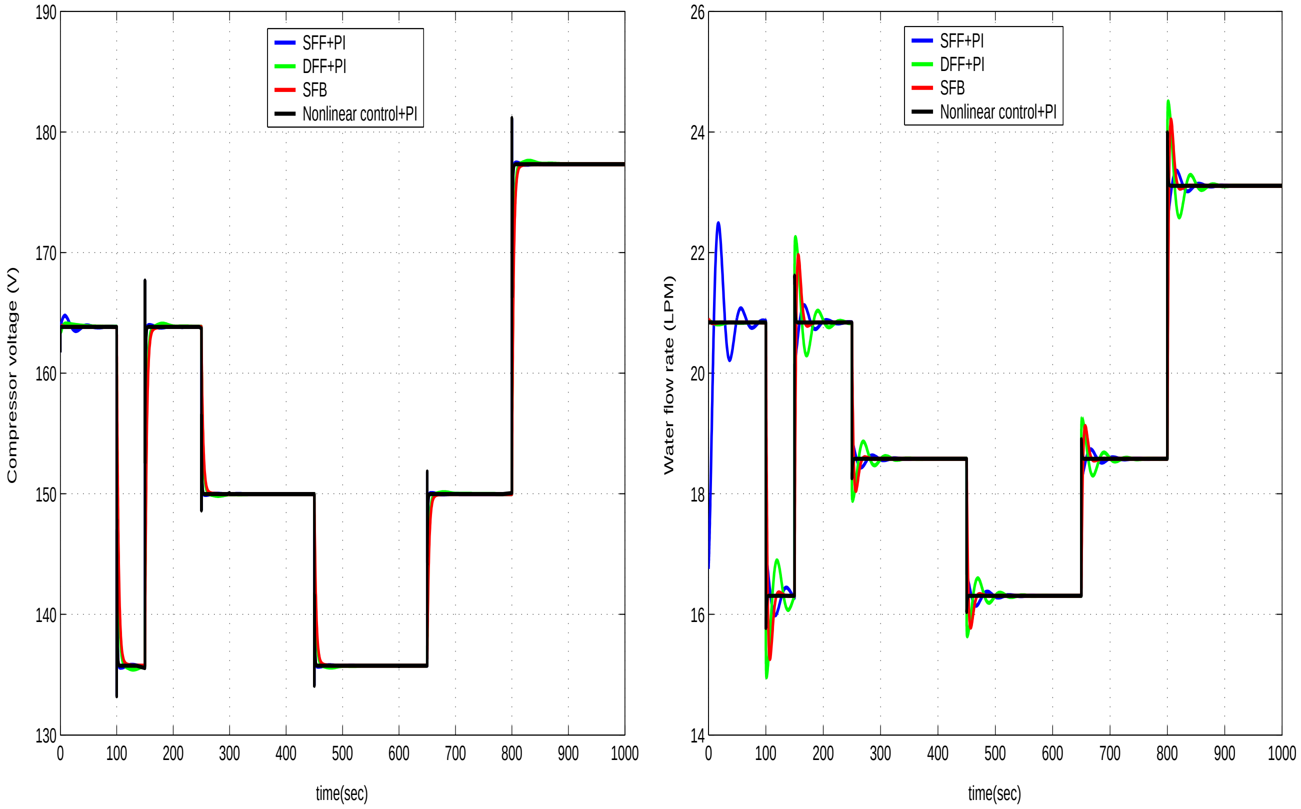
Multivariate state feedback control

- State feedback control is a powerful technique for multivariate systems. The control law is: $\mathbf{u} = -\mathbf{K}\mathbf{x}$
- Since states are measurable, an optimal LQR (linear quadratic regulator) scheme can be implemented. In practice, states may have to be estimated due to the presence of measurement noise.
- It allows one to impose weights on inputs and states, which exist in practice.
- Set-point problem is converted to a regulatory problem by augmenting the system with an integrator (essential for tracking)
- Multivariate control this way is better equipped to handle the interactions than the single-loop PID schemes.

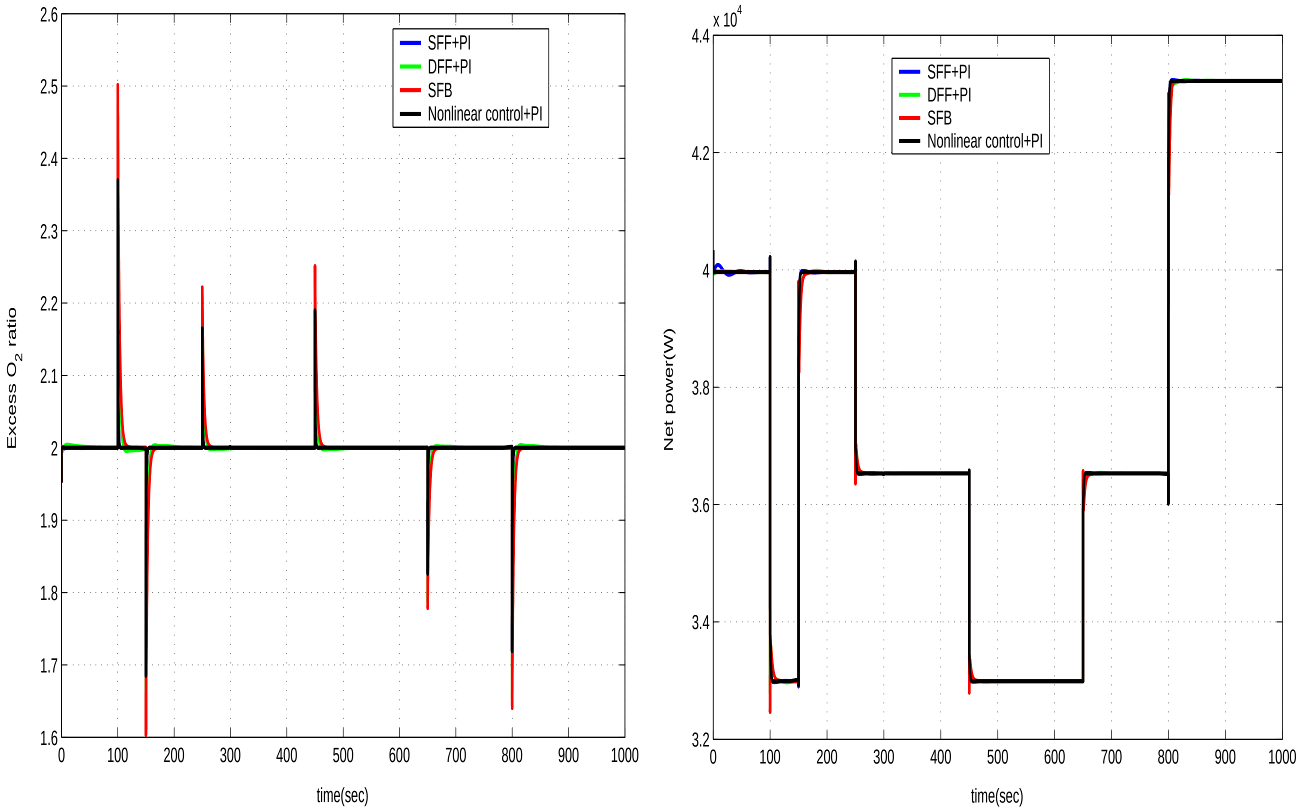
Regulatory problem: Controlled variables



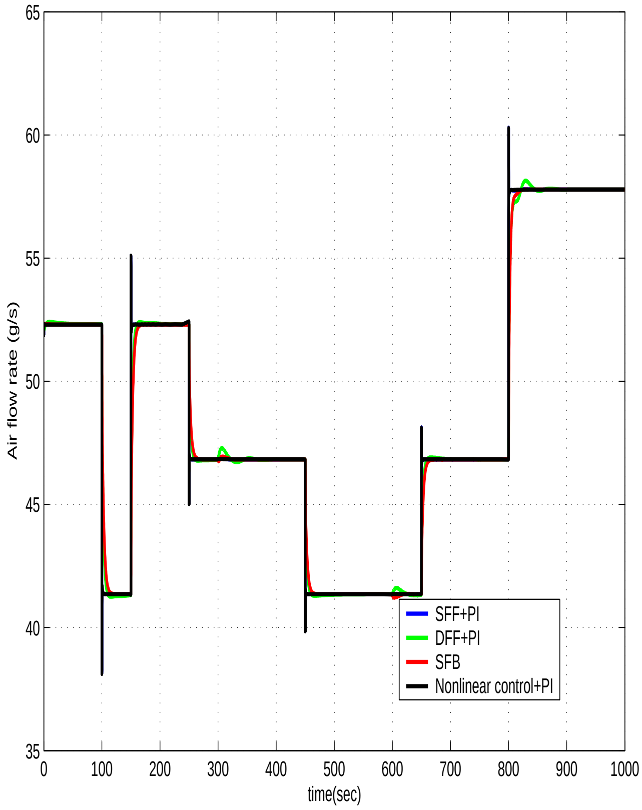
Regulatory problem: Manipulated variables

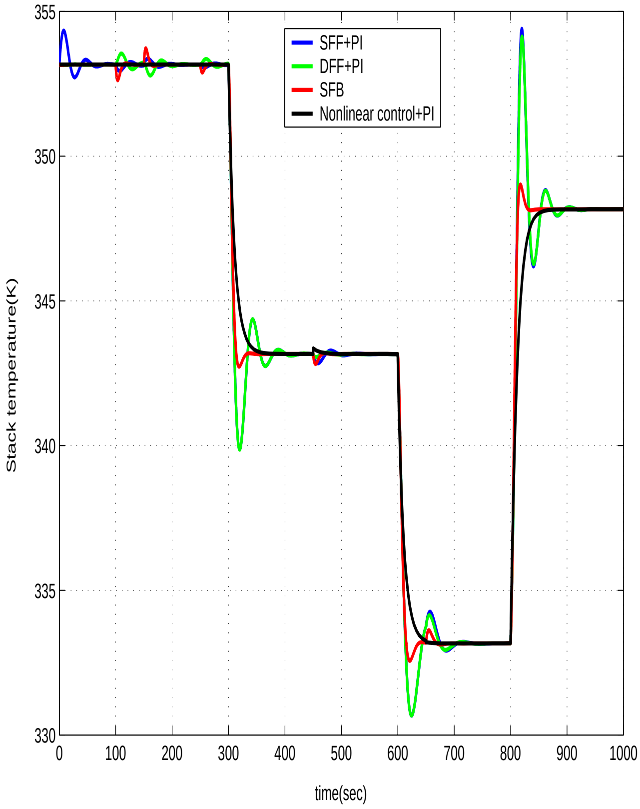


Regulatory problem: Performance variables

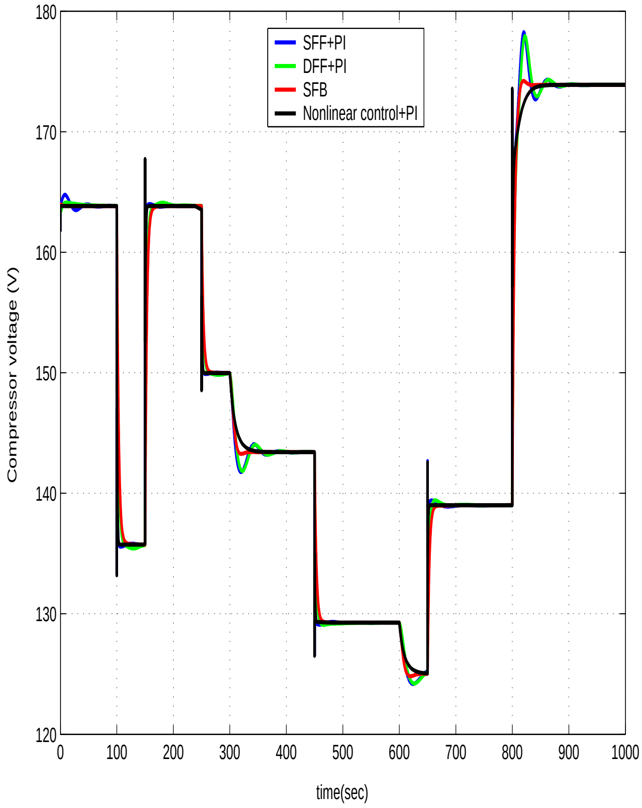


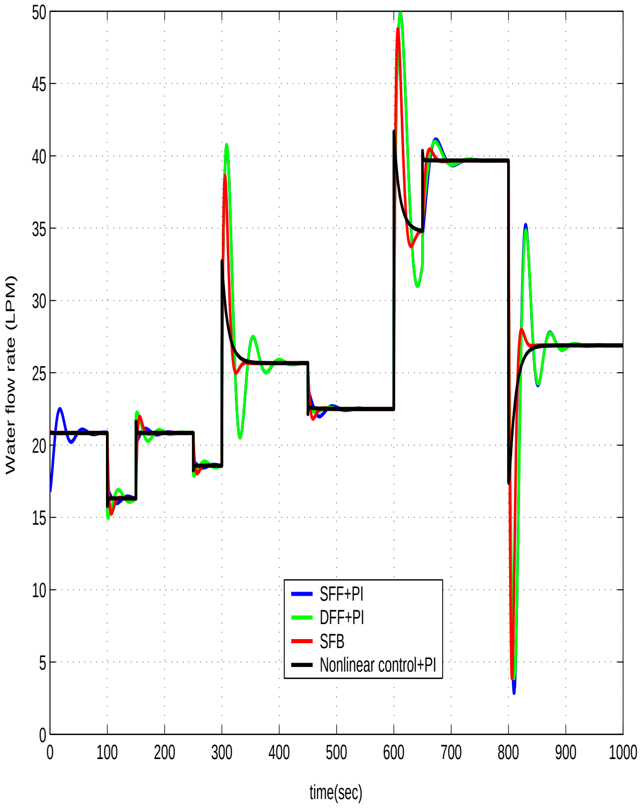
Servo problem: Controlled variables





Servo problem: Manipulated variables





Continuous external humidification of a PEMFC system: Design and Control

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Why is humidification required?

- Water management is essential to efficient performance of a PEM fuel cell, because the proton conductivity depends on hydration of polymer membrane.
- The net power of a stack is higher when hydrogen alone is humidified than both the reactants are being humidified and fed into the fuel cell stack.

Since the performance of the fuel cell is dependent more on hydrogen humidification than on oxygen humidification, the scope of the work is restricted to the hydrogen humidification.

Physical definitions

Dewpoint

It is the temperature at which the vapor starts to condense.

Relative humidity (RH)

RH is the ratio of the partial pressure of water vapor(P_V) present in the gas to the saturation vapor pressure(P_{sat}) of water at gas temperature. The measurement is expressed as a percentage.

$$\%RH = \frac{P_V}{P_{sat}} \times 100$$

where

$$log_{10}(P_{sat}) = -1.69 \times 10^{-10} T^4 + 3.85 \times 10^{-7} T^3 - 3.39 \times 10^{-4} T^2 + 0.143 T - 20.92$$

The dew/frost point temperature defines the saturation point for the water vapor in the gas. From this unique equilibrium temperature, all other reporting formats of gas humidity can be derived.

Influence of humidity on performance of PEMFC

Performance enhancement of PEMFC depends on the conductivity of proton through membrane, by migration of hydronium ion(H_3O^+) through membrane from anode to cathode.

- %RH of H_2 @100 has to be maintained in the fuel cell at various loads of current densities.
- %RH of air 80-90 and @95 have to be maintained at higher and lower current densities respectively.
- Activity coefficient(λ) of the membrane has to be maintained @14 to keep the the membrane completely hydrated.
- Temperature of fuel cell/stack @80^0C to be maintained (this is due to the trade off between the reaction kinetics and water transport across the membrane).

Need for humidity control in PEMFC

- To deliver power demand
- Optimum utilization of fuel in cell
- To avoid dehydration of the membrane
- To meet certain performance specifications in the process
- Ensure safety of the process.
- Minimize cost as well as increase productivity.

Types of humidification

The existing humidification systems are classified under the following types which are

External Humidification

The gases are heated and humidified externally in external humidification, thereby allowing us to maintain the %RH of gas at the desired value.

Internal Humidification

The gases are preheated before introducing into electrochemical active area of fuel cell. In internal humidification, %RH of gas can not be maintained at desired value.

Types of humidity sensors

- Wet/dry bulb psychrometer
- Displacement sensors
- Bulk polymer resistive sensors
- Capacitive sensors
- Saturated salt lithium chloride sensors
- Aluminium oxide dewpoint sensors
- Chilled mirror (optical condensation) hygrometer

Except chilled mirror hygrometer, all other sensors fail to respond actively during the humidification of gas at 100% RH. The chilled mirror optical dewpoint hygrometer is preferred in the range of -20°C to 90°C, and these are used as primary measurement device in calibration of other devices. The accuracy in temperature estimate is ±0.3°C

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Chilled mirror(optical condensation) hygrometer

Chilled mirror hygrometer is considered to follow the most precise method for dew point measurement. The response time is $\leq$ 4sec, so it can be used in control applications (online).

How does it work

- The sensor contains a small metallic mirror, the surface of which is chilled untill the vapour condenses the sample gas onto the mirror surface.
- The chilled mirror is illuminated by a source of light and the reflection is detected by a phototransistor.
- A control system keeps the temperature of the chilled mirror hygrometer at the point where a thin film is maintained.
- At the occurence of condensation, the reflected light is scattered therefore the intensity of light reduces. A PRT embedded in the mirror measures the respective dew point temperature.

1

Advantages of chilled mirror hygrometer (CMH) Contd

- A CMH provides one of the few truly direct physical measurements of humidity. It is recognized as the most precise method of determining the water vapor content of a gas above 5% RH. Used when maximum precision of measurement is needed.
- The CMH's optical sensor is a totally inert device. The sample gas contacts glass and non-reactive metals. Thus, it can be easily cleaned and can last indefinitely. Useful when the gas sample contains contaminants and particulates, which would damage other types of humidity sensors.
- Unlike polymer RH sensors, lithium chloride dew cells, and other chemically-based sensors, a CM sensor does not lose its calibration. Therefore, it possesses long-term calibration stability.

Literature review

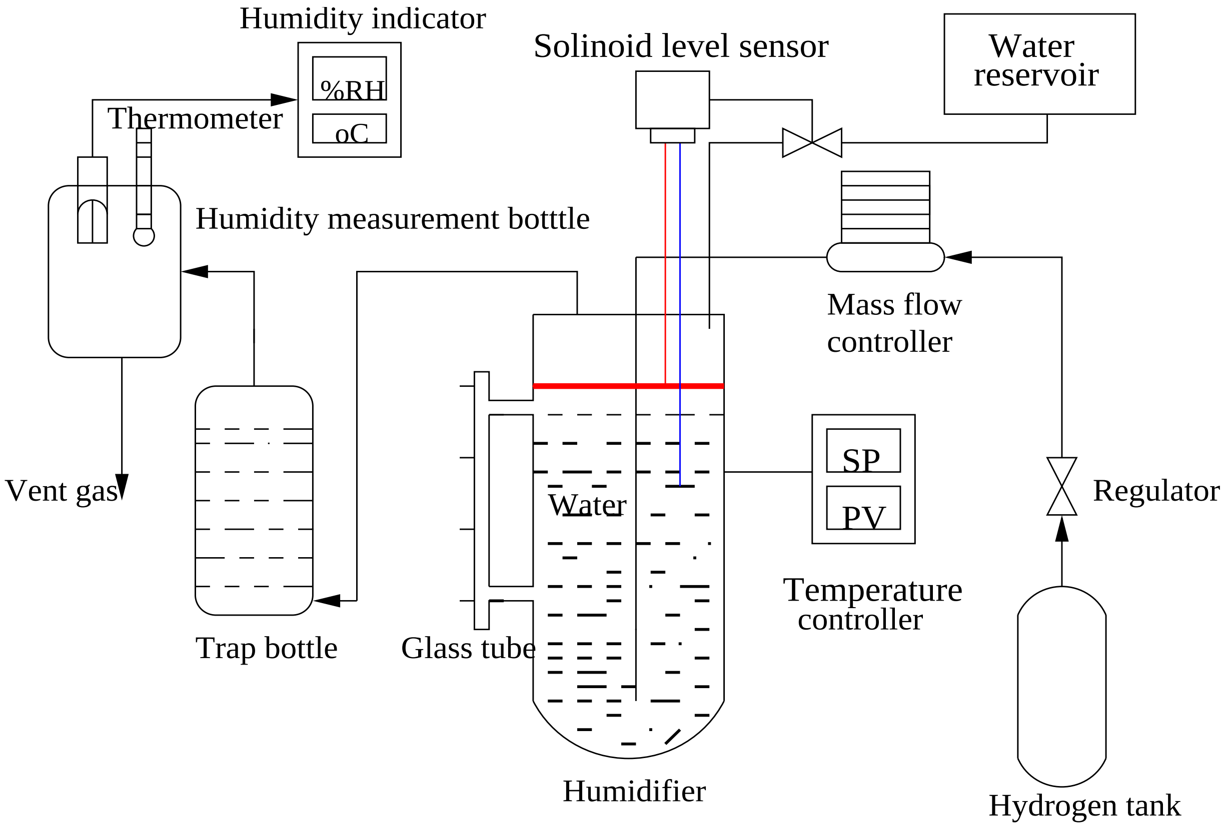
- Sridhar *et.al*[2001] have shown that the rate of water pick-up of H_2 gas at various flow rates in bubble humidification is lower when compared to membrane humidification. Hence they studied the effect of membrane thickness, area of membrane, gas flow rate and temperature of hot water on water pick up of H_2 in a membrane humidification.
- Rajalakshmi *et.al*[2002] have studied the effect of design parameters such as sparger diameter, number and diameter of sparger holes on relative humidity of H_2 besides the effect of gas flow rate and temperature of humidifier in a bubble humidifier. In their studies significant water carry over was observed at higher gas flow rates (above 15 lpm).

Literature review Contd...

- Duksu and Junbom [2004] have shown that the performance of PEM fuel cell is dependent more on H_2 humidifier temperature than the oxidant humidifier temperature.

To the best of authors knowledge the continuous humidification of H_2 gas has not been studied using a external or stack coolant water circulation in a bubble humidifier.

Existing bubble humidification system



Issues in the existing H_2 humidifier setup

- Water level has been maintained with solenoid level control.
- The running stack has to be stopped frequently for liquid water injection into the humidifier.
- Humidifier bottle has been heated with electrical jacketed heater.
- Water carry over occurs at high gas flow rates (above 5 lpm).

Issues in the existing H_2 humidifier setup Contd..

Disadvantages

- Water reservoir should kept at high elevation (10m) for operating the stack at 1 atm pressure (gauge). Therefore, it cannot be implemented in real time applications.
- Water level cannot be adjusted dynamically to avoid water carry over during high gas flow rates.
- External heat supply is needed for heating the humidifier bottle though the heating source is available in the form of stack coolant water.

Main features of proposed design

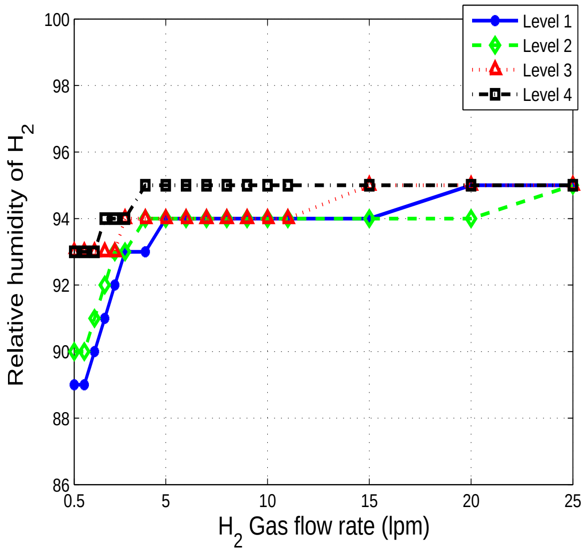
- It can be used for continuous humidification of H_2 gas.
- Water level can be maintained automatically between level 1 and level 4 at higher and lower gas flow rates respectively.
- Water-carry over can be avoided over a wide range of gas flow rates.

Scale-up: The proposed design can be scaled-up to a specified gas flow rate and stack operating pressure using the principles of geometric and kinematic similarity.

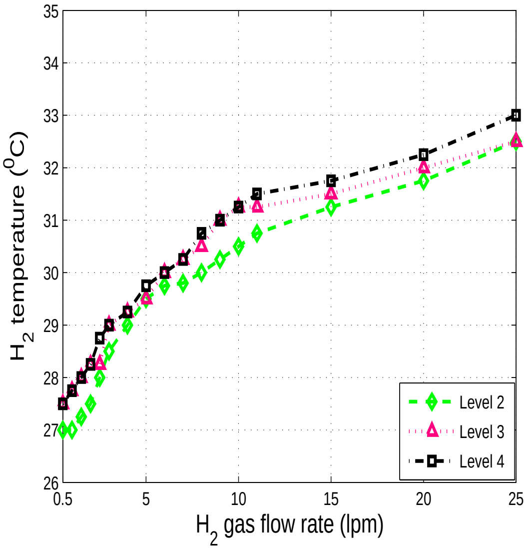
Studies required for a proposed design

- Effect of water level (gas residence time)
  - To determine the gas flow rate at which the water carry-over occurs
  - To study the effect of gas residence time on RH at constant humidifier temperature
- Effect of humidifier temperature
  - To study the relation between the humidifier and exit gas temperatures
  - To study the effect of humidifier temperature on relative humidity of H_2

Effect of water level (residence time)



RH of H_2 at $T_{humidifier}$=40^0C

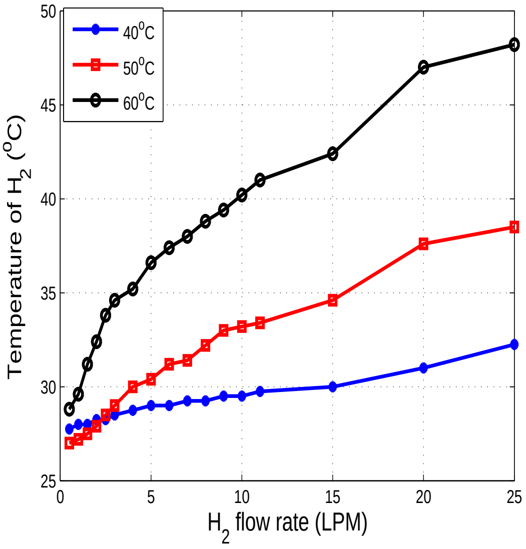


Temperature of H_2 gas

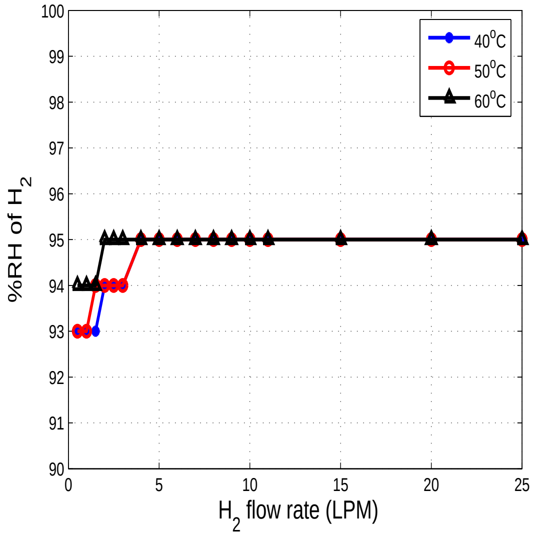
Effect of water level (residence time) Contd..

- The experiments were conducted for different levels of liquid volume (320 cc, 580 cc, 800 cc, 1000 cc) at humidifier bottle temperature 40^oC.
- The relative humidity of H_2 is dependent on gas residence at lower gas flow rates and is independent at higher gas flow rates.
- The variation in gas temperature at the exit of the humidifier bottle at any gas flow rate is due to changes in the gas residence time in the humidifier.

Effect of Temperature

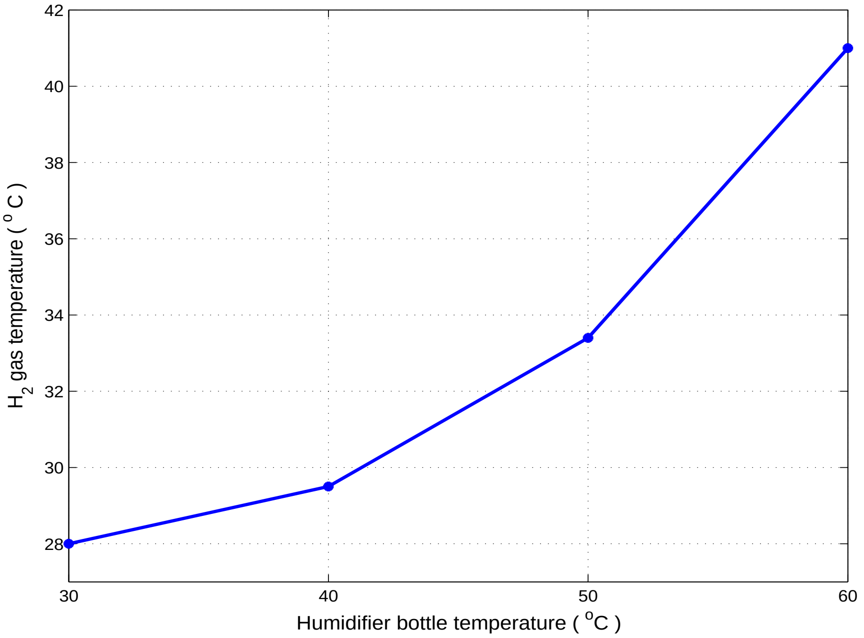


Relative humidity of H_2 gas



Temperature of H_2 in hygrometer

Effect of Temperature Contd...

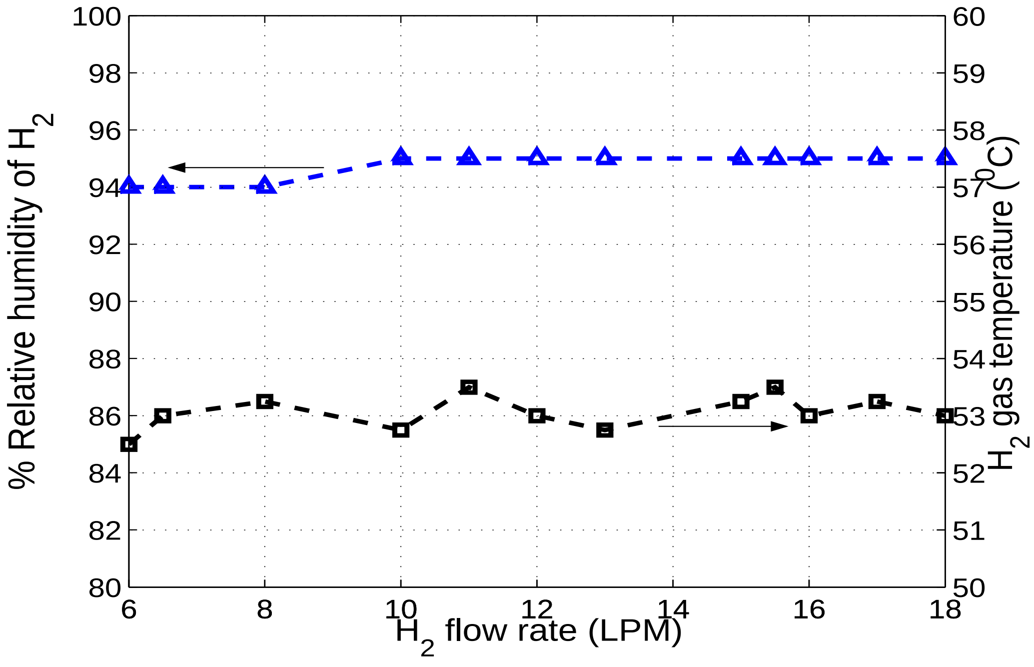


T_{H_2} at different temperatures of humidifier bottle, level 1 and gas flow rate 10 lpm

Effect of Temperature Contd...

- To study the effect of temperature, experiments were conducted at level 1 (lower) to avoid water carryover and thereby %RH was considered to be less dependent on liquid level at higher (4-25 lpm) gas flow rates.
- The relative humidity of H_2 is constant at higher gas flow rates for a wide range of gas flow rates.
- The temperature of H_2 gas increases exponentially with an increase in humidifier temperature. Using this chart, one can determine the humidifier temperature to achieve a desired exit temperature.

Results with continuous humidifier



Relative humidity of H_2 at exit temperature; Humidifier temperature 55^oC

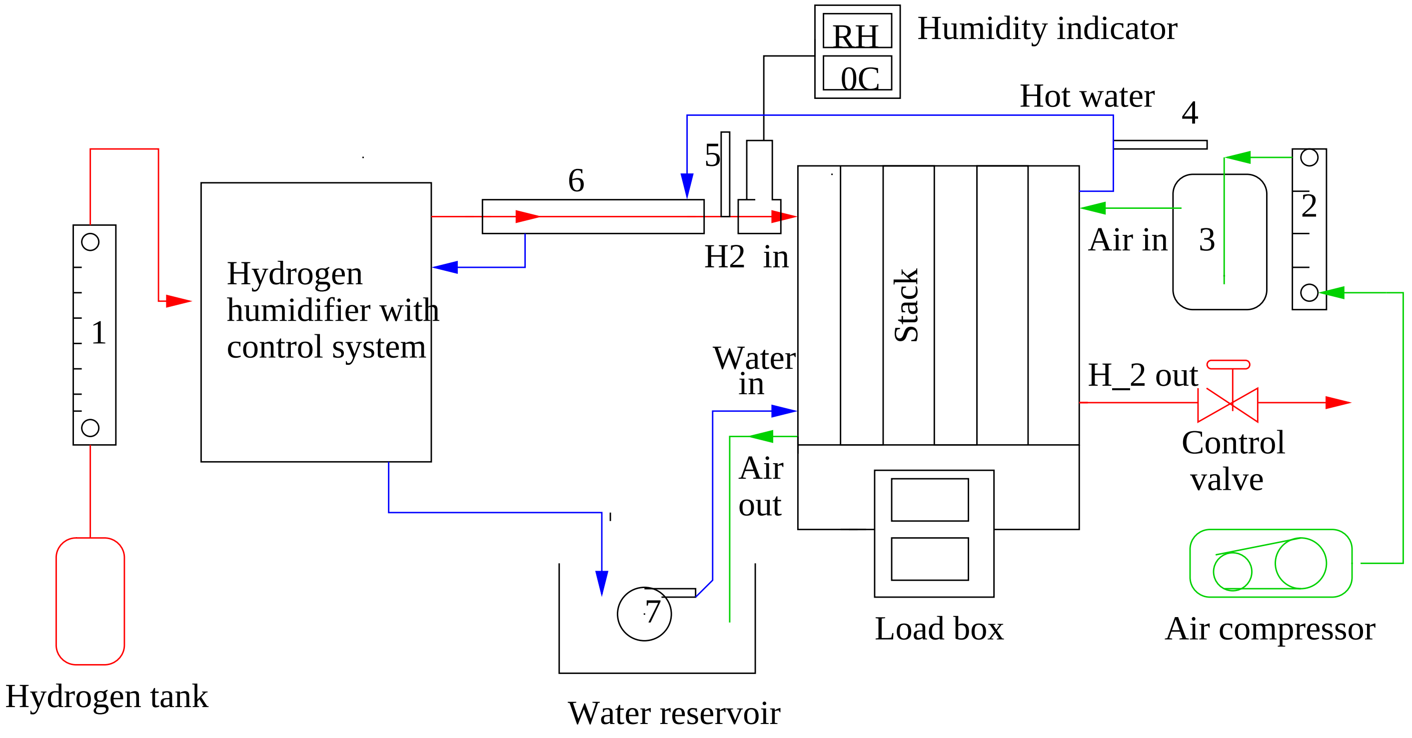
Design operating pressure of level control bottle

In order to know the design operating pressure of level control bottle, two types of float balls have been tested in the present experiments and the results obtained from Eq. 2 are compared.

Float ball type	Type of material	Diameter/ Height (cm)	Mass (grams)	Design pressure (mbar)	
				Experimental	Model
Hollow sphere	HDPE	Dia = 6.1	28.62	60	62
Cylinder	Thermo coal	Dia= 6.1 Height = 6.1	27.25	120	123

The cylindrical float ball is preferred to a hollow spherical ball since it gives a higher limiting pressure for the same diameter of the float ball.

Implementation on a 1 kW stack



1,2 Rotameters 3. Air humidifier 4,5 :Thermometers 6. Exit gas heating section 7. Water pump

Results with 1 kW stack Contd....

H_2 flow (lpm)	P_{H_2} (mbar)	current I (amp)	voltage (V)	$\triangle h_{water}$ (cm)	stack outlet T_{H_2O}(^{0}c)	Stack inlet	
						T_{H_2}(^{0}c)	%RH
17.5	120	20	23.6	0.6	58	53.5	94
16	100	18	24.6	0.8	56	53	94
15	85	16	26.5	1.3	56	52.5	94
14	75	14	27.2	2.1	54	51	94
12	65	12	29.2	2.7	52	50.5	94
10	55	10	32	3.1	51	49.5	94
8	45	8	32.4	3.3	50	48.5	94
5	30	6	34	4.0	50	48	94
4	15	4	35.2	4.9	49	47	93
3	10	2	37.7	5.3	48	45.5	93

Summary

- The condensation of water vapour is avoided at electrode/flow field interface during the start up of stack when the gas is humidified with recirculated stack coolant water.
- H_2 gas is being humidified continuously without water carry over by the gas.
- Constant relative humidity of H_2 is maintained over a wide range of gas flow rates.
- External heating is not required for continuous humidification H_2

Main contribution:

The conventional bubble humidifier has been converted to a continuous humidifier and designed to control the %RH of H_2 at the stack temperature without the water carry-over.