

3.014 MATERIALS LABORATORY
MODULE – BETA 2
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FUEL CELLS and ELECTROLYZERS

OBJECTIVES:

- Understand the relationship between Gibbs Free Energy and Electrochemical Cell Potential.
- Verify the effect of Temperature on the Cell Potential of the fuel cell.
- Verify the effect of Current on the Cell Potential of the fuel cell.

BACKGROUND:

A *fuel cell* is an electrochemical energy conversion system that takes a hydrogen-containing chemical, such as pure hydrogen gas, methanol or other hydrocarbons, and oxygen to form electricity. A fuel cell can continue to operate as long as it is continuously supplied with additional fuel. How does this differ from batteries?

There are many types of fuel cells [1-2]:

Proton exchange membrane/Polymer electrolyte membrane fuel cell (PEM)

Solid oxide fuel cell (SOFC)

Direct methanol fuel cell (DMFC)

Molten carbonate fuel cell

...

We will work with PEM fuel cells, which operate generally between room temperature and 80°C and function with hydrogen and oxygen. The electrochemical reactions that convert chemical energy into electrical energy in a PEM fuel cell are as follows [3]:

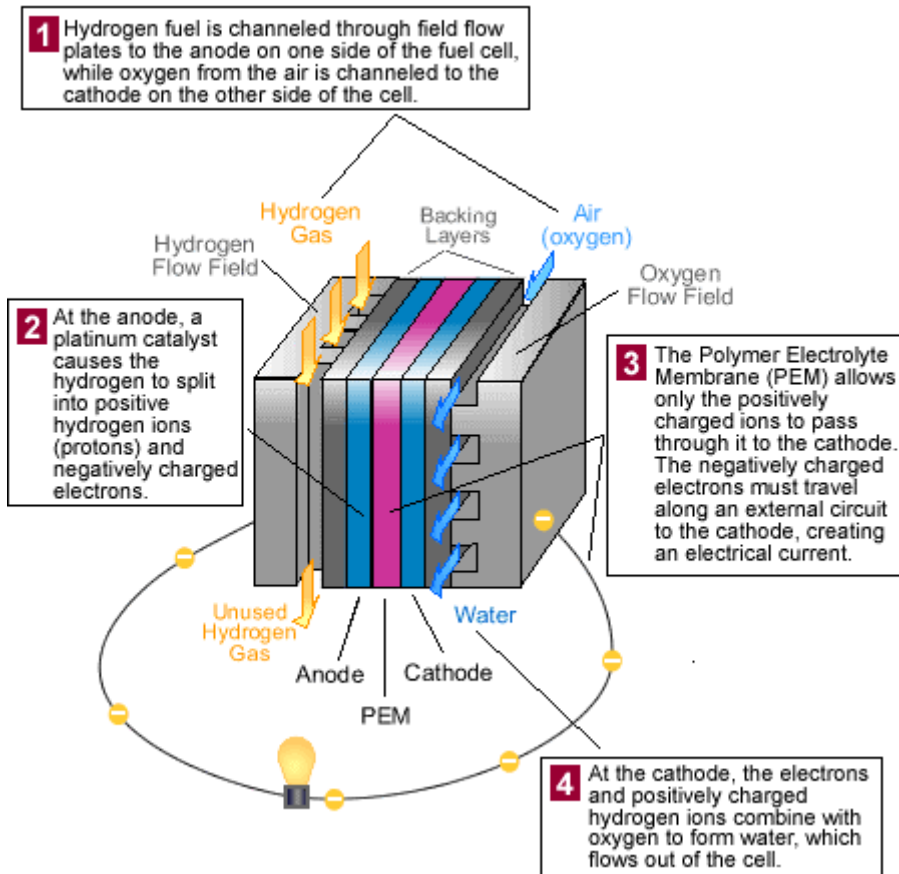
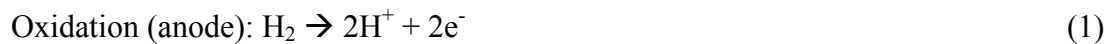
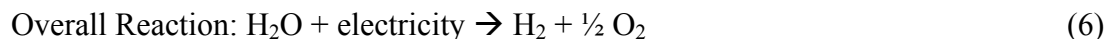
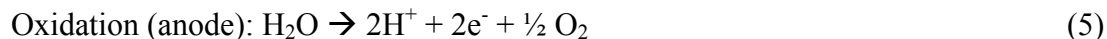


Figure 1: How a PEM fuel cell works [4]



When working in reverse, the fuel cell is called an electrolyzer. For a PEM electrolyzer the reactions are as follows [3]:



One advantage of PEM fuel cells is that they operate at relatively low temperatures (SOFC's operate above 600°C) and so the start-up time is short.

However, the reactions of reduction and oxidation are slow at low temperatures, so the PEM fuel cell requires use of a catalyst, such as platinum. This raises the cost of PEM fuel cells and is one of the main hurdles in the commercialization of this technology.

The cell potential (open circuit potential or *open circuit voltage* (OCV)) is a result of the electrochemical reactions occurring at the cell electrode interfaces. Reactions 1 and 2, are half-cell reactions occurring simultaneously, at the anode and cathode.

The maximum amount of electrical energy (or work done) that can be delivered, by an electrochemical cell (or fuel cell) in a given state, depends on the change in *Gibbs free energy*, ΔG as shown in equation 7 [5].

$$\Delta G = - nFE \quad (7)$$

where n is the number of moles of electrons exchanged in an electrochemical reaction ($n=2$ in equations 1 and 2), F is the Faraday's constant (96,485 C/mol), and E is the cell potential. For cell conditions in a standard state,

$$\Delta G^0 = - nFE^0 \quad (8)$$

where, E^0 represents *standard electrochemical cell potential*, and ΔG^0 represents the Gibbs free energy changes in the standard state. The standard state is measured at 25°C and atmospheric pressure.

The Gibbs Free Energy at standard temperature and pressure may be calculated from the Gibbs Free Energies of Formation of the products and reactants from equation 3, which are tabulated in the CRC Handbook [6].

$$\Delta G^0_f(\text{H}_2\text{O}) - \Delta G^0_f(\text{H}_2) - \frac{1}{2} \Delta G^0_f(\text{O}_2) = -237.1 \text{ kJ/mol} \quad (9)$$

Comparing Equations 3 and 6, one notes that the only difference would be the sign of the Gibbs free energy. A negative Gibbs free energy results in a positive cell potential which indicates the reaction is favorable thermodynamically. A positive sign indicates the opposite. In order to form hydrogen and oxygen from water, energy must be supplied.

The cell voltage is dependent on several factors, such as electrode chemistry, temperature and electrolyte concentration.

The temperature dependence may be calculated through the Gibbs-Helmholtz Equation:

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

In general, the ΔS term is positive for a favorable reaction and the overall ΔG term decreases with temperature. T , is the absolute temperature (K).

OPERATION OF A FUEL CELL

The standard electrochemical cell potential, E^0 , calculated from the Gibbs free energy is a theoretical value that does not account for the inefficiencies in a real fuel cell. The inefficiencies result in lower measured cell potentials, which result in a decrease in the power density that can be achieved from a fuel cell. The *power* achieved is equal to the voltage output of the cell multiplied by the current output.

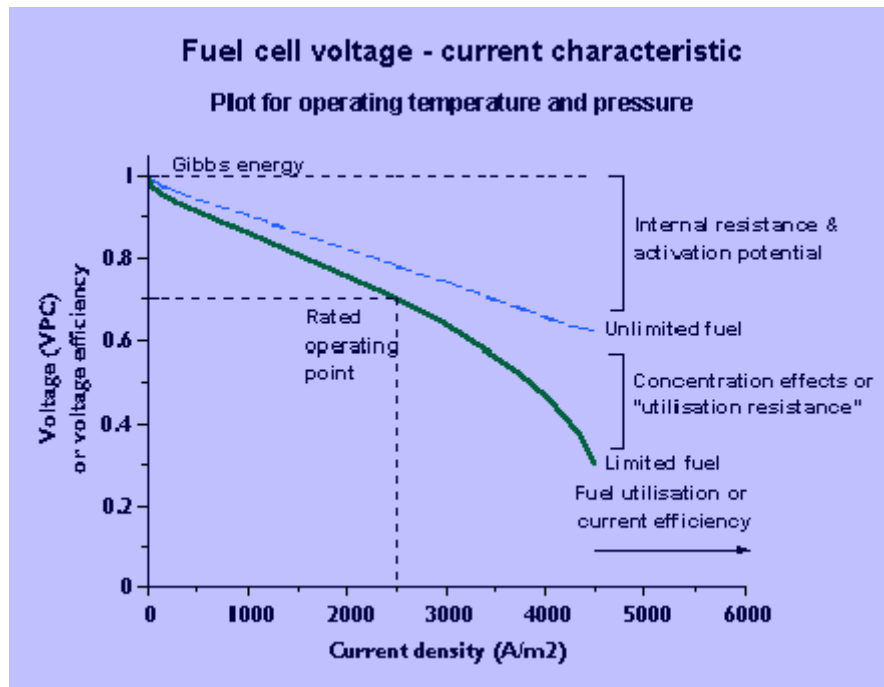
$$\text{Power: } P = VI$$

(11)

where P is power, V is cell voltage or cell potential, and I is the current. Power density is defined as the power achieved for a given fuel cell membrane area and is usually expressed in W/cm^2 .

In electrochemical systems, inefficiencies are termed *overpotentials*, because they result in a loss of the voltage that the system can achieve at a given current density.

The overpotentials can be measured as current is increased to produce a fuel cell performance curve.



Courtesy of John Simmons. Used with permission.

Figure 2: Typical fuel cell performance curve for given operating temperature and pressure [7].

The inefficiencies in a fuel cell originate from three sources [5]:

- activation overpotential due to sluggish electrode kinetics
- ohmic overpotential from internal cell resistance
- concentration overpotential due to generation of concentration gradients

The activation overpotential results in a potential drop at all current densities, but is the dominating loss at low current densities. The concentration overpotential dominates at high current densities. Ohmic losses affect the fuel cell performance at all current densities.

MATERIALS:

Reversible Fuel Cell kits : www.FuelCellStore.com

Deionized water

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