Sustainable Energy Future

Hydrogen Economy

“Water will one day be employed as fuel, that hydrogen and oxygen of which it is constituted will be used”

Jules Verne - The Mysterious Island, 1874

Current Energy Economy

Transportation Technologies

- Diesel
- Gasoline
- Other oil-derived fuels

CO_2-emitting nonrenewable

Stationary Power Technologies

- Coal
- Natural gas (heating)
- Nuclear
- Hydroelectric

CO_2-emitting nonrenewable

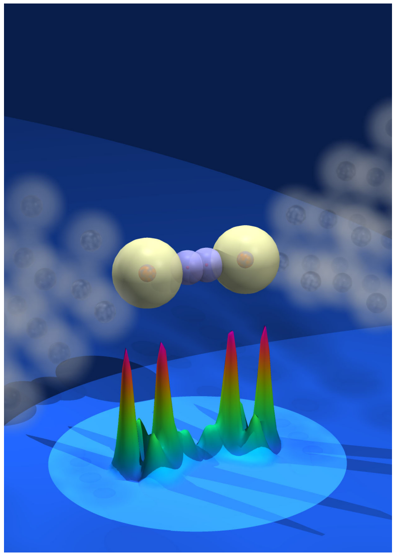
Sustainable Energy Future

Transportation Technologies

- Biofuels
- Hydrogen (i.e. fuel cells)
- Electric vehicles (EVs)

Stationary Power Technologies

- Wind
- Solar
- Geothermal
- Hydroelectric
- Hydrogen (i.e. fuel cells)



HYDROGEN ECONOMY

Energy Distribution by H_2

Hydrogen is energy carrier

- Advantages (over fossil fuels)
  - Environmentally cleaner
  - Cut greenhouse gases/pollution
  - More efficient (technical efficiency)
- Disadvantages
  - Low energy density (storage obstacles)
  - Non-green generation techniques (currently)

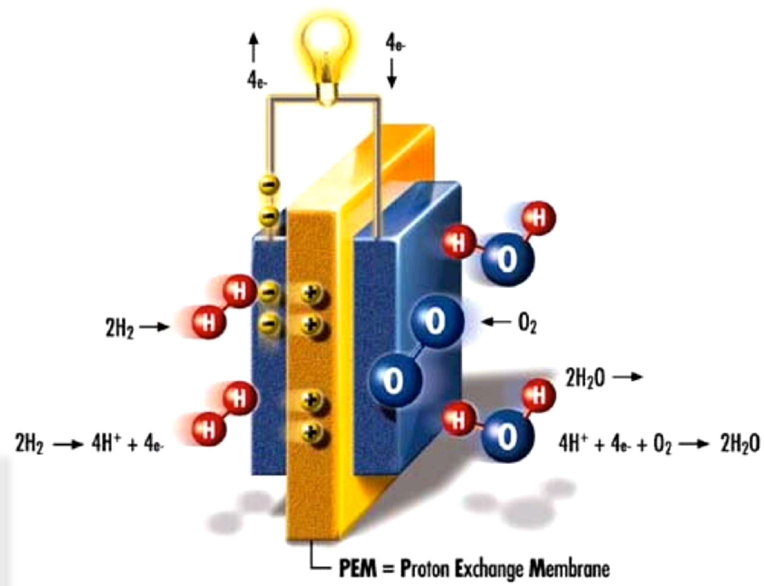
H_2 Economy: Applications

- Transportation
  - Personal
  - Commercial
  - Boats/ships
- Stationary
  - Buildings (commercial, residential)
  - Industry
- Portable electronics

Hydrogen: Three Components

- Generation
  - Thermal processes
  - Electrolytic processes
  - Photolytic processes
- Storage
  - Gaseous or Liquid
  - Materials-based
- Utilization
  - Combustion
  - Fuel Cells

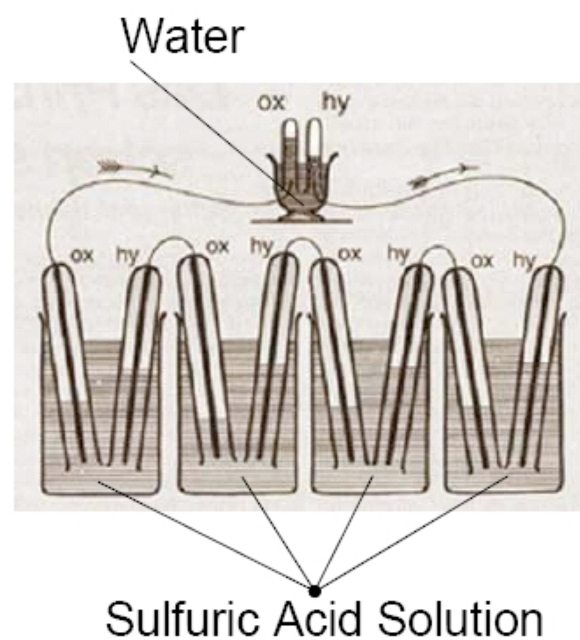
Why Fuel Cells?



HYDROGEN UTILIZATION

History of Fuel Cells

- Discovered by Sir William Grove (1839)
  - Bubbled H_2 around one electrode of electrolysis cell
  - 1st fuel cell principal: make electricity *directly* from chemicals
  - 50 cells in series generated 25-30V



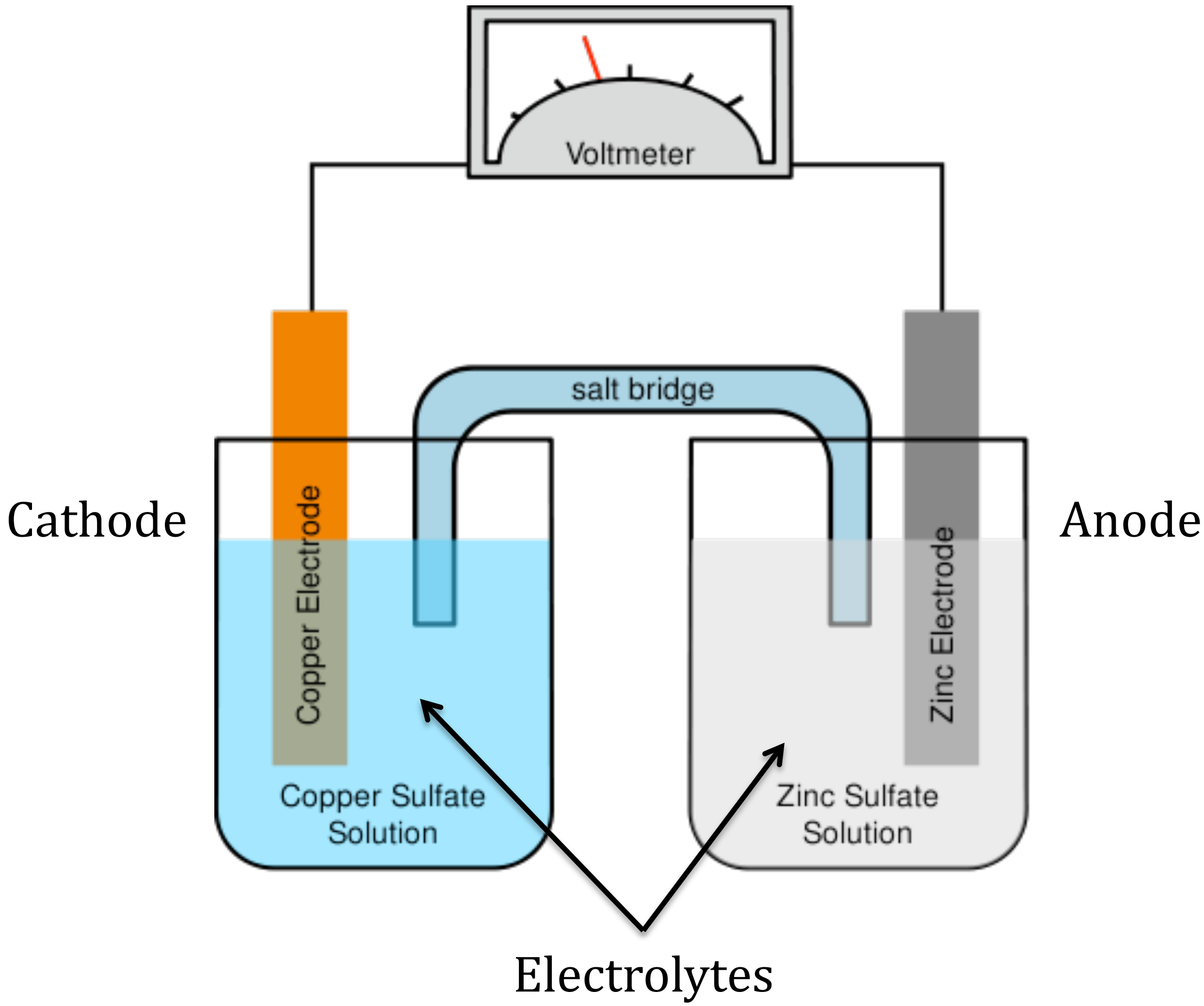
History of Fuel Cells: 1800s

- Work continued in Germany (mostly)
  - Improvements and replications
- Friedrich Wilhelm Ostwald
  - Determined interconnected roles of the various components of fuel cell (1893)
  - "Pollution for cities if the current path of combustion to obtain energy continued to be followed" (1894 prediction)

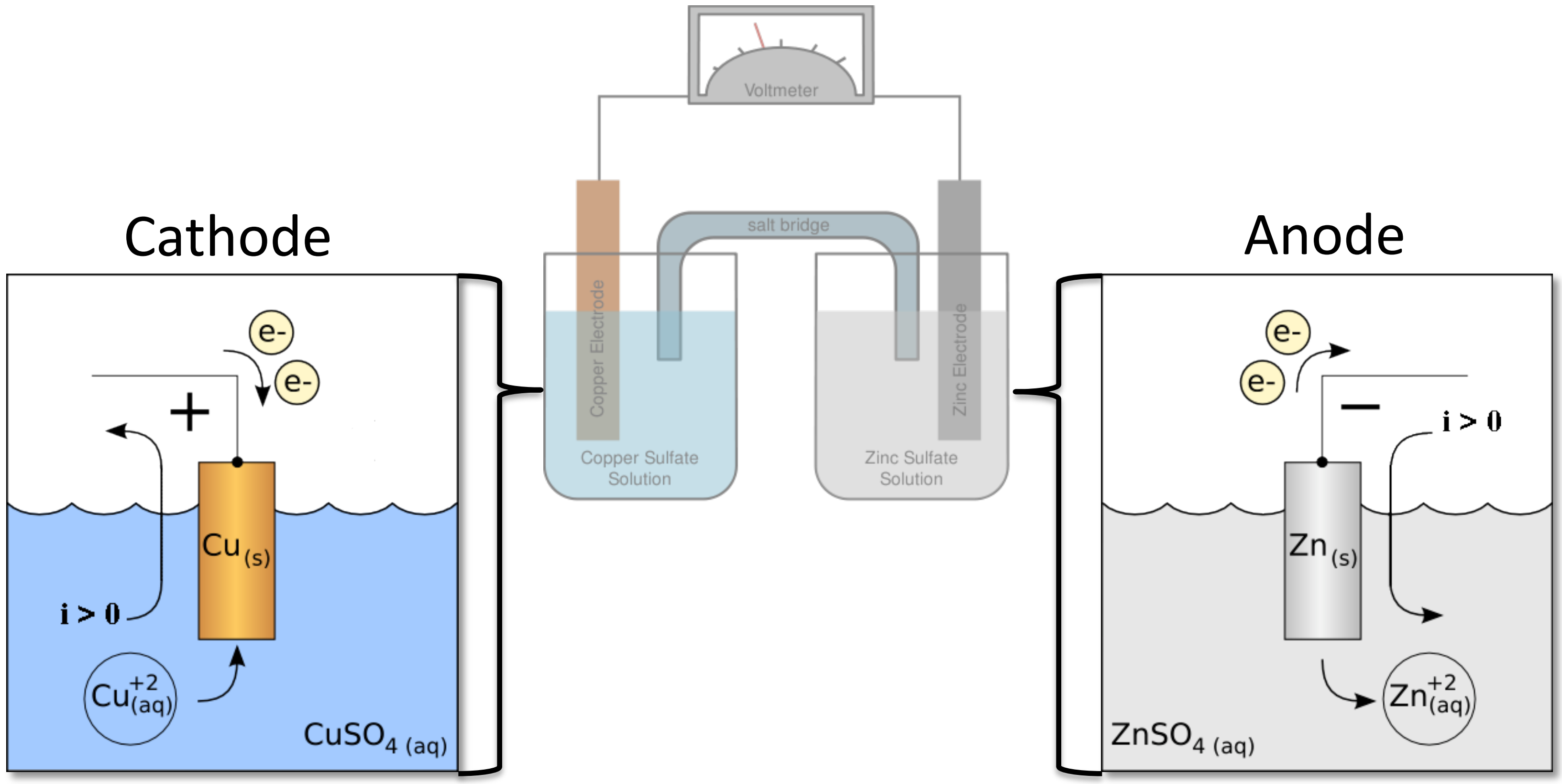
History of Fuel Cells (cont)

- Early 20th Century
  - Electric cars competed with I.C. engines
  - Long charging time for batteries
- Francis Thomas Bacon
  - Rediscovered fuel cells in 1939
  - 1959 developed 5-kW fuel cell
  - NASA implements fuel cells (Bacon) for Apollo

Electrochemical Cell (Battery)



Half-Cell Reactions



$$Cu^{2+} + 2e^{-} \longrightarrow Cu \qquad Zn \longrightarrow Zn^{2+} + 2e^{-}$$

(during discharge)

Batteries

- Electrical energy storage
  - Electricity produced elsewhere
- Charging (electricity input)
  - Electrode reactions → New material formation
- Discharging (electricity output)
  - Electrochemical reactions → Electricity

Fuel Cells = Batteries?

- Similarities
  - Chemical energy converted to electricity
  - Spontaneous reaction ($\Delta G < 0$)
    - Battery: only during discharge
    - Fuel Cell: while fueled
  - Energy (electricity) released
    - Proceeds down free energy gradient

Fuel Cells ≠ Batteries

- Batteries
  - Require charging (periodic device)
  - Consumption/formation of electrodes during operation
  - Degradation over time
- Fuel Cells
  - Continual operation (w/ fuel supply)
  - No change to electrodes (slow deterioration)

What are Fuel Cells?

- Electrical energy producer
  - Cathode: Oxygen reduced

$$1/2\,O_2 + 2\,e^- \longrightarrow O^{2-}$$

  - Anode: Fuel (H_2, CH_3OH, CH_4) oxidized

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

  - Free energy from fuel oxidation released as electricity

$$H_2 + 1/2\,O_2 \longrightarrow H_2O$$ (exothermic)

Fuel Cell Stack

- Individual cells combined into a "stack"
  - Number of fuel cells determines total voltage
  - Surface area of each cell determines total current.
  - Multiplying voltage by current yields total electrical power

Power (W) = Voltage (V) X Current (A)

Why Hydrogen?

Possible Fuel Cell Combinations

Reaction	Potential (V)
$H_2 + 1/2\,O_2 \longrightarrow H_2O$	1.229
$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$	1.060
$C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$	1.093
$C_{10}H_{22} + 15\,1/2\,O_2 \longrightarrow 10\,CO_2 + 11\,H_2O$	1.102
$CH_3OH + 3/2\,O_2 \longrightarrow CO_2 + 2\,H_2O$	1.222
$H_2 + Br_2 \longrightarrow 2\,HBr$	1.066

Alternative fuels

Pros: Liquid - easier to handle

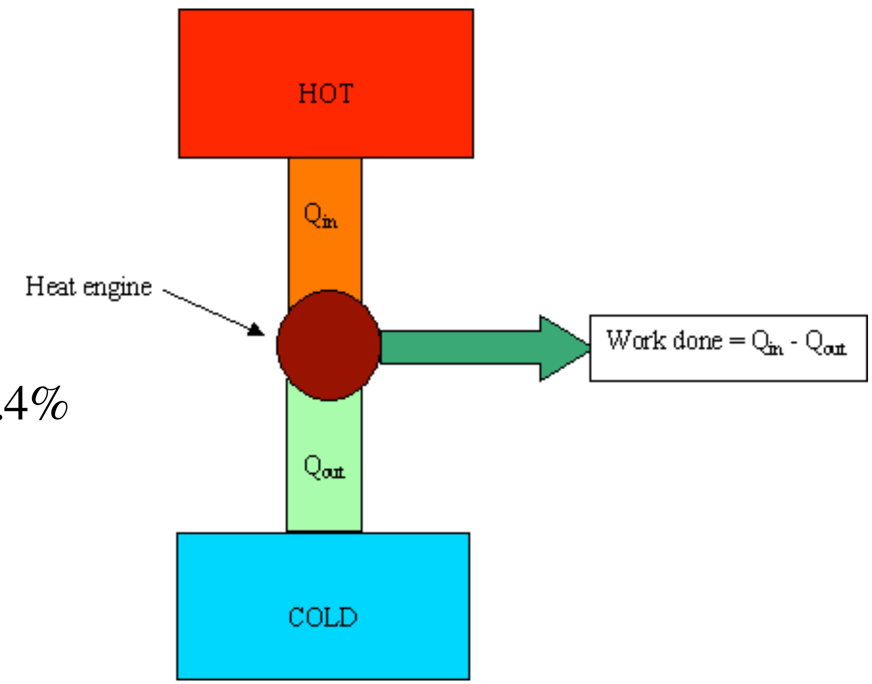
Why Not Combustion?

- Hydrogen combustion

$$H_2 + 1/2\,O_2 \longrightarrow H_2O + \text{heat} \quad (286\ \text{kJ/mol})$$

- Heat engine (ideal)
  - Carnot efficiency limit
  - i.e. auto-ignition temp

$$\frac{T_H - T_C}{T_H} = \frac{500\,^{\circ}C - 25\,^{\circ}C}{(500\,^{\circ}C + 273.15)} \times 100 = 61.4\%$$



What About Fuel Cells?

Electrochemical Efficiency (ideal)

$$-\Delta G = W_{rev} - P\Delta V$$

$$P\Delta V = 0 \Rightarrow -\Delta G = W_{rev}$$

$$W_{rev} = nFV_e \Rightarrow -\Delta G = nFV_e$$

$\Delta G =$ available energy

$\Delta H =$ total energy change

$$\text{maximum efficiency}\left(\varepsilon_{\max}\right) = \frac{\Delta G}{\Delta H} = -\frac{nFV_e}{\Delta H}$$

Fuel Cell Efficiency (ideal)

- For example: $H_2 + 1/2\,O_2 \longrightarrow H_2O$

$$V_e = 1.229V \qquad \Delta H = 285.85kJ$$

$$\text{Faraday's constant } (F) = 96{,}485.34C \cdot mol^{-1}$$

$$\text{maximum efficiency}\left(\varepsilon_{\max}\right) = 83\%$$

- Compared to fuel combustion
  - Higher T_H value, better efficiency
  - Heat engine T_H at 1500˚C ≈ fuel cell at 190 ˚C[1]

[1]Modern Electrochemistry 2B, p1798; Bockris, J., Reddy, A.

Two Categories of Fuel Cells

- High temperature
  - PAFC (phosphoric acid)
  - MCFC (molten carbonates)
  - SOFC (solid oxide)
- Low temperature
  - AFC (alkaline fuel cell)
  - PEMFC (polymer electrolyte fuel cells)

High Temperature Fuel Cells

- PAFC (phosphoric acid) – ≥200 ˚C
  - $H_4P_2O_7$ liquid electrolyte
  - Stationary power, 50 to 200 kW range (37-42%)
- MCFC (molten carbonates) – 600-700 ˚C
  - Na and K carbonates/$LiAlO_2$matrix (~60%)
  - electrical utility, industrial, and military applications
- SOFC (solid oxide) – 600-1000 ˚C
  - solid, nonporous metal oxide electrolyte
  - no Pt catalyst necessary

Low Temperature Fuel Cells

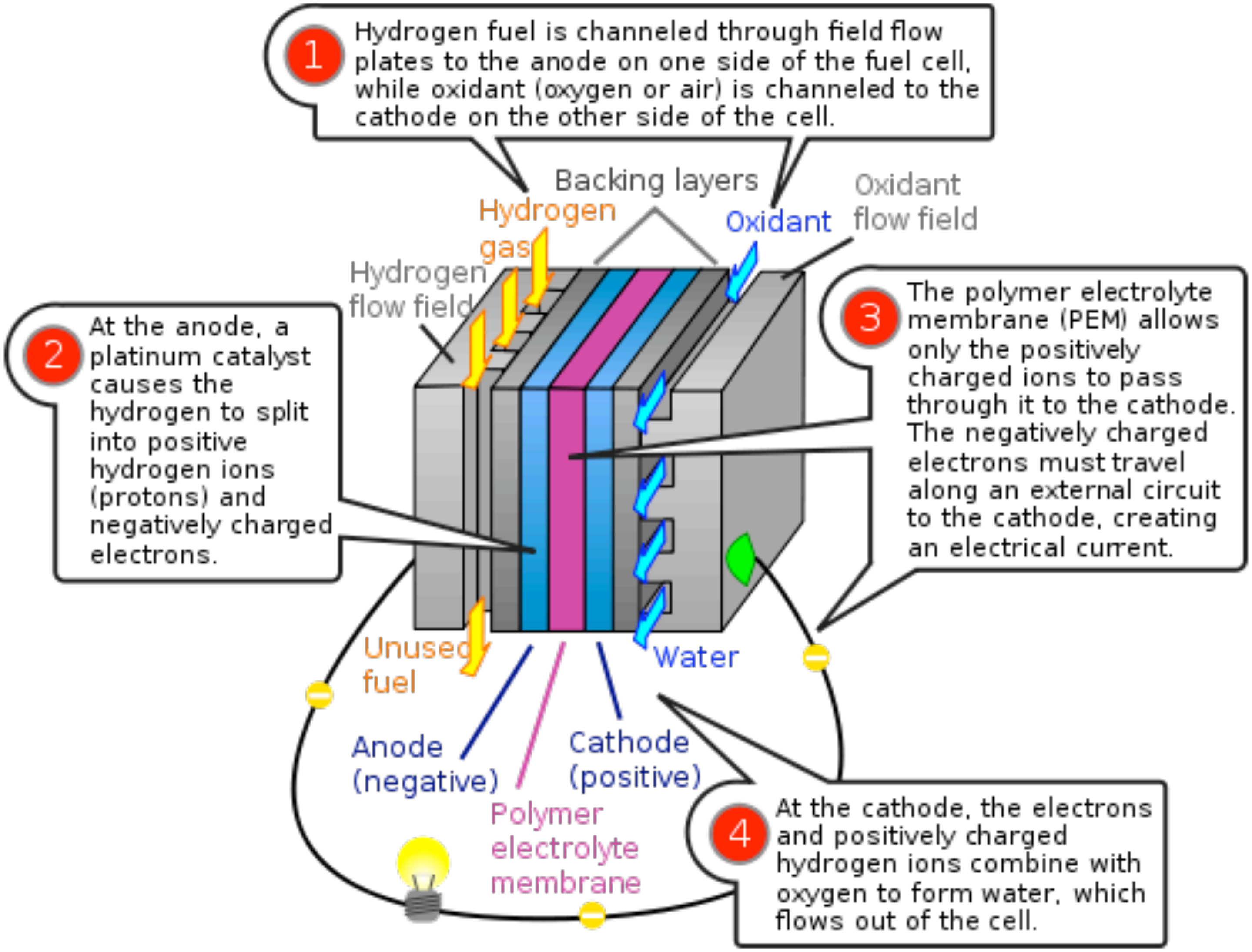
- AFC (alkaline fuel cell) – 80 ˚C
  - Oldest design (Bacon cell)
  - Aqueous alkaline (KOH) electrolyte
  - CO_2 intolerant -> requires purified air
  - Highly efficient (near 70%)
- PEMFC (polymer electrolyte fuel cells) – <200 ˚C
  - Stationary/portable applications
  - Solid polymer membrane as electrolyte

PEMFC

Polymer electrolyte fuel cells

- Proton conducting membrane as electrolyte
  - Perfluorosulphonic acid polymer (typical)
- Operating temperature <100 ˚C
- Pt-impregnated electrodes
  - Catalyze cell reactions
- Only membrane is hydrated
  - Sufficient conductivity

PEMFC



1 Hydrogen fuel is channeled through field flow plates to the anode on one side of the fuel cell, while oxidant (oxygen or air) is channeled to the cathode on the other side of the cell.
Backing layers
Hydrogen gas
Oxidant
Oxidant flow field
Hydrogen flow field
2 At the anode, a platinum catalyst causes the hydrogen to split into positive hydrogen ions (protons) and negatively charged electrons.
3 The polymer electrolyte membrane (PEM) allows only the positively charged ions to pass through it to the cathode. The negatively charged electrons must travel along an external circuit to the cathode, creating an electrical current.
Unused fuel
Water
Anode (negative)
Cathode (positive)
Polymer electrolyte membrane
4 At the cathode, the electrons and positively charged hydrogen ions combine with oxygen to form water, which flows out of the cell.

PEMFC

- Higher power density (compared to other FCs)
  - Compact
  - Lightweight
- Solid electrolyte
  - Less expensive to manufacture
  - Less corrosion
- Applications
  - Transportation
  - Portable electronics

Fuel Cells: Major Hurdles

- Proton-conducting membrane
  - Must maintain proper hydration
- CO intolerant catalyst
  - Purified fuel to prevent catalyst poisoning
- Pt electrocatalysts (electrodes)
  - Very limited supply => $$$$
- Manufacturing costs
  - $75 to $100/kW (2005)
  - Need to be ~$30/kW

H_2: Fuel Cell Summary

Fuel Cell Type	Output	Electrical Efficiency	Cost (estimated)
Polymer Electrolyte Membrane (PEM)	<1kW –250kW	53-58% (transport) 25-35% (stationary)	$75-110/kW
Alkaline (AFC)	10kW – 100kW	60%	$80–200/kW
Phosphoric Acid (PAFC)	50kW – 1MW (250kW module typical)	>40%	$1500-2000/kW (target)
Molten Carbonate (MCFC)	<1kW – 1MW (250kW module typical)	45-47%	$1200/kW (target) >$2400/kW
Solid Oxide (SOFC)	<1kW – 3MW	35-43%	$400/kW (target)