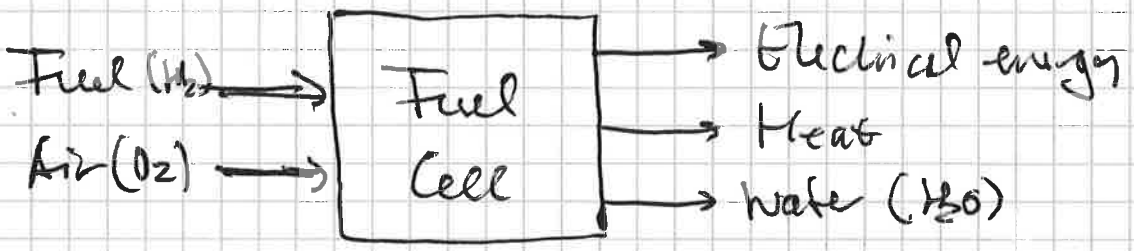
Some basic notes about Fuel cells

William Grove was the first scientist who studied this technique 1839. Fuel cells was developed during the 60-to 80-ties in the space industry. This was done due to its properties with hydrogen (H_2) as fuel among other things

Principal sketch for a Fuel cell:



Fuel cells may be made in
1, Big scale - Power-plants
2, Medium scale - Vehicle
3, small scale - Laptops

Any fuel can be used which can be oxidazed. Hydrogen as fuel and energy carrier is only one example.

Properties

Clean
Silent
High efficiency

Expensive
Material problems
Short lifetime

The construction of a fuel cell

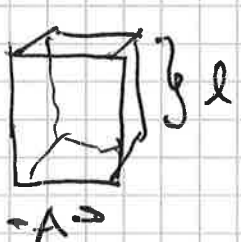
Anode reaction $H_2 \rightarrow 2H^+ + 2e^-$

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

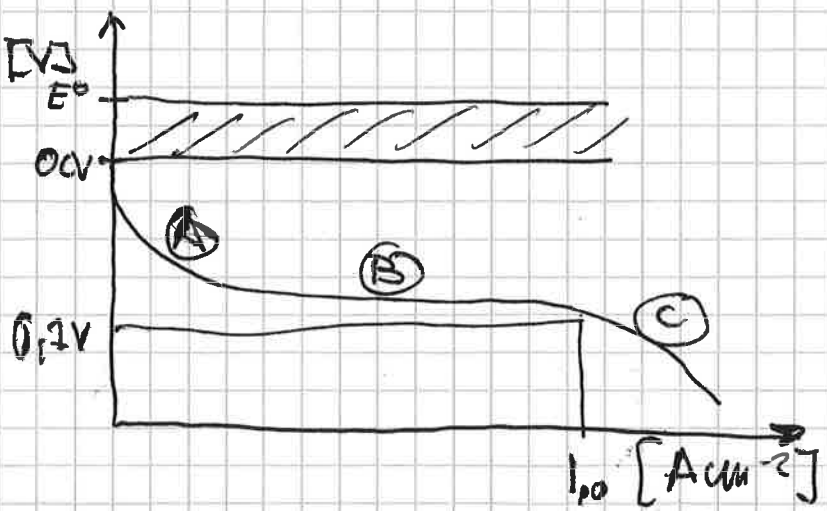
Main reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

The electrolyte: The aim is to transport ions from the anode to the cathode or the opposite. It should have a high conductivity

$\sigma = \frac{1}{R} \cdot \frac{l}{A}$ R = the membrane resistance



A fuel cells properties when running can be estimated by a Polarization curve



E^0 = The theoretical voltage
OCV = Open Current voltage
(A) = Activation losses (slow reactions)
(B) = Ohmic losses (resistance due to ionic transport)
(C) = Concentration losses (slow transport of reactants)

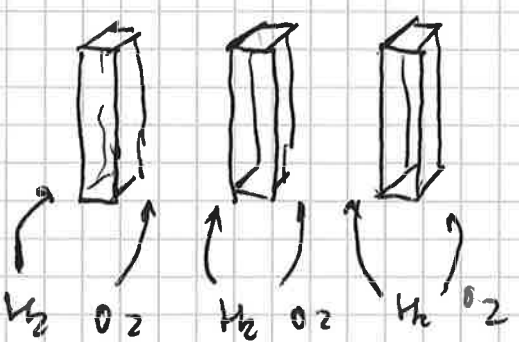
Each cell has a current density of 0,8 $A cm^{-2}$ at a voltage of 0,7 V. $P = U \cdot I = 0{,}7V \cdot 1{,}0 A = 0{,}7 W/cm^2$

The voltage can be estimated by

$$\Delta V = E_{OCV} - A \ln i - iR - m e^{n \cdot i}$$

(A) → η_{act} (B) → η_{ohm} (C) → η_{conc}.

The cells are set into series or in parallell to get the desired Powe ($P = \sum_i U_i I_i$) in stacks.



The cells are separated by a bipolar plate which is transporting the electrons.

18 cells in series give $18 \cdot 0{,}7 = 12{,}6 V$
A cell of $10 \times 10 cm^2 = 100 cm^2$ gives the power of $12{,}6 \cdot 100 = 1260$ Watt

Components in the fuel cell.

- Air pump / compressor
- Regulation of fuel, oxidant
- Regulation of the temperature
- Cooling of the cell
- Heat exchangers
- Regulation of air humidity, (supply of water)
- DC/AC or AC/DC converters
- Computer regulation of the system

Fuel cell thermodynamics

The first theorem of thermodynamics $\Delta U = \delta q - \delta w$

The second theorem of thermodynamics $dS = \delta q_{rev} / T$

ΔU = Internal energy = energy of rotation, vibration, translation and of electrons

Enthalpy $= H = U + PV$

Free energy $= G = H - TS = U + PV - TS$

Chemical equilibrium $\Delta G = -RT \ln K \quad K = \prod a_i^{\nu_i}$

$E^{eq} K = \Delta g = -nFE$

Kinetics of reaction $r = A e^{-E_a/RT} \cdot \prod a_i^{\nu_i}$

Chemical energy $\Delta H_{reaction} = \Delta H_{products} - \Delta H_{reactants}$

$\Delta H < 0 \Rightarrow$ exothermic reaction

$\Delta H > 0 \Rightarrow$ endothermic reaction

Gibbs function of reaction $g = h - Ts$ [mol]

For a reaction this yields $\Delta g_{reaction} = \Delta g_{products} - \Delta g_{reactants}$

The maximum cell voltage is when $W_{max} = -\Delta g_{products}$

The electrical work may be noted as $W_E (nN_{Ac}) = E \cdot (nF)$

A general electrochemical reaction gives by

$$\sum \nu_i' a_i \rightarrow \sum \nu_i'' a_i$$

The degree of energy conversion

η = obtained energy / supplied energy

Examples $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\eta = 83\%$

$H_2(g) + \frac{1}{2}O_2(g) \Rightarrow H_2O(l)$ $\eta = 95\%$

The reversible potential of the cell is dependent on temperature, pressure and concentration

The actual potential of the cell is E

$$E = E_{rev.} - (\eta_{act} + \eta_{ohm} + \eta_{conc})$$

The cell potential efficiency of degree is $\eta_E = \frac{E}{E_{rev.}}$

$H_2O(l) \Rightarrow \eta_E = 57\%$

$H_2O(g) \Rightarrow \eta_E = 47\%$

The average free energy conversion efficiency $= \eta_{FC}$

$$\eta_{FC} = \eta_F \cdot \eta_E \cdot \eta_I$$

η_F = fuel efficiency

η_I = the current efficiency

The Fuel cell total system efficiency $= \eta_S$

$$\eta_S = \eta_{FC} \cdot \eta_{aux.}$$

Fuel cell electrochemistry

Some electrochemical concepts.

In an acidic electrolyte

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

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

In an acalic electrolyte

Anod reaction $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

Cathode reaction $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$

TOTAL REACTIONS: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

Elementary reactions:

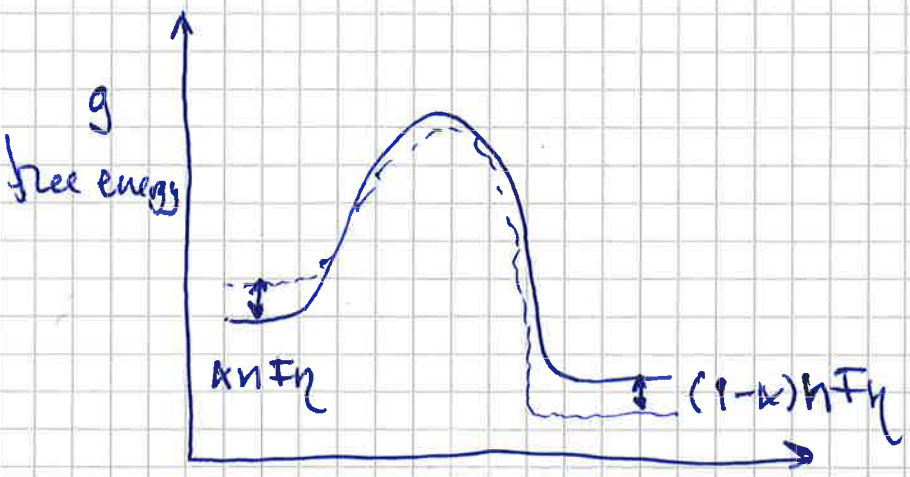
Tafels equation $H_2 \rightleftharpoons H_{ad} + H_{ad}$

Volmers reaction $H_{ad} \rightleftharpoons H^+ + e^-$

Butler Volmers equation for the current density is

$$j_{FC} = j_0 \left\{ \exp\left(\frac{n\alpha F\eta}{RT}\right) - \exp\left(-\frac{(1-\alpha)nF\eta}{RT}\right) \right\}$$

j_0 is a property of the catalysator which is used in the fuel cell. $\sim 10^{-10}\ Acm^{-2}$



Transport phenomena in fuel cells.

The transport of motion, energy, mass and current are taking place at the same time in fuel cells.

Transport processes are as important as electrochemical reactions for the estimating efficiency of the fuel cell.

For Newtons law of viscosity in Cartesian coordinates we have

$$\rho D\vec{V}/Dt = -\nabla p + \mu \nabla^2 \vec{V} + \rho \vec{g}$$

These are written as

$$\rho\left(\frac{\partial v_x}{\partial t} + v_x\frac{\partial v_x}{\partial x} + v_y\frac{\partial v_x}{\partial y} + v_z\frac{\partial v_x}{\partial z}\right) = \frac{\partial p}{\partial x} + \mu\left[\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2}\right] + \rho g_x$$

$$\rho\left(\frac{\partial v_y}{\partial t} + v_x\frac{\partial v_y}{\partial x} + v_y\frac{\partial v_y}{\partial y} + v_z\frac{\partial v_y}{\partial z}\right) = \frac{\partial p}{\partial y} + \mu\left[\frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} + \frac{\partial^2 v_y}{\partial z^2}\right] + \rho g_y$$

$$\rho\left(\frac{\partial v_z}{\partial t} + v_x\frac{\partial v_z}{\partial x} + v_y\frac{\partial v_z}{\partial y} + v_z\frac{\partial v_z}{\partial z}\right) = \frac{\partial p}{\partial z} + \mu\left[\frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2} + \frac{\partial^2 v_z}{\partial z^2}\right] + \rho g_z$$

The equation of energy is written

$$\rho \hat{C}_p DT/Dt = k\nabla T + \mu \Phi_v$$

and in detail:

$$\rho \hat{C}_p\left(\frac{\partial T}{\partial t} + v_x\frac{\partial T}{\partial x} + v_y\frac{\partial T}{\partial y} + v_z\frac{\partial T}{\partial z}\right) = -\left[\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} + \frac{\partial q_z}{\partial z}\right] -$$

$$-\left(\frac{\partial \ln \rho}{\partial T}\right)_p \frac{DT}{Dt} - \tau : \nabla V$$

The equation of continuity is

$$\frac{\partial \rho}{\partial t} + \nabla \rho V = 0 \quad [kg/m^2 s]$$

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho v_x) + \frac{\partial}{\partial y}(\rho v_y) + \frac{\partial}{\partial z}(\rho v_z) = 0$$

The continuity equation of each component A is

$$\rho D w_A / Dt = \rho \mathcal{D}_{AB} \nabla w_A + r_A \quad [kg/m^2 s]$$

$$\rho\left(\frac{\partial w_A}{\partial t} + v_x \frac{\partial w_A}{\partial x} + v_y \frac{\partial w_A}{\partial y} + v_z \frac{\partial w_A}{\partial z}\right) = \rho \mathcal{D}_{AB} \cdot \left[\frac{\partial^2 w_A}{\partial x} + \frac{\partial^2 w_A}{\partial y^2} + \frac{\partial w_A}{\partial z^2}\right] + r_A$$

In these equations is Newtons law, Fouriers law and Ficks law included.

Domensless heat transport is made by Nusselts number

$$Nu = \frac{h_H x}{k} = f_1(Re, Pr)$$

Domensless mass transport is made by Sherwoods number

$$Sh = \frac{h_m x}{D_{ij}} = f_2(Re, Sc)$$

Help with Reynolds analogy is

$$C_f\left(\frac{Re}{2}\right) = Nu = Sh$$

$Pr = \frac{\nu}{\alpha}$ = transport of motion / transport of energy

$Sc = \frac{\nu}{D_{ij}}$ = transport of motion / transport of mass

$$Re = \frac{\rho V_\infty x}{\mu} = \frac{V_\infty \cdot x}{\nu} = \text{velocity} \cdot \text{Length} / \text{viscosity}$$

PEM Fuel Cells

Applications are stationary, vehicles and portable units.

The electrolyte is a proton leading membrane in a fast polymer.

Compact cell construction and operation simple design, easy to construct, low corrosion, long lifetime, 50-250 µm thick

stationary units 10-350 kW
vehicles transport 85 kW (cars)
busses 300 kW

The reaction is taking place on a three-phase point where hydrogen gas, the catalysator and the electrolyte is in one point.

The catalysator is made by platine particles on coal particles.

The current density is 0,3-0,5 A cm^{-2} with air
1,0 A cm^{-2} with oxygen

No oxidant.

Properties for PEMFC

Temperature in operation	50-80°C
Power density	350-580 mW cm^{-2}
Power	0,01-1000 kW
Efficiency chemical to electric	45-60%
lifetime	>40.000h (projected)
Capital cost	2000 US$/kW
Application	portable, mobile, space stationary

PEMFCs are also used for hydrogen production since they is a reversible process. These PEMFCs are competing with ordinary electrolysers.

Fuels for fuel cells:

1, hydrogen (H_2)
2, Methanol (CH_3OH)
3, ammoniak ($2NH_3 \rightarrow N_2 + 3H_2$) a converter as for hydrogen storage

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