Fuel Cells: The Electrochemical and Thermodynamical Models

Lecture #7

Outline

- What is a fuel cell?
- Basic operation of a fuel cell
- Fuel cell types
- Hydrogen as a fuel
- Fuel cell performance
- Dynamic response
- Generated heat
- Fuel cell controllers
- Conclusions

What is a Fuel Cell?

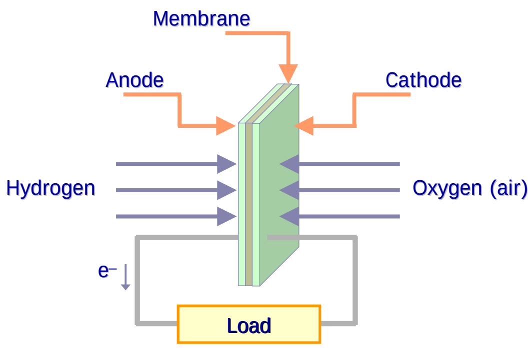
- It is a device that converts chemical energy into electrical energy
- First demonstrated by sir William Grove (1839)
- Used in the 50's by NASA
- A fuel cell is characterized by what separates the anode from the cathode (electrolyte)
- It conducts ions from the anode to the cathode to form water and heat as by-products
- Uses a catalyst to speed the reaction (Pt, Ni)
- The operation temperature depends on the fuel cell type (from about 50ºC to 1000ºC)

What is a Fuel Cell?

- Major Components:

- **anode:** fuel oxidation
- **cathode:** oxidant reduction
- **electrolyte:** ion transport
- **catalyst:** reaction speed

Basic Operation of a Fuel Cell



Basic Operation of a Fuel Cell

Anode reaction (oxidation):

$$\mathbf{H_2 \rightarrow 2H^+ + 2e^-}$$

Cathode reaction (reduction):

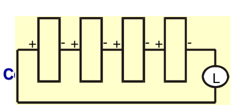
$$\mathbf{{}^1\!/_2 O_2 + 2H^+ + 2e^- \rightarrow H_2O + heat}$$

Overall reaction:

$$\mathbf{H_2 + {}^1\!/_2 O_2 \rightarrow H_2O}$$

Fuel Cell Stacks

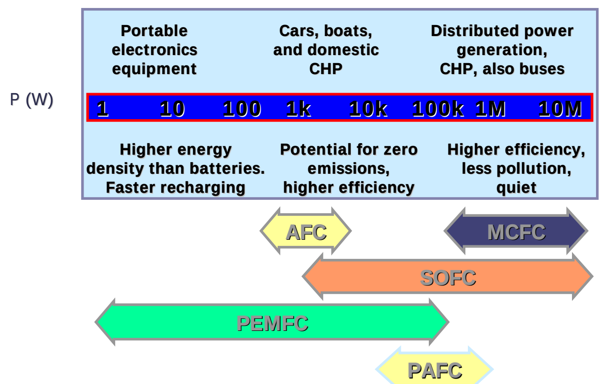
- **Single cell: 0.6 V (dc), 0.7 A/cm²**
- **5-10 kW for residences**
- **Multiple cells for higher power**
- **Connect in series: $V_S = nV_{FC}$**
- **C**



Fuel Cell Types

Characteristic	PEMFC	DMFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Proton Exchange Membrane	Proton Exchange Membrane	Potassium Hydroxide	Phosphoric Acid	Molten Carbonates (Li, K, Na)	Solid Oxide ZrO_2-$Y2O_3$
Temperature (ºC)	50-90	50-130	50-250	180-200	650	750-1050
Charge Carrier	H^+	H^+	OH^-	H^+	CO_3^{2-}	O^{2-}
Catalyst	Pt	Pt	Pt, Ni	Pt	Ni, LiNi	Ni
Fuel	H_2 (Pure or Reformed)	CH_3OH	H_2 (Pure)	H_2 (Reformed)	H_2 and CO reformed & CH_4	H_2 and CO reformed & CH_4
Poison	CO>10ppm	Adsorbed intermediates	CO, CO_2	CO>1% H_2S>50ppm	H_2S>0.5ppm	H_2S>1ppm
Main Applications	Portable, Transportation	Portable, Transportation	Space	Power gener., Co-generation, Transportation	Power gener., Co-generation	Power gener., Co-generation

Fuel Cell Types



Hydrogen as a Fuel

- **Safety**
- **H_2 generation**
  - reformation of natural gas
  - electrolysis of H_2O
  - controlled CO_2 production
- **H_2 delivery**
  - pipelines
  - tanks
  - compressors

- **Energy density**

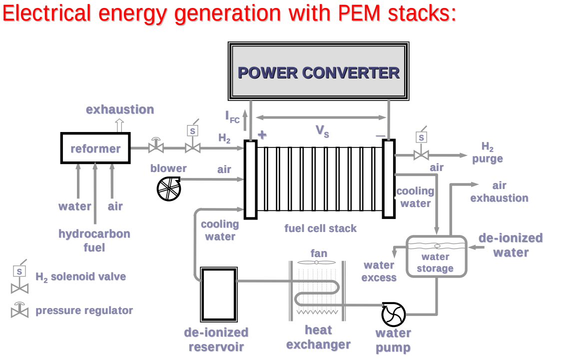
Fuel	Wh/g	kWh/L
Hydrogen	33	???
Diesel Fuel	13.2	21.1
Gasoline	8.4	12.6
Methanol	6.2	5.0

- **Energy requirements**
  - Power: 0.7 kW average
  - Energy: 0.7 x 30 x 24 = 504 kWh/month
  - H_2: 33 Wh/g $\Rightarrow$ 15.28 kg

Volume depends on the pressure and temp.

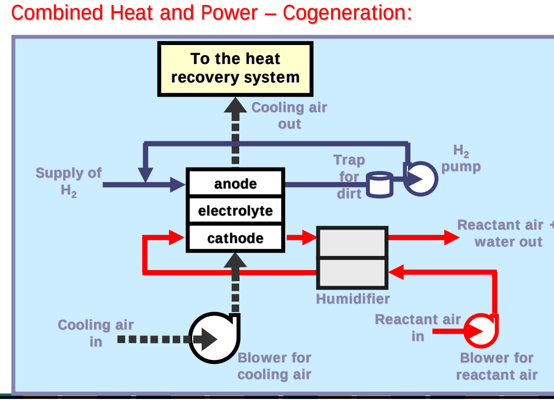
Fuel Cell Power Plants

Electrical energy generation with PEM stacks:



Fuel Cell Power Plants

Combined Heat and Power – Cogeneration:



Fuel Cell Performance

- **The fuel cell electrical efficiency can be defined as:**

$$\eta = \frac{\text{electrical energy produced per mol of fuel}}{\text{change in the enthalpy of formation}}$$

$$\eta = \frac{V_{FC} . i_{FC} . t}{-\Delta \bar{h}_f} \left(\frac{J / mol}{J / mol} \right)$$

- $\Delta \bar{h}_f$ =-241.83 kJ/mol (water ⇒ steam – LHV)
  -285.84 kJ/mol (water ⇒ liquid – HHV)

Fuel Cell Performance

- FC electrical work ⇒ change in the Gibbs free energy of formation
- The fuel cell maximum efficiency can be defined as:

$$\eta_{max} = \frac{\text{change in the Gibbs free energy of formation}}{\text{change in the enthalpy of formation}}$$

$$\eta_{max} = \frac{\Delta \bar{g}_f}{\Delta \bar{h}_f}$$

Fuel Cell Performance

- Reversible OCV for a hydrogen fuel cell: $E_o = \frac{-\Delta \bar{g}_f}{2.F}$

State of water	Temp (ºC)	$\Delta \bar{g}_f$ (kJ/mol)	E_o (V)	η_{max}
Liquid	25	-237.2	1.23	83%
Liquid	80	-228.2	1.18	80%
Gas	100	-225.3	1.17	79%
Gas	400	-210.3	1.09	74%

Referred to the HHV (-285.84 kJ/mol)

Fuel Cell Performance

- The maximum theoretical voltage, using all the hydrogen enthalpy of formation, is given by:

$$E_{max,t} = \frac{-\Delta \bar{h}_f}{2.F} = \begin{cases} \text{1.48 V, using the HHV} \\ \text{1.25 V, using the LHV} \end{cases}$$

- These voltages are related to a 100% efficient system. So, the FC efficiency can be obtained by:

$$\eta = \mu_f \cdot \frac{V_{FC}}{1.48}$$

μ_f ⇒ fuel utilization coeficient; generally about 95%.

Fuel Cell Electrical Equations

Current density: $J = \frac{i_{FC}}{A}$ (A/cm^2)

Electrical power: $P_{FC} = V_{FC}.i_{FC}$ (W)

Stack voltage: $V_S = n.V_{FC}$ (V)

Stack power: $P_S = V_S.i_{FC} = n.V_{FC}.i_{FC}$ (W)

Fuel Cell Performance - Example

- From the basic FC operation, we know that for 1 molecule of H_2 2 electrons circulate through the external circuit.
- In one mole of H_2 we have N molecules of H_2 (N=6.022×10^{23} - Avogadro's number)
- Now, for one mole of H_2 ⇒ 2×N electrons circulate through the external circuit.
- Considering the charge of one electron (-e = 1.602×10^{-19} C), the charge that flow is equal to:

$$q = -2.N.e = -2.F \quad \text{(C)}$$

F: Faraday constant or the charge in one mole of electrons = 96485 C

Fuel Cell Performance - Example

- The equation shows the charge for one mole of H_2. For a certain amount of H_2 (certain number of moles):

$$q = -2.F.(H_2 \text{ moles}) = -2.F.H_2 \quad \text{(C)}$$

- Now, dividing this equation by time and not considering the signal:

$$\frac{q}{t} = I_{FC} = 2.F.H_2.\frac{1}{t} = 2.F.\left(\frac{H_2}{t}\right) \quad \text{(C/s=A)}$$

$$I_{FC} = 2.F.\dot{H}_2 \quad \text{(A)}$$

$\dot{H}_2$: Hydrogen flow rate (moles/s)

Fuel Cell Performance - Example

- The last equation showed the resulting current from a certain H_2 flow rate. If we rearrange the equation, we have the necessary H_2 for a certain current (or the H_2 usage flow rate):

$$\dot{H}_{2,u} = \frac{I_{FC}}{2.F} \quad \text{(moles/s)}$$

- This equation is valid for one cell. For a stack, with *n* cells:

$$\dot{H}_{2,u} = \frac{n.I_{FC}}{2.F} \quad \text{(moles/s)}$$

Fuel Cell Performance - Example

- Considering the power supplied by the stack, the FC current is given by:

$$\mathbf{P_S = n.V_{FC}.I_{FC} \Rightarrow I_{FC} = \frac{P_S}{n.V_{FC}}} \quad \text{(W)}$$

- Replacing this value in the previous equation:

$$\mathbf{\dot{H}_{2,u} = \frac{n.I_{FC}}{2.F} = \frac{n}{2.F}.\frac{P_S}{V_{FC}.n}} \quad \text{(moles/s)}$$

Fuel Cell Performance - Example

- Or:

$$\mathbf{\dot{H}_{2,u} = \frac{P_S}{2.F.V_{FC}}} \quad \text{(moles/s)}$$

- Considering the molar mass of H_2 (2.02×10^{-3} kg/mole):

$$\mathbf{\dot{H}_{2,u} = \frac{P_S}{2.F.V_{FC}}\left(\frac{moles}{s}\right).\frac{2.02\times10^{-3}}{1}\left(\frac{kg}{mole}\right)}$$

$$\mathbf{\dot{H}_{2,u} \cong 1.05\times10^{-8}.\frac{P_S}{V_{FC}}} \quad \text{(kg/s)}$$

Fuel Cell Performance - Example

- Finally, including the fuel utilization factor:

$$\mathbf{\dot{H}_{2,u} \cong 1.05\times10^{-8}.\frac{P_S}{V_{FC}}.\frac{1}{\mu_f}} \quad \text{(kg/s)}$$

- Consider a FC stack supplying a certain load with:

P_S = 5 kW, V_{FC} = 0.65 V, μ_f = 0.95:

$$\mathbf{\dot{H}_{2,u}} = 1.05\times10^{-8}.\frac{5000}{0.65}.\frac{1}{0.95}$$

$$\mathbf{\dot{H}_{2,u}} \cong 8.5\times10^{-5} \quad \text{(kg/s)}$$

Fuel Cell Performance - Example

- The stack efficiency can be calculated as:

$$\eta = \mathbf{\frac{P_S}{-\Delta\bar{h}_f}}$$

- Considering the stack supplying 5 kW:

$$\eta = \frac{\mathbf{5000\left(\frac{J}{s}\right)}}{\mathbf{285.84\times10^3\left(\frac{J}{mole}\right).\left(\frac{1mole}{2.02\times10^{-3}kg}\right).8.5\times10^{-5}\left(\frac{kg}{s}\right)}}$$

Fuel Cell Performance - Example

$$\eta = \frac{\mathbf{5000}\left(\frac{\mathbf{J}}{\mathbf{s}}\right)}{\mathbf{141505}\times\mathbf{10^3}\left(\frac{\mathbf{J}}{\mathbf{kg}}\right).8.5\times10^{-5}\left(\frac{\mathbf{kg}}{\mathbf{s}}\right)}$$

$$\eta = \frac{\mathbf{5000.(J/s)}}{\mathbf{12028(J/s)}} \Rightarrow \eta \cong 41.6\%$$

- Using the following equation:

$$\eta = \mu_f \cdot \frac{\mathbf{V_{FC}}}{\mathbf{1.48}} = 0.95.\frac{0.65}{1.48} \Rightarrow \eta \cong 41.7\%$$

Fuel Cell Performance

Fuel cell output voltage:

$$V_{FC} = E_{Nernst} - V_{act} - V_{ohmic} - V_{con}$$

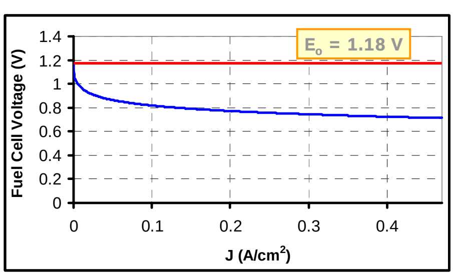
Voltage drops:

- Activation (reaction kinetics)
- Ohmic (electrolyte + contact resistances)
- Concentration or mass transport (mass flow limitations)
- Internal currents or fuel crossover

J. M. Corrêa (Ph.D. Brazilian Student Under CAPES Scholarship), F. A. Farret, V. A. Popov, M. G. Simões "Simulation of Fuel Cell Stacks Using a Computer Controlled Power Rectifier with the Purposes of Actual High Power Injection Applications," IEEE Trans. on Industry Applications, July/August 2003, pp. - .

Fuel Cell Performance

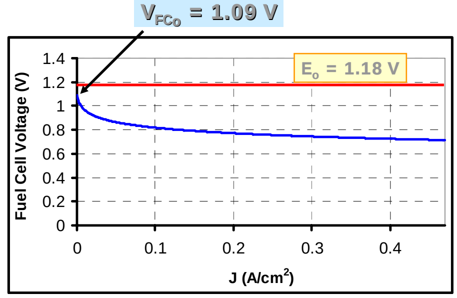
For a fuel cell operating at 80ºC $\Rightarrow \bar{\Delta} g_f$ = -228.2 kJ/mol and E_o = 1.18 V.
Considering just the activation voltage drop:



Fuel Cell Performance

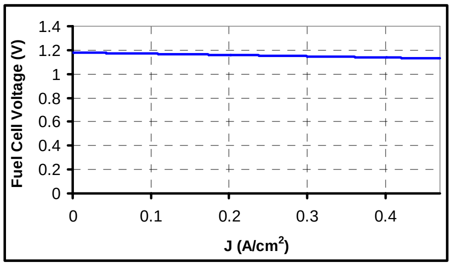
Considering just the internal current (J_n = 1.8 mA/cm^2) and the activation voltage drops:

V_{FC_o} = 1.09 V



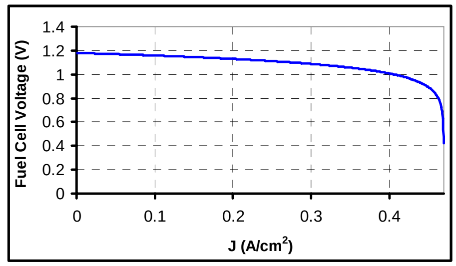
Fuel Cell Performance

Considering just the internal current and the ohmic voltage drops:



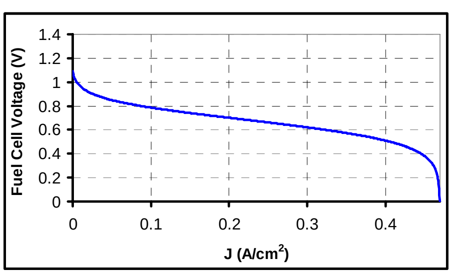
Fuel Cell Performance

Considering just the internal current and the concentration voltage drops:

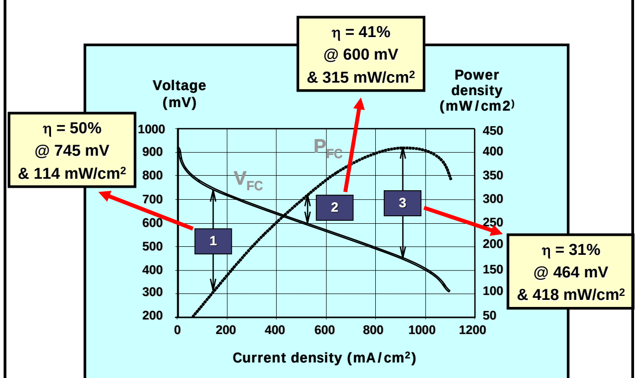


Fuel Cell Performance

Considering all voltage drops:

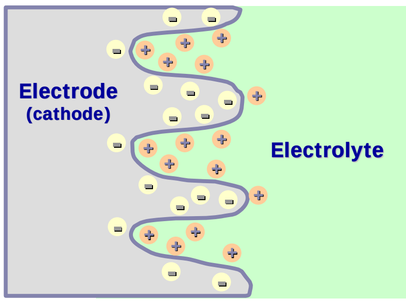


Fuel Cell Performance

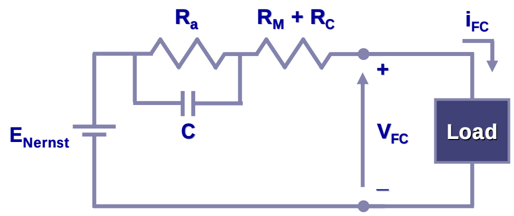


Dynamic Response

Charge double layer effect:



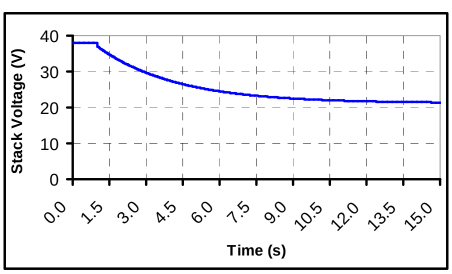
Dynamic Response



Time constant: $\tau = C.R_a$

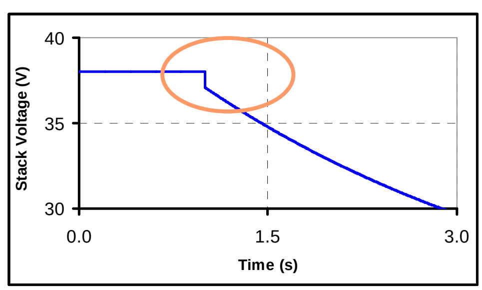
Dynamic Response

Example: for an application of a 15 A step load current:



Dynamic Response

Example: for an application of a 15 A step load current:



Generated Heat and Temperature Variation

$$\dot{Q}_g = P_S \cdot \left(\frac{1}{\eta} - 1 \right) \quad \text{(W)}$$

$$\dot{Q}_{rem} = \varsigma \cdot \dot{Q}_{ger} \quad \text{(W)}$$

$$\frac{dT}{dt} = \frac{\dot{Q}_g - \dot{Q}_{rem}}{M \cdot C_p} = \frac{\dot{Q}_g - \dot{Q}_{rem}}{C}$$

Overall Efficiency

$$\dot{Q}_u = \eta_h . \dot{Q}_g \quad \text{(W)}$$

$$\eta_t = \frac{P_S + \dot{Q}_u}{P_S + \dot{Q}_g} = \frac{P_S + \eta_h . \dot{Q}_g}{P_S + \dot{Q}_g}$$

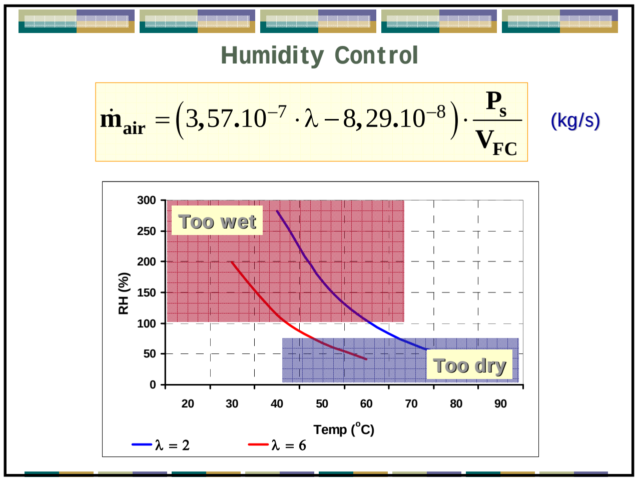
Fuel Cell Control Systems

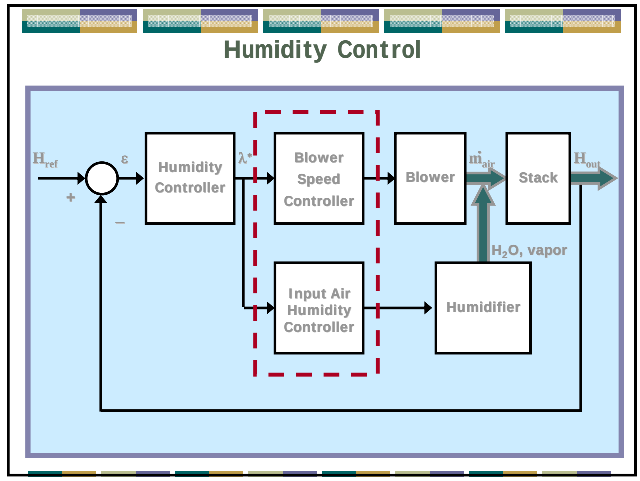
- **Humidity control**
- **Temperature control**
- **Reactants flow and/or pressure control**
- **Electrical control (P,V,I)**

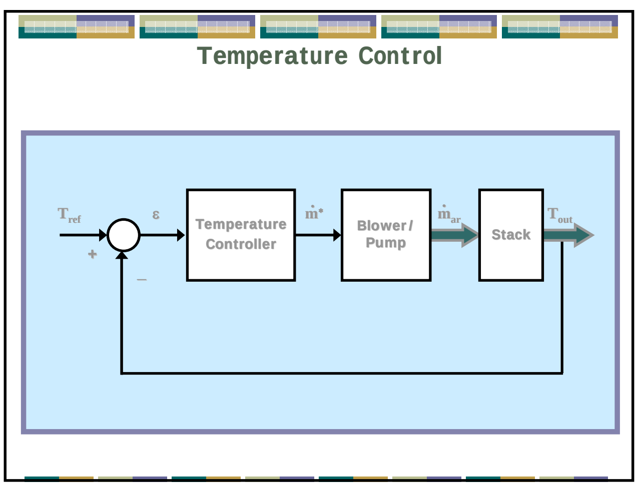
Humidity Control

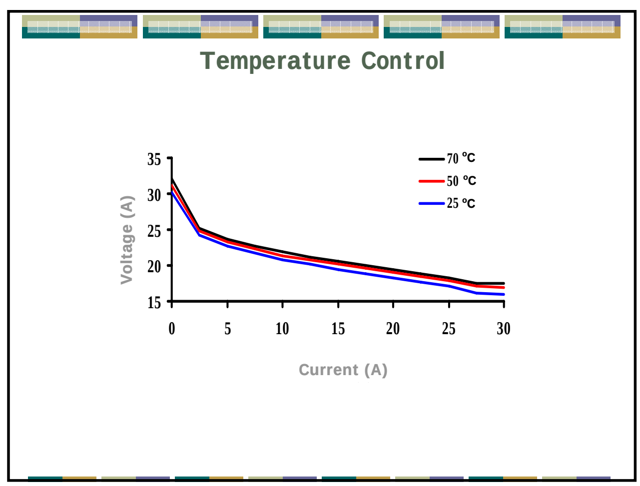
Exit air humidity (input air: Temp. 20ºC, RH 70%)

Temp (ºC)	λ = 1.5	λ = 2	λ = 3	λ = 6	λ = 12	λ = 24
20					218	145
30				199	120	79
40		282	201	114	69	46
50	215	169	120	68	41	27
60	133	104	74	42		
70	85	67	48			
80	56	44	31			
90	38	30				

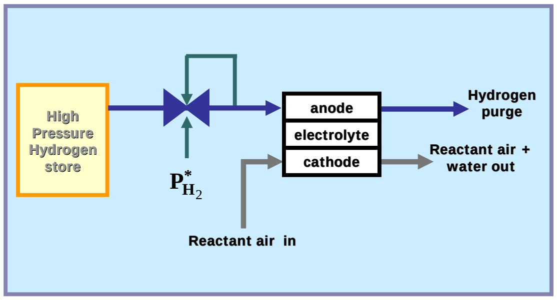

Humidity Control
$\dot{m}_{air} = \left(3,57.10^{-7} \cdot \lambda - 8,29.10^{-8}\right) \cdot \frac{P_s}{V_{FC}}$
(kg/s)
Too wet
Too dry
RH (%)
Temp (°C)
λ = 2
λ = 6


Humidity Control
H_{ref}
ε
Humidity Controller
λ*
Blower Speed Controller
Blower
$\dot{m}_{air}$
Stack
H_{out}
H_2O, vapor
Input Air Humidity Controller
Humidifier


Temperature Control
T_{ref}
ε
Temperature Controller
$\dot{m}$*
Blower / Pump
$\dot{m}_{ar}$
Stack
T_{out}

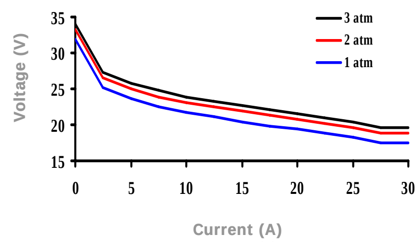

Temperature Control
70 °C
50 °C
25 °C
Voltage (A)
Current (A)

Pressure/flow Control

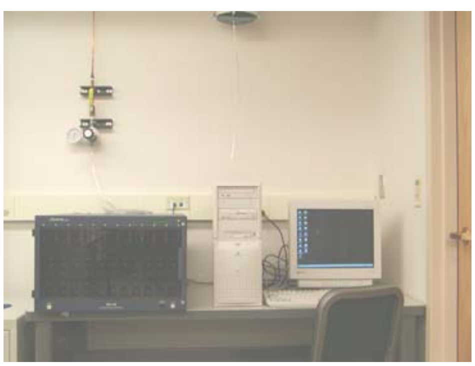


Pressure/flow Control

$$\Delta V = 0.02.\ln\left(\frac{P_2}{P_2}\right)$$



Example of a Practical System



Conclusions

- This module presented the fundamentals of a fuel cell and the basic operation. The fuel cell types and the use of hydrogen as a fuel were also discussed.
- Evaluation of a PEM fuel cell performance considered static and dynamic responses with considerantions on efficiency and generated heat.
- Fuel cell controllers for temperature, humidity pressure and flow were discussed and an experimental setup was presented.


Questions ?