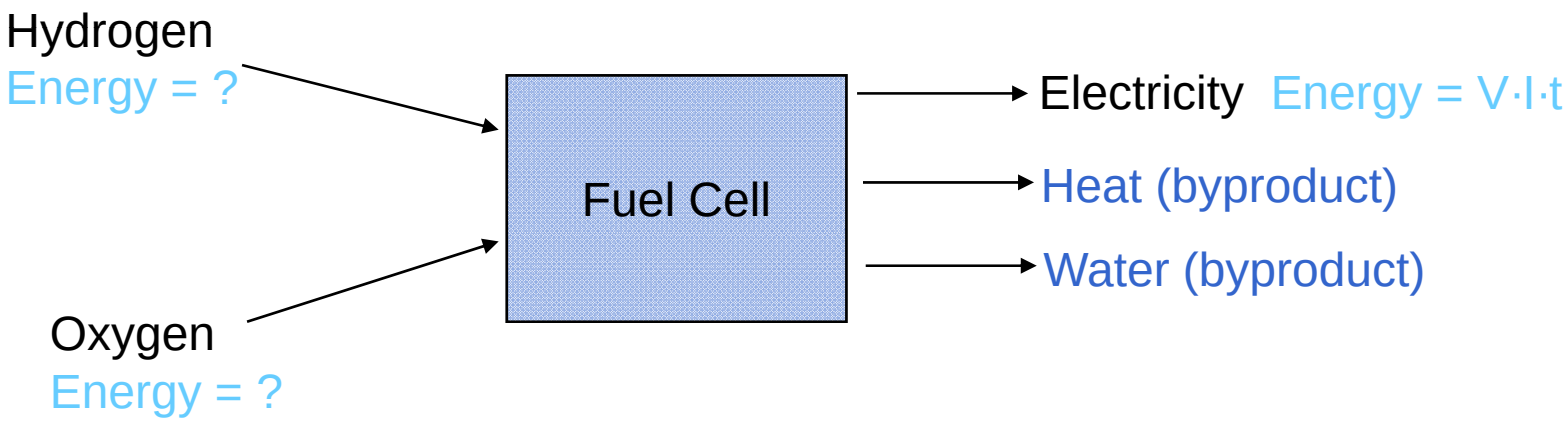
Describing a fuel cell's performance and efficiency

Basic energy conversion of a fuel cell was described as:

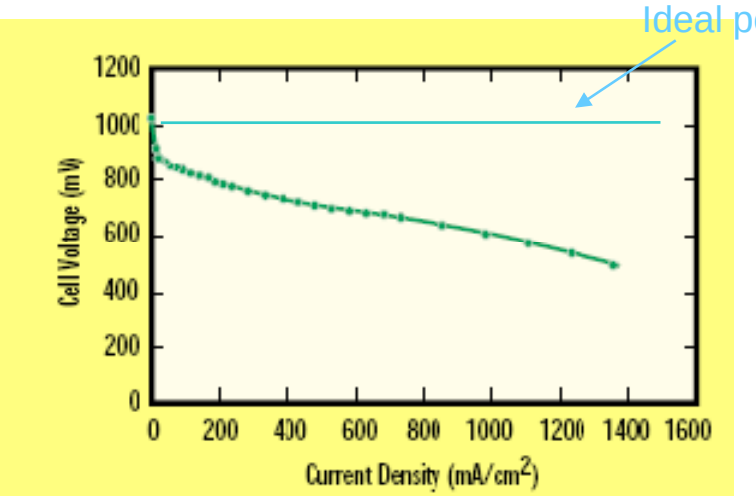
Chemical energy of fuel = Electrical energy + Heat energy



The input energy is that produced during reactions at the electrodes.
In this section we will describe the above energy balance in more detail using the first and second laws of thermodynamics.

Performance (cont.)

The performance of a fuel cell is governed by its Polarization Curve.



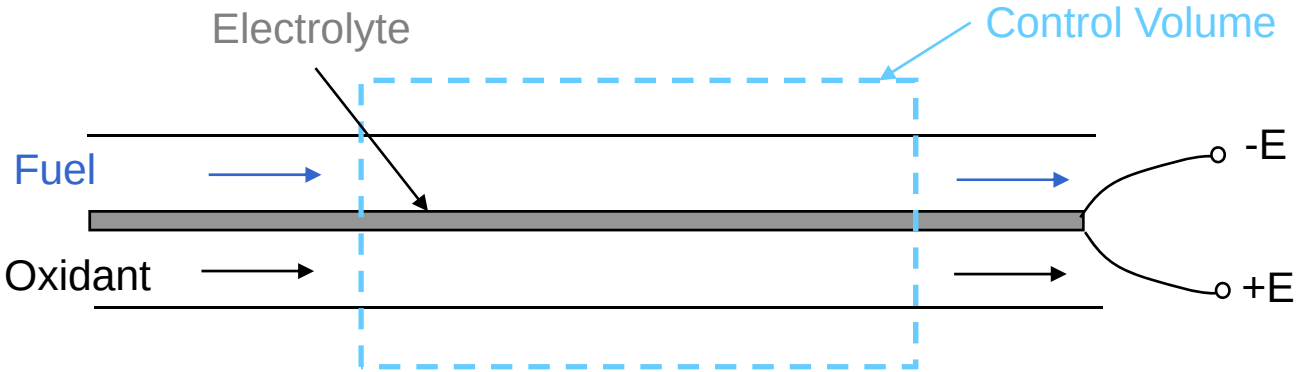
Graph of voltage vs. current density of a hydrogen/air polymer electrolyte membrane fuel cell. (ref. 1)

This type of performance curve shows the DC voltage delivered at the cell terminals as a function of the current density (current per unit area of membrane) being drawn by the external load.

This curve and the losses associated with its shape will be discussed later.

One measure of the energy conversion efficiency of a fuel cell is the ratio of the actual voltage at a given current density to the maximum voltage obtained under no load (open circuit) conditions.

Thermodynamic Analysis: 1st Law



1st Law for a control volume:

$\Delta E = Q - W$ where $\Delta E = \Delta KE + \Delta PE + \Delta U + \Delta(PV) = \Delta H$

=> $\Delta H = Q - W$

For a fuel cell, the work is obtained from the transport of electrons across a potential difference, not by mechanical means, such as turning of turbine blades.

Defining the work term

Electrical work is, in general, described by the relation: $W = EI\Delta t$

where E is the cell voltage and I is the current

In a fuel cell reaction, electrons are transferred from the anode to the cathode, generating a current. The amount of electricity ($I\Delta t$) transferred when the reaction occurs is given by NF, where

N = number of electrons transferred
F = Faraday's constant = 96,493 coloumbs

So the electrical work can be calculated as: $W = NFE$

The First Law then becomes: $\Delta H = Q - NFE$

Thermodynamic Analysis: 2nd Law

Will consider the fuel cell to be ideal for now, meaning that it is reversible and thus behaves as a perfect electrochemical apparatus (Gibbs):

" If no changes take place in the cell except during the passage of current, and all changes which accompany the current can be reversed by reversing the current, the cell may be called a perfect electrochemical apparatus."

Recall that the heat transferred during a reversible process was expressed as:

$$Q = T \Delta S$$

Combining the First and Second Law analysis, we get:

$$\boxed{\Delta H = T\Delta S - NFE}$$

Gibb's Free Energy (chemical potential)

From our previous result for a cell operating reversibly:

$$dH = TdS - FEdN$$

Under these conditions:
- the losses are minimal
- the useful work obtained is maximized

This maximum work is represented by the Gibbs free energy: $dG = -FEdN$

So the thermodynamic expression for the maximum useful work obtained from a fuel cell becomes:

$$\boxed{dG = dH - TdS}$$

Physical Interpretation of dG = dH - TdS

dH represents the total energy of the system.

TdS represents the “unavailable” energy (that which cannot be converted to useful work).

Therefore G represents the “free” energy or the energy available to do useful work.

More on Gibbs Free Energy

The electrons released to generate the electrical work are, of course, inherently related to the chemical reaction taking place. So ΔG can also be associated with the chemical energy released during the reaction occurring in the fuel cell.

Typically, a "free energy of formation", ΔG_f or ΔG^o is computed for these reactions, where the free energy is referenced with respect to standard temperature and pressure (STP) conditions.

For a given reaction, $\Delta G^o = G^o_{products} - G^o_{reactants}$

See example problem 15.2 for calculation of ΔG^o

Electrochemistry: Fuel Cell Reactions

Hydrogen fuel cell:

Oxidation half reaction $2H_2 \rightarrow 4H^+ + 4e^-$

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

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

Methanol fuel cell:

Cell reaction: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Energy formation (kJ/mol)	
$-\Delta H^o$	$-\Delta G^o$
286	237
890	818

Maximum Voltage Produced by a Single Cell

The reversible open circuit voltage (i.e. the maximum voltage that could be generated) can be calculated based on ΔG^o as:

$$E = \frac{\Delta G^o}{NF}$$

For example, in the previous reaction where ΔG^o was 237 kJ/mol, the open circuit voltage would be:

E = 237,000(2 mol H_2)/(4 electrons)(96,493) = 1.23 volts

Fuel Cell Vs. Carnot Cycle Efficiency

The efficiency limit of a Carnot heat engine is defined as:

$$\eta_{carnot} = 1 - \frac{T_L}{T_H}$$

So the higher the hot temperature source, the higher the efficiency.

If, for example, one wanted to calculate the maximum efficiency of a steam turbine operating at 400° C with the water exhausted through a condenser at 50° C, it would be:

$$\eta_{car} = 1 - \tfrac{675}{325} = 0.52$$

Under these conditions, the turbine could be no more than 52% efficient.

Fuel Cells Vs. Carnot Engines (cont.)

Fuel cells, on the other hand:

- Operate isothermally – no temperature cycling.
- Operate with less energy lost in maintaining the temperature of the "hot source."
- Are inherently less irreversible.

Fuel cells are not limited by the Carnot efficiency limit.

Fuel Cell Efficiency

Since fuel cells use materials that are typically burnt to release their energy, the fuel cell efficiency is described as the ratio of the electrical energy produced to the heat that is produced by burning the fuel (its enthalpy of formation or Δh_f).

From the basic definition of efficiency: $\eta = W / Q_{in}$

where W is given by ΔG (or NFE)

Q_{in} is the enthalpy of formation of the reaction taking place. Since two values can often be computed depending on the state of the reactant, the larger of the two values ("higher heating value") is used (HHV).

$$\boxed{\eta = \frac{\Delta G}{HHV} = \frac{NFE}{HHV}}$$

Maximum Fuel Cell Efficiency

The maximum efficiency occurs under open circuit conditions (reversible) when the highest cell voltage is obtained.

$$\eta_{\max} = \frac{\Delta G^o}{HHV} = \frac{NFE^o}{HHV}$$

For the hydrogen fuel cell reactions shown previously where ΔG^o was 237 kJ/mol and ΔH^o was 286 kJ/mol, the maximum efficiency of the fuel cell would be 83%.

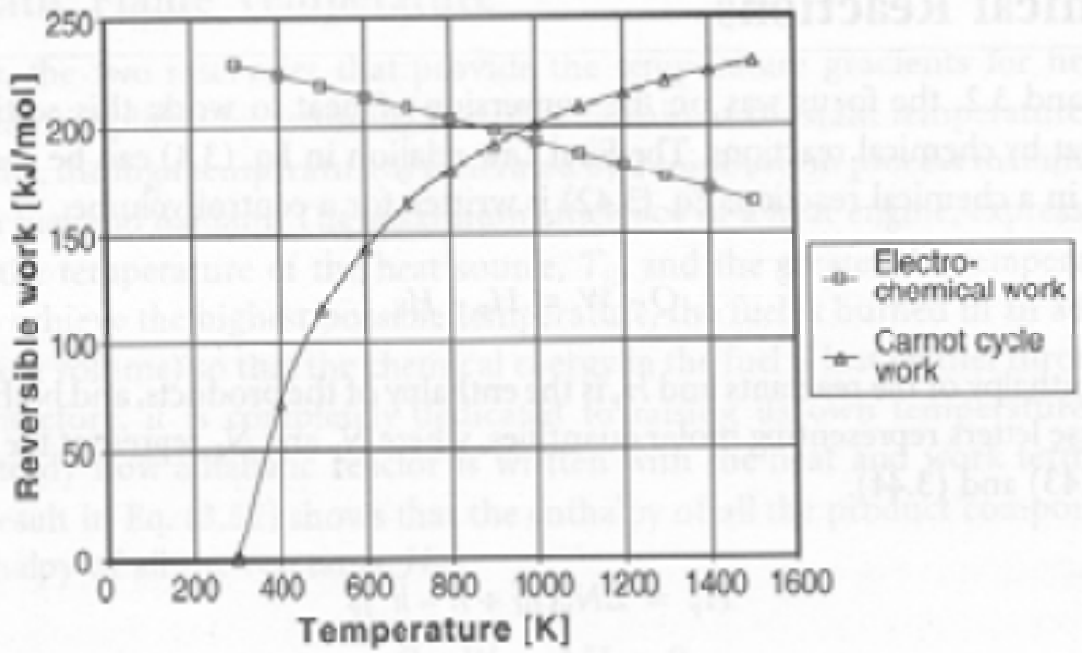
How does a Carnot engine match up?

A Carnot engine would have to have a high temperature of 1753 K, with a corresponding low temperature of 298 K, to achieve an efficiency of 83%!

However, the work done by a Carnot engine increases with increasing temperature.

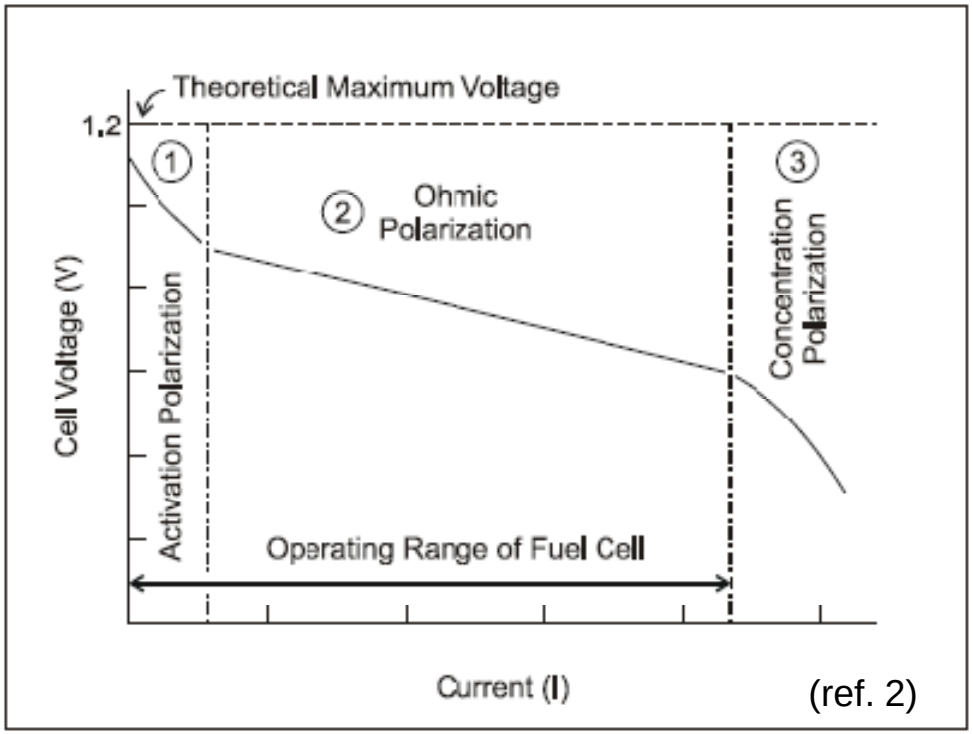
The reverse is true for the ΔG based fuel cell work (and hence efficiency) because ΔG decreases with increasing temperature.

Fuel Cell Vs. Carnot Efficiencies



As can be seen, there exists a temperature above which the fuel cell efficiency is *lower* than the Carnot efficiency. This temperature is approximately 950 K for a H_2-O_2 system.

Losses Associated With Fuel Cell Operation



(ref. 2)

In reality fuel cells achieve their highest output voltage at open circuit (no load) conditions and the voltage drops off with increasing current draw. This is known as polarization.

The polarization curve shows the electrochemical efficiency of the fuel cell at any operating current.

Classification of Losses in an Actual Fuel Cell[3]

Activation Losses: These losses are caused by the slowness of the reaction taking place on the surface of the electrodes. A proportion of the voltage generated is lost in driving the chemical reaction that transfers the electrons.

Ohmic Losses: The voltage drop due to the resistance to the flow of electrons through the material of the electrodes. This loss varies linearly with current density.

Concentration Losses: Losses that result from the change in concentration of the reactants at the surface of the electrodes as the fuel is used.

Fuel Crossover Losses: Losses that result from the waste of fuel passing through the electrolyte and electron conduction through the electrolyte. This loss is typically small, but can be more important in low temperature cells.

References

[1]Thomas, S. & Zalbowitz,M. "Fuel Cells- Green Power", Los Alamos National Laboratory, http://education.lanl.gov/resources/fuelcells/fuelcells.pdf

[2]Fuel Cell Technology.pdf

[3]Larmanie, J. & Dicks, A. 2000 Fuel Cell Systems Explained, John Wiley & Sons.