Workshop on Fuel Cells for Automotive Applications

A.M. Kannan (amk@asu.edu)
Arizona State University

Chulalongkorn University
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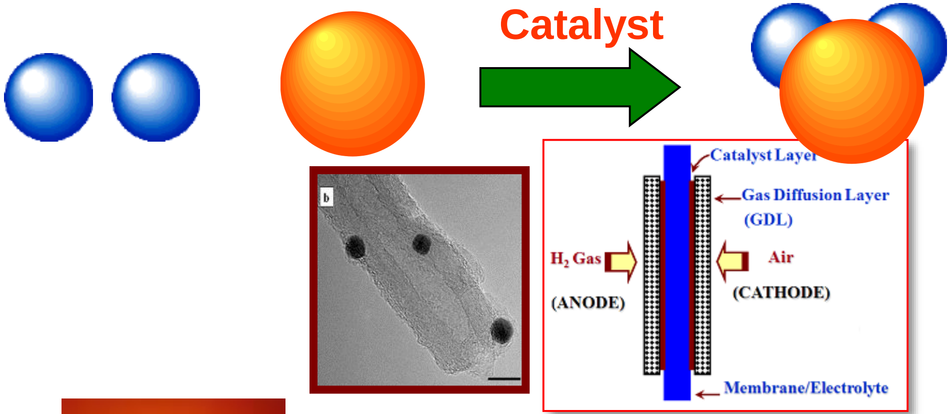
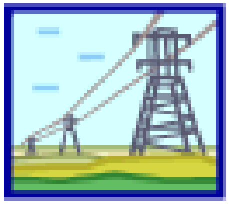
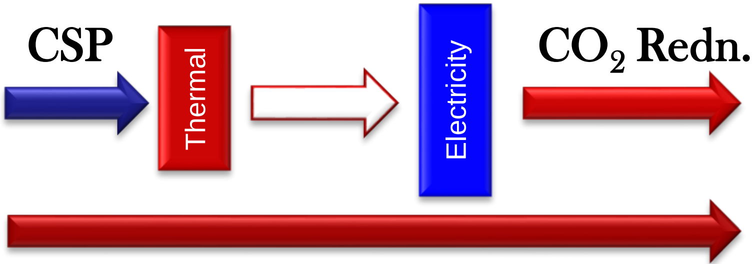
FC Lab Research

Electrocatalysis for Water Electrolyzer, Fuel Cells, and CO_2 Reduction







CSP

Thermal

Electricity

CO_2 Redn.

Photoelectrochemical cell

Photocatalysis – Cu_2O

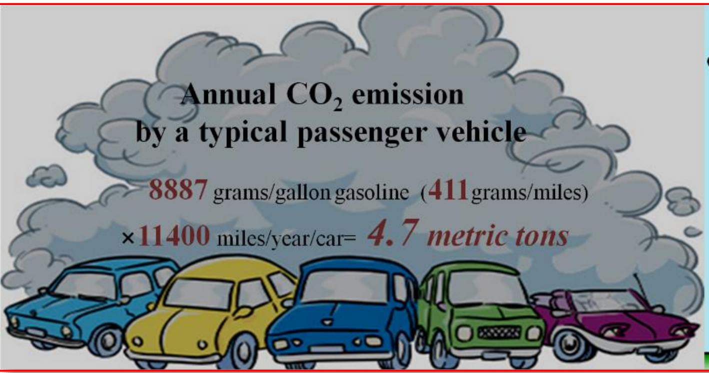
Chemical Energy

Solar Fuels

H_2

Methanol

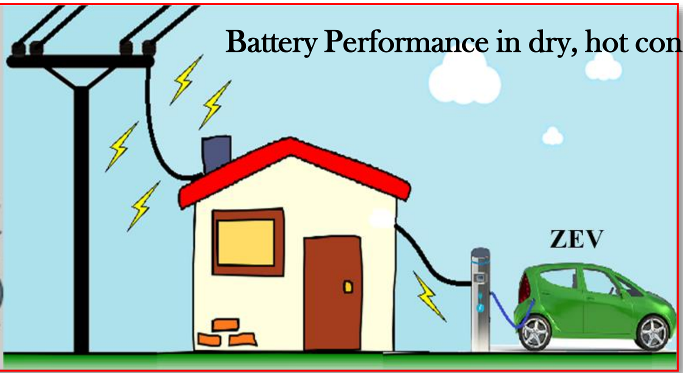
Hydrocarbon



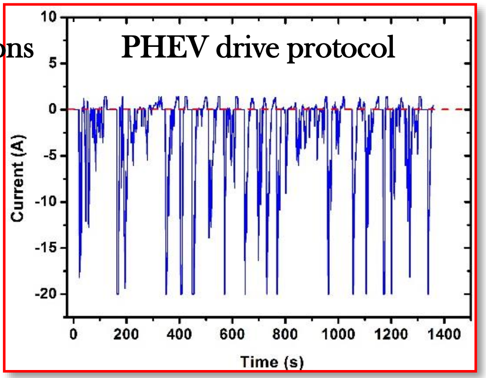
Annual CO_2 emission
by a typical passenger vehicle

8887 grams/gallon gasoline (411 grams/miles)

×11400 miles/year/car= *4.7 metric tons*

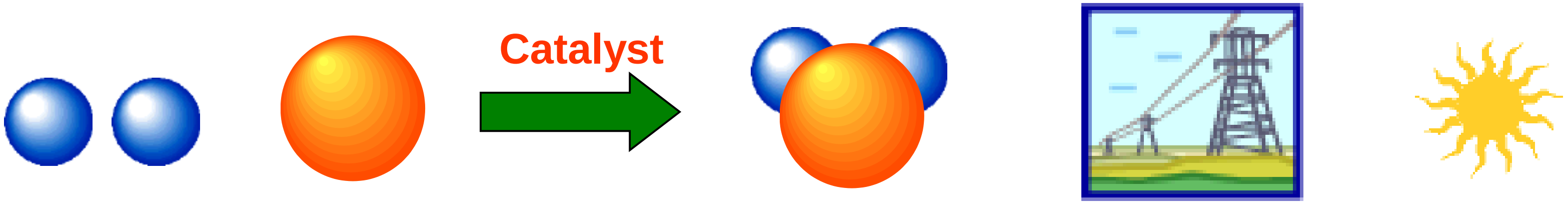


Battery Performance in dry, hot conditions



PHEV drive protocol

WHAT IS A FUEL CELL?

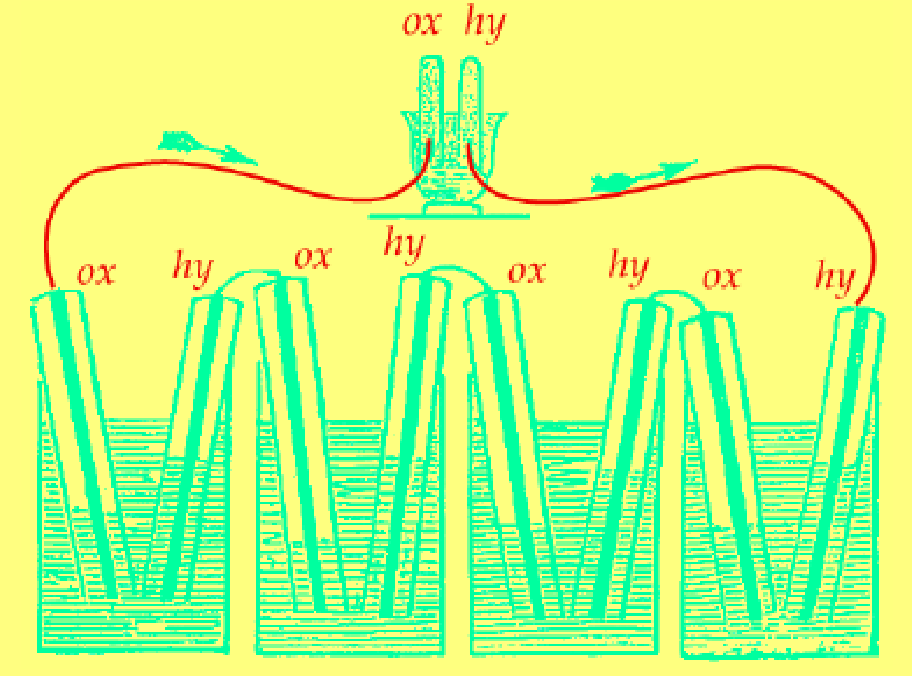


$$H_2 + \tfrac{1}{2} O_2 \xrightarrow{\text{Catalyst}} H_2O + \text{Electricity} + \text{Heat}$$

- Fuel cell is an Energy Conversion Device (like battery), which converts continuously the free energy change of a chemical reaction between a fuel and oxygen directly into electricity and heat with invariant electrodes and electrolyte
- Although the operation of a FC is similar to a battery, it does not require the time consuming process of recharging
- Fuel cells can provide electricity continuously, unlike the batteries, as long as the fuel and oxidant are supplied

History of fuel cells

- First known demonstration by Sir William Robert Grove in 1839
  - It operated with separate Pt Electrodes in O2 and H2 gases, submerged in a dilute sulfuric acid electrolyte, essentially reversing a water electrolysis reaction



History of fuel cells

- Ludwig Mond – 1889
  - Charles Langer
  - First practical device using air and industrial coal gas
- Dr. Francis Thomas Bacon – 1932
  - Bacon cell - AFC
  - Developed a fuel cell stack capable of producing 5kW – 1959
- Harry Karl Ihrig – 1959 Allis Chalmers Tractor
  - Fuel cell vehicle
  - 1008 cells – 15kW

History of fuel cells (cont.)

- NASA's Gemini program
  - Developed the first PEMFC by William Grubb at the GE in 1955
- NASA's Appolo program
  - Switched to AFC due to shorter life of PEMFC
- LANL – 1980s
  - An order of magnitude reduction of noble metal loading
- Ballard – 1993
  - First marketable fuel cell stack for vehicles

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History of fuel cells (cont.)

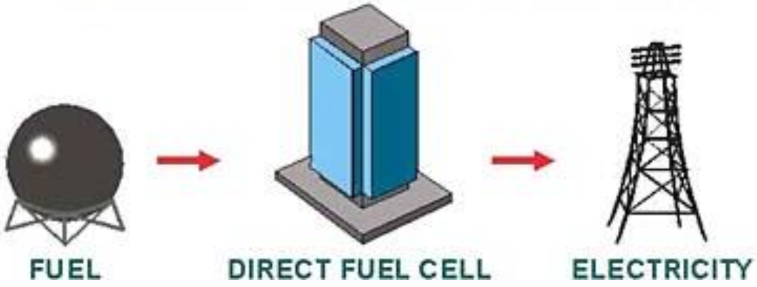
- Currently, the PEMFC and SOFC are the most promising candidates for conventional power system replacement, with MCFC also under continued development
- The AFC and PAFC have all ceased development efforts, with exception of niche applications
- Based on the continued market drivers of dwindling petroleum resources and environmental concerns, it is evident that, despite lingering technical challenges, continued development of various FC systems will evolve towards potential [illegible] applications.

WHY FUEL CELLS?

COVENTIONAL POWER PLANT

- Carnot cycle limited
- Low efficiency
- Air Pollution

DIRECT FUEL CELL POWER PLANT



- No Carnot limitation
- High Efficiency
- Clean Energy System
- No pollution
- Quiet
- No Photochemical smog precursor
- No VOC
- Modular
- Local

Smog

- Under the right conditions, the smoke and sulfur dioxide produced from the burning of coal can combine with fog to create **industrial smog**.
- The most famous London smog event occurred in December, 1952 when five days of calm foggy weather created a toxic atmosphere that claimed about 4000 human lives.
- However, the burning of fossil fuels like gasoline can create another atmospheric pollution problem known as **photochemical smog**.

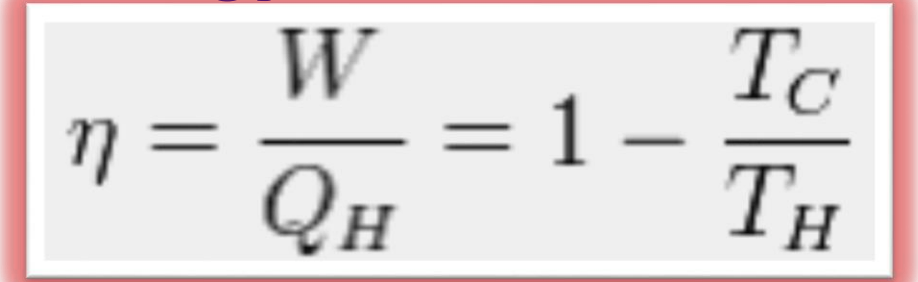
GEOGRAPHY

Photochemical Smog

- Photochemical smog is a condition that develops when **primary pollutants** (oxides of nitrogen and volatile organic compounds created from fossil fuel combustion) interact under the influence of **sunlight** to produce a mixture of hundreds of different and hazardous chemicals known as **secondary pollutants**.

Carnot Cycle

- Efficient existing cycle capable of converting a given amount of thermal energy into work.



$$\eta = \frac{W}{Q_H} = 1 - \frac{T_C}{T_H}$$

W : Work done by the system (energy exiting the system as work),

Q_H : Heat put into the system (heat energy entering the system),

T_C : Absolute temperature of the cold reservoir, and

T_H : Absolute temperature of the hot reservoir.

What is the Motivation for H2 Energy?

- **Market forces, Greenery and Innovation** are shaping the future of our industry and propelling us inexorably towards H2 energy.
- Those who don’t pursue it . . . Will rue it

-Frank Ingriselli, President, Texaco Technology Ventures

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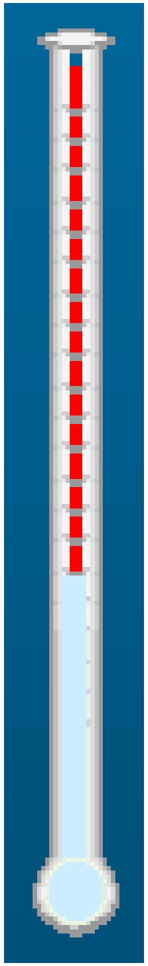
Fuel cell types

FC Technologies	Efficiency	Temp.
➢Solid Oxide	45-65 %	800 °C
➢Molten Carbonate	50 %	650 °C
➢Phosphoric Acid	40%	200 °C
➢Alkaline	50-60 %	100 °C
➢Direct Methanol	40 %	80 °C
➢Proton Exchange Membrane (PEM)	40%	80 °C



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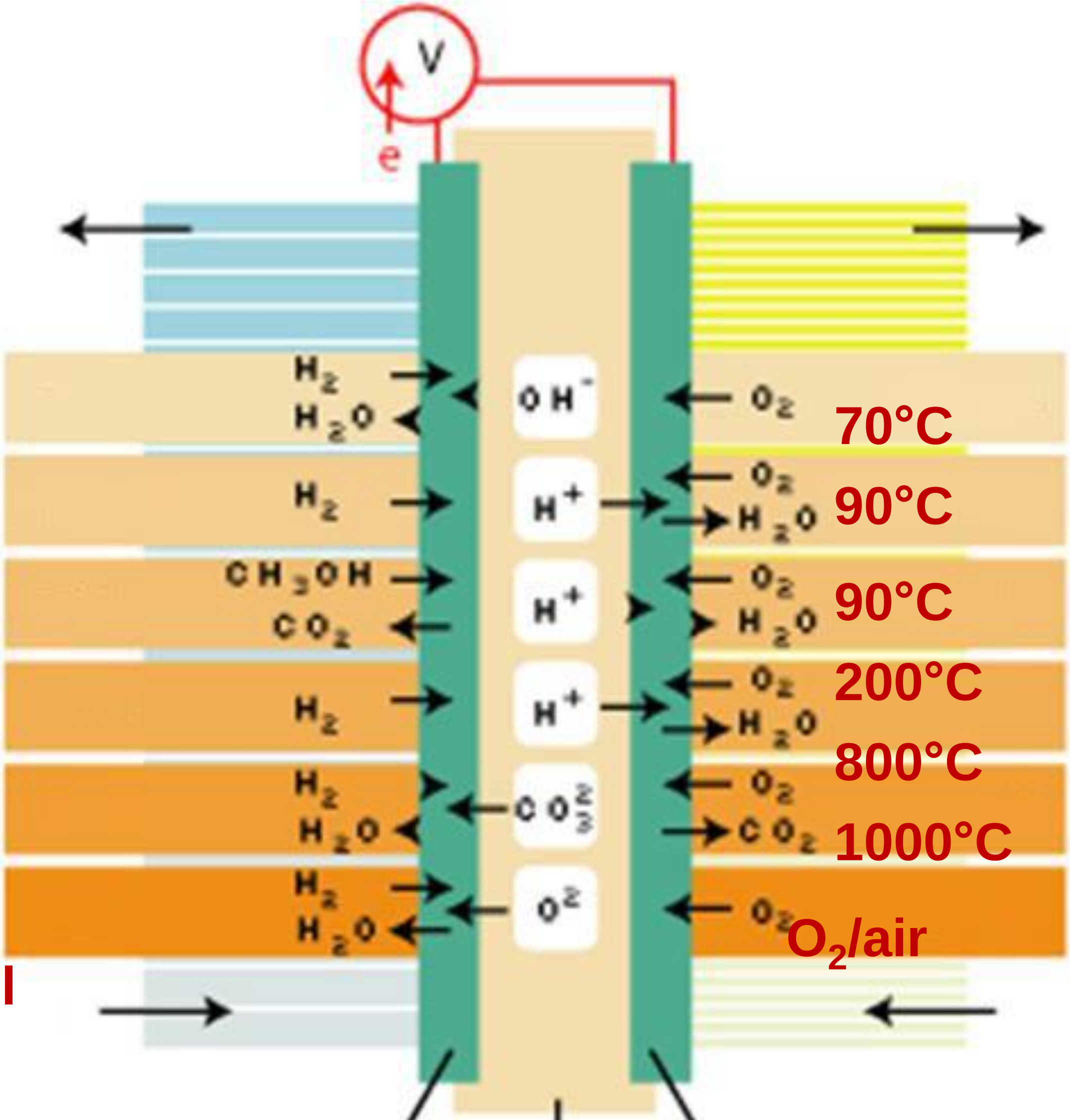
Types of fuel cells

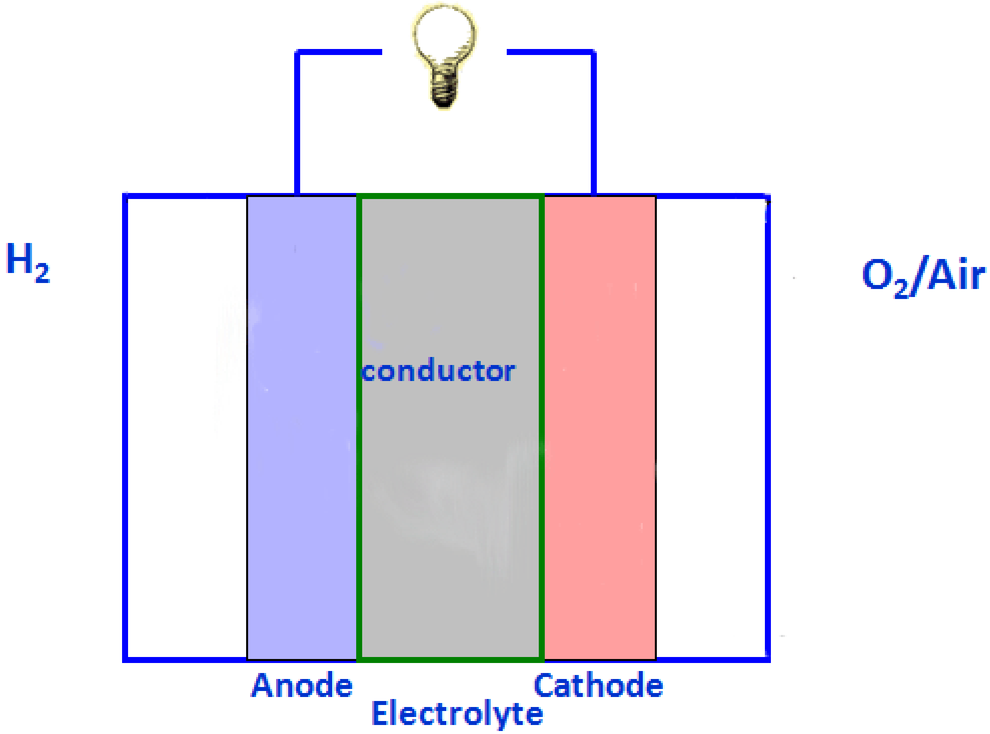


AFC
PEMFC
DMFC
PAFC
MCFC
SOFC
Fuel

70°C
90°C
90°C
200°C
800°C
1000°C
O_2/air

Anode
Electrolyte
Cathode

Proton Exchange Membrane Fuel Cell



Electrolyte	Nafion membrane
Catalyst	Platinum-carbon
Anode fuel	Hydrogen
Cathode gas	Oxygen/air
Temperature	90°C
Efficiency	35-60%

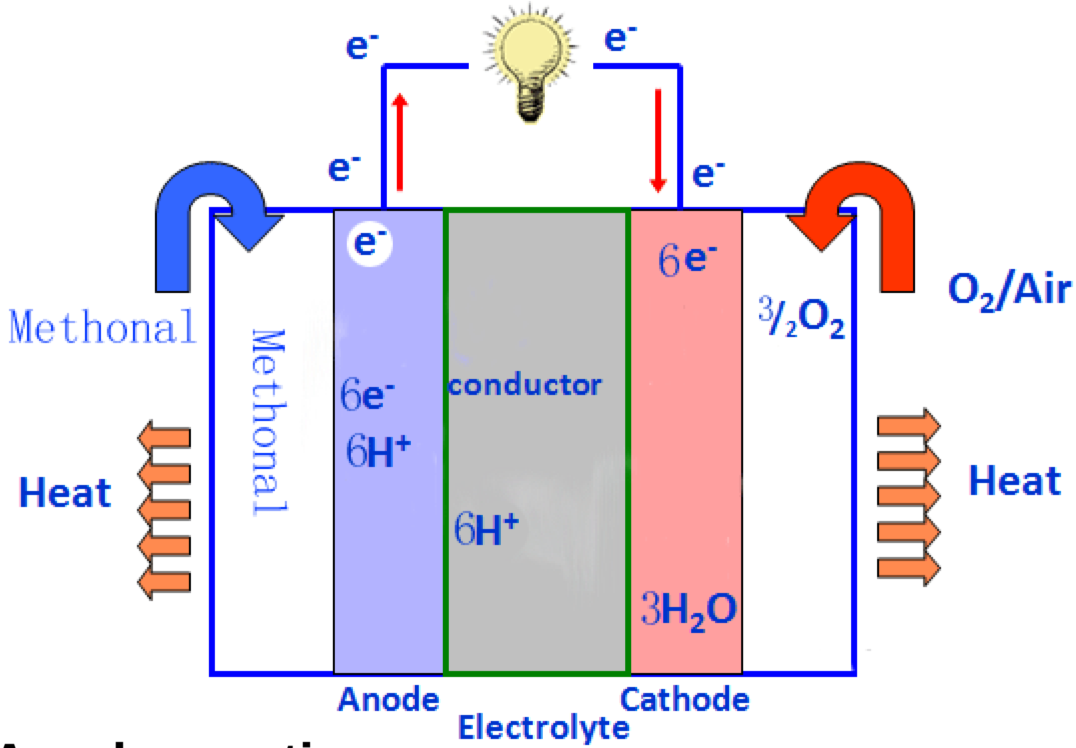
Anode reaction:

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

Cathode reaction:

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

Direct Methanol Fuel Cell



Electrolyte	Nafion membrane
Catalyst	Platinum based alloys
Anode fuel	Methanol solution in water
Cathode gas	Oxygen/air
Temperature	90°C
Efficiency	35-40%

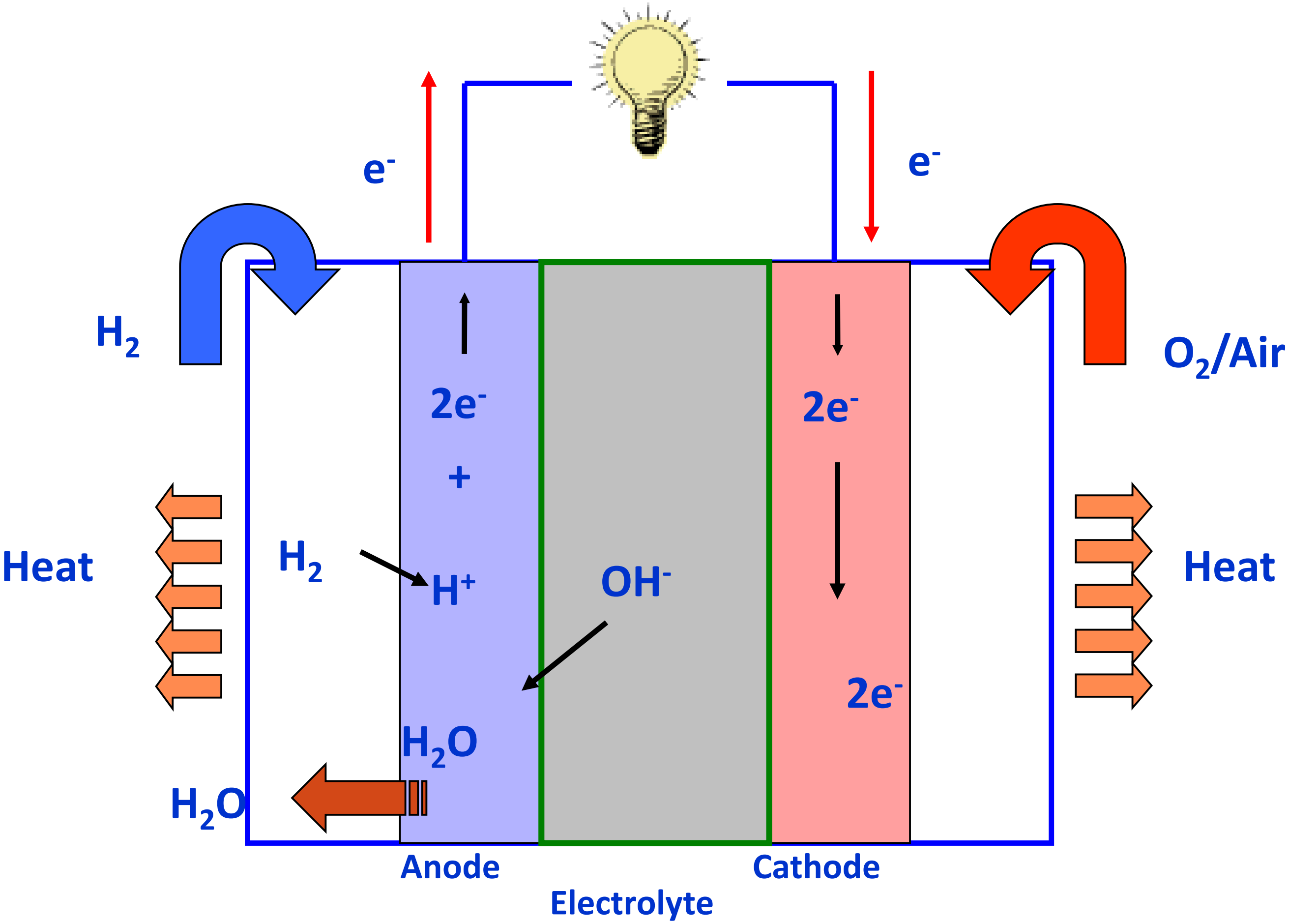
Anode reaction:

$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode Reaction:

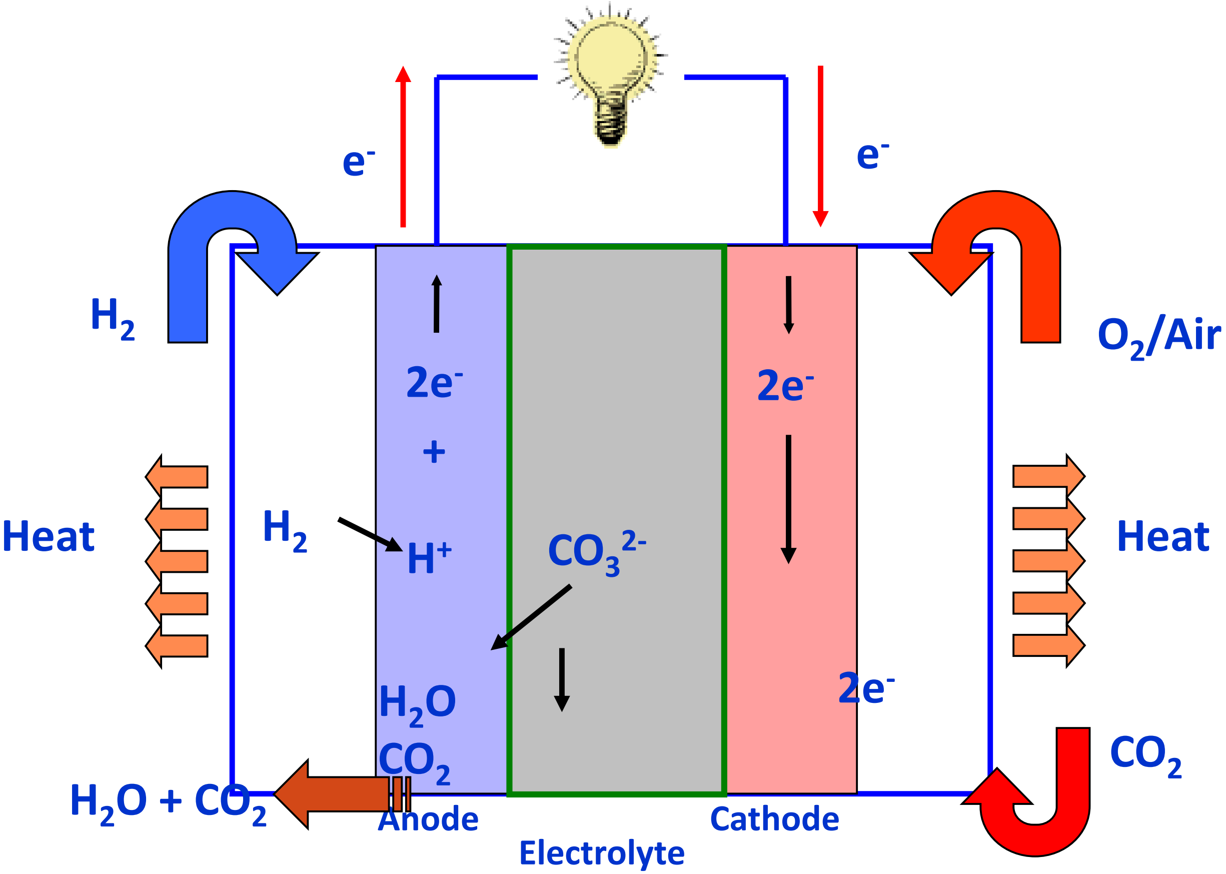
$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

AFC



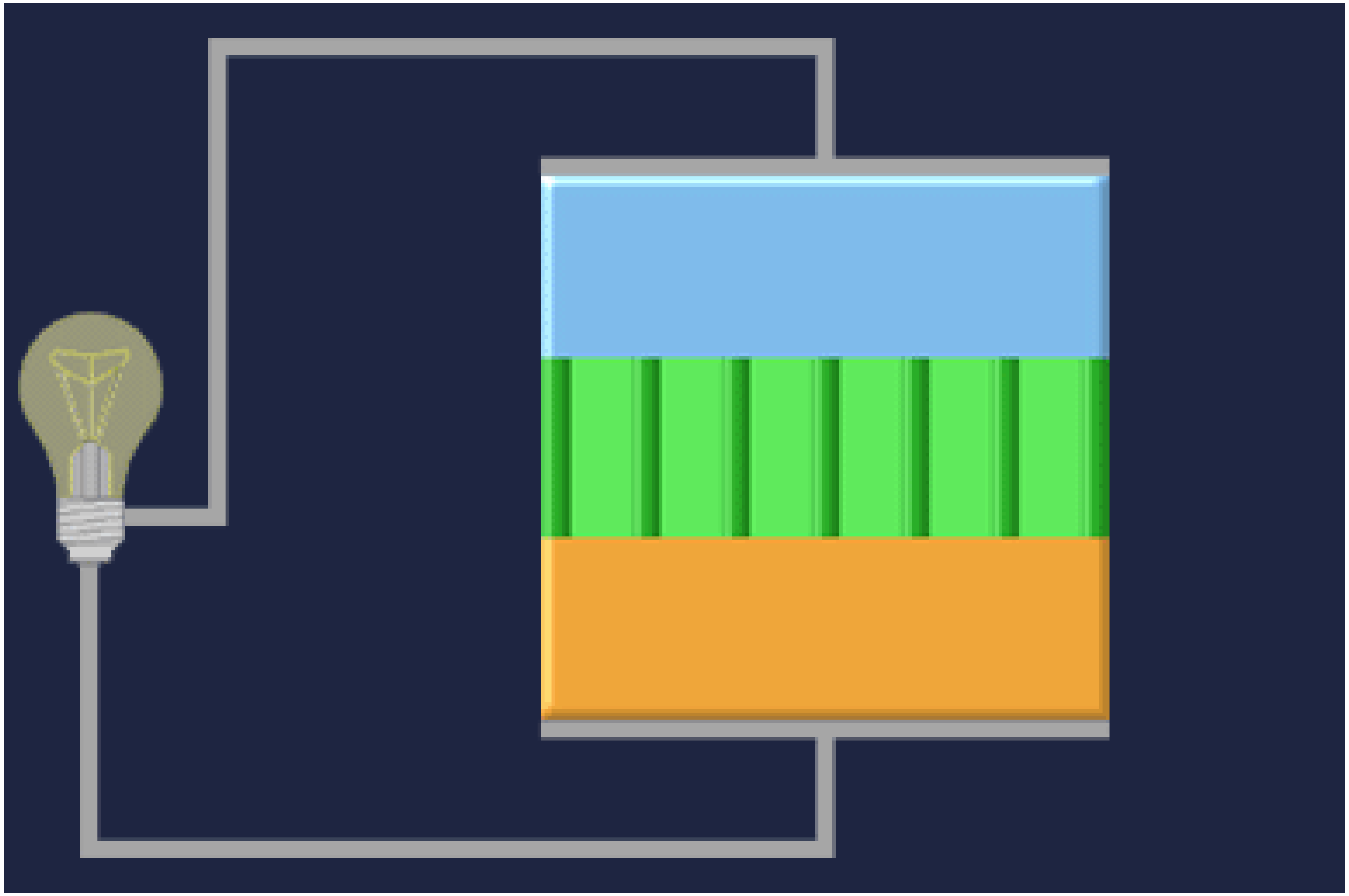
Net reaction: $H_2 + ½O_2 \rightarrow H_2O$ + heat

MCFC



Net reaction: $CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$ + heat

SOFC

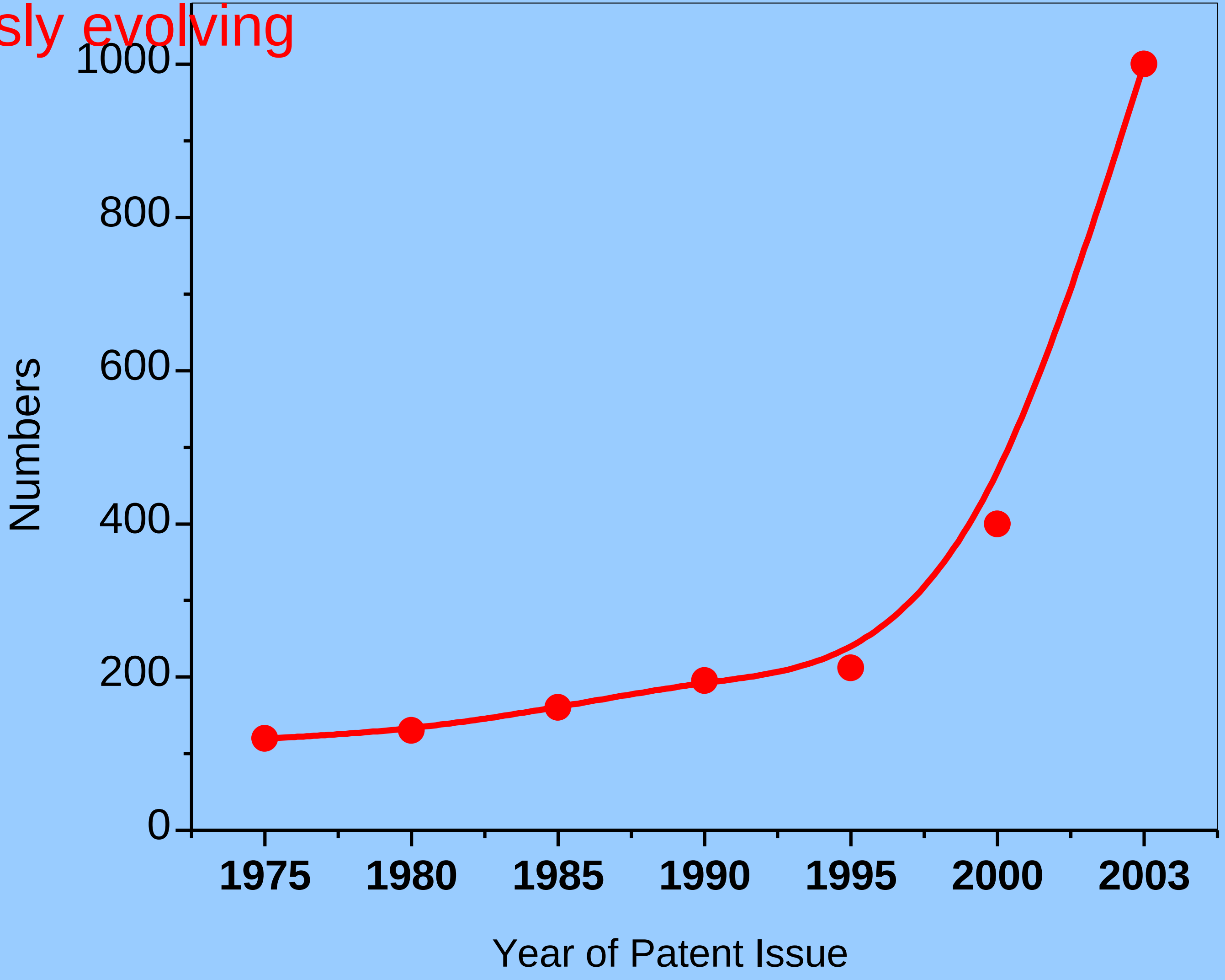


Reactants for FCs

	Electrocatalyst	Anode fuel	Cathode gas
PEMFC	Platinum based	Hydrogen	Oxygen or air
DMFC	Platinum based alloys	Methanol solution in water	Oxygen or air
BFC	Glucose oxidase – carbon nanotubes	Glucose solution in water	Oxygen
PAFC	Platinum based	Hydrogen	Oxygen or air
AFC	Platinum based	Hydrogen	Oxygen
MCFC	Non-precious metals	Hydrogen or methane	Air
SOFC	Non-precious metals	Hydrogen or methane	Air

Timeline of US Patents

The Science and Technology of FCs are fascinating and continuously evolving



Top 10 Patent applns. in 2010

1 Toyota	381
2 Panasonic	141
3 UTC	118
4 Honda	103
5 General Motors	103
6 Samsung	79
7 Daimler	75
8 Toshiba	61
9 Nissan	52
10 Sony	52

All the Toyota's FC patents are open to public now

Fundamental Advantages

- A potential for relatively **high operating efficiency**, scalable to all size power plants
- If H_2 is used as a fuel, **pollution emissions are strictly a result of H_2 production processes**
- **No moving parts**, with the exception of pumps, compressors, and blowers to drive fuel and air
- **Multiple choices of potential fuel feedstocks**, from petroleum products/natural gas to renewable ethanol or biomass H_2 production
- **A nearly instantaneous recharge** capability compared to batteries

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Technical Limitations of FCs

- Before FCs can make a major impact on future power generation for various applications, the following technical limitations common to all the FC systems must be overcome:

1. **Cost:**
    1. To be competitive with ICE and stationary power generations systems, FC should reach ~$ 30 and ~$1000/kW through alternative materials and construction methods
    2. Cost of catalysts is still significant but not dominant
    3. Mass production methods are key components to commercial viability of FC systems

FCs should not be seen as a panacea for every power generating applns in the world

Technical Limitations of FCs

2. Durability and Reliability:

1. The performance of every FC gradually degrades with time due to a variety of phenomena
2. Automotive FC must withstand load cycling and freeze-thaw environmental swings with an acceptable level of degradation from the beginning-of-life (BOL) performance over a life time of 5500 h (~ 165,000 miles at 30 mph)
3. A stationary FC must withstand over 50000 h of steady operation under vastly changing external temperature conditions

FCs should not be seen as a panacea for every power generating applns in the world

Direct H_2 Fuel Cell

- 50,000 h, 100 % RH

- 5,500 h, 30 % RH

Technical Limitations of FCs

3. System Power Density and Specific Power:

US DOE year 2010 targets for system power density and specific power are:

1. 650 W/kg and 650 W/L for automotive (50 KW) applications.
2. 150 W/kg and 170 W/L for auxiliary (5 to 10 kW peak) applications.
3. 100 W/kg and 100 W/L for portable (mW to 50 W) applications.

FCs should not be seen as a panacea for every power generating applns in the world

Technical Limitations of FCs

4. Fuel:

Fuel **Storage**, **Generation** and **Delivery** technologies must be advanced if pure hydrogen is to be used.

5. Performance:

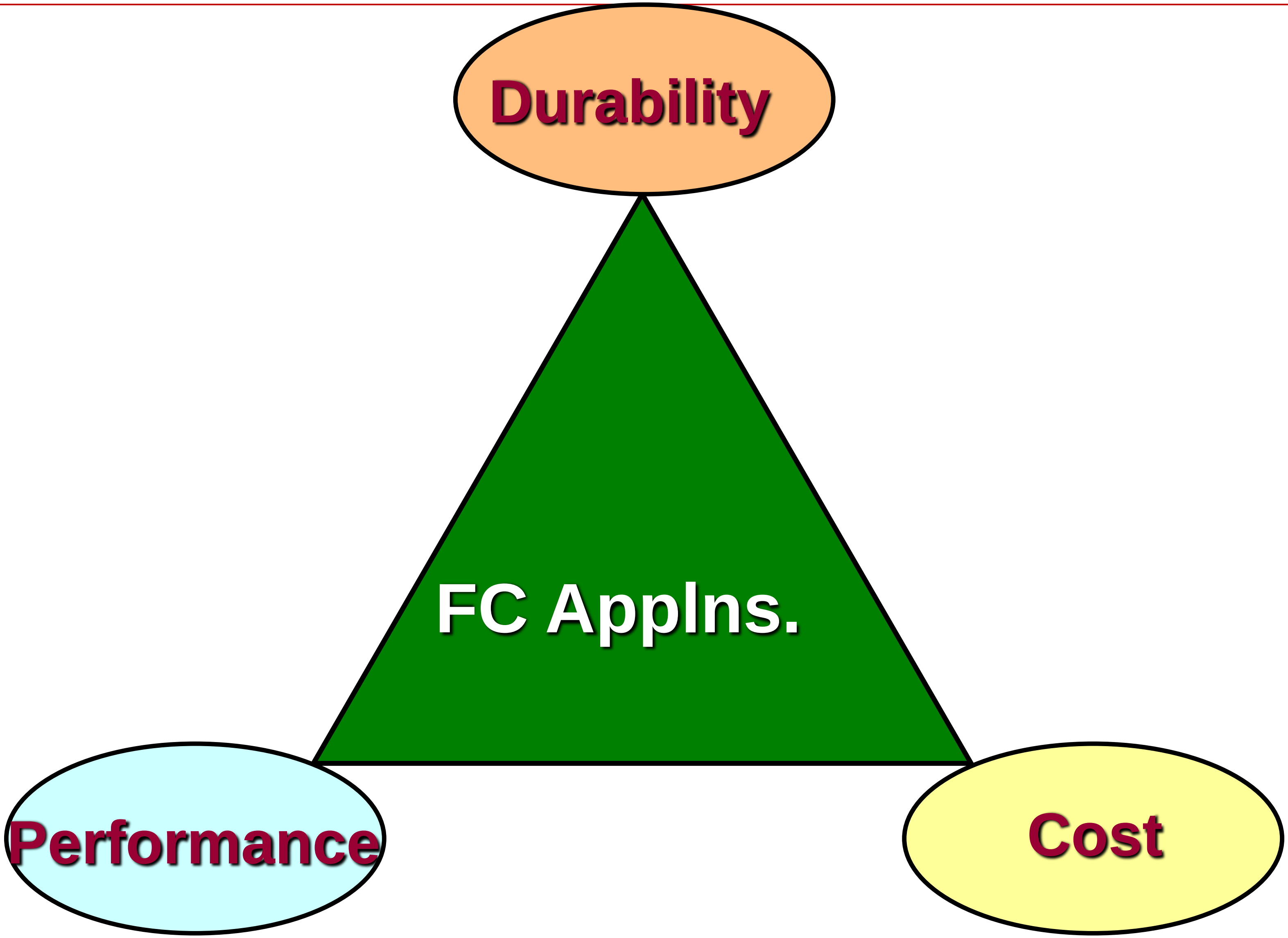
1. Desired performance and longevity of system components must be achieved.
2. New hardware (e.g., high volume blowers and efficient power conditioners) must be developed to suit the needs of the FC power systems

6. Controls:

Sensors and online control systems for FC systems are needed for transient operation, where performance instability can become a major issue,

FCs should not be seen as a panacea for every power generating applns in the world

The key Triad



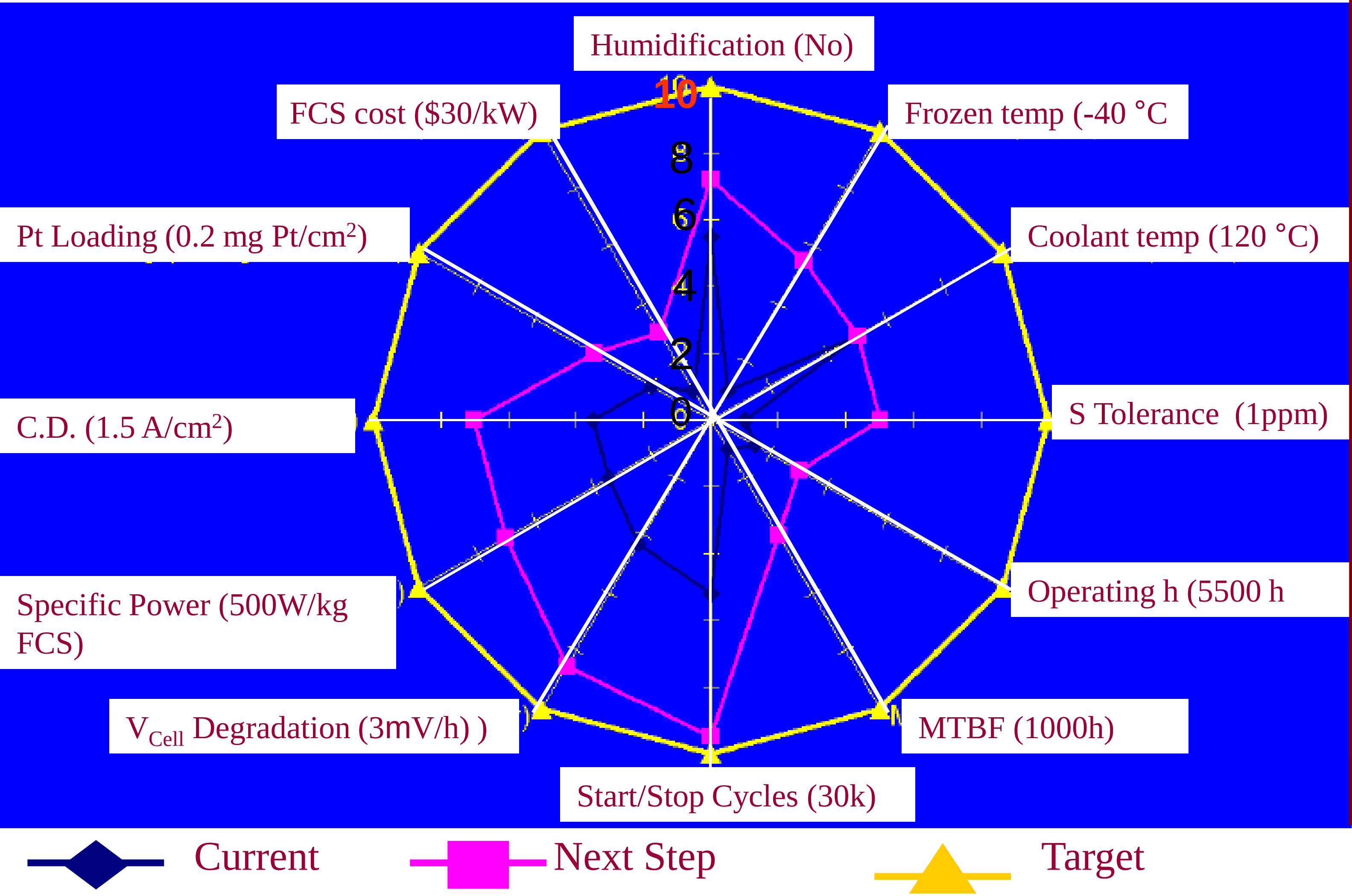
Durability

FC Applns.

Performance

Cost

Barriers on the way to FCVs



Reliability

Performance

Cost

Electromotive Force (EMF)

- If *E is the voltage of the fuel cell, then the electrical work done moving this charge* round the circuit is

Electrical work done = charge × voltage = $-2F*E$ *joules*

- If the system is reversible (or has no losses), then this electrical work done will be equal to the Gibbs free energy released $\Delta\overline{g}_f$.
- So $\Delta\overline{g}_f = -2F*E$
- Thus $E = -\Delta\overline{g}_f/2F$ This fundamental equation gives the EMF or reversible OCV of the H2 FC.

Problem

- Calculate the Open Circuit Voltage values of a Hydrogen fuel cell operating at 25 and also 800 ºC.

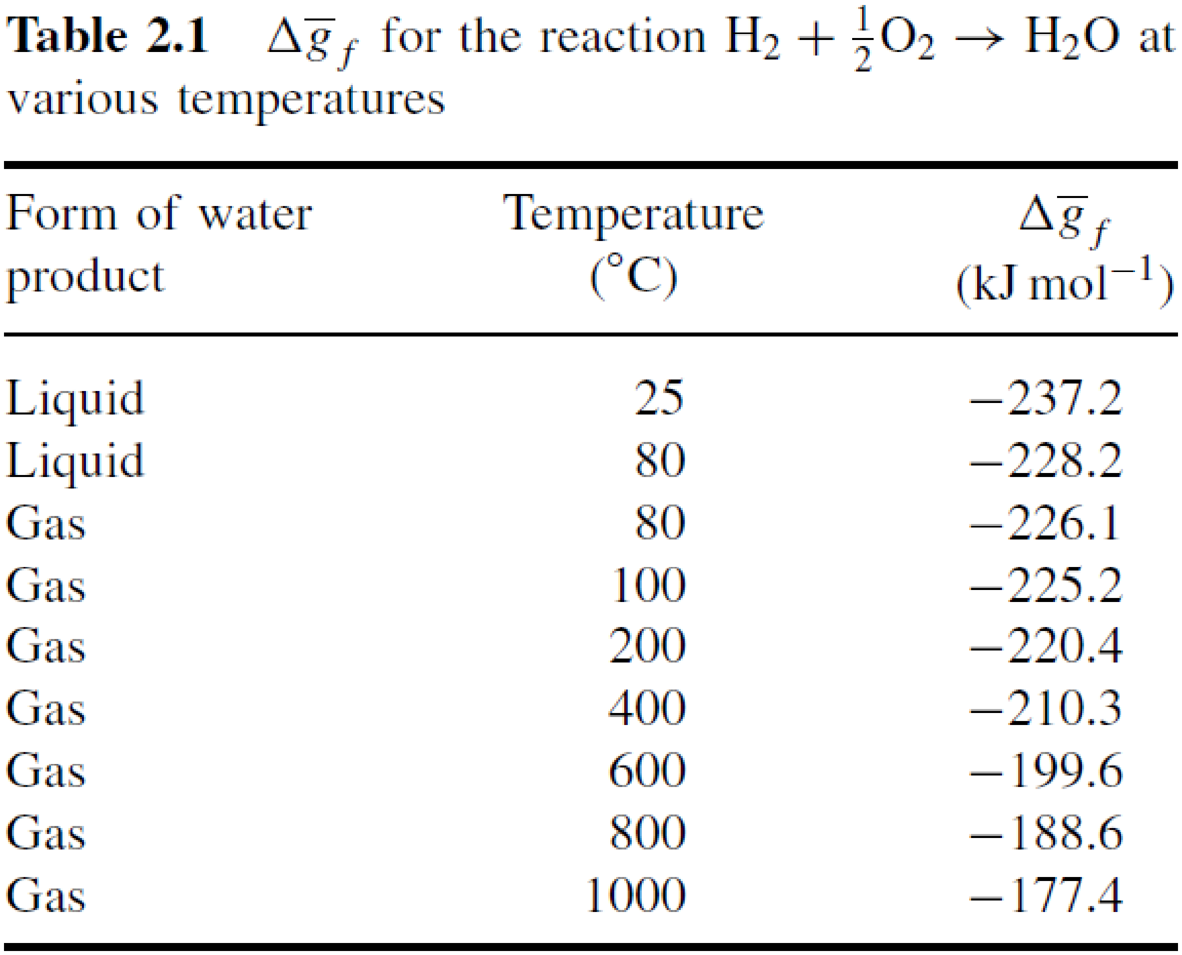


Table 2.1 $\Delta \overline{g}_f$ for the reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ at various temperatures

Form of water product	Temperature (°C)	$\Delta \overline{g}_f$ ($kJ\,mol^{-1}$)
Liquid	25	−237.2
Liquid	80	−228.2
Gas	80	−226.1
Gas	100	−225.2
Gas	200	−220.4
Gas	400	−210.3
Gas	600	−199.6
Gas	800	−188.6
Gas	1000	−177.4

Efficiency

- A more well-known example of an efficiency limit is that for heat engines – such as steam and gas turbines.
- If the maximum temperature of the heat engine is T_1, *and* the heated fluid is released at temperature T_2, *then Carnot showed that the maximum* efficiency possible is
- **Carnot limit = $(T_1 - T_2)/T_1$**
- As an example, for a steam turbine operating at 400°C (675 K), with the water exhausted through a condenser at 50°C (325 K), the **Carnot efficiency limit is (675 – 325)/675 = 0.52 = 52%**

Effect of Pressure and Gas Concn.

- We noted that the Gibbs free energy changes in a chemical reaction vary with temperature.
- Equally important, though more complex, are the changes in **Gibbs free energy with reactant pressure and concentration**.
- A general reaction such as

$$\boxed{j\mathrm{J} + k\mathrm{K} \rightarrow m\mathrm{M}}$$

- *j moles of J react with k moles of K to produce m moles of M.*

Effect of Pressure and Gas Concn.

- *Each of the* reactants, and the products, has an associated ‘activity’.
- This ‘activity’ is designated by *a, aJ, and aK being the activity of the reactants, and aM the activity of the product.*
- *It is* beyond the scope of this course to give a thorough description of ‘activity’.
- However, in the case of gases behaving as ‘ideal gases’, it can be shown that

$$\boxed{\text{activity } a = \frac{P}{P^0}}$$

where *P is the pressure or partial pressure of the gas and P^o is standard pressure, 0.1 MPa.*

Effect of Pressure and Gas Concn.

$$\Delta \bar{g}_f = \Delta \bar{g}_f{}^{0} - RT \ln\left(\frac{a_{\mathrm{J}}^{j} \cdot a_{\mathrm{K}}^{k}}{a_{\mathrm{M}}^{m}}\right)$$

$\Delta \bar{g}_f{}^{0}$ **is the change in molar Gibbs free energy of formation at standard pressure**

- For the FC reaction **$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$**

$$\Delta \bar{g}_f = \Delta \bar{g}_f{}^{0} - RT \ln\left(\frac{a_{\mathrm{H_2}} \cdot a_{\mathrm{O_2}}^{\frac{1}{2}}}{a_{\mathrm{H_2O}}}\right)$$

If the activity of the reactants increases, $\Delta \bar{g}_f$ *becomes more negative, that is, more energy is released.*

Effect of Pressure and Gas Concn.

- To see how this equation affects voltage, the equation in the previous page becomes,

$$E = \frac{-\Delta \bar{g}_f{}^0}{2F} + \frac{RT}{2F} \ln\left(\frac{a_{H_2} \cdot a_{O_2}^{\frac{1}{2}}}{a_{H_2O}}\right) = E^0 + \frac{RT}{2F} \ln\left(\frac{a_{H_2} \cdot a_{O_2}^{\frac{1}{2}}}{a_{H_2O}}\right)$$

This is Nernst equation

where E^o *is the EMF at standard pressure*

- The equation shows precisely how raising the activity of the reactants increases the voltage.
- *The EMF calculated is* 'Nernst voltage' and is the reversible cell voltage that would exist at a given temperature and pressure.

Effect of Pressure and Gas Concn.

- In a mixture of gases, the total pressure is the sum of all the ‘partial pressures’ of the components of the mixture.
- For example, in air at 0.1MPa, the partial pressures are as shown

Gas	Partial pressure (Mpa)
Nitrogen	0.07809
Oxygen	0.02095
Argon	0.00093
Others (including CO2)	0.00003
Total	0.10000

Effect of Pressure and Gas Concn.

- At high temperature (e.g. in a SOFC at 1000°C) we can assume that the steam behaves as an ideal gas, and so

$$a_{H_2} = \frac{P_{H_2}}{P^0}, \qquad a_{O_2} = \frac{P_{O_2}}{P^0}, \qquad a_{H_2O} = \frac{P_{H_2O}}{P^0}$$

- The Nernst Equation is

$$E = E^o + \frac{RT}{2F} \ln \left(\frac{\frac{P_{H_2}}{P^o} \cdot \left(\frac{P_{O_2}}{P^o} \right)^{\frac{1}{2}}}{\frac{P_{H_2O}}{P^o}} \right)$$

- If all the pressures are given in bar, then *Po = 1*

$$E = E^0 + \frac{RT}{2F} \ln \left(\frac{P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \right)$$

Effect of Pressure and Gas Concn.

- H_2 gas might be part of a mixture of H_2 and CO_2 from a fuel reformer, together with product steam.
- The O_2 will nearly always be part of air.
- It is also often the case that the pressure on both the cathode and the anode is approximately the same – this simplifies the design.
- If this system pressure is *P, then*

$$P_{H_2} = \alpha P \qquad P_{O_2} = \beta P \qquad P_{H_2O} = \delta P$$

- where *α, β, and δ are constants depending on the molar masses and concentrations of* H_2, O_2, and H_2O.

$$E = E^0 + \frac{RT}{2F}\ln\left(\frac{\alpha\cdot\beta^{\frac{1}{2}}}{\delta}\cdot P^{\frac{1}{2}}\right) = E^0 + \frac{RT}{2F}\ln\left(\frac{\alpha\cdot\beta^{\frac{1}{2}}}{\delta}\right) + \frac{RT}{4F}\ln(P)$$

This is also Nernst equation

Problem

- Calculate the Open Circuit Voltage value of a Hydrogen fuel cell operating at 205 °C with pure oxygen and Hydrogen containing 5 % CO_2. System pressure is 1 atm.

$$E = E^0 + \frac{RT}{2F} \ln \left(\frac{P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \right)$$

Hydrogen partial pressure

- Hydrogen can either be supplied pure or as part of a mixture.
- If we isolate the pressure of hydrogen term

$$E = E^0 + \frac{RT}{2F}\ln\left(\frac{P_{O_2}^{\frac{1}{2}}}{P_{H_2O}}\cdot\right) + \frac{RT}{2F}\ln(P_{H_2})$$

- So, if the hydrogen partial pressure changes, say, from *P1 to P2 bar, with* P_{O_2} *and* P_{H_2O} *unchanged, then the voltage will change by*

$$\Delta V = \frac{RT}{2F}\ln(P_2) - \frac{RT}{2F}\ln(P_1) = \frac{RT}{2F}\ln\left(\frac{P_2}{P_1}\right)$$

Problem

- Calculate the increase in Open Circuit Voltage value of a Hydrogen fuel cell operating at 90 °C, when the Hydrogen pressure is increased from 1 to 2 atm (with pure oxygen, pressure is 1 atm).

$$\boxed{E = E^0 + \frac{RT}{2F}\ln\left(\frac{P_{O_2}^{\frac{1}{2}}}{P_{H_2O}}\cdot\right) + \frac{RT}{2F}\ln(P_{H_2})}$$

$$\Delta V = \frac{RT}{2F}\ln(P_2) - \frac{RT}{2F}\ln(P_1) \quad = \frac{RT}{2F}\ln\left(\frac{P_2}{P_1}\right)$$

Hydrogen partial pressure

- The use of H2 mixed with CO2 occurs particularly in phosphoric acid fuel cells, operating at about 200°C.
- Substituting the values for *R, T , and F gives*

$$\Delta V = 0.02 \ln\left(\frac{P_2}{P_1}\right) \text{V}$$

- As an example, changing from pure hydrogen to 50 % H_2/CO_2 mixture will reduce the voltage by 0.015V per cell.

System pressure

- The Nernst equation (page 34) shows that the EMF of a fuel cell is increased by the system pressure according to the term $\frac{RT}{4F}\ln(P)$

- So, if the pressure changes from *P1 to P2 there will be a change of voltage*

$$\Delta V = \frac{RT}{4F}\ln\left(\frac{P_2}{P_1}\right)$$

- For an SOFC operating at 1000°C, this would give

$$\Delta V = 0.027\ln\left(\frac{P_2}{P_1}\right)$$

Problem

- Calculate the increase in Open Circuit Voltage value of a Hydrogen fuel cell operating at 90 ^{o}C, when the Hydrogen and Air pressure are increased from 1 to 3 atm.

$$\Delta V = \frac{RT}{4F} \ln\left(\frac{P_2}{P_1}\right)$$

Air or Oxygen

- A similar effect occurs when studying the change from air to oxygen.
- This effectively changes *β in Nernst equation (page 34) from 0.21 to 1.0.*
- *Isolating β gives*

$$E = E^0 + \frac{RT}{4F}\ln(\beta) + \frac{RT}{2F}\ln\left(\frac{\alpha}{\delta}\right) + \frac{RT}{4F}\ln(P)$$

- For the change in *β from 0.21 to 1.0, with all other factors remaining constant,*

$$\Delta V = \frac{RT}{4F}\ln\left(\frac{1.0}{0.21}\right)$$

- For a proton exchange membrane (PEM) fuel cell at 80◦C this would give *V* = 0.012*V*

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Problem

- Calculate the Open Circuit Voltage value of a Hydrogen fuel cell operating at 50 °C with pure Hydrogen and air. System pressure is 2 atm.

$$E = E^0 + \frac{RT}{2F} \ln\left(\frac{P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \right)$$

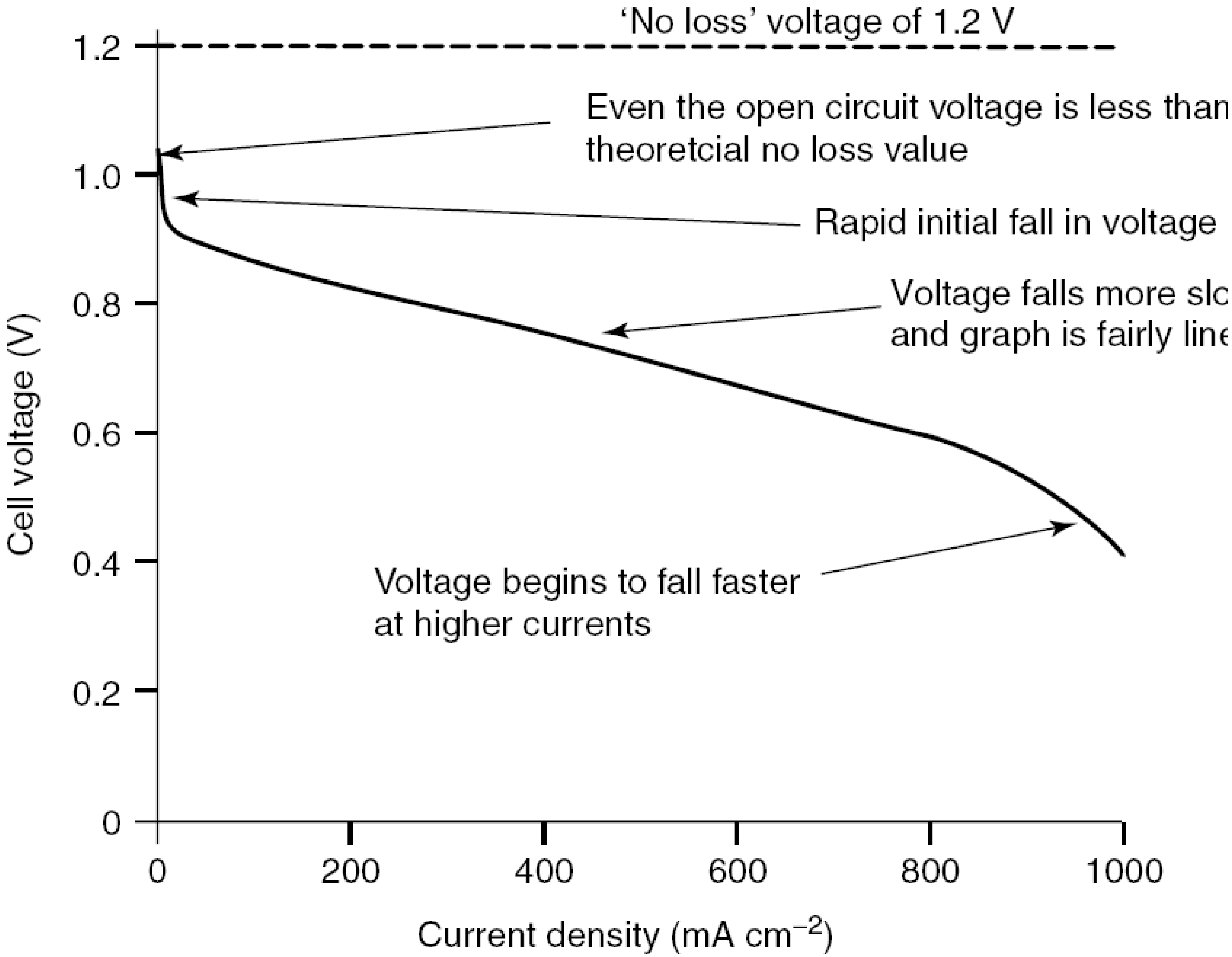
Operational Voltage

- Theoretical value of the OCV of a H_2 FC is given by the formula

$$E = \frac{-\Delta \overline{g}_f}{2F}$$

- This gives a value of about **1.2V** for a cell operating below 100 ◦C.
- However, when a fuel cell is made and put to use, it is found that the voltage is less than this, often considerably less.
- Figure in next page shows the performance of a typical FC operating at ~ 70◦C, at normal air pressure.

Low Temp FC Performance



Low Temp FC Performance

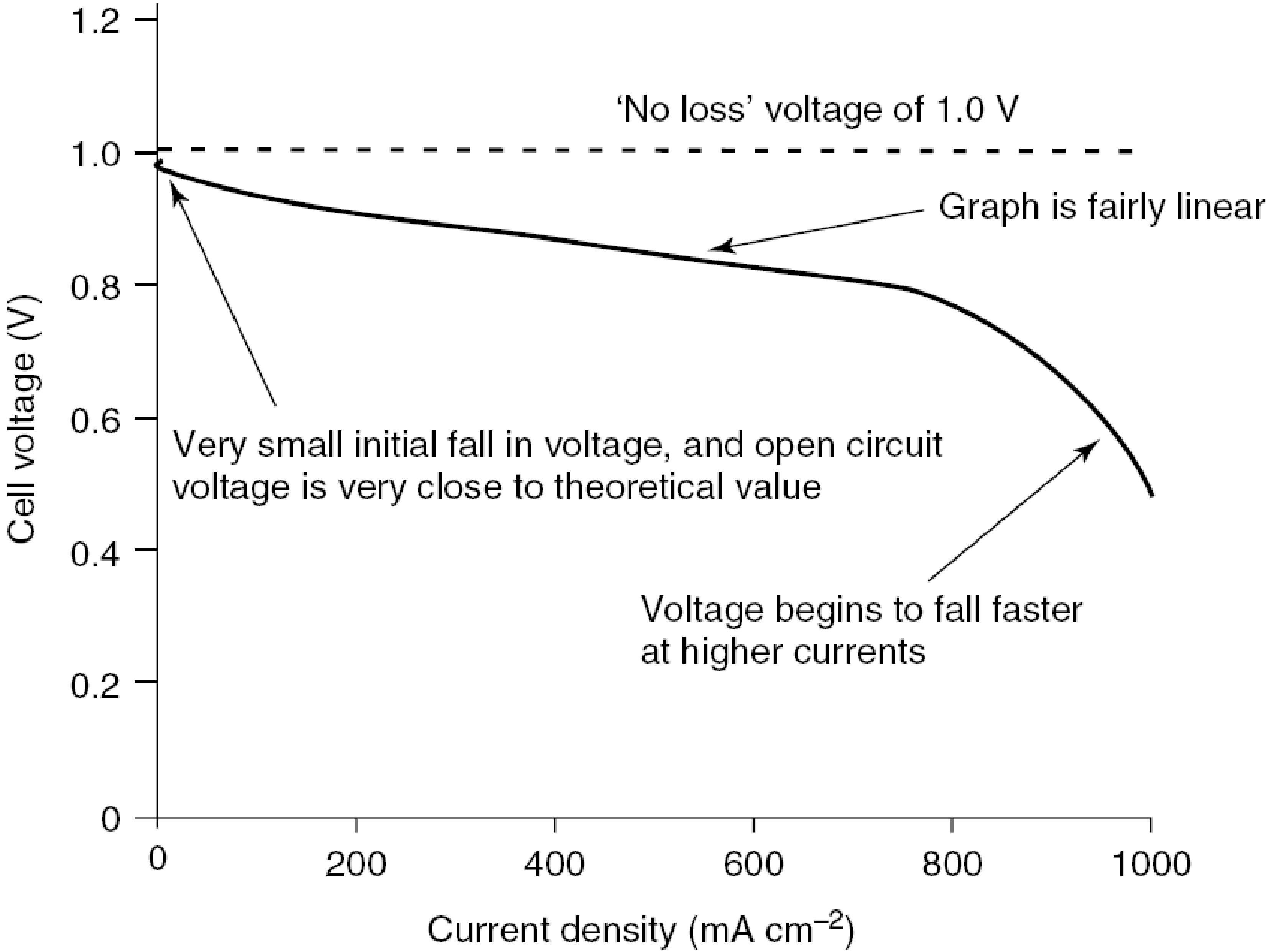
The key points to notice about this graph of the cell voltage against current density are as follows:

- Even the open circuit voltage is less than the theoretical value.
- There is a rapid initial fall in voltage.
- The voltage then falls less rapidly, and more linearly.
- There is sometimes a higher current density at which the voltage falls rapidly.

High Temp FC Performance

- If a fuel cell is operated at higher temperatures, the shape of the voltage/current density graph changes.
- As we have seen earlier, the reversible ‘no loss’ voltage falls.
- However, the initial fall in voltage as current is drawn from the cell is markedly less.
- Figure in next page shows the situation for a typical SOFC operating at about 800 ◦C.

High Temp FC Performance



High Temp FC Performance

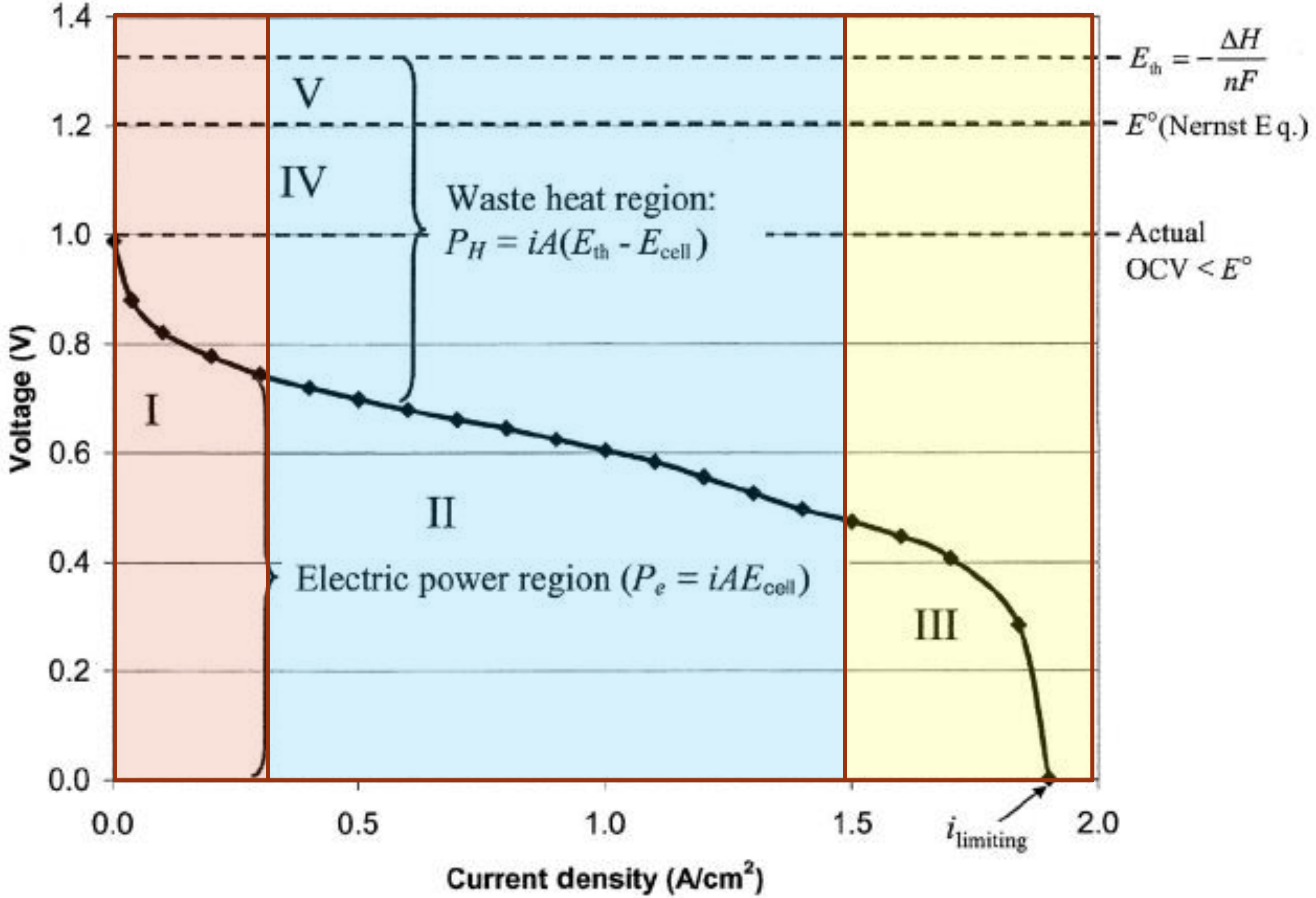
The key points here are as follows:

- The open circuit voltage is equal to or only a little less than the theoretical value.
- The initial fall in voltage is very small, and the graph is more linear.
- There may be a higher current density at which the voltage falls rapidly, as with lower-temperature cells.

Voltage Loss

- The graphs of Figures show the difference between the expected voltage from a fuel cell operating ideally (reversibly) and the actual voltage.
- ***Overvoltage or overpotential*** *is the term often used by electrochemists.*
- *This is because* it is a voltage superimposed over the reversible or ideal voltage.
- ***Polarisation*** *is another term much used by some electrochemists and others.*

Polarization Curve for FC



Causes of Voltage Drop

- The characteristic shape of the voltage/current density graphs of Figures results from four major irreversibilities.

1. *Activation losses.*
2. *Fuel crossover and internal currents.*
3. *Ohmic losses.*
4. *Mass transport or concentration losses.*

Tafel Equation

Tafel equation

$$\Delta V_{\text{act}} = A \ln\left(\frac{i}{i_0}\right)$$

- The constant *A is higher for an electrochemical reaction that is slow.*
- *The constant* i_o is higher if the reaction is faster.
- The current density i_o *can be considered as the current* density at which the overvoltage begins to move from zero.
- It is important to remember that the Tafel equation only holds true when $i > i_o$.
- i_o *is usually* called the ***exchange current density***

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Tafel Equation constant, A

For a H_2 fuel cell with two electrons transferred per mole, the constant *A*

$$A = \frac{RT}{2\alpha F}$$

- The **constant *α is called the charge transfer coefficient***
- Its value depends on the reaction involved and the material the electrode is made from.
- For H_2 electrode, it is ~0.5 for a great variety of electrode materials.
- For O_2 electrode, it is between ~0.1 & 0.5 in most circumstances.

Exchange Current Density, i_o

- At zero current, the reaction is taking place all the time, but the reverse reaction is also taking place at the same rate.
- There is an equilibrium expressed as

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

- Thus, there is a continual backwards and forwards flow of electrons from and to the electrolyte.
- This current density is i_o, *the 'exchange' current density.*

Operating Voltage

- Imagine a fuel cell that has no losses at all except for this activation overvoltage on *one electrode.*
- *Its voltage would then be given by the equation*

$$V = E - A \ln\left(\frac{i}{i_0}\right)$$

- where *E is the reversible OCV.*
- If we plot graphs of this equation using values of i_o *of 0.01, 1.0, and 100* $mAcm^{-2}$, *using a typical value for A of 0.06 V,* we get the curves shown in next page.

Problem

- Calculate the Activation Polarization value at an operating current density of 50 $mA.cm^{-2}$ (25 deg C for a H_2/air fuel cell with an exchange current density value of 0.1 $mA.cm^{-2}$ and α value of 0.4.

$$\Delta V_{\text{act}} = A \ln\left(\frac{i}{i_0}\right)$$

$$A = \frac{RT}{2\alpha F}$$

Problem

- Calculate the cell voltage at an operating current density of 50 mA.cm^{-2} (25 deg C) for a H_2/air fuel cell at 2 atm, with an exchange current density value of 0.1 mA.cm^{-2} and α value of 0.4.

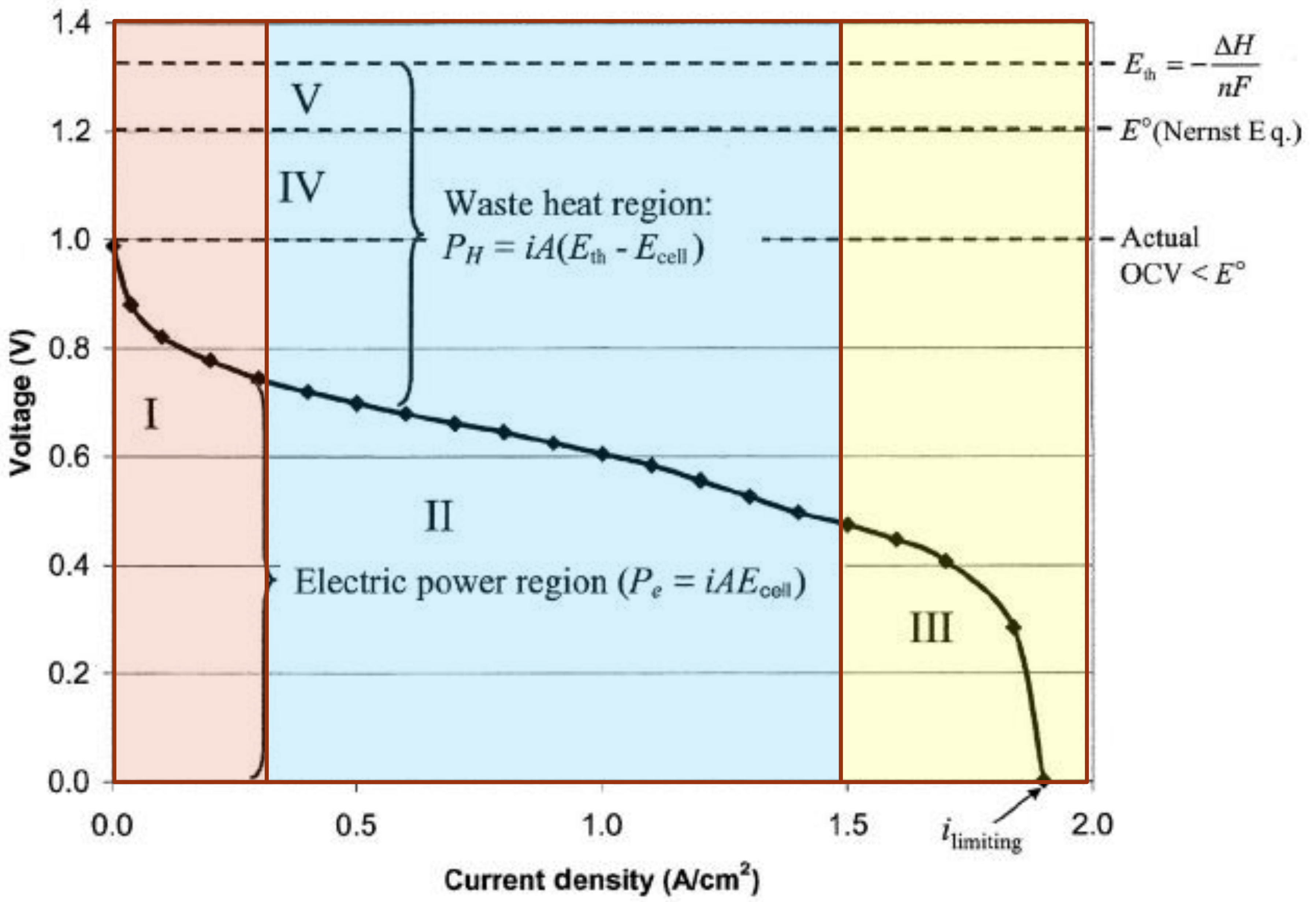
$$E = E^0 + \frac{RT}{2F} \ln\left(\frac{P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}}{P_{H_2O}}\right)$$

$$V = E - A \ln\left(\frac{i}{i_0}\right)$$

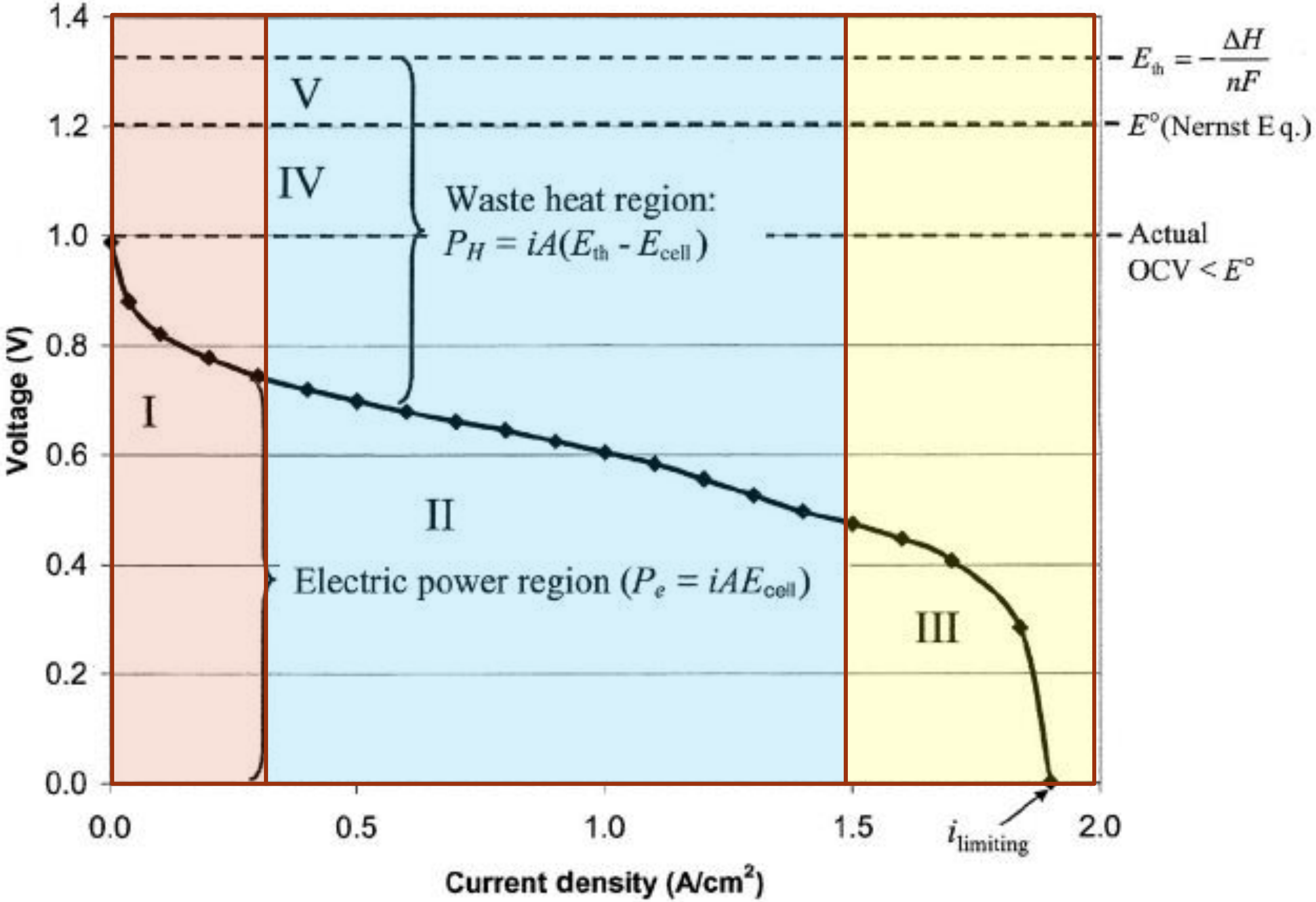
Reducing Activation Loss

- A crucial factor in improving fuel cell performance is, to increase the value of i_o, *especially at the cathode.*
- ***This can be done in the following ways:***
- ***Raising the cell temperature***
- ***Using more effective catalysts***
- ***Increasing the roughness of the electrodes***
- ***Increasing reactant concentration, for example, using pure O2 instead of air***
- ***Increasing the pressure***

Polarization Curve for FC



Polarization Curve for FC



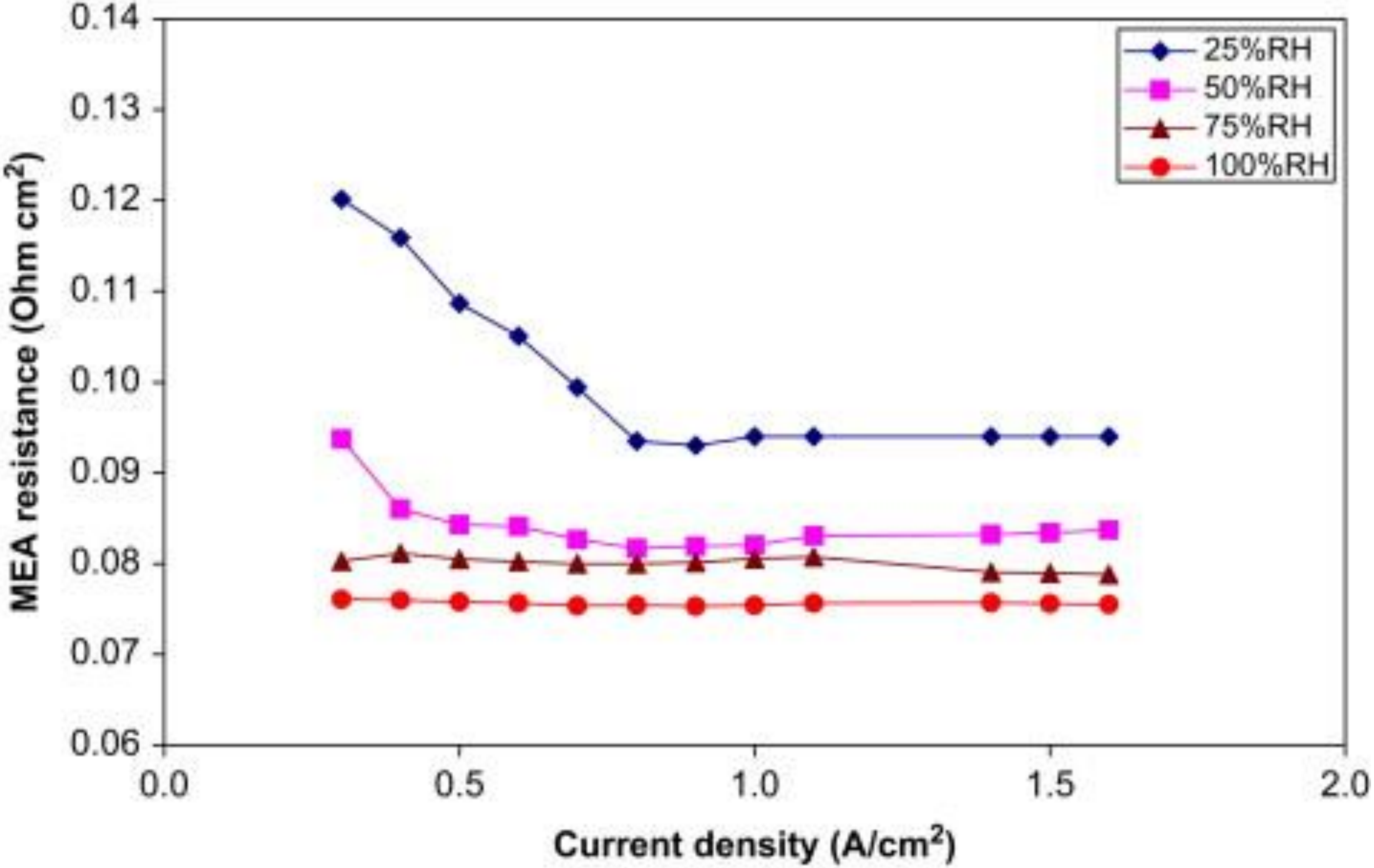
Ohmic Losses

- The losses due to the electrical resistance of the electrodes, and the resistance to the flow of ions in the electrolyte, are the simplest to understand and to model.
- The size of the voltage drop is simply proportional to the current, that is,

$$V = IR$$

- In most fuel cells the resistance is mainly caused by the electrolyte, though the cell interconnects or bipolar plates can also be important.

Cell Resistance



Problem

- Calculate the Ohmic Polarization loss values at various operating current densities of 200, 500, 800, 1000 mA.cm^{-2} for fuel cells with MEAs showing 0.075 and 0.1 Ohm. cm^{2}

Mass Transport or Concentration Losses

- If O_2 at the cathode of a FC is supplied in the form of air, then it is self-evident that during FC operation there will be a slight reduction in the concentration of the oxygen in the region of the electrode, as the O_2 is extracted.
- The extent of this change in concentration will depend on the current being taken from the fuel cell, and on physical factors relating to how well the air around the cathode can circulate, and how quickly the oxygen can be replenished.
- This change in concentration will cause a reduction in the partial pressure of the oxygen

Mass Transport or Concentration Losses

- The reduction in gas pressure will result in a reduction in voltage.
- These give the change in OCV caused by a change in pressure of reactants.

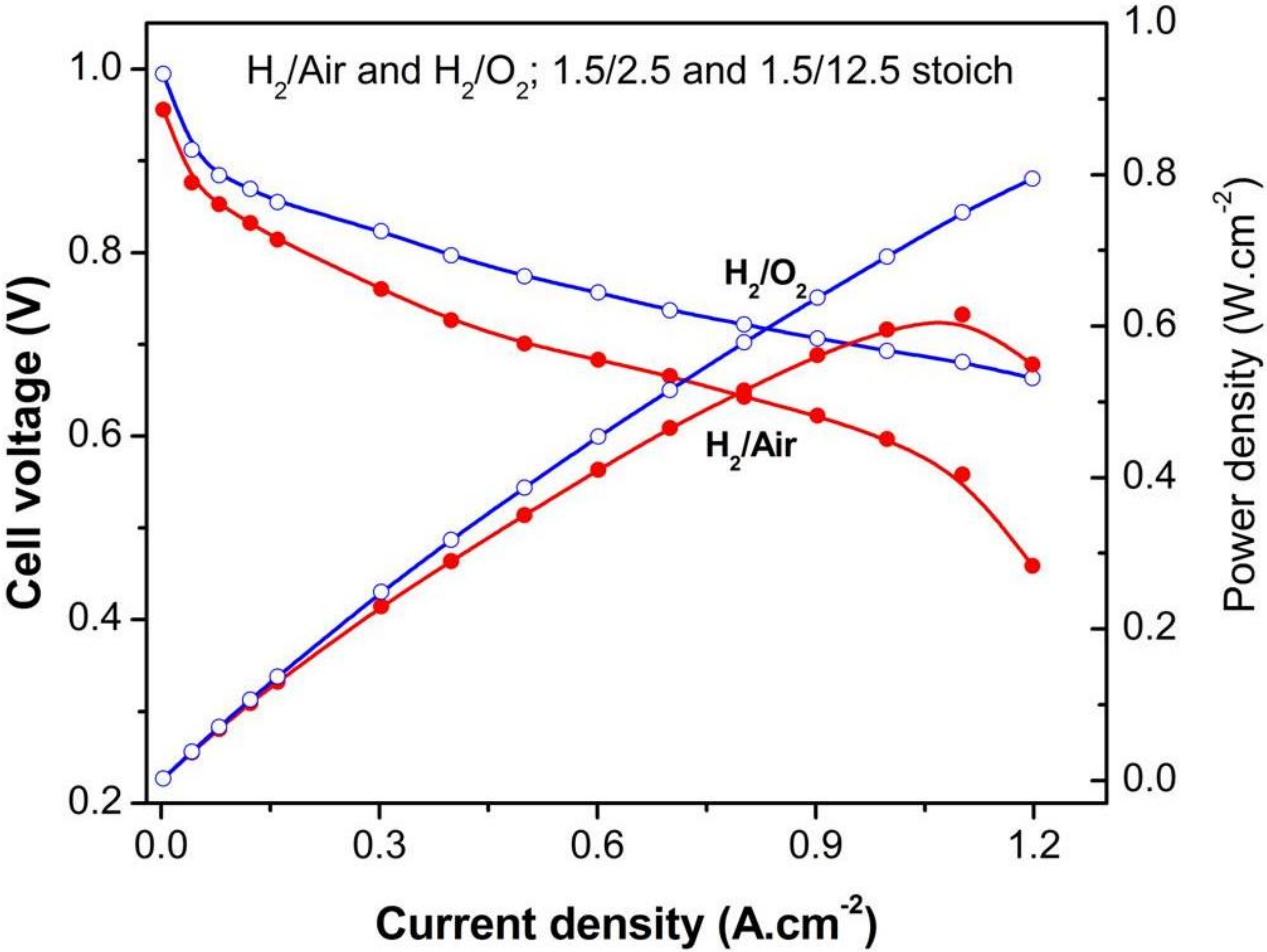
There are also problems with lower-temperature cells, and those supplied with hydrogen mixed with other gases such as carbon dioxide for the fuel.

$$\boxed{\Delta V = \frac{RT}{2F}\ln\left(\frac{P_2}{P_1}\right)}$$

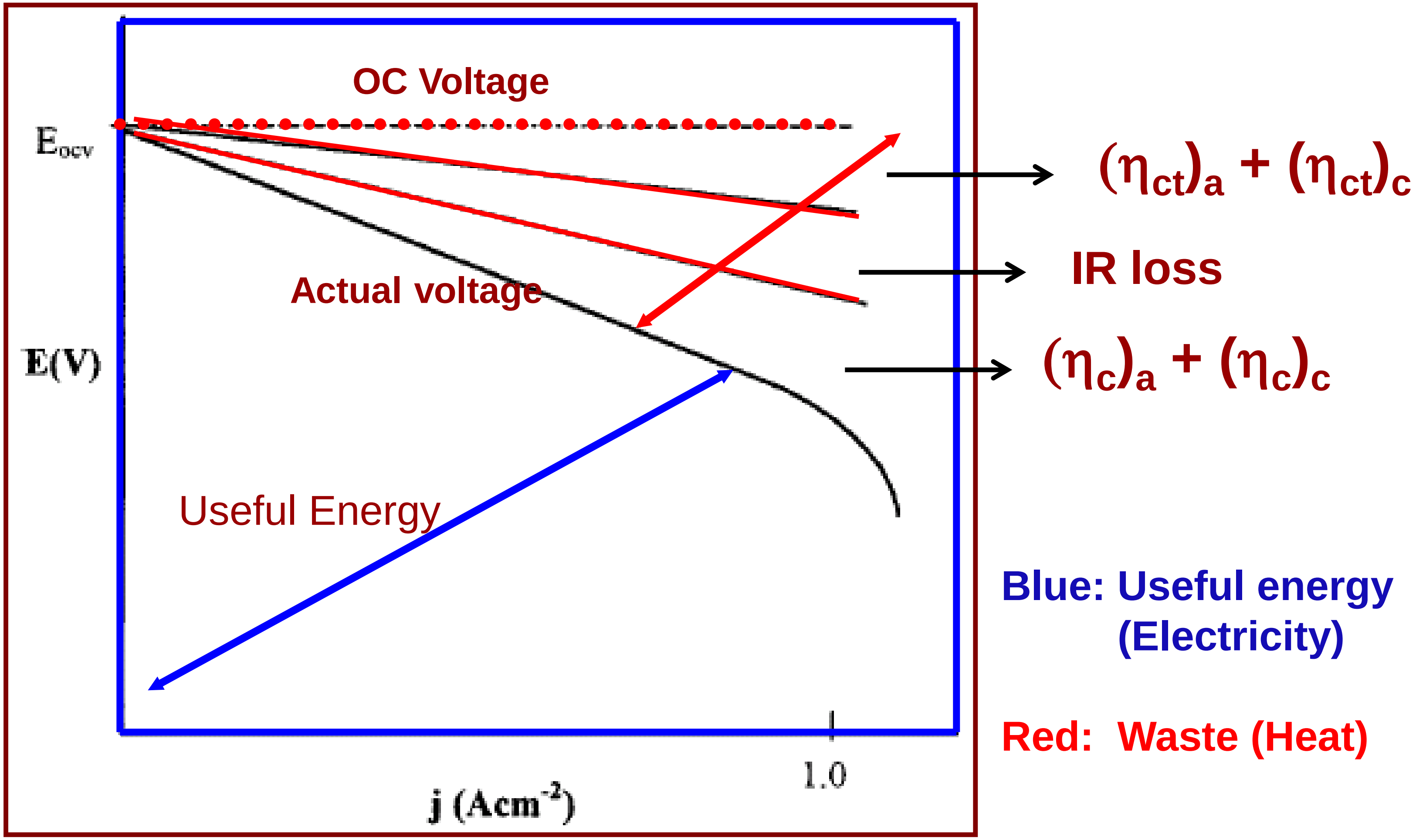
Mass Transport or Concentration Losses

- The mass transport or concentration overvoltage is particularly important in cases where the hydrogen is supplied from some kind of reformer, as there might be **a difficulty in increasing the rate of supply of hydrogen quickly to respond to demand**.
- Another important case is at the air cathode, if the air supply is not well circulated.
- **A particular problem is that the nitrogen that is left behind after the oxygen is consumed can cause a mass transport problem at high currents – it effectively blocks the oxygen supply.**
- In PEMFCs, the **removal of water** can also be a cause of mass transport or concentration overvoltage.

What happens with O2 to Air?



Operational Voltage of single cell



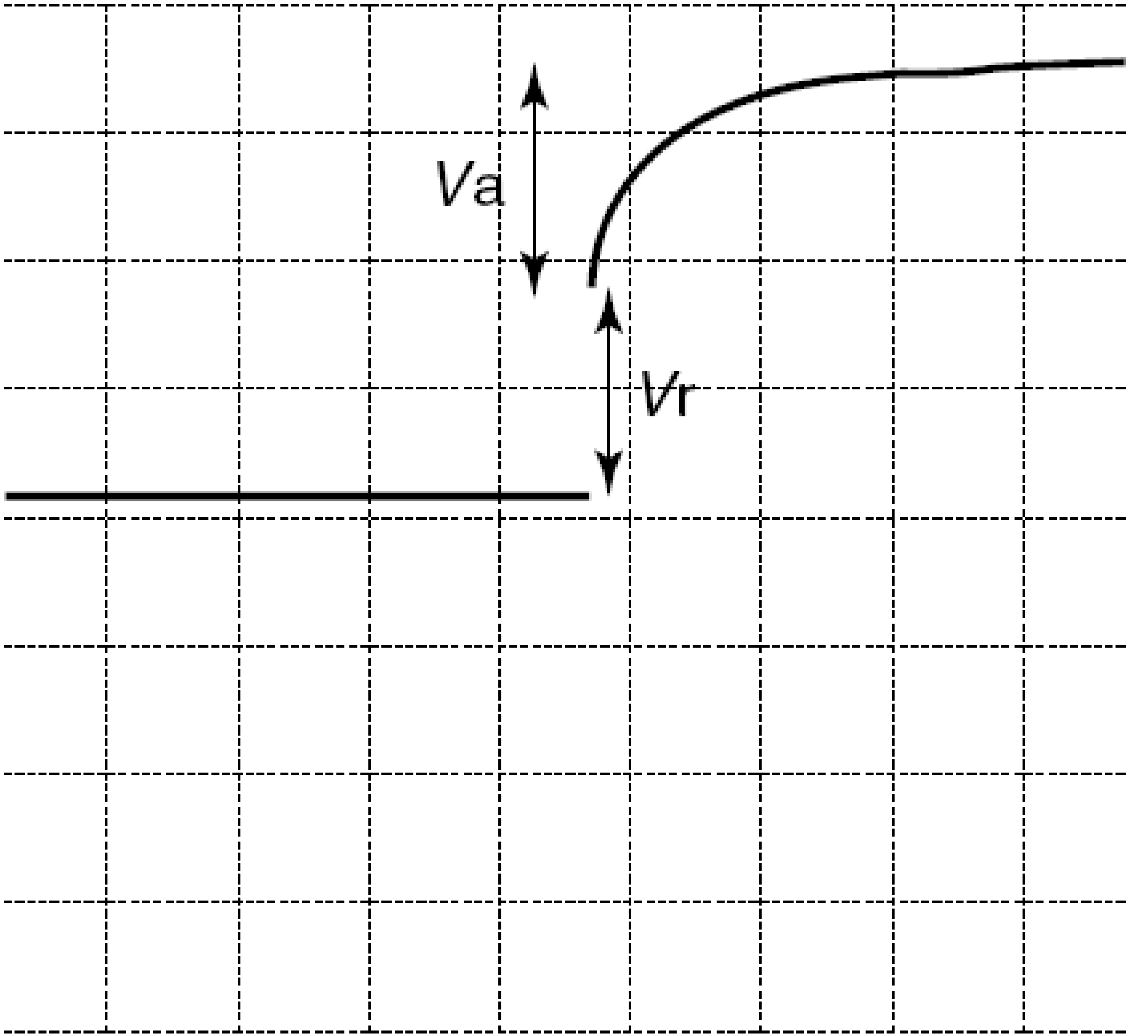
Blue: Useful energy (Electricity)

Red: Waste (Heat)

$$E = E_{ocv} - ((\eta_{ct})_a + (\eta_{ct})_c) - ((\eta_c)_a + (\eta_c)_c) - IR$$

PEM Fuel Cell

- Current interrupt test for a low-temperature, ambient pressure, hydrogen fuel cell.

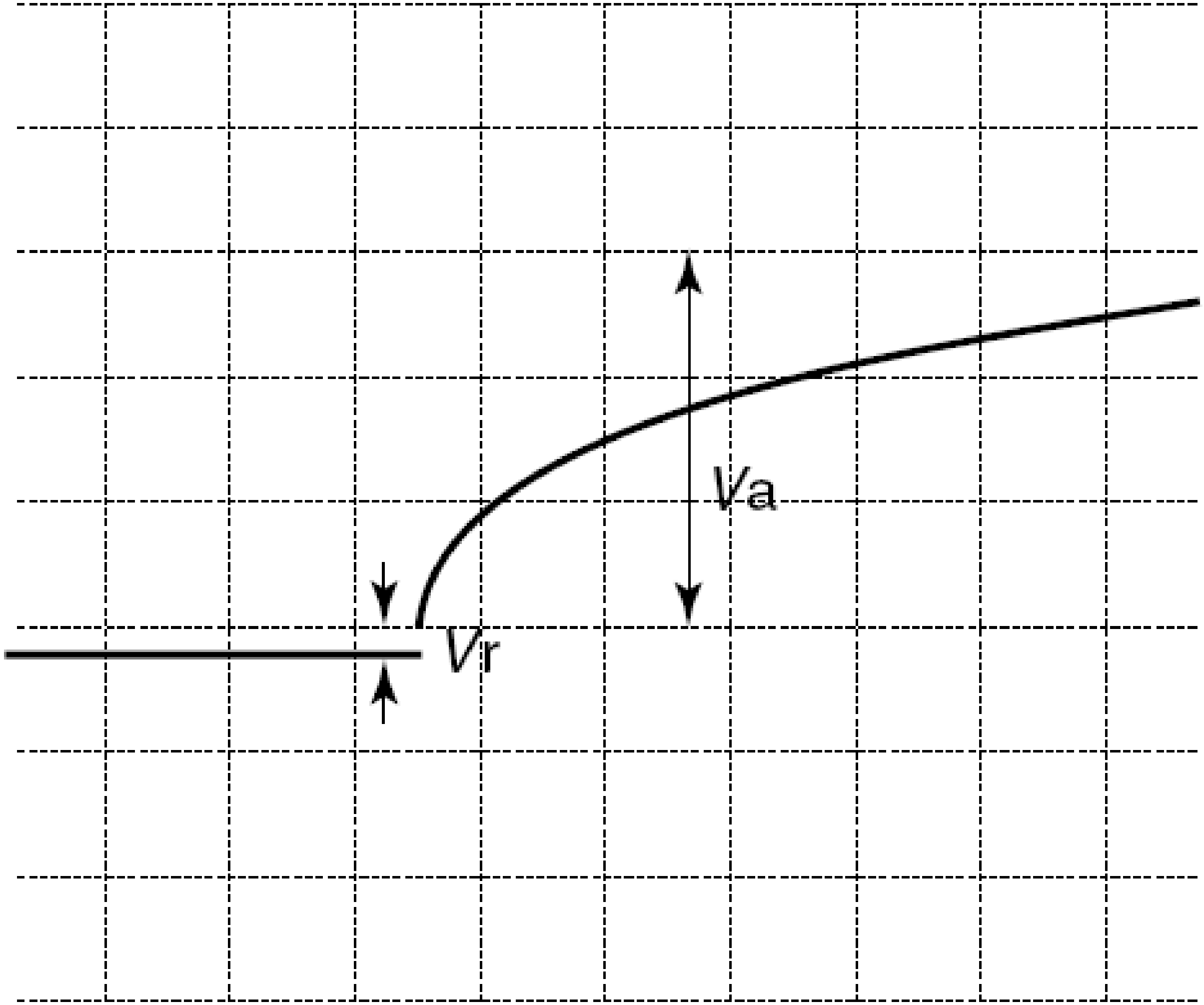


The ohmic and activation voltage drops are similar. (Time scale 0.2 s/div, $i = 100\,mA\,cm^{-2}$.)

Direct Methanol Fuel Cell

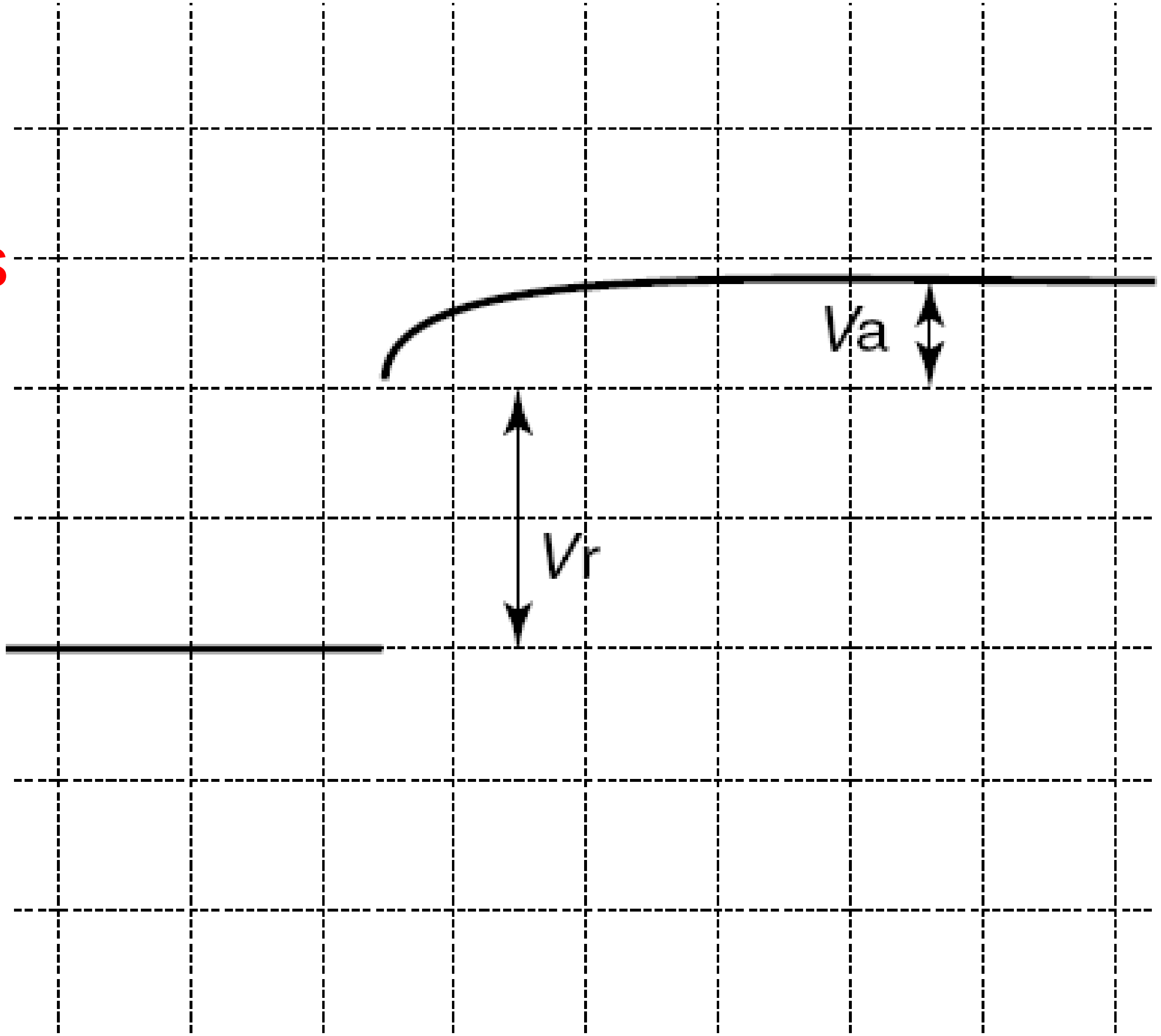
- Current interrupt test shows a large activation overvoltage at **both electrodes.**

As a result, the activation overvoltage is much greater than the ohmic, which is barely discernible. (Time scale 2 s/div. *$i = 10 mAcm^{-2}$*.)



SOFC

Current interrupt test for a small solid oxide fuel cell working at ~ 700°C



The large immediate rise in voltage shows that most of the voltage drop is caused by ohmic losses.(Time scale 0.02 s/div.
$I = 100 mA cm^{-2}$.)

Water Production

- In a hydrogen-fed fuel cell, water is produced at the rate of one mole for every two electrons.

$$\text{Water production} = \frac{P_e}{2 \cdot V_c \cdot F} \ \text{moles s}^{-1}$$

- The molecular mass of water is 18.02×10^{-3} kg mole^{-1}, so this becomes

$$\text{Water production} = 9.34 \times 10^{-8} \times \frac{P_e}{V_c} \ \text{kg s}^{-1}$$

as a rough guide, 1 kWh of fuel cell generated electricity produces about 1 pint or 0.5 L of water

Problem

- Calculate the amount of water produced for a 1-kW fuel cell operating for 1 h, at a cell voltage of 0.7 V.
- Calculate the amount of water produced for a 100 kW fuel cell operating for 1 min, at a cell voltage of 0.6 V.

$$\text{Water production} = 9.34 \times 10^{-8} \times \frac{P_e}{V_c}\ \mathrm{kg\,s^{-1}}$$

O_2, Air and H_2 Flow Rates

$$O_2 \text{ usage} = 8.29 \times 10^{-8} \times \frac{P_e}{V_c} \text{ kg s}^{-1}$$

$= 3.5\ P_e/Vc$ SCCM

$$\text{Air usage} = 3.57 \times 10^{-7} \times \lambda \times \frac{P_e}{V_c} \text{ kg s}^{-1}$$

$= 16.7\ P_e/Vc$ SCCM

with stoich = 1

In other words, 3.5 SCCM **of O_2 or 16.7** SCCM **of air and 7 SCCM of H_2 would produce 1 A current**

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Useful numbers……

- To produce 1 A current with 100 % utilization (or stoichiometry of 1):
  - **Flow rate of H2 Gas: 7 cc per min**
  - **Flow rate of O2 Gas: 3.5 cc per min**
  - **Flow rate of air: 16.66 cc per min**

Problem

- If there is 10 m^3 of hydrogen in compressed bottle, how long (hours) can it last for a 2 kW fuel cell stack operating at 0.5 V per cell (capable of generating 1 A/cm^2 having 200 cm^2 area) with fuel utilization of 90 % ?

- H2 required per hour per A with 90 % utilization

  = 7*60/0.9

For 2 kW → 7*60*2000/0.5/0.9 = 2048000cc per h

Total hours: 10,000,000 cc /2048000 = 5.36 h

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Heat Produced

- The cases in which water finally ends in liquid form are so few and so we will restrict ourselves to the vapor case.
- For a stack of n cells at current I , the heat generated is thus

$$\boxed{\text{Heating rate} = nI(1.25 - V_c)\ \text{W}}$$

- In terms of electrical power, this becomes

$$\boxed{\text{Heating rate} = P_e\left(\frac{1.25}{V_c} - 1\right)\ \text{W}}$$

Problem

- Calculate the heat produced in Joules/sec for a 1kW fuel cell stack operating at 0.6 V/cell if the product is water vapor. Also calculate the heat produced if the FC stack operates 0.5 V/cell. Which operating condition is better and why?

$$\text{Heating rate} = P_e\left(\frac{1.25}{V_c} - 1\right)\ \text{W}$$

Problem

- Calculate the heat produced for a 3 MW solid oxide fuel cell stack operating at 0.5 V/cell.

$$\boxed{\text{Heating rate} = P_e\left(\frac{1.25}{V_c} - 1\right)\ \text{W}}$$

Fuel Cell Performance Variables

- The performance of fuel cells is affected by
  - **Operating variables**
    - **Current density**
    - **Temperature**
    - **Pressure**
    - **Gas composition**
    - **Reactant utilization**
  - **Cell design and**
  - **Other factors** (impurities, cell life)
- These variables influence the ideal cell potential and the magnitude of the voltage losses

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PROGRESS IN FUEL CELL TECHNOLOGY

- **Blast from the past. A picture of the original UTC fuel cells used in a number of NASA missions**

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