FUEL CELLS IN THE CHEMICAL ENGINEERING CURRICULUM

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ABSTRACT

Fuel cells are an emerging technology that promise high conversion efficiencies of chemical fuels to electricity. Additionally, fuel cell technology can also greatly decrease the release of pollutants during energy conversion. This promising new technology has created a demand from chemical engineering students for more information and practical experience. This demand has generated new course content across our curriculum. Courses in Material and Energy Balances, Thermodynamics, Heat and Mass Transfer, Chemical Reactor Design, Senior Capstone Design, Air Pollution Control, Material Science and Engineering, and Introduction to Chemical Engineering have all added discussion, examples, and problems concerning fuel cells. Additionally, hands-on experience has been added to the Unit Operations Laboratory through purchase of a fuel cell/ solar cell combination. The unit demonstrates the renewable creation of hydrogen fuel, its subsequent use in a fuel cell, as well as the working characteristics of a fuel cell. The students in the Senior Design course have participated in the AIChE ChemE Car Competition and a student group used fuel cells to power their car. Students are very excited about this technology, and that desire is used to generate a working interest in the curriculum. This is also an excellent way to provide students with a knowledge of contemporary issues and the ability to use modern engineering tools necessary for engineering practice (ABET Criteria 3, program outcomes j and k).

INTRODUCTION

Fuel cells are devices used to convert chemical energy into electricity and heat. A fuel cell operates like a battery as it consists of two electrodes separated by an electrolyte. It is different in that it never becomes discharged and requires a continuous supply of fuel. Types of fuel cells include Phosphoric Acid, Proton Exchange Membrane or Solid Polymer, Molten Carbonate, Solid Oxide, Alkaline, Direct Methanol Fuel Cells, Regenerative Fuel Cells, and Zinc Air Fuel Cells. This paper will only discuss the proton exchange membranes. The curious reader may want to examine the web site http://www.fuelcells.org/ for more information concerning other types.

There are many uses for fuel cells — right now, all of the major automakers are working to commercialize a fuel cell car. Fuel cells are powering buses, boats, trains, planes, scooters, even bicycles. There are fuel cell-powered vending machines, vacuum cleaners, and highway road signs. Miniature fuel cells for cellular phones, laptop computers, and portable electronics are on their way to market. Hospitals, credit card centers, police stations, and banks are all using fuel cells to provide power to their facilities. Wastewater treatment plants and landfills are using fuel cells to convert the methane gas they produce into electricity. Fuel cells are ideal for power generation, either connected to the electric grid to provide supplemental power and backup assurance for critical areas, or installed as a grid-independent generator for on-site service in areas that are inaccessible by power lines. Since fuel cells operate silently, they reduce noise pollution as well as air pollution and the waste heat from a fuel cell can be used to provide hot water or space heating for a home. Many of the prototypes being tested and demonstrated for residential use extract hydrogen from propane or natural gas. Miniature fuel cells, once available to the commercial market, will help consumers talk for up to a month on a cellular phone without recharging. Fuel cells will change the telecommuting world, powering laptops and palm pilots hours longer than batteries. Other applications for micro fuel cells include pagers, video recorders, portable power tools, and low power remote devices such as hearing aids, smoke detectors, burglar alarms, hotel locks, and meter readers. These miniature fuel cells generally run on methanol, an inexpensive wood alcohol.

HISTORY

Fuel cells have been known to science for more than 160 years. Though generally considered a laboratory curiosity in the 1800s, fuel cells have become the subject of intense research and development, with several companies currently trying to make them a commercial success.

The first working fuel cells were called gas batteries, and were built in the early nineteenth century. Christian Freidrich Schoenbein and William Robert Grove may have been the first to systematically report on the phenomena, though there are earlier reports that Johann Ritter also observed the ability to generate electricity from hydrogen gas. Their experiments were quite simple, and are very instructive in understanding how a fuel cell works.

Schoenbein observed that during the preparation of chlorine and hydrogen gas from electrolysis of a sodium chloride solution, which forms gas bubbles at the anode (chlorine) and cathode (hydrogen), that after disconnecting the electrical source several bubbles remained stuck to the electrodes. The hydrogen bubbles disappeared when the two electrodes were reconnected electrically, but without a source of electricity. Schoenbein quickly realized that reverse electrolysis was occurring and after several systematic experiments conducted in 1838, he published the results in 1839. This source of electricity however was not economical since the hydrogen had to be generated using electricity, and the research was not greatly expanded upon at that time.

Grove realized that by combining several sets of these electrodes in a series circuit he might "effect the decomposition of water by means of its composition." He soon accomplished this feat with the device he named a "gas battery"– the first fuel cell built in 1839. Grove discovered that by arranging two platinum electrodes with one end of each immersed in a container of sulfuric acid and the other ends separately sealed in containers of oxygen and hydrogen, a constant current would flow between the electrodes. The sealed containers held water as well as the gases, and he noted that the water level rose in both tubes as the current flowed.

The technology advanced slowly over the years but took a giant leap in the 1960's. During the early 1960’s, General Electric produced the first practical application for a fuel cell when it provided onboard electrical power for the Gemini and Apollo space capsules. In the early 1970’s, DuPont introduced the Nafion® membrane from which all PEM (Proton Exchange Membrane) fuel cells had been constructed. This material is quite expensive to manufacture which has limited the market application of fuel cells. Also, the operating conditions for this type of PEM cell are very specialized, and not applicable to wide-scale use.

However, new materials and equipment are currently in development, and many research groups and a few businesses have found ways to reduce the cost of fuel cells. None of these systems have reached the cost necessary for wide scale adoption. Yet, the potential is there and there does not appear to be an insurmountable technical challenge to lower costs. In this paper, we will discuss the details of only one fuel cell type – the proton exchange membrane. They all work in a very similar way, with the chief difference being the electrolyte and the cell operating conditions.

PEM FUEL CELL

The Proton Exchange Membrane (PEM) fuel cell operates at relatively low temperatures (about 175 degrees F or 80 degrees C), have high power density, and can vary their output quickly to meet shifts in power demand. According to the U.S. Department of Energy, "they are the primary candidates for light-duty vehicles, for buildings, and potentially for much smaller applications such as replacements for rechargeable batteries." The proton exchange membrane is a thin plastic sheet that allows hydrogen ions to pass through it. The membrane is coated on both sides with highly dispersed metal catalysts (usually platinum). The electrolyte used is a solid organic polymer polyperflourosulfonic acid. The solid electrolyte is an advantage because it reduces corrosion and management problems. This type of fuel cell is, however, sensitive to fuel impurities, especially sulfur. Cell outputs generally range from 50 to 250 kW.

The PEM fuel cells use hydrogen or hydrogen containing fuels as the source of chemical energy. Hydrogen gas is fed to the anode of the fuel cell. Oxygen (or air) is fed to the cathode. The hydrogen atom splits into a proton and an electron with the aid of the catalyst at the anode. The two ions take different paths to the cathode. The proton passes through the electrolyte. The electrons create a current that can be utilized as electricity as they return to the cathode to be reunited with the hydrogen ion and oxygen to form a molecule of water. There is no combustion occurring in this process, so the common problems associated with combustion (air pollution, low efficiency) are not concerns for fuel cells. The chemical reactions and some thermodynamic data for this fuel cell are:

Anode: H2(g) -> 2H+(aq) + 2e-

Cathode: _O2(g) + 2H+(aq) + 2e- -> H2O(l)

Overall Cell: H2(g) + _O2(g) -> H2O(l)

Heat of reaction:	_H = -285.8 KJ/mol
Entropy	_S = -163.3 J/mol/K
Free Energy	_G = -237.2 KJ/mol
Cell Potential	V = 1.229 Volt

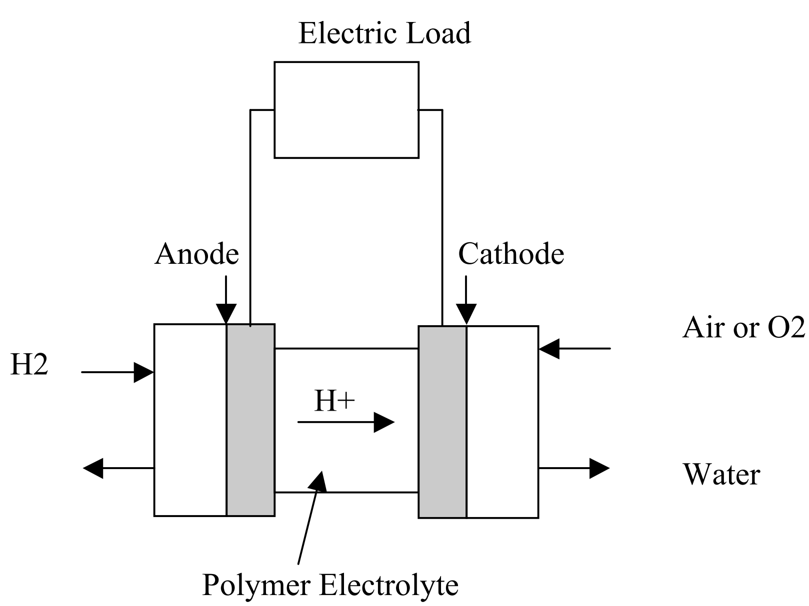
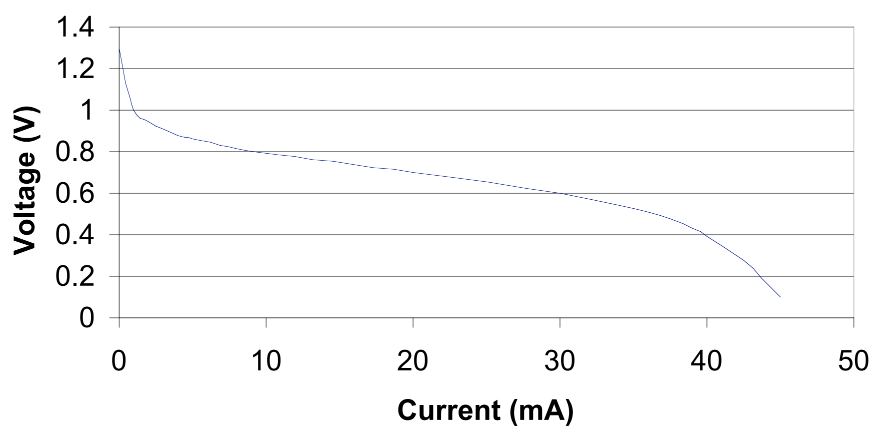


Figure 1. Fuel Cell Schematic

The typical efficiency of a fuel cell is approximately 70%, so a real cell develops a useful potential of 0.8 V rather than the theoretical maximum of 1.229 V. There are three basic types of inefficiencies related to the PEM cell – reaction inhibition, internal resistance, and gas diffusion - and they are generally termed overvoltage. Figure 2 shows a graph relating voltage generated with current. Reaction inhibition (in the 0 to 8 mA region) is due to limitations of the catalyst to convert hydrogen gas to hydrogen ions (protons) at the anode or to recombine the electrons, protons, and oxygen to make water. This is often due to the relatively slow speed of transferring electrons between the platinum catalyst and the electrolyte. Internal resistance (in the 8 to 25 mA region) is caused by the mass transfer resistance of the protons into the electrolyte from the anode catalyst, resistance as it moves across the electrolyte, and back to the cathode catalyst. It may also be caused by the electron motion at the electrical connectors, conductors, and in the external load. Gas diffusion (in the 25 + mA region) can limit the reaction due to mass transfer of the hydrogen and oxygen gas going to the electrodes. It happens when the gas is used faster than diffusion can replace them. The electrode becomes starved for the gas, and the reaction can be nearly halted.

Fuel cell research is aimed at reducing all elements of overvoltage in an economical manner. This may be accomplished by finding better electrocatalysts, using more highly conductive materials and contacts between phases, and using optimized electrode structures and gas ducts.

Figure 2. Characteristic Current/Voltage curve for a PEM Fuel Cell



FUELS

PEM fuel cells use hydrogen gas as an energy source. Hydrogen -- the most abundant element on Earth -- is used directly in the cell, however hydrogen gas does occur naturally in quantities of economic interest. Hydrogen can be obtained from fossil fuels (methane especially) or renewable fuels such as biomass, wind power, or solar power. Fuel cells can utilize any fuel containing hydrogen, including methanol, ethanol, natural gas, and even gasoline or diesel fuel. However, these fuels require a transformation using a "fuel reformer" to extract hydrogen. Energy also could be supplied by wind or solar power, which can use hydrogen to store extra energy for use when there is no wind or sunlight.

There are three main methods being considered for inexpensive hydrogen generation. All three generate hydrogen from a hydrogen source such as oil, gas, or water - but each by very different means – fuel reformers, enzymes, and renewable electricity.

Fuel Reformers - Fuel cells generally run on hydrogen, but any hydrogen-rich material can serve as a possible fuel source. When using a fuel other than pure hydrogen, a reformer or fuel processor is required. A reformer is a device that produces hydrogen from fuels such as gasoline, methanol, ethanol, or naphtha. Three basic reformer designs are being evaluated for fuel cells for use in vehicles: steam reforming, partial oxidation and auto-thermal reforming. Steam reformers combine fuel with steam and heat to produce hydrogen. The heat required to operate the system is obtained by burning fuel or excess hydrogen from the outlet of the fuel cell stack. Partial oxidation reformers combine fuel with oxygen to produce hydrogen and carbon monoxide. The carbon monoxide then reacts with steam to produce more hydrogen. Partial oxidation releases heat, which is captured and used elsewhere in the system as either heat (for making hot water for example) or to create steam to power a turbine in order to generate electricity. Auto-thermal reformers combine the fuel with both steam and oxygen so that the reaction is in heat balance. Auto-thermal reforming, while not as fully developed as the others, offers the most flexibility in heat management. In general, both methanol and gasoline can be used in any of the three reformer designs. Differences in the chemical nature of the fuels, however, can favor one design over another. In all three cases, if the hydrogen source fuel contains carbon, then CO2 and CO will be emitted in the reforming process. However the other air pollutants normally associated with electricity production (NOx, SOx, and particulates) are greatly reduced. For these systems to work properly, the fuels must be desulfurized to a greater extent than currently done, as sulfur will poison the fuel cell catalyst.

Enzymes - Another method to generate hydrogen is with bacteria and algae. The cyanobacterium, an abundant single-celled organism, produces hydrogen through its normal metabolic function. Cyanobacteria can grow in the air or water, and contain enzymes that absorb sunlight for energy and split the molecules of water, thus producing hydrogen. Since cyanobacteria take water and synthesize it to hydrogen, which is used in the fuel cell to create water (and energy), this is considered a renewable energy source.

Solar- and Wind- powered generation - The renewable energy of the sun and wind can be used to generate electricity. This electricity can then be used to create hydrogen, which acts as energy storage for times when there is no sun or wind. It can also be used to generate hydrogen for transportation. In this manner, hydrogen becomes an energy carrier – able to transport the power from the generation site to another location for use in a fuel cell. Here the fuel cell compliments the power generation of wind or solar, making them much more useful as a main energy source.

FUEL CELLS IN THE CHEMICAL ENGINEERING CURRICULUM.

Fuel cells are simple, but interesting chemical devices. They blend together issues from many sections of the curriculum, such as chemical reaction engineering, heat and mass transfer, thermodynamics, general chemistry, and material and energy balances. Actual experience with them may be included in laboratory classes, design classes, and in the student group competitions. In this section we will discuss how fuel cells can be included in different courses.

Introduction to Chemical Engineering is a freshman class that provides an overview of chemical engineering courses and the profession. Students can learn about what fuel cells are, how they work in general, and see them demonstrated. They can be part of a discussion on energy and society, provide an example of how chemical engineers can work with other engineers (electrical, mechanical, and civil to name a few) as well as scientists and businessmen. If you give students chemical industry related research projects, fuel cells are an excellent topic.

Material and Energy Balances (also called stoichiometry in some curricula) is usually a sophomore level course and covers the general tools needed in chemical engineering. In this class the basic fuel consumption models can be introduced, as well as the concept of efficiency (these are not particular to fuel cells and can be simply added to any lecture / discussion about energy production). An example problem may involve comparing the amount of useful electricity produced by one mol of fuel using combustion and using a fuel cell.

Thermodynamics – calculate the heat of reaction as well as general discussion of electricity production efficiency. Note that fuel cells are not subject to the Carnot heat cycle limitations for efficiency, since it is based on chemical energy and not heat cycles. The standard galvanic cell calculation shows that a hydrogen-powered cell could generate, as a maximum, 1.229 V potential. Additional work can demonstrate why it will always be less.

Heat and Mass transfer. A typical problem will look at the mass transfer of protons between electrodes in various electrolytes, or obtaining sufficient oxygen at the cathode. The problem can be coupled with the heat removal required and the effect of heat on the mass transfer problem, and can be solved as a heat transfer problem, a mass transfer problem, or a combined problem. For example, at high loads, the fuel cell will be limited by gas and ion diffusion to the electrodes. This can form a basis for a mass transfer problem.

Chemical Reaction Engineering – Fuel cells are catalytic chemical reactors. They are an excellent way to introduce catalyst based reactions, and the concepts of catalyst limitations and diffusion limitations to a chemical reaction. Under different conditions, a fuel cell can encounter both types of problems.

Laboratory class – Students can gain hands on experience with using a fuel cell. They can generate hydrogen, or examine the workings of a fuel reformer. Explore equipment to deliver the hydrogen to the electrode, delivery of air or oxygen to the other electrode, measure the voltage output at different loads, look at how differing loads changes the efficiency of the cell, etc. Students can explore how changes in catalyst surface area, pure oxygen vs. oxygen from air, and variation of internal and external loads change the operating characteristics of a cell.

ChemE car competition. Many student groups have chosen to use fuel cell powered cars for this AIChE competition. The chemical reaction of converting hydrogen to water and power is an acceptable and useful reaction. The system seems to calibrate almost linearly between amount of hydrogen and distance traveled. Problems include the generation and storage of hydrogen, obtaining oxygen, and the somewhat slow startup for the car.

ABET

Introducing fuel cells into the chemical engineering curriculum was student driven at UMD. Students had heard about them in the general news media and became curious and excited about their prospects. However, they were unable to find all the information they needed to satisfy their curiosity. The students asked their professors for more information and several members of the faculty decided to include fuel cell technologies into their basic course material, either as example problems or even just as discussion points.

Many of these students may spend their careers working on or with fuel cells if they reach commercial success. The possibilities include applications for cell phones, computers, remote sensing equipment, automobiles and transportation, residential power supply, as well as commercial and industrial scale power generation. The material is still new enough to be a contemporary issue but not so undeveloped as to be difficult to include in an engineering curriculum.

Finally, since the technology seems to be a real possibility for major adoption within five to ten years, the fuel cell (in whatever form) may become one of the common engineering tools all engineers need to know and understand.

CONCLUSION

Students are demanding to learn about new technologies, and are very interested in fuel cells in particular. The fuel cell appears to have a good potential to be adapted as another method for generating electricity.

We have found several places to include information about fuel cells into the curriculum, without needing to add another course, or dilute any other course. The information can be blended into existing content through the use of discussion of standard course topics and example problems. Finally, several such areas are identified in this paper.

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