Tfy-56.4332
Fuel cells and hydrogen
Lecture #1

Introduction to fuel cells

Basics of fuel cells

Source: Ryan O'Hayre et al: Fuel Cell Fundamentals. Wiley, 2006.

Slides: Peter Lund (+Janne Halme)

Lecturing 2015: Janne Halme

Course outline

Components Period: III - IV (alternate years, lectured spring 2015)

- 8 **Lectures** Wednesdays 12:15 – 14:00 K215
  - Lecturers: Doc. Janne Halme (main), Prof. Peter Lund, Dr. Olli Himanen (VTT)
- 6 **Exercises** Mondays 12:50 – 14:00 K326
  - Assistants: Dr. Imran Asghar, Mr. Erno Kemppainen
- 6 **Homework** returned exercises, 5/6 required
- 2 hours **lab work** in groups in March, 3 page lab report
- Sit in **exam**, or alternatively a **project work**

Workload

- Lectures 16 h; Exercises 12 h + assistant reception times 8 hours; Home work 14 h; Group work: 20 h; Independent studies and exam: 60 h

Passing and evaluation

Spring 2015: Written assignments AND (exam OR project work)

- Homework 5/6, group labwork & lab report 1/1
- exam OR group project work & report
- evaluation: homework (20 %), lab report (20%), exam OR project work (60 %)

After Spring 2015: Exam (100 %)

Course material

- Lecture notes and exercises are delivered through NOPPA
- Books:
  1) **Fuel Cell Handbook 7th edition**. U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory (through NOPPA)
  2) **Frano Barbir: PEM Fuel Cells, Theory and Practice**. Elsevier B.V. 2005. ISBN-13: 978-0-12-078142-3 / ISBN-10: 0-12-078142-5. Available in the main library. On-line access at campus (Ebrary, Knovel, Elsevier)
  3) **Ryan O'Hayre et al: Fuel Cell Fundamentals**. Wiley, 2006.
- Group Work will be based on 1)-2) and other material

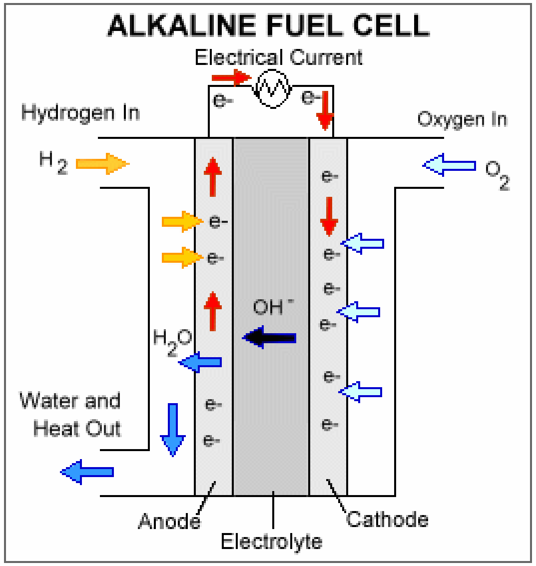
Additional: Plenty of E-books available via Aalto Library

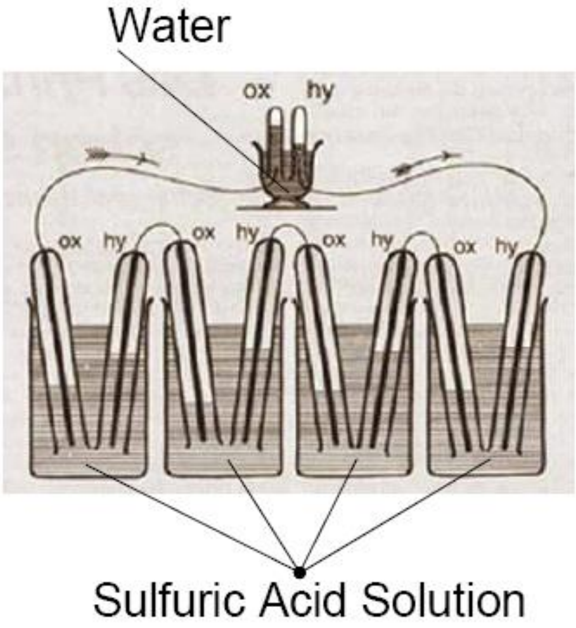
Examples:

- Fuel cell technology handbook / edited by Gregor Hoogers, 2003, (link)
- Fuel cells : current technology challenges and future research needs / Noriko Hikosaka Behling. 2013 (Link)

What is a fuel cell ?

- A fuel cell is an electrochemical device that converts chemical energy from a fuel into electrical energy without any moving parts
- Fuel cells are operationally equivalent to a battery, but the reactants or fuel in a fuel cell can be replaced unlike a standard disposable or rechargeable battery



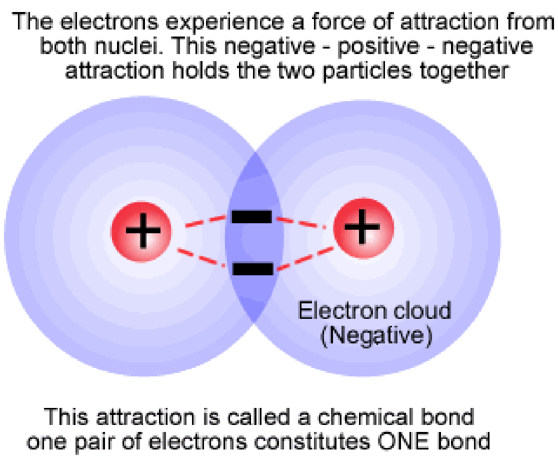


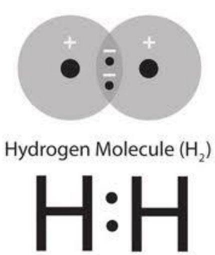
Examples of applications

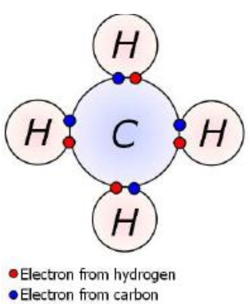
- Mobile, stationary and portable power applications
- Power range from mWs to few hundred kWs

Chemical energy release – reconfiguring of bonds

- Atoms are connected through bonds that lower their total energy
- Bond is formed → energy is released
- Bond is broken → energy is absorbed
- Net release of energy : energy released > energy absorbed







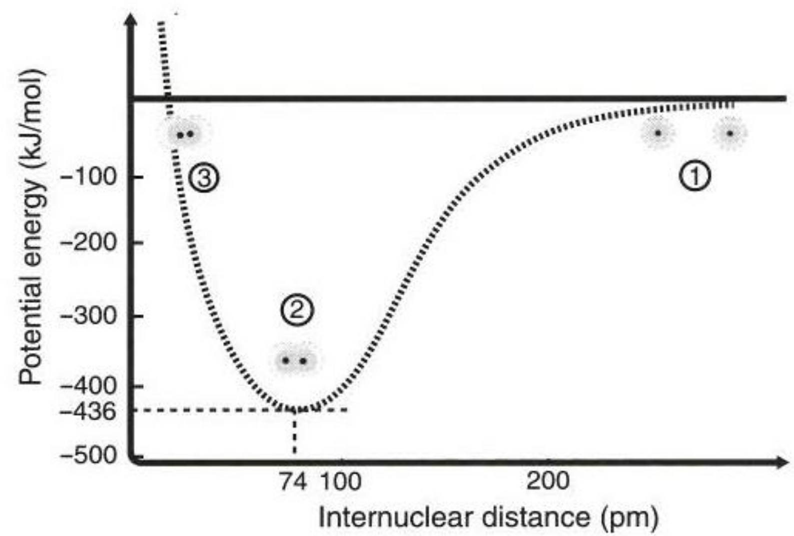


Figure 1.3. Bonding energy versus internuclear separation for hydrogen–hydrogen bond. (1) No bond exists. (2) Most stable bonding configuration. (3) Further overlap unfavorable due to internuclear repulsion.

Simple combustion reaction

- Basic combustion equation: $H_2 + ½\ O_2 \rightleftharpoons H_2O$ + heat
- Collision of molecules → O_2 and H_2 bonds break → New H_2O bonds formed → Energy of new configuration lower → Heat released
- Reconfiguration of bonds involves fast electron transfer;

  Q: how can we slow the e^- transfer from fuel species to oxidant species ?

  A: separate reactants so that electron reconfiguration is much slower

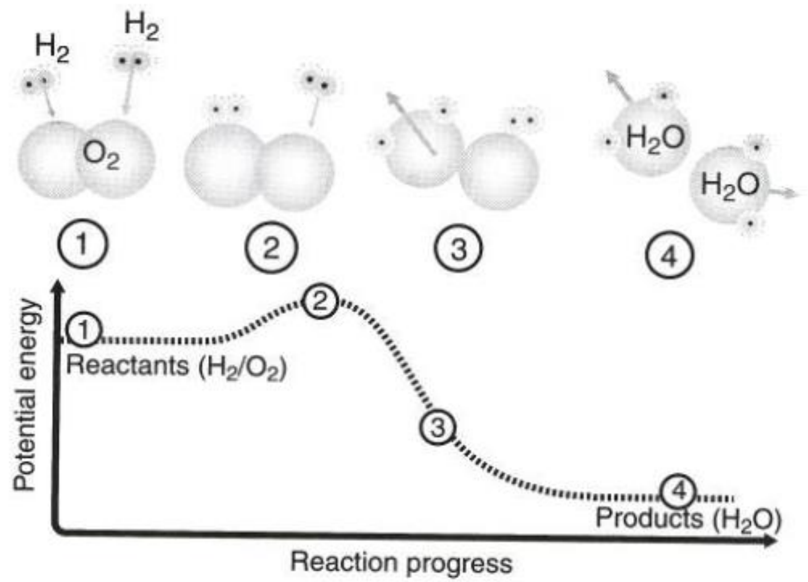


Figure 1.2. Schematic of H_2–O_2 combustion reaction. (Arrows indicate the relative motion of the molecules participating in the reaction.) Starting with the reactant H_2–O_2 gases (1), hydrogen–hydrogen and oxygen–oxygen bonds must first be broken, requiring energy input (2) before hydrogen–oxygen bonds are formed, leading to energy output (3, 4).

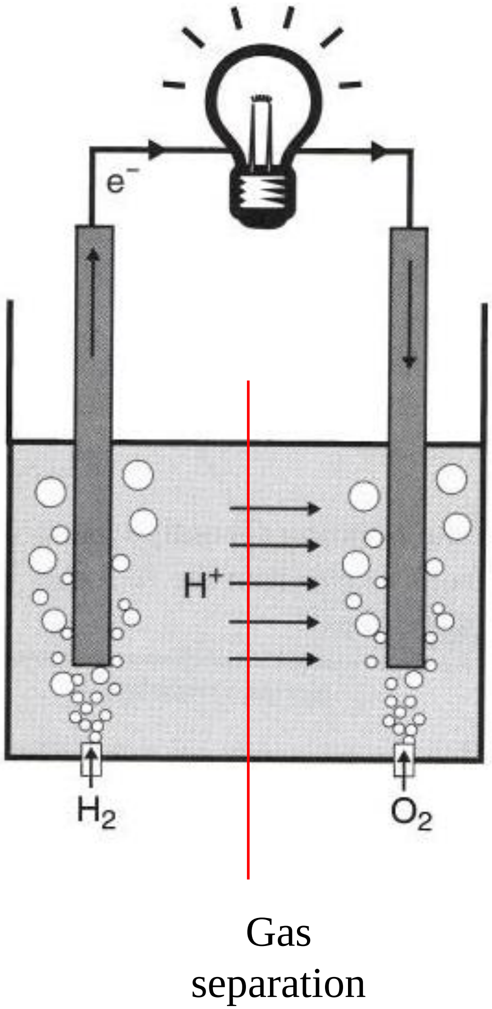
Physical principle of a fuel cell

- In a fuel cell, electrons are forced to move through an external circuit before completing the reaction (i.e. reconfiguring the bonds)

$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O$$

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

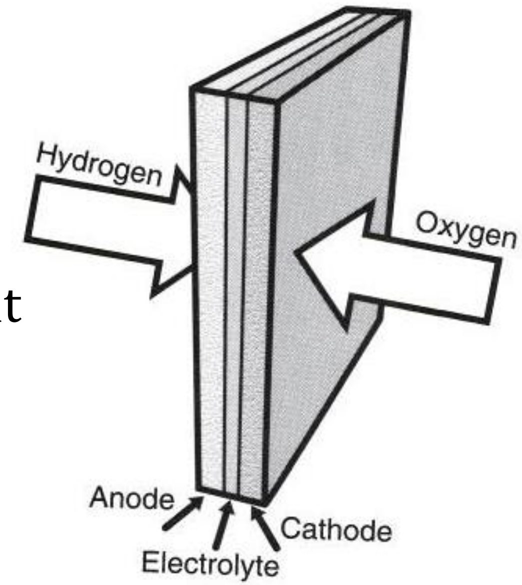
$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$$



- How ? An electrolyte is employed to allow ions (e.g. H^+, O^{2-}) but not electrons (e^-) to flow
- Electrolyte = ionic conductor
- A simple fuel cells has two electrodes (for both half reactions) and an electrolyte
- An ionically permeable membrane may be used to keep the gases separate

Basic operation of FC

- Reaction area determines the current (electricity) production → large areas lead to large current → maximize surface-to-volume → thin and porous structures
- Anode = oxidation reaction (electrons liberated)
- Cathode = reduction reaction (electrons consumed)
- Good gas access necessary; oxidant (air) and reactant (fuel) separated by the electrolyte



Major steps in a fuel cell

1. Flow field plates (channels, groves) distribute the reactants over the electrodes
2. Fast electrochemical reactions result in high current; catalysts needed; kinetics is a limiting factor
3. Charge balance requires ion transport (by hopping), slow and losses → thin electrolyte preferred
4. Product removal. Similar to 1)

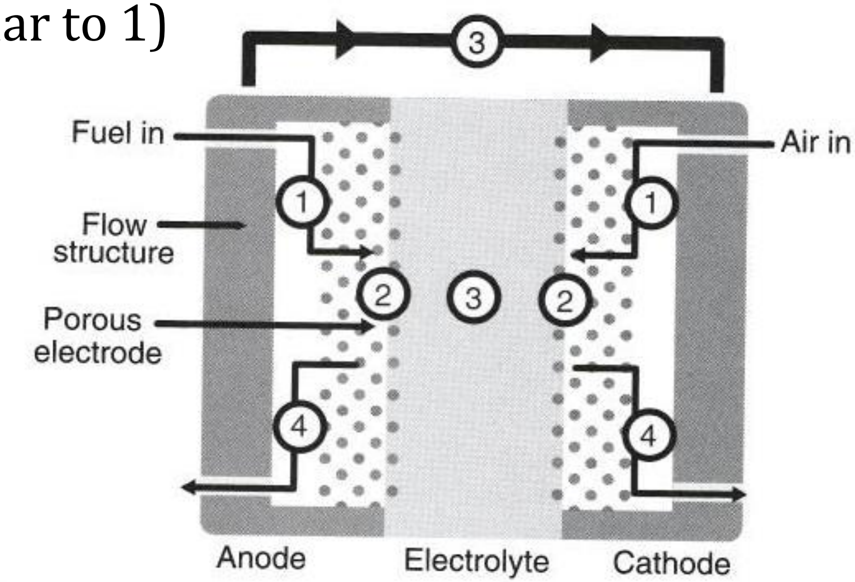
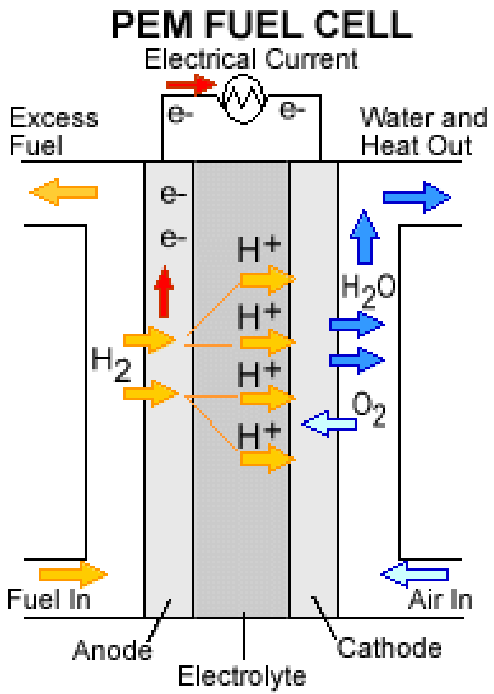


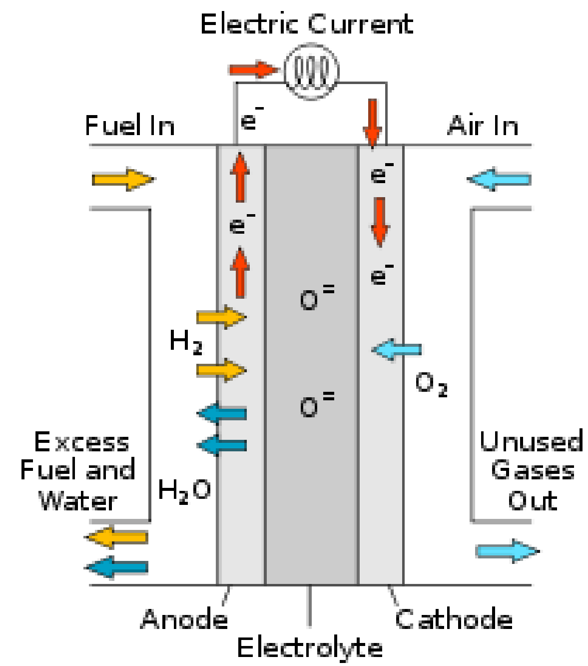
Figure 1.8. Cross section of fuel cell illustrating major steps in electrochemical generation of electricity: (1) reactant transport; (2) electrochemical reaction; (3) ionic and electronic conduction; (4) product removal.

Fuel cell types

- Fuel cells are distinguished based on the electrolyte used
- All have same underlying operation principle, but operate at different temperatures, use different materials, differ in performance, etc.
- Most important fuel cells are: Polymer electrolyte membrane fuel cell (**PEMFC**) and solid oxide fuel cell (**SOFC**).



SOFC



Fuel cell general characteristics

Fuel cell type	Electrolyte material	Transported ion	Operating temperature
Polymer electrolyte membrane fuel cell (PEMFC)	Cation conducting polymer membrane	H^+	20-80 °C
Direct methanol/ethanol fuel cell (DMFC/DEFC)	Cation conducting polymer membrane	H^+	20-80 °C
Direct formic acid fuel cell (DFACF)	Cation conducting polymer membrane	H^+	20-80 °C
Direct borohydride fuel cell (DBFC)	Aqueous alkaline solution (e.g. KOH), Anion or cation conducting polymer membrane	OH^- or Na^+	20-80 °C
Phosphoric acid fuel cell (PAFC)	Molten phosphoric acid (H_3PO_4)	H^+	150-200 °C
Alkaline fuel cell (AFC)	Aqueous alkaline solution (e.g. KOH)	OH^-	<250 °C
Molten carbonate fuel cell (MCFC)	Molten alkaline carbonate (e.g. $NaHCO_3$)	CO_3^{2-}	600-700 °C
Solid oxide fuel cell (SOFC)	O^{2-} conducting ceramic oxide (e.g. Y_2O_3-stabilized ZrO_2)	O^{2-}	600-1000 °C

Comparison of fuel cell technologies

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

FUEL CELL TECHNOLOGIES PROGRAM

Comparison of Fuel Cell Technologies

Fuel Cell Type	Common Electrolyte	Operating Temperature	Typical Stack Size	Efficiency	Applications	Advantages	Disadvantages
Polymer Electrolyte Membrane (PEM)	Perfluoro sulfonic acid	50-100°C 122-212° typically 80°C	< 1kW–100kW	60% transportation 35% stationary	• Backup power • Portable power • Distributed generation • Transporation • Specialty vehicles	• Solid electrolyte reduces corrosion & electrolyte management problems • Low temperature • Quick start-up	• Expensive catalysts • Sensitive to fuel impurities • Low temperature waste heat
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90-100°C 194-212°F	10–100 kW	60%	• Military • Space	• Cathode reaction faster in alkaline electrolyte, leads to high performance • Low cost components	• Sensitive to CO_2 in fuel and air • Electrolyte management
Phosphoric Acid (PAFC)	Phosphoric acid soaked in a matrix	150-200°C 302-392°F	400 kW 100 kW module	40%	• Distributed generation	• Higher temperature enables CHP • Increased tolerance to fuel impurities	• Pt catalyst • Long start up time • Low current and power
Molten Carbonate (MCFC)	Solution of lithium, sodium, and/ or potassium carbonates, soaked in a matrix	600-700°C 1112-1292°F	300 kW-3 MW 300 kW module	45-50%	• Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Suitable for CHP	• High temperature corrosion and breakdown of cell components • Long start up time • Low power density
Solid Oxide (SOFC)	Yttria stabilized zirconia	700-1000°C 1202-1832°F	1 kW–2 MW	60%	• Auxiliary power • Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Solid electrolyte • Suitable for CHP & CHHP • Hybrid/GT cycle	• High temperature corrosion and breakdown of cell components • High temperature operation requires long start up time and limits

For More Information

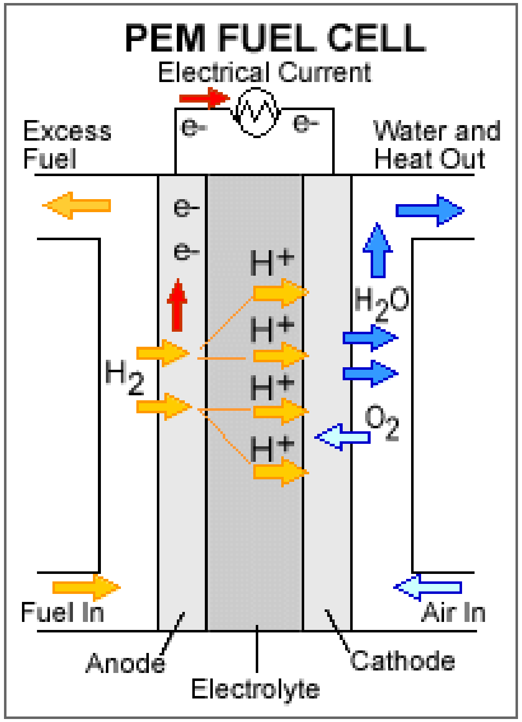
More information on the Fuel Cell Technologies Program is available at *http://www.hydrogenandfuelcells.energy.gov*.

PEM Fuel Cell

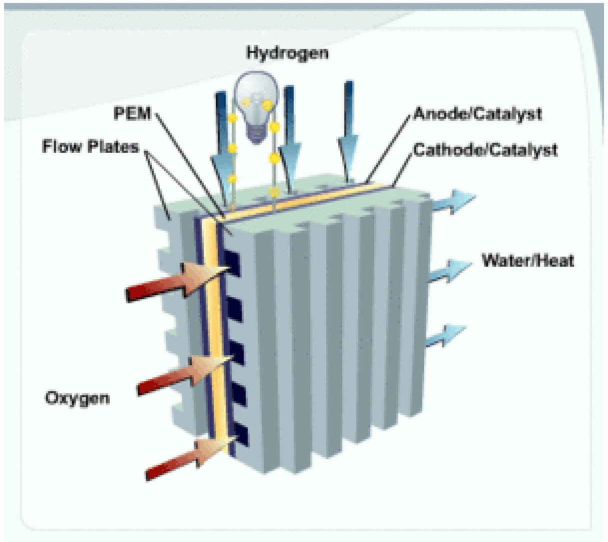
Anode: $$H_2 \rightleftharpoons 2H^+ + 2e^-$$

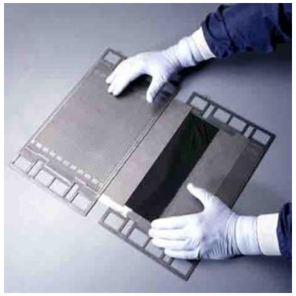
Cathode: $$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$$

Overall: $$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$$



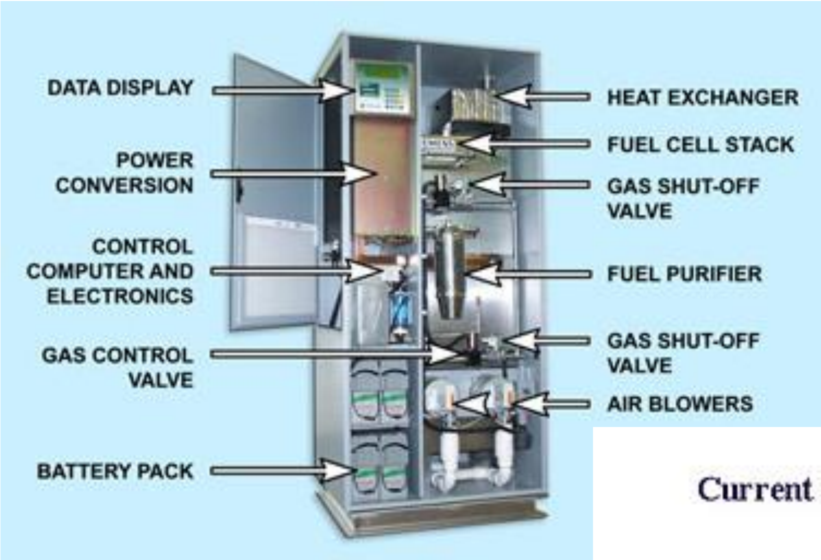
- The most popular fuel cell type used in mobile, stationary and portable applications (1 mW-100 kW); low temperature operation (<<100 °C)
- Solid electrolyte (polymer) that requires water to make H^+ conductive; slow electrochemistry on the cathode (air) requiring a Pt-catalyst
- Mass and heat flow management important





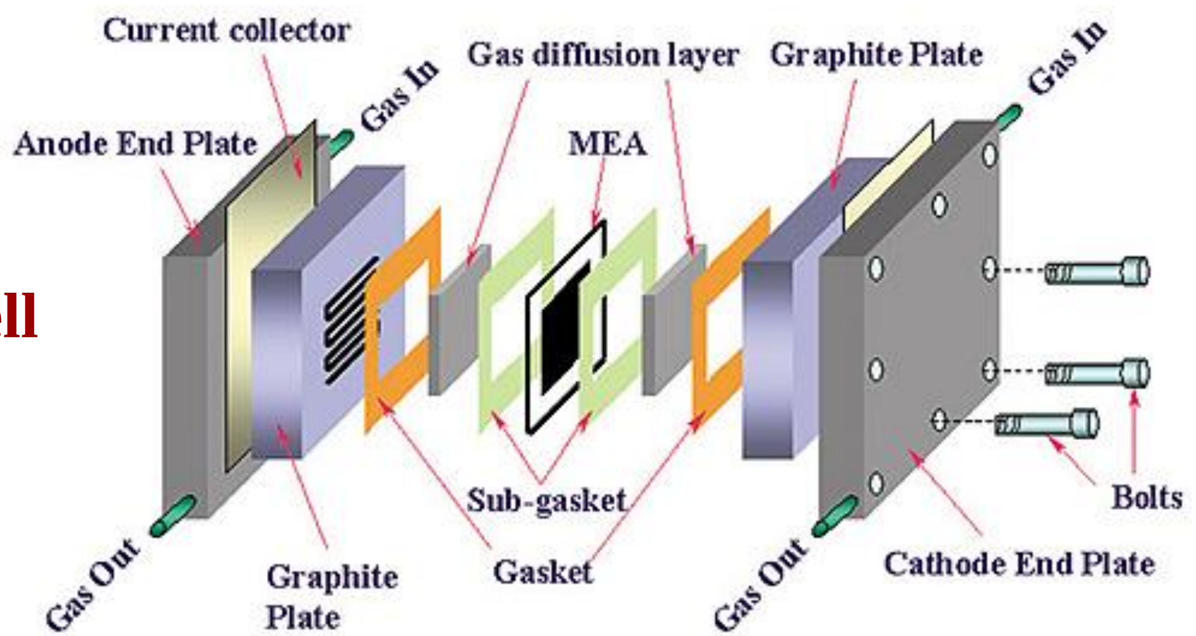
Fuel cell components (example: PEMFC)

System



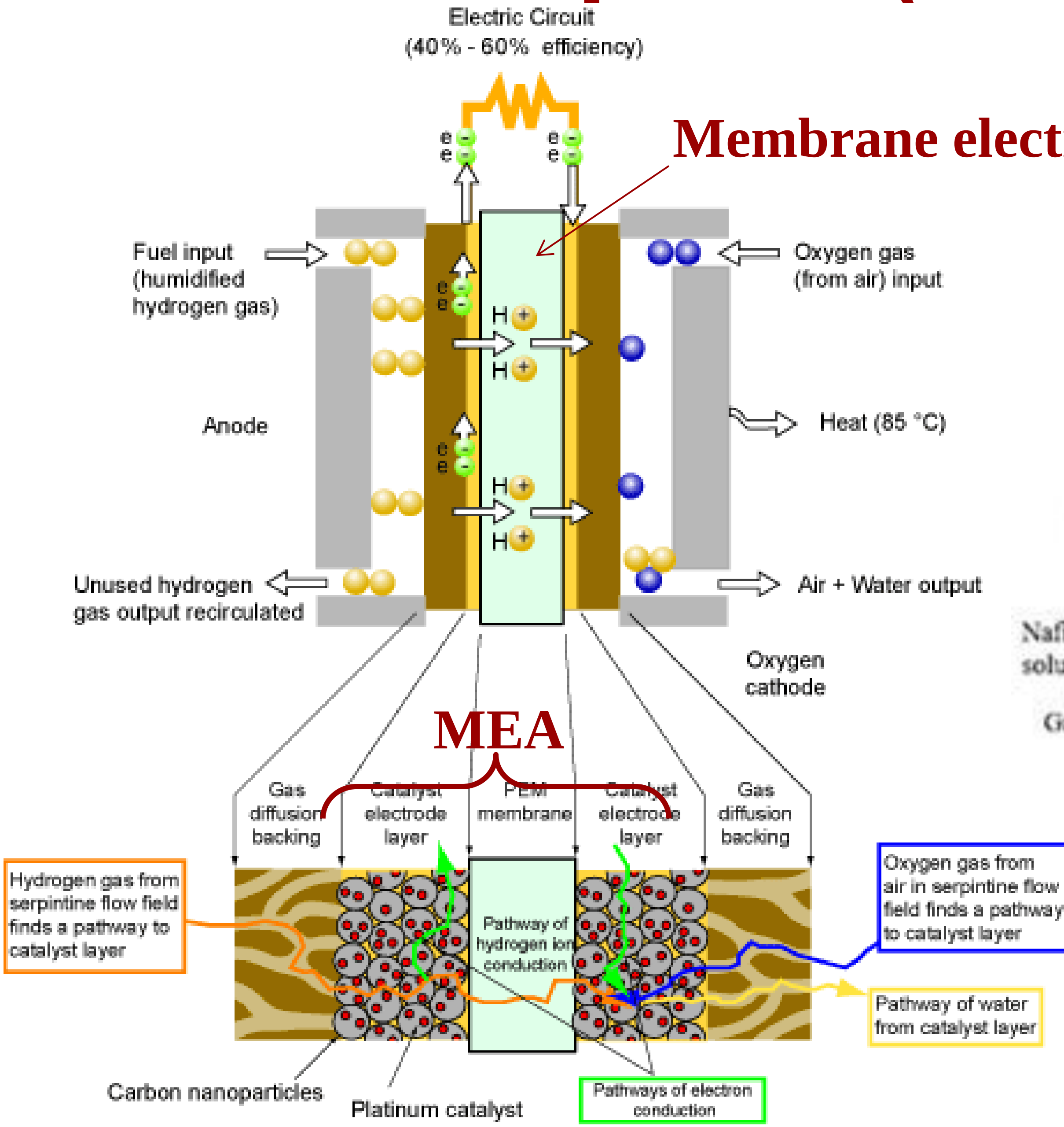
Stack

Cell

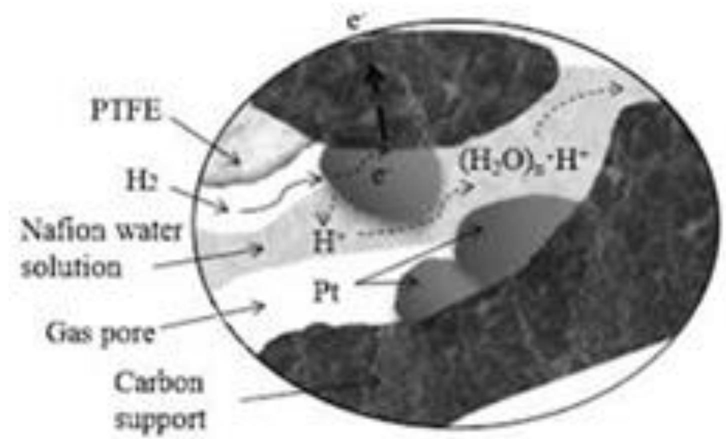


Fuel cell components (example: PEMFC)

Membrane electrode assembly (MEA)



Reaction sites at the electrodes (three-phase boundary)



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

SOFC Fuel Cell

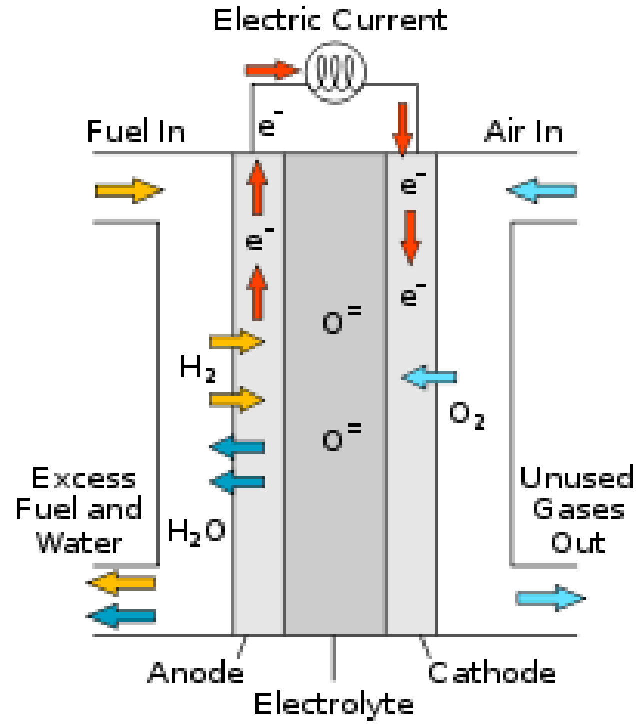
Anode:

- $H_2 + O^{2-} \rightarrow 2H_2O + 2e^-$
- $CO + O^{2-} \rightarrow CO_2 + 2e^-$
- $CH_4 + 4O^{2-} \rightarrow 2H_2O + CO_2 + 8e^-$

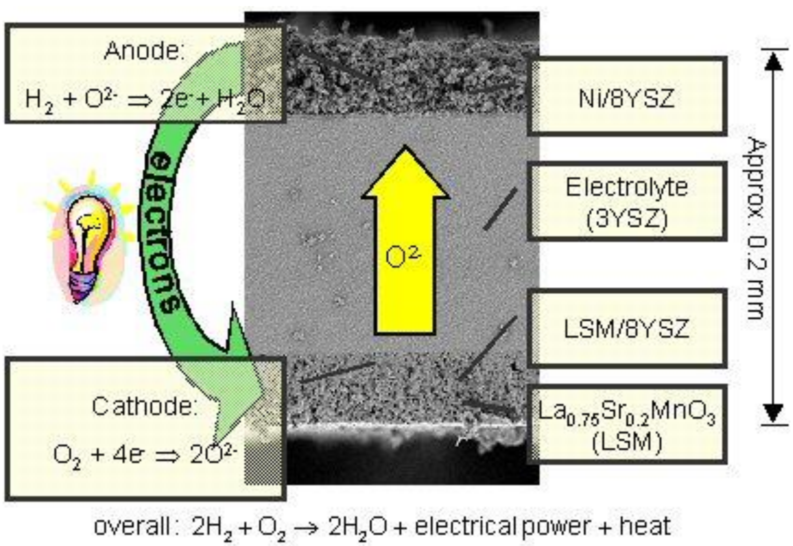
Cathode: $\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$

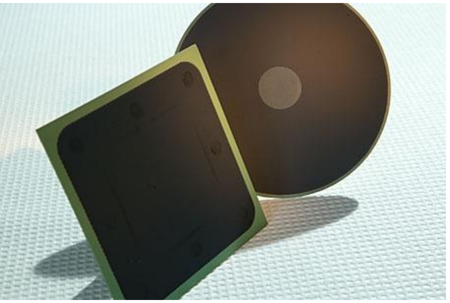
Overall:

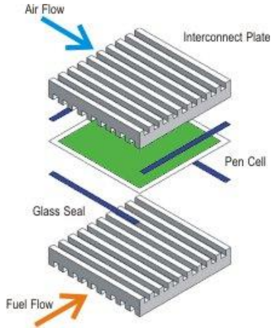
- $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
- $CO + \frac{1}{2}O_2 \rightarrow CO_2$
- $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



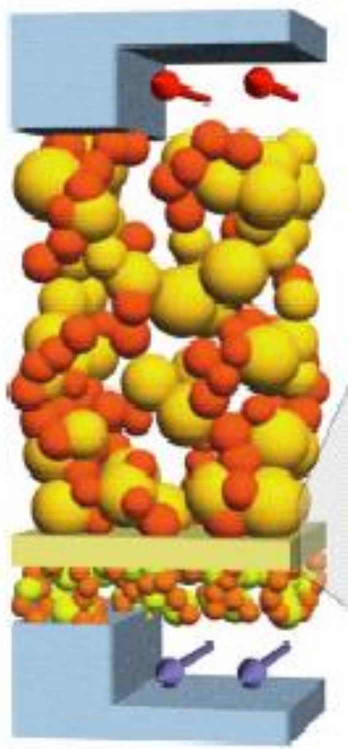
- SOFC= high temperature fuel cells (>700 °C); ceramic electrolyte with T-dependent ion conductivity
- High T → flexible to fuels, no catalysts
- High T → material problems, slow response
- Well suitable for co-generation

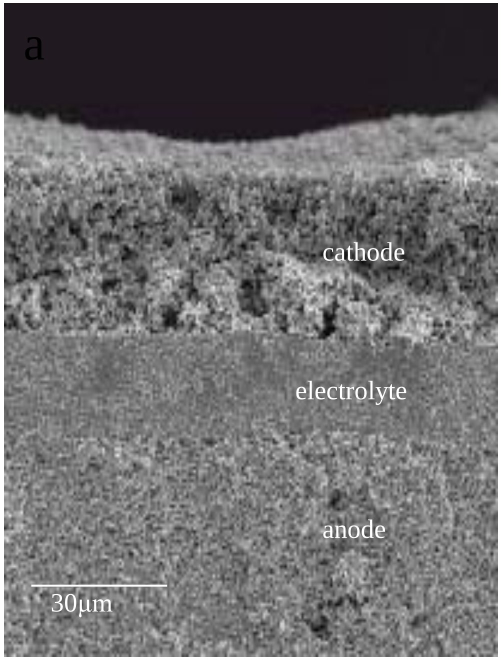




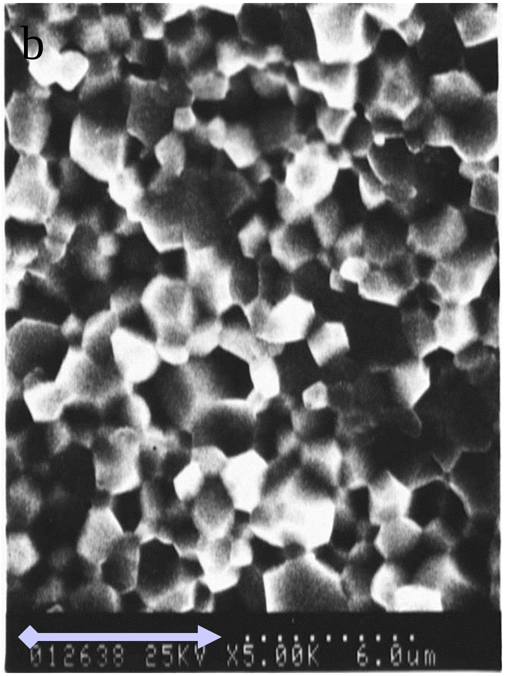


SOFC Fuel Cell





Electrolyte 25µm



b) porous anode

Fuel cell performance

- Fuel cell performance is described by the current-voltage (I-V) curve
- Normalized : current density mA/cm^2, power density W/cm^2 (kW/L, W/kg))
- Ideal thermodynamical voltage versus real voltage with loss mechanisms
  - Activation losses (electrochemical reactions, kinetics)
  - Ohmic losses (ionic and electronic conduction)
  - Concentration losses (mass transport)

$$V = E_{\text{thermo}} - \eta_{\text{act}} - \eta_{\text{ohmic}} - \eta_{\text{conc}}$$

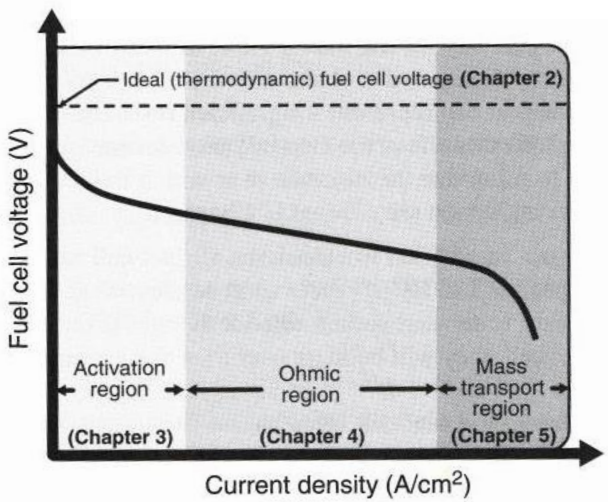
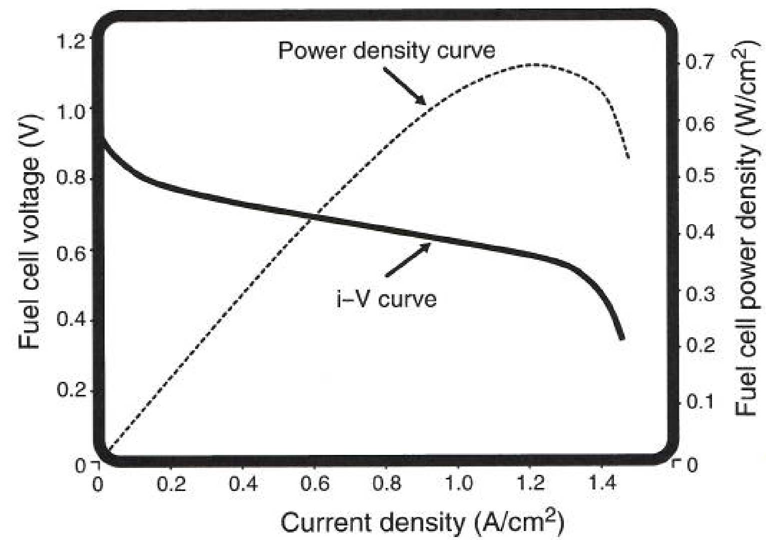


Figure 1.9. Schematic of fuel cell i–V curve. In contrast to the ideal, thermodynamically predicted voltage of a fuel cell (dashed line), the real voltage of a fuel cell is lower (solid line) due to unavoidable losses. Three major losses influence the shape of this i–V curve; they will be described in Chapters 3–5.



Fuel cell advantages and disadvantages

- Advantages:
  - More efficient than combustion engines
  - Power and capacity can easily be scaled
  - No moving parts, silent, no emissions

- Disadvantages
  - Costs
  - Volumetric power density poor, gravimetric power density better
  - Fuel (e.g. Hydrogen)
  - Several operational issues