Sharif University of Technology

Fuel cell Technology

Lecture 4

Ramin Roshandel

Energy Engineering Department

Current Energy system

Hydro
Oil
Natural Gas
Coal
Nuclear

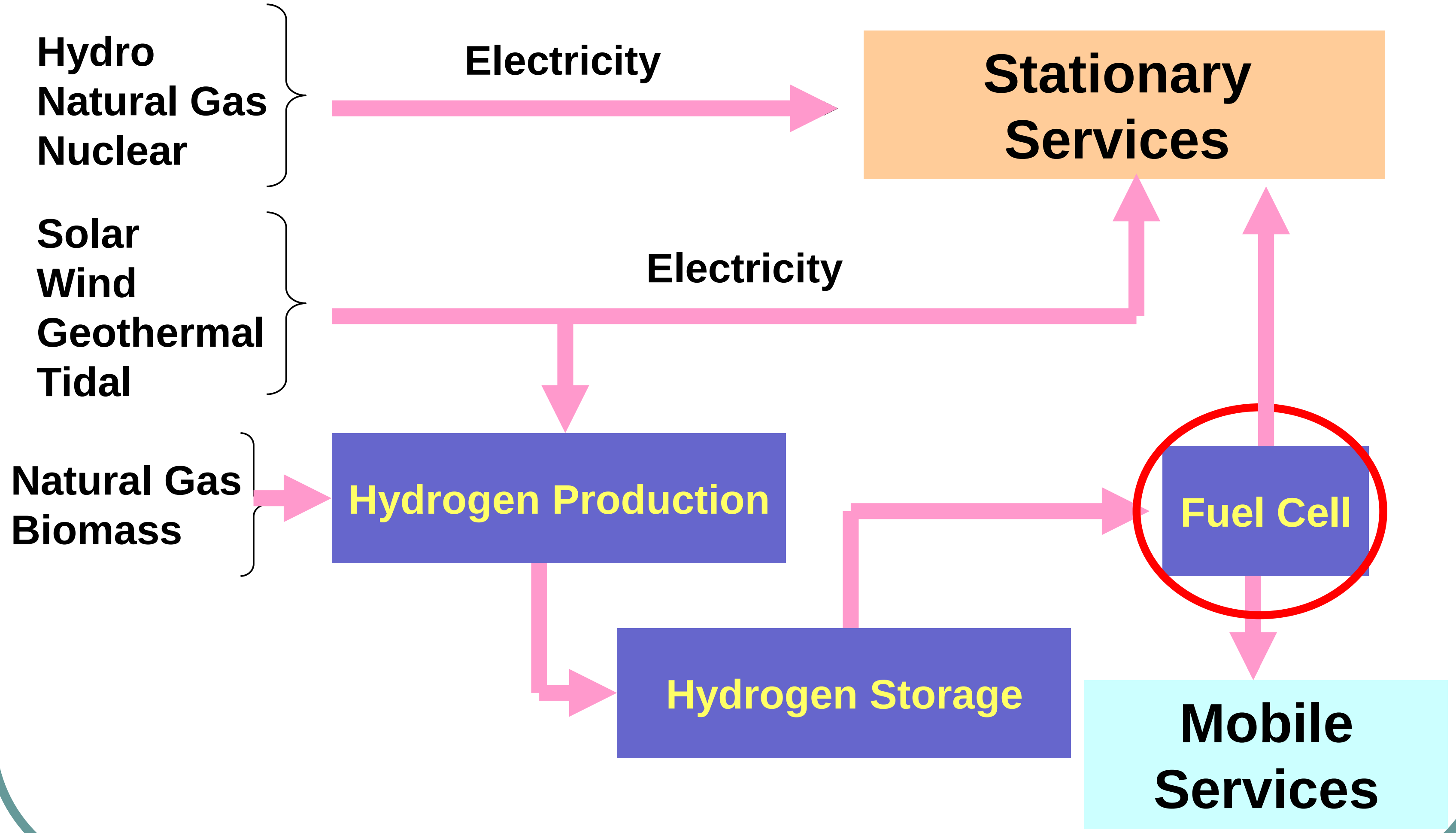
Electricity → **Stationary Services**

Solar
Wind
Geothermal
Biomass
Tidal

Solar power is a big growth area

Oil → **Mobile Services**

Fuel cell Role in future energy system



Fuel cell application

- Transportation



- Off-Grid Power

- Grid-Integrated Power

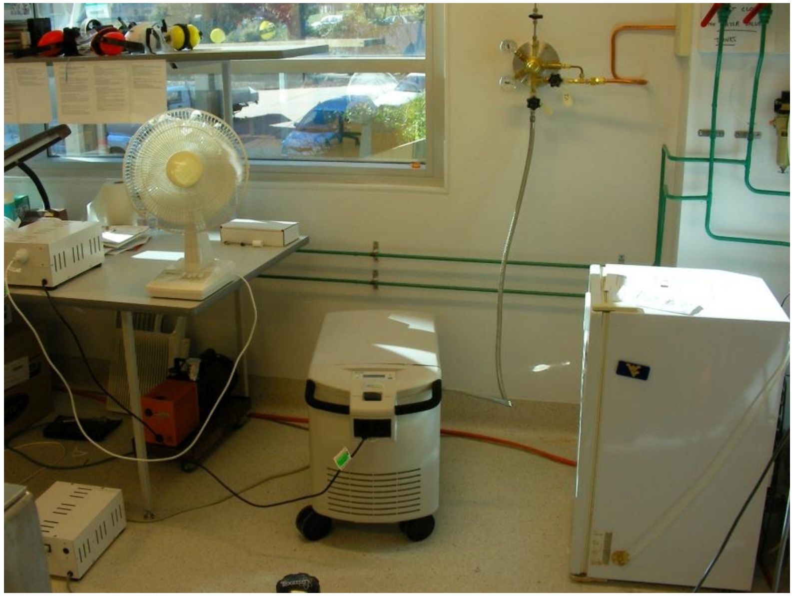
- Portable Electronics


Off- grid Power

Australian National University

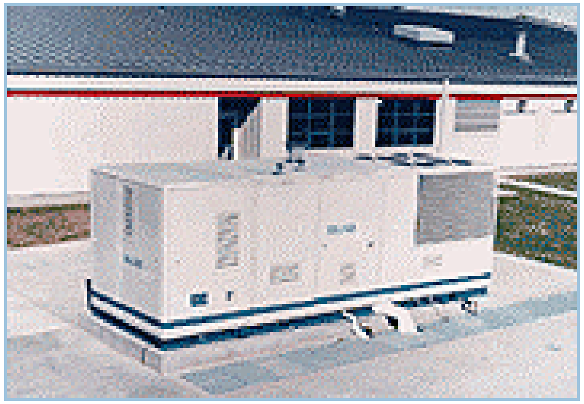
1 KW Ballard PEM Fuel cell

20 Single cell, 20 L/min H_2



On grid power

Fuel cell Submarine
9X 34KW



Fuel cell power plant

Micro CHP

Microgen

ENATEC

Whispergen

Disenco

Energetix

Ceres Power - Fuel Stack only

Accumentric

Why Fuel Cells?

Global Reasons!

- Fossil fuel reserves are diminishing at high rates!
- Environmental issues and pollutant!
- There is no way to powering the future!
- We should think of more efficient energy conversion devices

National Reasons!

- We live in a energy based country!
- More than 80% of Iran's budget is come from energy export!
- Every technology in energy supply section should be well considered!
- Iran is a resource-rich power having the world’s second largest natural gas proven reserves which can be used as a main fuel for fuel cells

Why Fuel Cells?

From Scientific view

Fuel cell technology is a multi disciplinary field which covers series of Science and Engineering branches

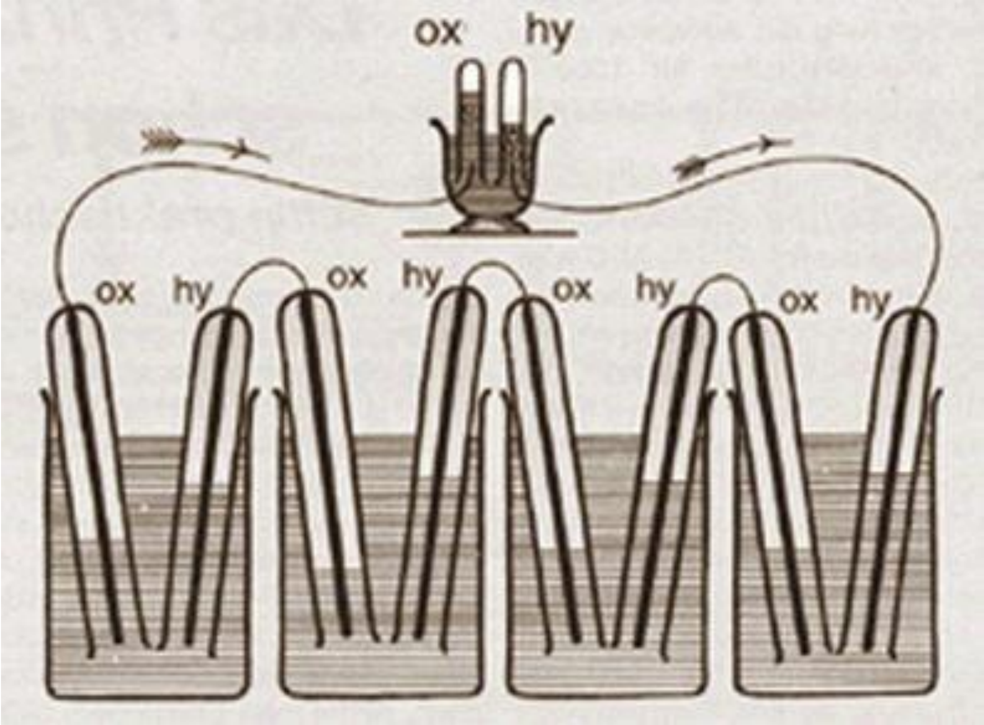
Fuel cell is a new technology which is in the state of the art, it can open new windows in Science and Technology

Fuel cell R&D activities are one of the hottest fields in research centers and universities

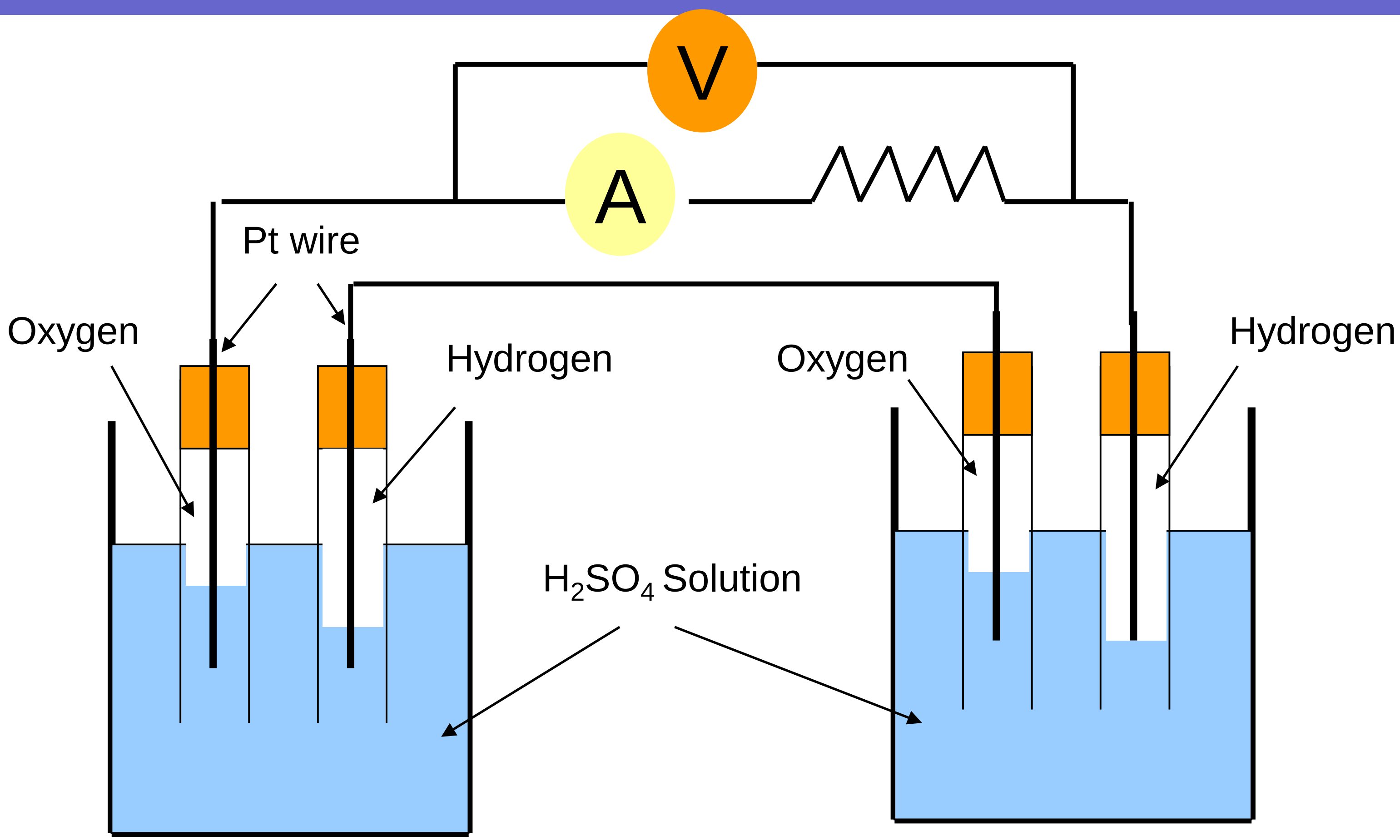
Fuel cell History

1839

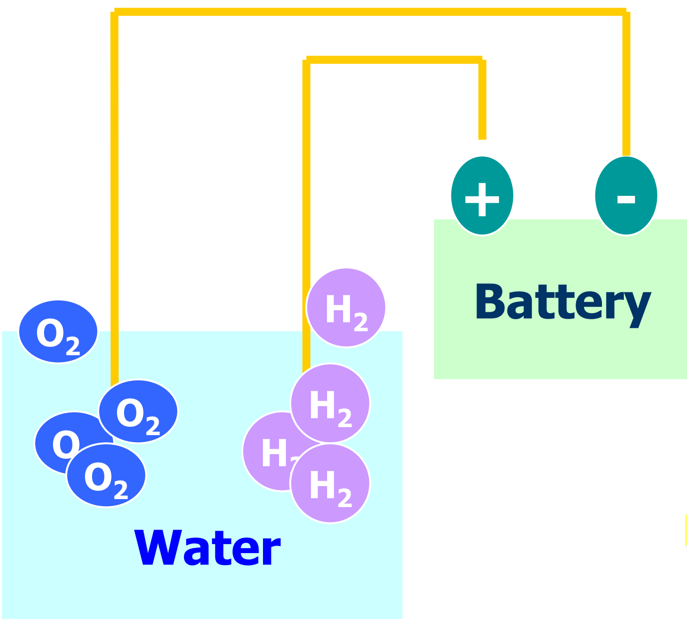
Grove's Device: Oxygen and hydrogen in the tubes over the lower reservoirs react in sulfuric acid solution to form water. That is the energy producing chemical reaction.
The electrons produced electrolyze water to oxygen and hydrogen in the upper tube that was actually used as a voltmeter.



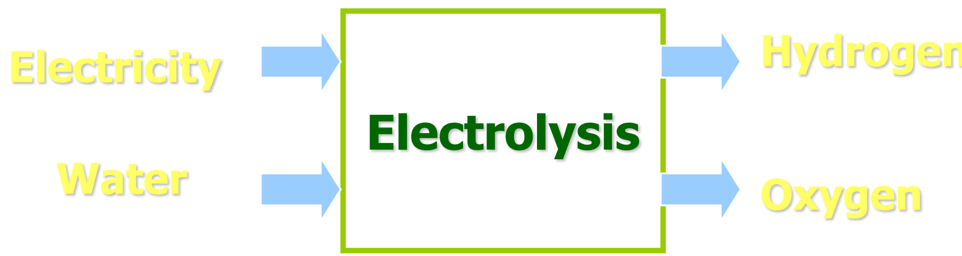
Grove Fuel cell



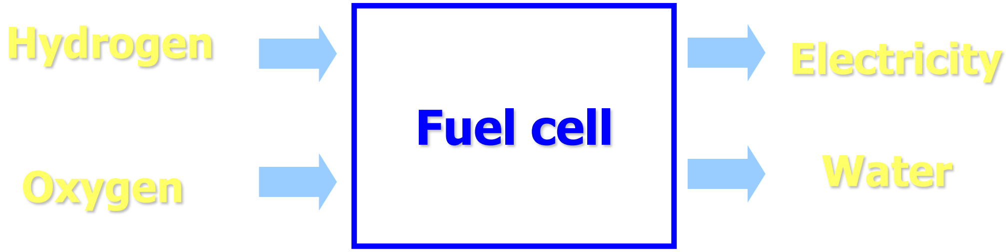
Electrolysis Experiment



$$2H_2 + O_2 \rightarrow 2H_2O$$



Fuel cell introduction

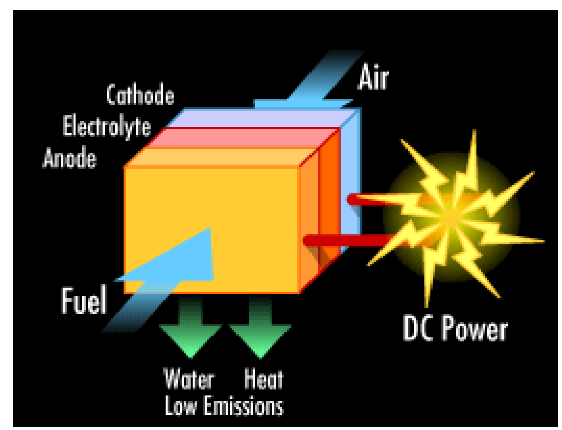


Fuel Cell Elements

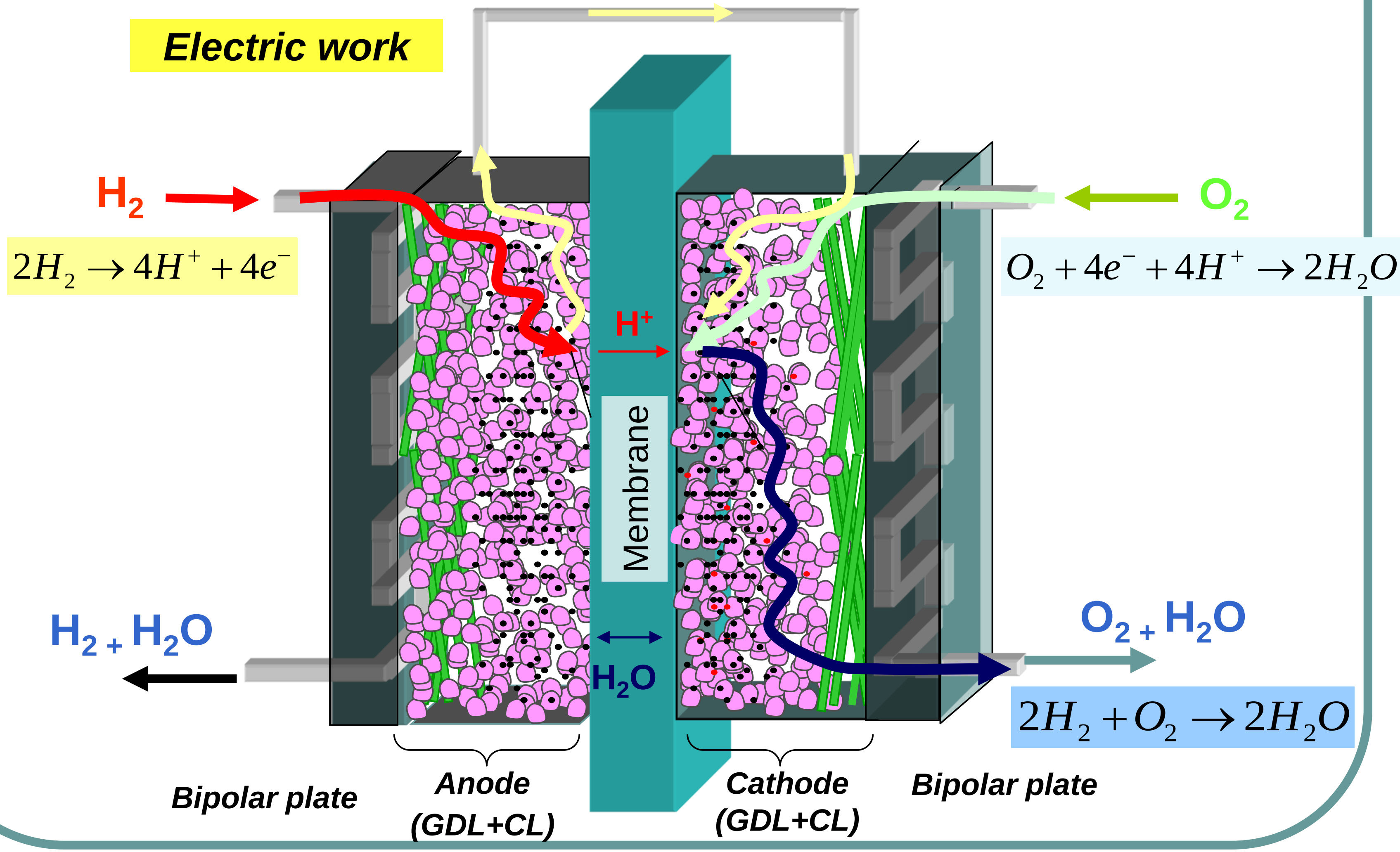
- Anode
- Cathode
- Electrolyte

Fuel Cell Advantages

- High Efficiency
- Low Emission
- Scalability
- Fuel Flexibility
- Reliability
- Quiet Operation

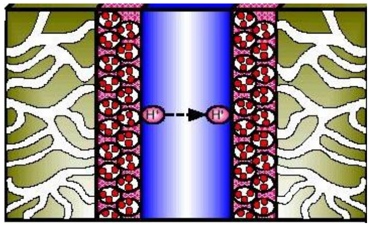


Fuel cell, Base of Operation



Fuel cell Majors

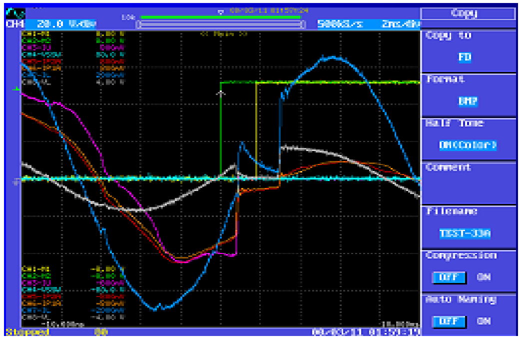
- **Membrane**
- **Catalyst layer**
- **GDL**



MEA

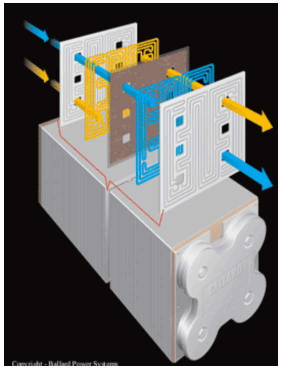
- *Chemistry*
- *Material Engineering*
- *Chemical Engineering*
- *Physics*
- *Nano Technology*

Fuel Cell Control



- *Electrical Engineering*
- *Mechanical Engineering*

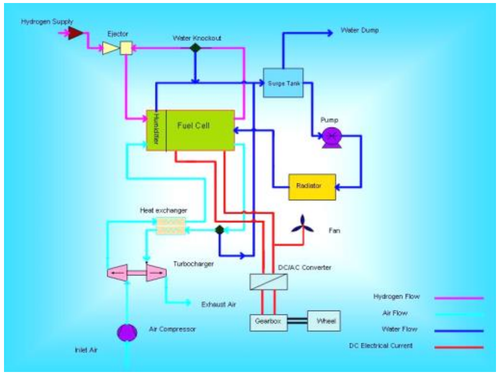
Fuel Cell Stack



- **Stack Design**
- **Bipolar plate**
- **Water management**
- **Heat management**

- *Mechanical Engineering*
- *Chemical engineering*

Fuel Cell System and Accessory



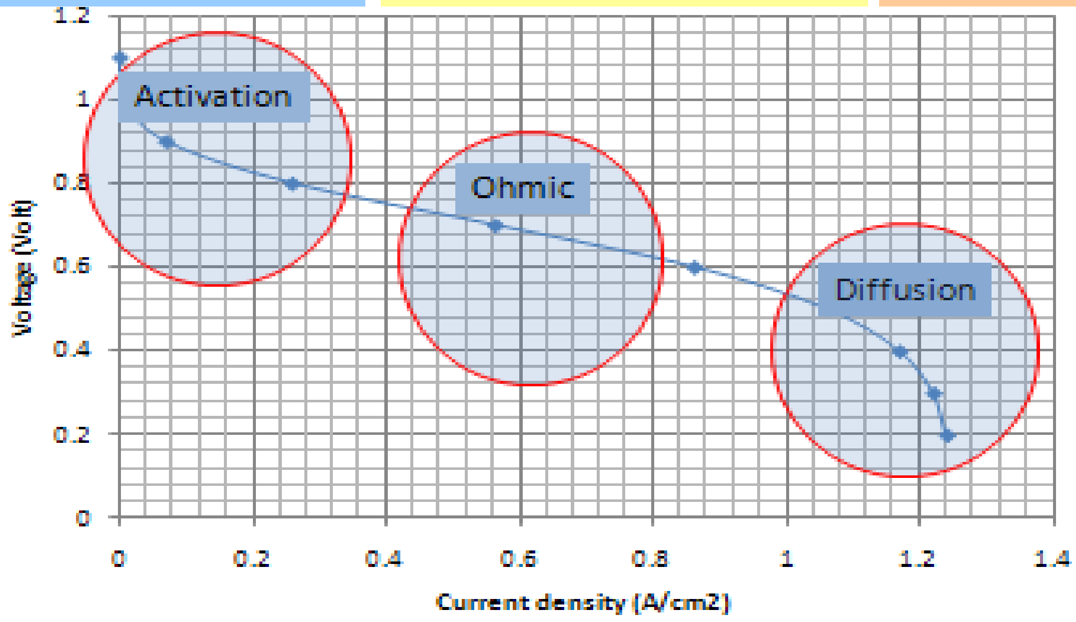
- **Fuel Supply Subsystem**
- **Air Supply Subsystem**
- **Cooling subsystem**
- **Output power**
- **CHP**

- *Mechanical Engineering*
- *Chemical Engineering*
- *Electrical Engineering (Power)*

Fuel cell performance

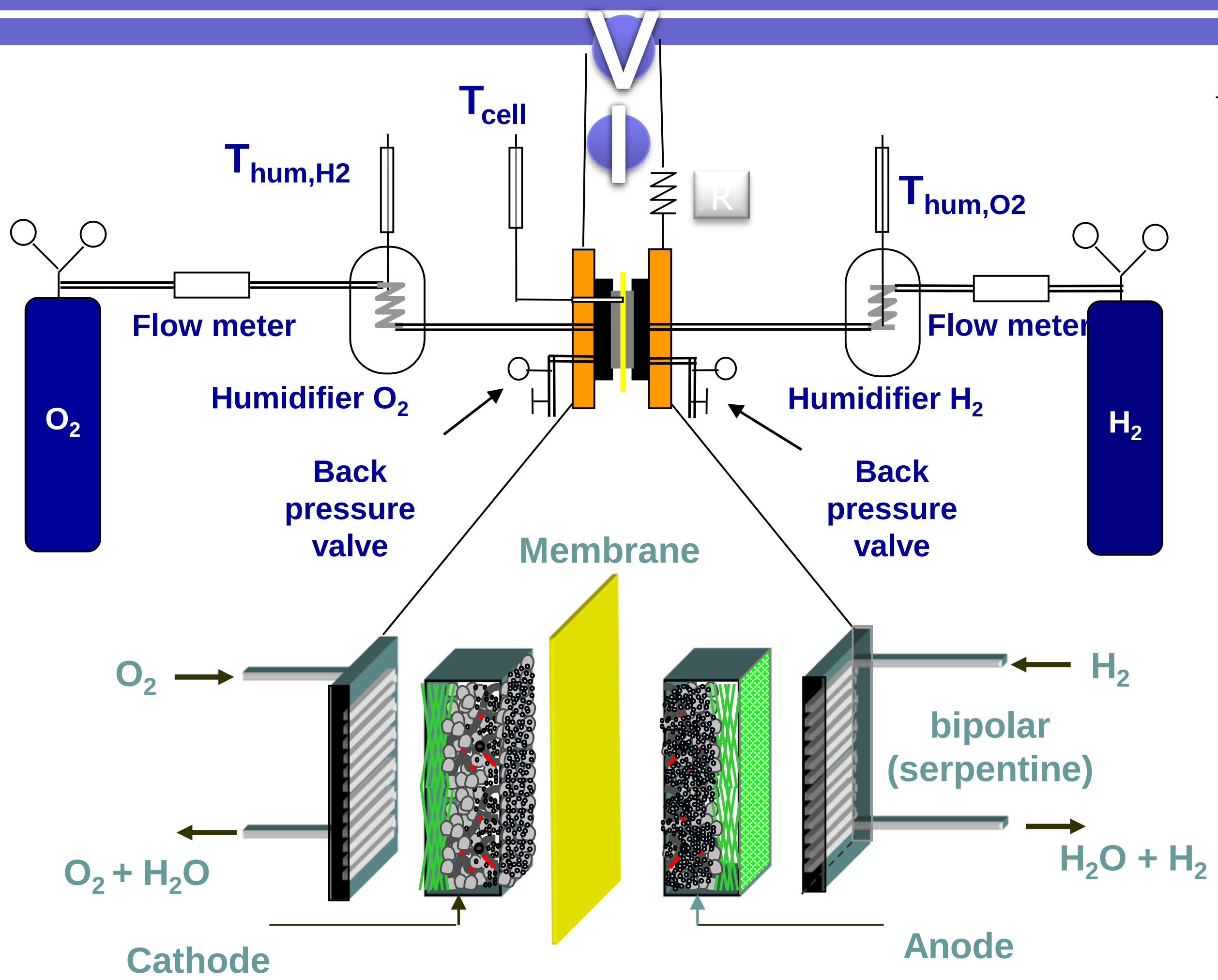
Polarization Curve

Chemical Engineering ***Electrical Engineering*** ***Mechanical Engineering***



$$V = V_{OCV} - \eta_{act} - \eta_{ohm} - \eta_{dif}$$

Fuel cell Test station



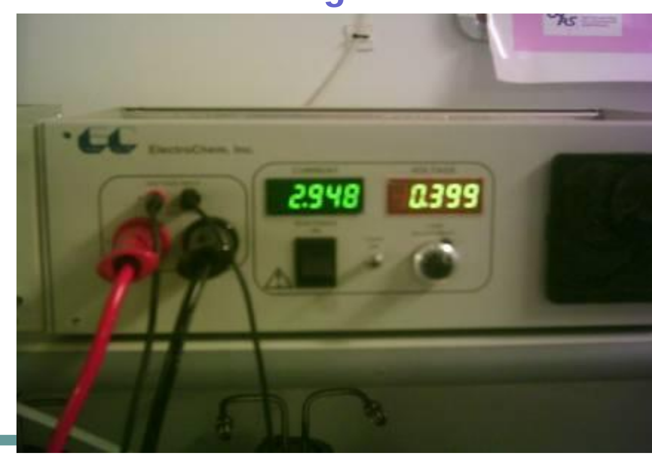
H_2/O_2 , Nafion 115, 80°C, 3 bars.

Fuel cell Test station

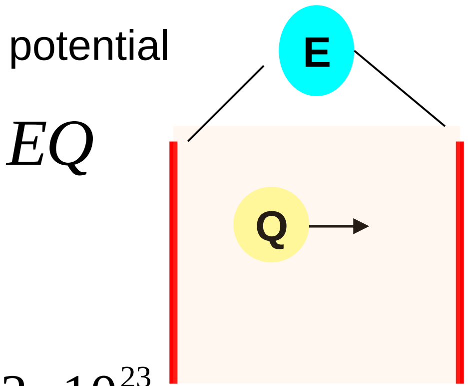
Fuel cell test station
MTS – 150 Electrochem

Gas management unit

Load management unit



Gibbs free energy and Voltage!



$$W_{elec} = EQ$$

$$Q = nF$$

$$N_A = 6.02 \times 10^{23}$$

$$q = 1.6 \times 10^{-19}$$

$$F = 96487$$

$$\Rightarrow \begin{cases} W_{elec} = nFE \\ \Delta g_{rxn} = -nFE \end{cases}$$

$$\Delta g_{rxn} = \Delta g(product) - \Delta g(reactant)$$

PEM Fuel cell ⇒ $H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O$

$$\Delta g_{rxn} = (\Delta g)_{H_2O} - (\Delta g)_{H_2} - \tfrac{1}{2}(\Delta g)_{O_2}$$

$$E^0 = -\frac{\Delta g^0_{rxn}}{nF}$$

$$E^0 = -\frac{-237000\, {}^{J}\!/\!{}_{mol}}{2\, {}^{mole}\!/\!{}_{mol} \times 96487\, {}^{C}\!/\!{}_{mol}} = 1.23V$$

Direct Methanol Fuel Cell

DMFC ⇨ $$CH_3OH + \tfrac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

$$\Delta g_{rxn} = (\Delta g)_{CO_2} + 2(\Delta g)_{H_2O} - (\Delta g)_{CH_3OH} - \tfrac{3}{2}(\Delta g)_{O_2}$$

$$E^0 = -\frac{\Delta g^0_{rxn}}{nF} = 1.199 \text{ V}$$

$$\begin{cases} CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- & \textbf{Anode} \\ \tfrac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O & \textbf{Cathode} \end{cases}$$

Nernst Equation

$$E = E^0 - \frac{RT}{nF} \ln \frac{\prod a_{product}^{v_i}}{\prod a_{reactant}^{v_i}}$$

How reversible Voltages vary as a function of concentration, pressure and temperature

For PEM Fuel cell $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{H_2O}}{a_{H_2} a_{O_2}^{1/2}} \quad \Rightarrow \quad E = E^0 - \frac{RT}{2F} \ln \frac{1}{p_{H_2} p_{O_2}^{1/2}}$$

Practical examples

H_2- Air Fuel cell **Air instead of oxygen?**

$$E = E^0 - \frac{RT}{2F}\ln\frac{1}{1\times(0.21)^{1/2}}$$

$$E = 1.229 - \frac{(8.314)\times(298.15)}{2\times 96487}\ln\frac{1}{(1)(0.21)^{1/2}} = 1.219V$$

Pressurized H2- Air Fuel cell **Using compressor?**

$$E = E^0 - \frac{RT}{2F}\ln\frac{1}{3\times(5\times 0.21)^{1/2}}$$

$$E = 1.229 - \frac{(8.314)\times(298.15)}{2\times 96487}\ln\frac{1}{(3)(5\times 0.21)^{1/2}} = 1.244V$$

Ideal reversible Fuel cell efficiency

$$\eta = \frac{Useful}{Total}$$

$$\eta = \frac{work}{\Delta h} \longrightarrow \eta_{FC} = \frac{\Delta g}{\Delta h}$$

$$\begin{cases} \Delta g^0 = -237.3\, {}^{kJ}\!/_{mol} \\ \Delta h^0 = -286\, {}^{kJ}\!/_{mol} \end{cases} \Rightarrow \eta_{FC} = \frac{-273.3}{-286} = 0.83$$

$$\eta_{Carnot} = \frac{T_H - T_L}{T_H}$$

Practical, real or operational Fuel cell Efficiency

$$\eta = (\eta_{thermo}) \times (\eta_{voltage}) \times (\eta_{fuel})$$

$$\eta_{FC} = \frac{\Delta g}{\Delta h}$$

$$\eta_{voltage} = \frac{V}{E}$$

$$V = E - V_{act} - V_{ohm} - V_{dif}$$

$$\eta_{fuel} = \frac{i/2F}{\upsilon_{fuel}}$$

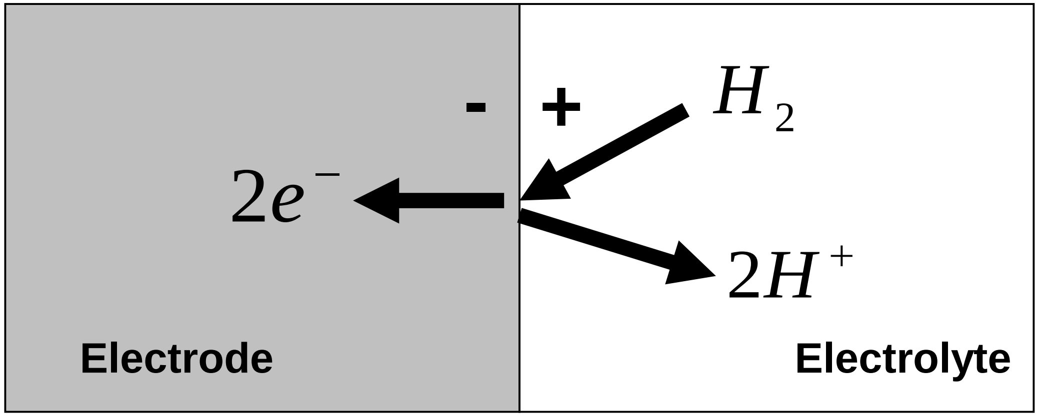
$$\eta_{fuel} = \frac{1}{\lambda}$$

$$\eta = \left(\frac{\Delta g}{\Delta h}\right)\left(\frac{V}{E}\right)\left(\frac{1}{\lambda}\right)$$

Chemical and Electrochemical reactions

- In chemical reactions charge transfer occurs directly between two chemical species
- In electrochemical reactions charge transfer occurs between electrode and a chemical species

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



Charge, Current and Mass Flow!

$$i = \frac{dQ}{dt}$$

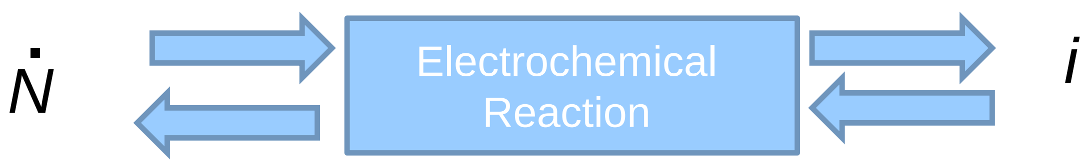
$$Q = nFN$$

Electron production in reaction for each mole

Total Charge

Charge of one mole electron

Number of total moles



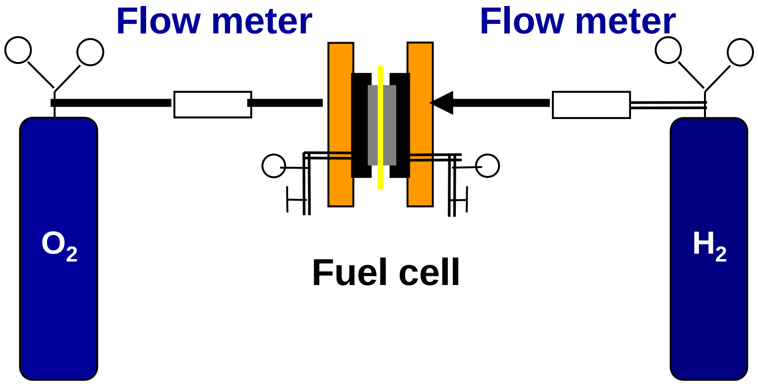
$$i = nF\frac{dN}{dt}$$

Electrical current

Molar rate: mol/s

Example

How much current can a PEM fuel cell produce if the Hydrogen flow rate is 5 sccm at STP?



$$PV = NRT$$

$$\frac{dN}{dt} = \frac{P(dV/dt)}{RT}$$

$$\frac{dN}{dt} = \frac{(1atm)(0.005L/\min)}{(0.08314L.atm/(molK))(298K)} = 2.05\times10^{-4}\, molH_2/\min$$

$$i = nF\frac{dN}{dt} = 2\times(96487C/mol)\times(2.05\times10^{-4}\, molH_2/\min)\times(1\min/60s)$$

$$\boxed{i = 0.657A}$$

Butler- Volmer equation

$$j_0 = j_0^0 \frac{c^*}{c^{0*}}$$

Fuel cell current density A/cm²

Reactant concentration mol/cm³

Transfer coefficient

product concentration mol/cm³

$$j = j_0^0 \left(\frac{c_R^*}{c_R^{0*}} e^{\alpha nF\eta/(RT)} - \frac{c_P^*}{c_P^{0*}} e^{-(1-\alpha)nF\eta/(RT)} \right)$$

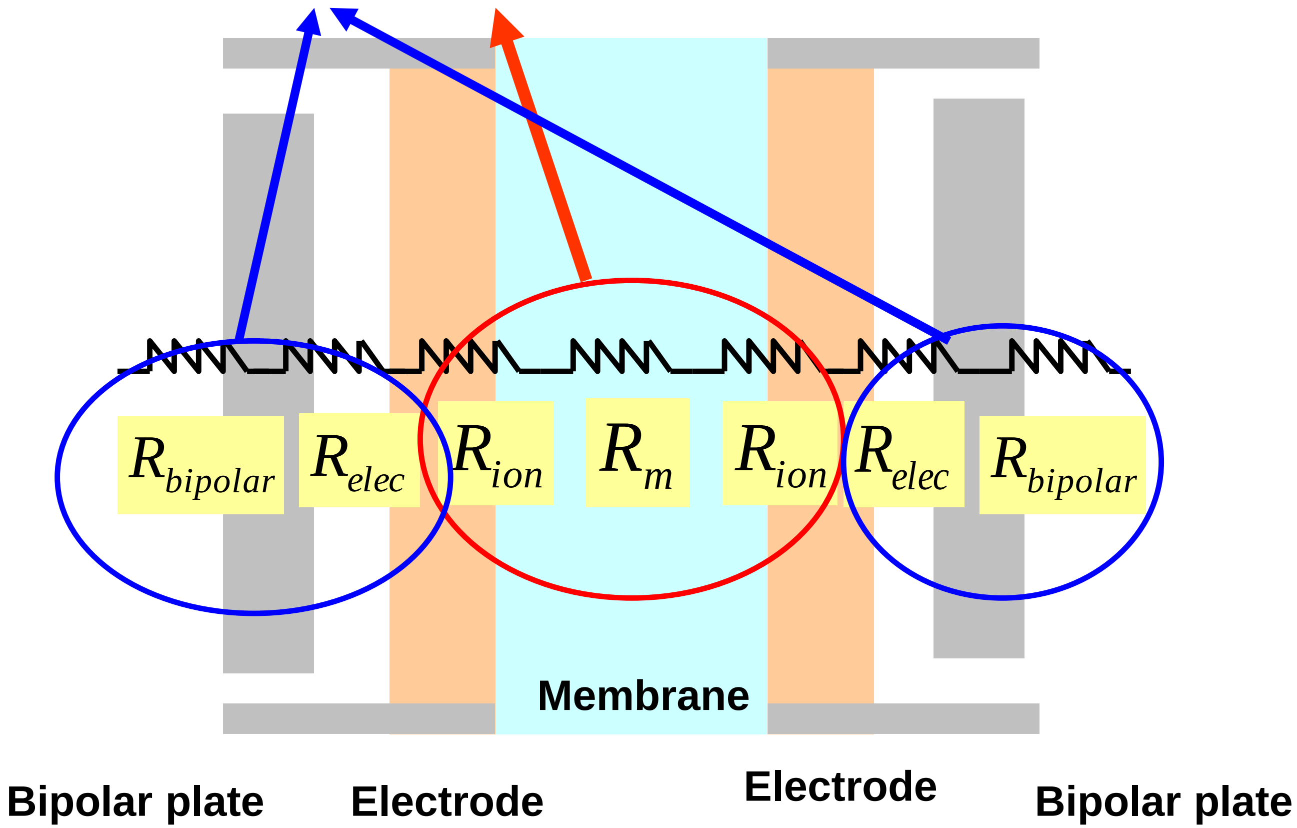
Reference product concentration mol/cm³

Reference reactant concentration mol/cm³

Exchange current density
A/cm² at reference condition

Fuel cell resistances

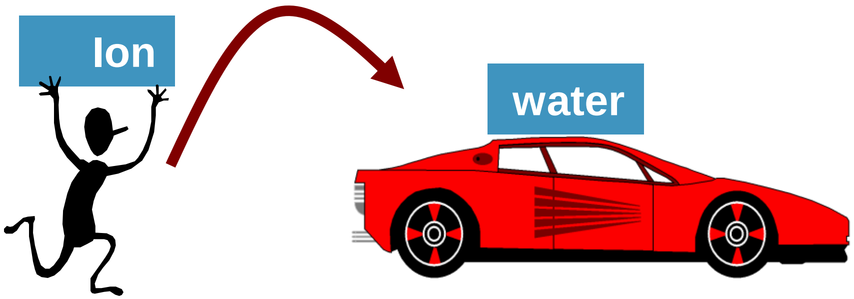
$$\eta_{ohmic} = iR_{ohmic} = i\left(R_{elec} + R_{ion}\right)$$



Vehicle mechanism

Ion Transport Mechanism

Ions are transported through free volume space by hitching a ride

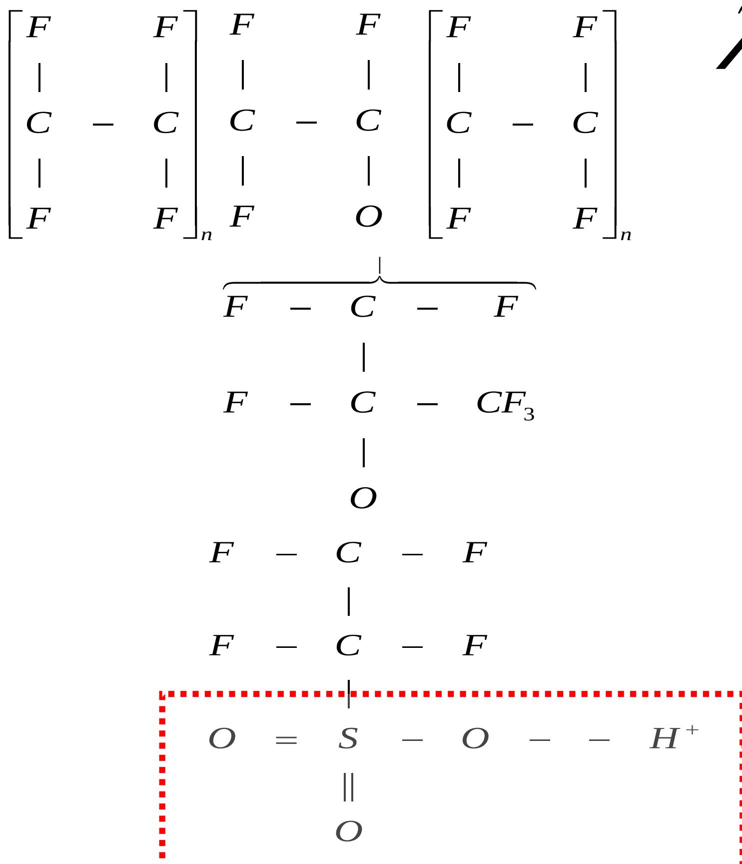


$$H^{+} + H_2O \rightarrow H_3O^{+}$$

- **Water is a common vehicle**
- **Ion conductivity is strongly dependent on Membrane water content**
- **Membrane should maintained near full water saturation**

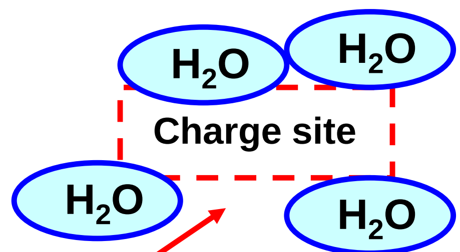
Nafion®

Nafion Structure



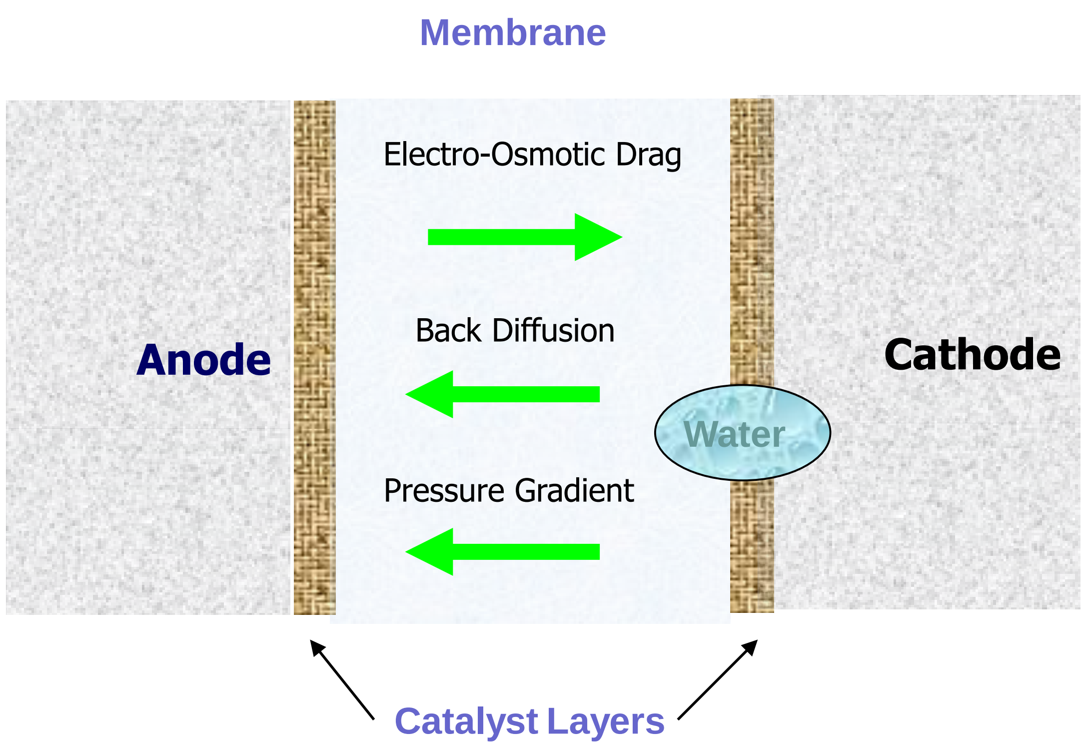
$$\lambda = \frac{\text{The number of the absorbed water molecules}}{\text{Number of ionic site}}$$

(0-22) Water content

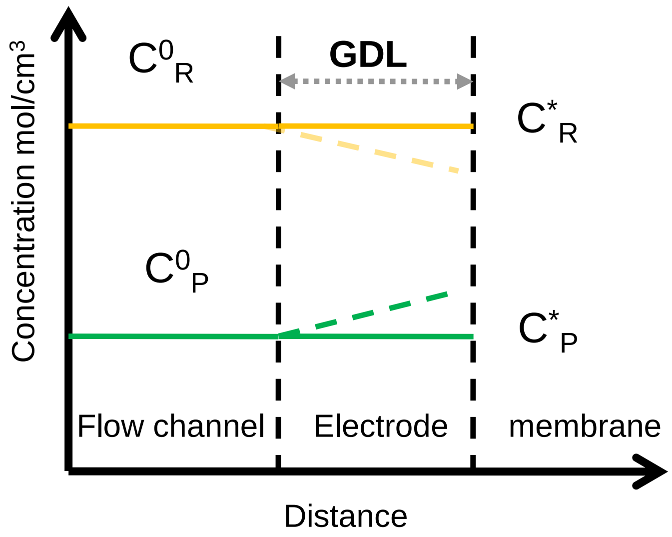


Conductivity and water content are strongly related

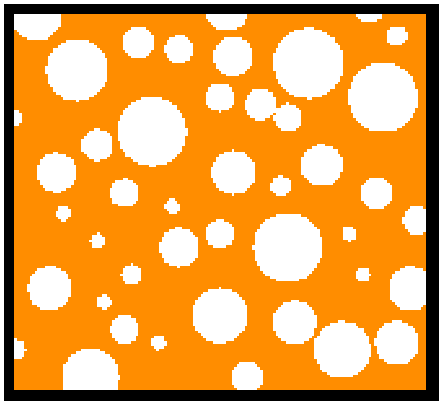
Water transport in membrane

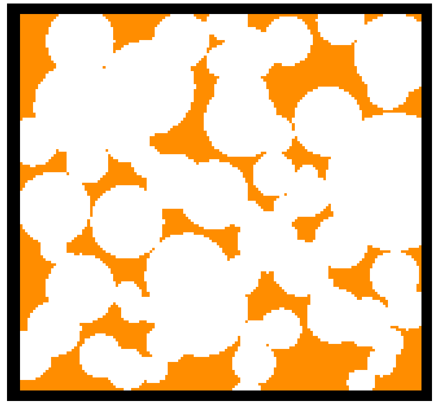


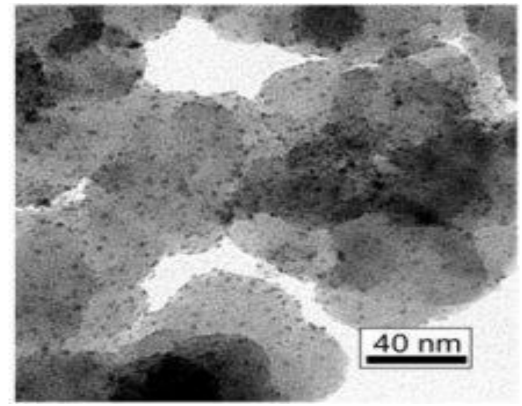
Electrochemical reaction drives diffusion



Porous media







Total volume

Pore volume

$$V = V_s + V_p$$

Solid volume

Specific Area, 1/cm

$$A_a = \frac{S_p}{V}$$

Porosity

$$\varepsilon = \frac{V_p}{V}$$

$$D^{eff} = D\,\varepsilon^{1.5}$$

Mass transport in electrodes

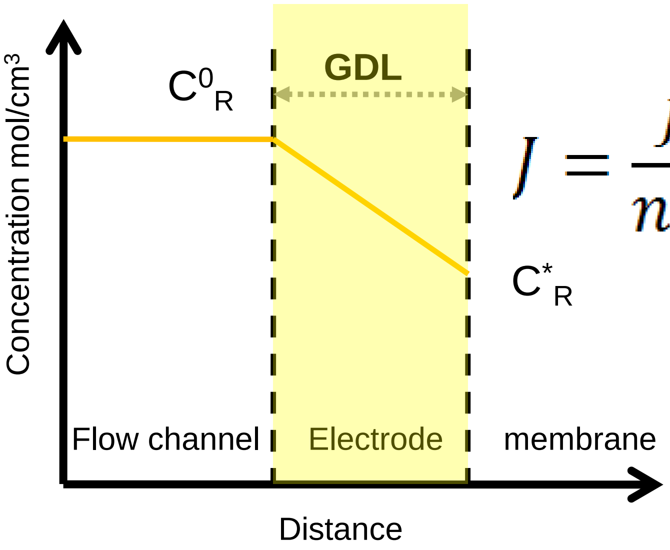
$$J_{diff} = -D\frac{dc}{dx}$$

Ficks law

$$J_{diff} = -D^{eff}\frac{c_R^* - c_R^0}{\delta}$$

$$j = -nFD^{eff}\frac{c_R^* - c_R^0}{\delta}$$

$$c_R^* = c_R^0 - \frac{j\delta}{nFD^{eff}}$$



$$J = \frac{j}{nF}$$

Limiting current density

$$j = -nFD^{eff}\frac{c_R^* - c_R^0}{\delta}$$

$$c_R^* = 0 \Rightarrow j_L = nFD^{eff}\frac{c_R^0}{\delta}$$

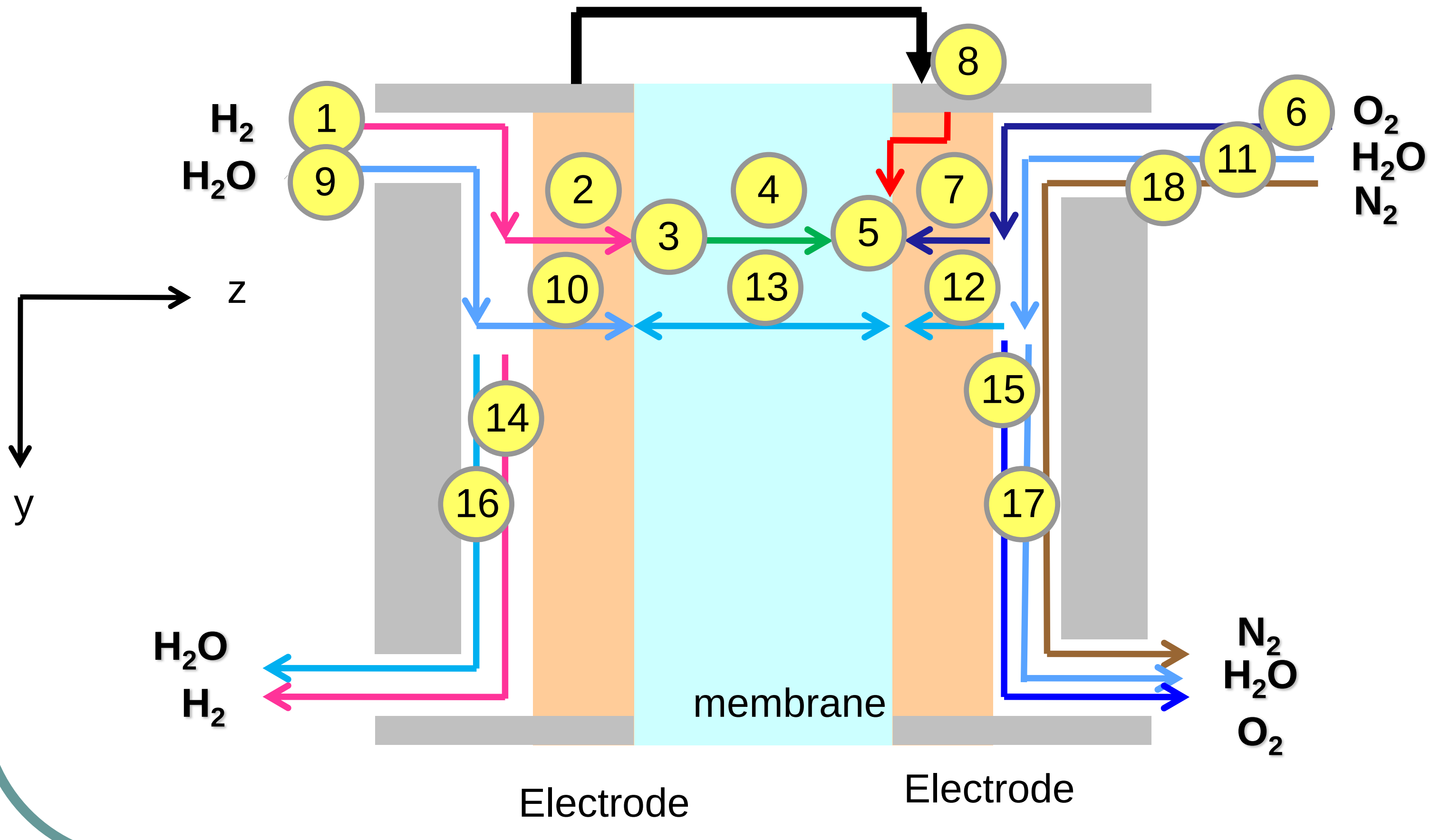
$c_R^0 \nearrow$ By designing good flow structure

$D^{eff} \nearrow$ And $\delta \searrow$ By optimizing fuel cell operation condition and electrode design

Put all together

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

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



1D Model

1 6 9 11 16 14 15 16 17 18 Reactant transport in channel

2 7 10 12 Reactant transport in porous electrode

3 Electrochemical reaction, Hydrogen decomposition

4 Ion transport in polymer membrane

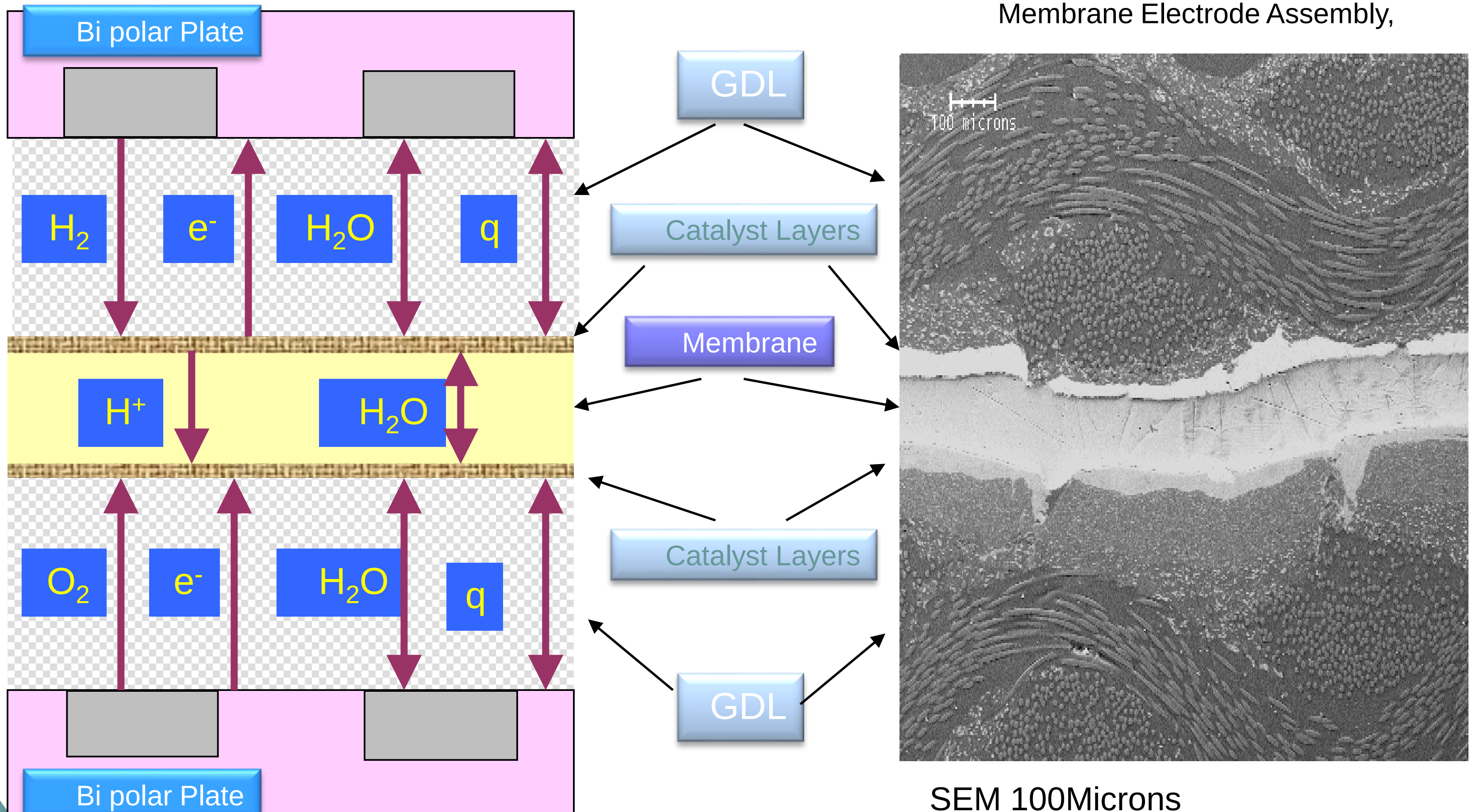
5 Electrochemical reaction, water production

8 Electron transport in porous electrodes and bipolar plates

13 Water transport in polymer membrane

Move to 2D and 3D

Membrane Electrode Assembly,

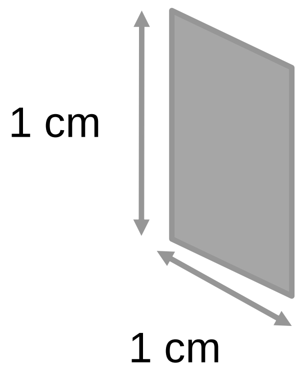


SEM 100Microns

From Single cell to Stack

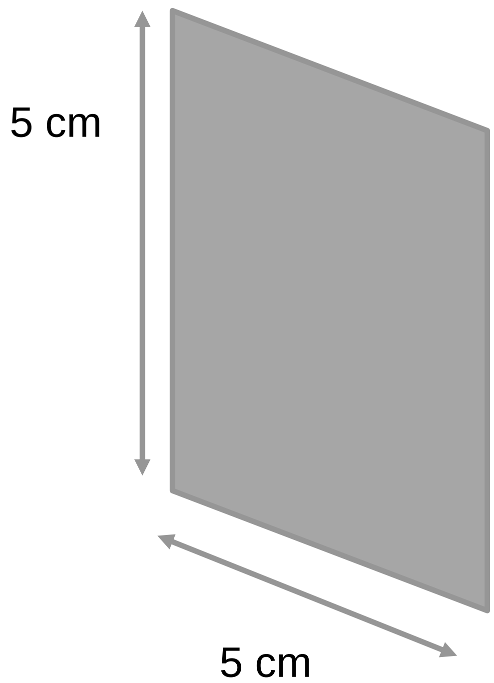
MEA

$1\ A/cm^2$



I=1 A
V=0.6 V

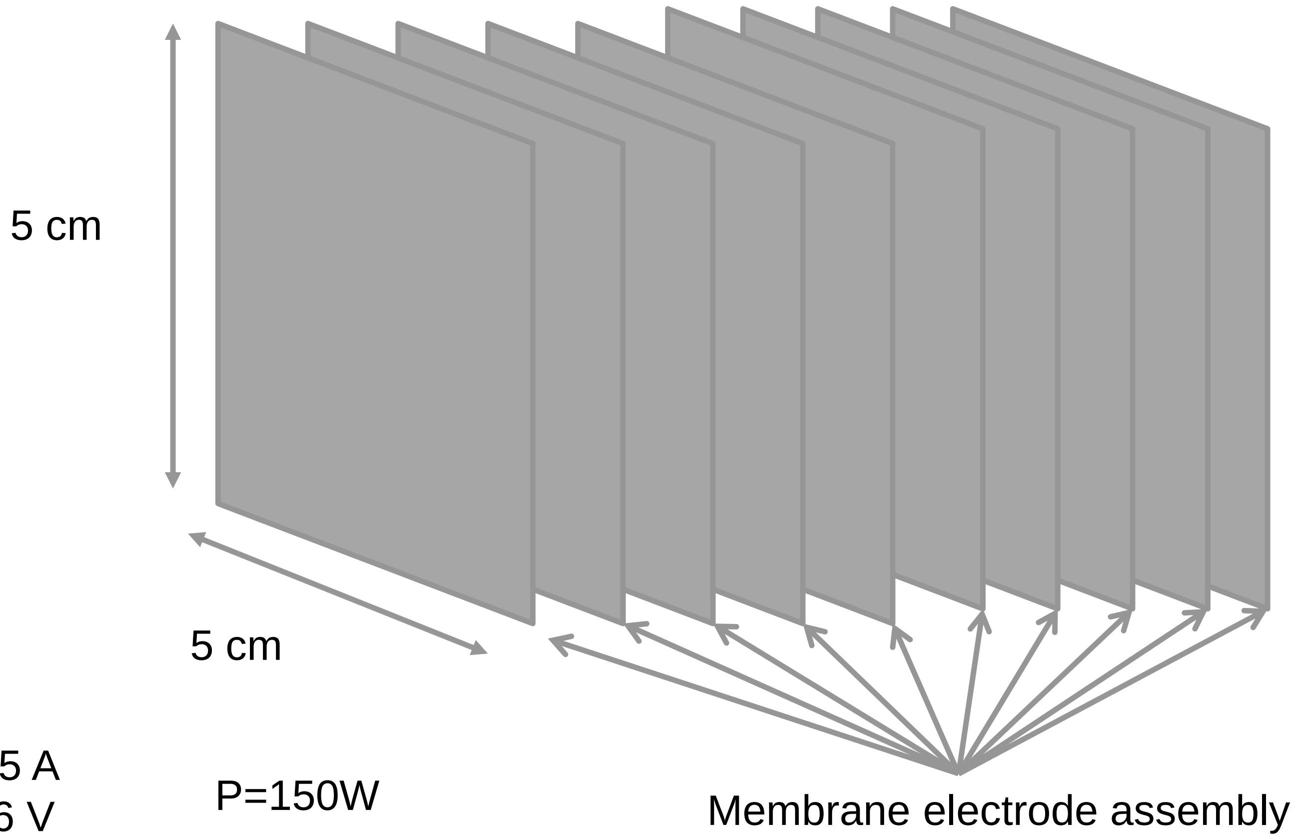
P=0.6W



I=25 A
V=0.6 V

P=15W

Fuel cell stack



I=25 A
V=6 V

P=150W

Storage effectiveness and efficiencies

$$\text{Mass storage density} = \frac{\text{Mass of } H_2 \text{ stored}}{\text{Total system mass}} \times 100 \quad \%H_2/\text{Kg}$$

$$\text{Volume storage density} = \frac{\text{Mass of } H_2 \text{ stored}}{\text{Total system volume}} \quad \text{Kg } H_2 /\text{L}$$

$$\text{Gravimetric energy density} = \frac{\text{Stored enthalpy of fuel}}{\text{Total system mass}} \quad \text{kWh/Kg}$$

$$\text{Volumetric energy density} = \frac{\text{Stored enthalpy of fuel}}{\text{Total system volume}} \quad \text{kWh/L}$$

Hydrogen storage

Compressed H_2 300-700 bar

About 10% of energy content of hydrogen should be expended to pressurized It to 300 bar

Liquid H_2 22 K

About 30% of energy content of hydrogen should be expended in this case

Metal Hydride Iron, titanium, manganese, nickel and chrome alloys

Metal hydride can absorb large amount of hydrogen in form of H atoms

Upon slight heating, the hydrides will release their stored hydrogen

But: Metal Hydrides are expensive and heavy