

2006-705: DO FUEL CELL TOPICS BELONG IN A COMBUSTION COURSE?

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Do Fuel Cell Topics Belong in a Combustion Course?

Abstract

Combustion technologies are responsible for a lion's share of the country's electric power production and virtually a hundred percent of the conversion of fuels to power in the transportation sector. In spite of this domination, there is a growing competition from cleaner, more efficient energy technologies and a demand for distributed power generation. This is an area of engineering in which fuel cells are beginning to play a noticeable role. Fairly often combustion and fuel cells are referred to as opposing and quite different technologies. For example, one of the most reputable Thermodynamics textbooks¹ emphasizes that the chemical reactions in fuel cells are "*not* a combustion process." Despite the differences, a careful inspection of the topics associated with fuel cells surprisingly reveals a great deal of parallels with combustion.

The traditional sequence of topics in a combustion course proceeds from stoichiometry thru the second law to the Gibbs function and to the chemical equilibrium of combustion products. This coverage of material allows a straightforward extension into the thermochemistry of fuel cells with the derivation of the Nernst equation. This equation contains important fuel cell operating parameters, such as temperature and pressure. For example, the temperature affects the ideal voltage of a fuel cell, while partial pressures are responsible for fuel utilization. Along the same lines, both pressure and temperature influence the product outcome in combustion.

Fuel cell topics also include fuel-reforming applications. Depending on the operating temperature, fuel cells utilize internal or external reforming. There are three main technologies of fuel reforming. First, partial oxidation is a combustion process where fuels are burned in fuel-rich conditions. Second, steam reforming and the water-gas shift reaction are chemical reactions already common in combustion textbooks². Third, thermal autoreforming is a combination of the two methods. All of them present an excellent opportunity to expand students' experiences with relevant chemical equilibrium homework problems as well as course projects.

The authors fully agree that fuel cell reactions are not combustion. Nevertheless, the similarity of the underlying theories and applications is undeniable. This paper will introduce a way of interweaving fuel cell topics in a combustion course. This is especially beneficial in a curriculum that is not ready or does not have room for a full course on fuel cells.

Introduction

It is surprising to learn that fuel cell technology is over 165 years old, and yet it has made only marginal inroads in the modern power production world. William Grove, a British investigator, is generally acknowledged as the inventor of the fuel cell. However, some sources indicate that it might have been Humphrey Davy who should be credited with this invention in 1801, almost forty years earlier³. The successful development of combustion-mechanical power-dynamo technology in the early 1900 overshadowed any attempts to commercially develop fuel cells' direct conversion for many years to come. Most fuel cell work was done in a laboratory setting. However, this hard research eventually paid off in the mid 1950s in the work of Francis Thomas Bacon, whose fuel cells flew NASA's Apollo missions. Still much lighter than comparable

batteries of the time, these cells were complex, sensitive to impurities, expensive and short-lived. The next generation of fuel cells produced by International Fuel Cells (now United Technologies Corp., UTC) flew Space Shuttle missions in 1970-1990. Occasional commercial demonstrations existed throughout this period, but it was not until the mid-1980s to the early-1990s that the development of commercial systems took place. Westinghouse-Siemens and UTC were joined in 1969 by Energy Research Corp. (now Fuel Cell Energy), in 1979 by Ballard Research, Inc. (now Ballard Power Systems, Inc.), and in 1997 by Plug Power. All currently are the main North American fuel cell market players.

The introduction of fuel cells as a power production technology will be accompanied with many benefits. Regardless of the fuel cell type, sulfur is poisonous for fuel cells and is removed from the feed; as a result, sulfur oxides are not produced. Due to low operating temperature, the formation of nitrogen oxides is minimized with the exception of SOFC. Fuel cells are also part of distributed power generation technology, therefore reducing electrical transmission losses. Utilizing the waste heat further increases the efficiency. The target markets in this category are hotels, hospitals, schools, universities, wastewater treatment plants, etc. These authors' two favorite examples of such combined heat and power applications are the utilization of considered low grade heat produced by a phosphoric acid fuel cell in a company's cafeteria (Copel Solutions, Brazil⁴), and Sierra Nevada's brewing plant where the methane produced in the brewing process fuels the Direct Fuel Cell™ by FCE. In return, the fuel cell provides the heat for brewing, meanwhile supplying the electric grid with excess electricity⁵. The fuel pumping losses need not to be taken into consideration, unless the fuel would not be at the point of consumption for any other reason but the fuel cell.

The greatest fuel cell promise lies with its higher power conversion efficiency than the efficiency of Carnot-limited combustion-based power. In combustion the very same process of raising temperature, and consequently Carnot efficiency, is responsible for the destruction of the work potential (exergy) through the products attaining the adiabatic temperature. This even further degrades the efficiency of combustion-based technologies. All that and other considerations limit the electrical conversion efficiency to 20-30 % and 30-37 % for micro turbines and reciprocating engines⁶, respectively. Beyond the scope of this paper, an extended comparison of exergy destruction in combustion and fuel cells is given by Chen¹¹. The fuel cells do not operate in a cycle, but rather in a constant temperature-pressure environment, so that the efficiency is based on the reversible electrical work available, with theoretical values approaching 83% for a hydrogen-oxygen fuel cell operating at standard conditions. However, the operation of a fuel cell is not entirely an ideal process with conversion losses present. To function, a fuel cell also requires auxiliary equipment (so-called balance of plant). All that brings the individual electrical conversion efficiency to 40%. Operating at a higher temperature reduces the theoretical efficiency of fuel cells, while irreversible losses decrease thus raising the overall performance to 45%. In addition, thermal power becomes available with co-generation potential, thus boosting the overall performance. Fuel cells have two major drawbacks: the price of the stack per KW of power produced and long-term reliability (currently the stacks need to be replaced every 3-5 years). These are the factors whose influence will diminish with the economy of scale. Altogether, the many advantages make a strong case for fuel cells to play a significant role in the future energy market.

Fuel cells are now taken from the space technology realm into commonplace, especially automotive applications. The news anchors do their best to learn the proper vocabulary and details of the technology. Unfortunately, one misconception still lingers around the news channels — that hydrogen is the most abundant element on earth. While true, the statement suggests that hydrogen is available plentifully in free form ready for consumption. The sad reality is that a great deal of effort is required to produce hydrogen in a form acceptable to fuel cells. Regardless, the media attention and the rising fuel prices have made fuel cells acceptable by society with the promise of cleaner air and longer mileage per dollar spent, though the latter may not come true for quite a while.

According to the 2005 Worldwide Fuel Cell Industry Survey⁷, fuel cells are a \$330 million in sales industry with over 6300 employees worldwide, 47% of whom are employed in the US. The R&D expenses rose by 9% in 2004 to a total of \$716 million. The survey shows that of 158 companies that responded, more than two thirds located in North America and more than 50% have been in the business less than ten years. This demonstrates that the fuel cell industry is a growing sector of the economy and could be an important contributor to the power market in the future.

The automotive sector's vision is well represented by Mitsuhiko Yamashita⁸, Executive President of Nissan Corp. in charge of R&D. According to Yamashita, fuel cell powered vehicles will reach a market share of a few percent only in 30 years, but they will gain more than 15% only ten years later. Despite such slow developing prospects, Nissan has built a new fuel cell research center where it tests its own fuel cells, rather than being dependent on other manufacturers. In addition, the major competition to fuel cells will come from hybrid gasoline and diesel engines. All these factors suggest that there will be a strong market for an engineering workforce versed in both combustion and fuel cell applications.

The recent progress in fuel cell technology combined with the growing market share dictates the need of preparing more engineers fluent in fuel cells. This is due to the steadily growing fuel cell industry and the need for further development of fuel cell technology and manufacturing capabilities.

Introduction to fuel cells in an undergraduate engineering program would be preferred as a separate course or, alternatively, as a part of an advanced course in Thermodynamics⁹. But can it be a part of a combustion course? Most certainly.

The Grand Valley State University (GVSU) undergraduate ABET-accredited mechanical engineering program includes the following thermo-fluid science courses: required Thermodynamics, Fluid Mechanics and Heat Transfer, and elective HVAC and Combustion Applications. All, except Thermodynamics, are 4 credit courses with a laboratory component. The advent of new technologies requires a response from the academia. However, introducing a separate lab-based fuel cell course will require a considerable effort and demand on resources. So the academia could employ creative solutions within the existing curriculum offered. The Combustion Applications course sets as its goals to educate students about combustion phenomena and the most important technologies based on combustion. These include rocket engines, jet engines/gas turbines, spark and compression ignition engines, gas burners, and coal

combustion. Most of these topics closely relate to power production, and fuel cells naturally fall into this category. The technical depth for exploration of underlying fuel cell principles surpasses that available in traditional Thermodynamics or Energy Systems courses because of the deeper look into the chemical equilibrium and kinetics subjects required. However, these topics are essential in a combustion course and are well covered in the classroom, thus preparing students for absorbing fuel cell fundamentals. This further strengthens the argument about the appropriateness of fuel cell topics in a Combustion course. The overall goals of introducing fuel cells in such a setting would be to demystify the seemingly complex topic of fuel cells, educate on alternatives to combustion, prepare students as future engineers for potential independent study or an advanced course on fuel cells, and even give them a slight edge in employment opportunities.

The 2004 US electricity consumption was 3,971 billion kilowatt-hours¹⁰: 2-3% of that came from renewable energy resources, 27 % came from hydroelectric and nuclear sources, and a whopping 70% came from the combustion of fossil fuels. 70% of the total electricity produced from fossil fuels comes from the combustion of coal. Practically the entire transportation sector is powered by burning fossil fuels. Both the power and automotive sectors of the economy have a tremendous environmental impact. Much research and implementation work needs to be done to cut down pollution. As petroleum is estimated to run out in the next 50 years with the prices going up already, new hybrid engine technologies are coming on board, and updated gasoline engines employ direct fuel injection and cylinder deactivation. Coal, estimated to last for another 250-300 years, is a significant source of environmental concern. Innovative methods of its preparation or combustion are continuously researched and tried with a steady progress being made. Therefore, despite the advent of new renewable and alternative energy technologies teaching combustion foundations will remain essential for a long time.

Fuel Cell Thermodynamics

Combustion theory is a challenging study of complex phenomena. Despite the observed variety of processes, combustion theory is built upon the foundations of chemical equilibrium and kinetics adapted to each phenomenon. A study of these topics can take from several weeks to almost the entire course depending on the desired depth, although the subject is close to bottomless. Good understanding of chemical equilibrium modeling by the student is emphasized even at the undergraduate level. A careful look into fuel cell topics surprisingly reveals a lot of similarities between the two subjects, especially in the derivation of the Nernst equation, issues of performance related to chemical kinetics, and certainly fuel preparation and consumption. Teaching these topics in a fuel cell course will also consume several weeks (probably not in the listed order) of class time to do a good job. Three to four credit hour courses are used as a reference here. There will be an appreciable benefit to an engineering student to learn about fuel cells as a fascinating technology as well as direct alternative to combustion. So how to accomplish that without introducing a whole new course and diverting significant resources to this effort? Blending it in the framework of a combustion course just might be the answer. On the other hand, a combustion course would have very little time to spare. This paper outlines what material to cover about fuel cells in about 3-4 hours of lecture. Not only is this material beneficial in terms of fuel cells, but it also reinforces student understanding of chemical equilibrium and its widespread occurrence. The coverage of fuel reforming is somewhat brief,

savoring the enjoyment of chemical equilibrium for fuel utilization in a molten-carbonate fuel cell. This can become an advanced homework or a medium level project.

There are several types of fuel cells. A first look at their names is extremely confusing, and it might seem questionable why such different devices are grouped together. A brief overview will explain the few similarities and the many variations of fuel cells. A fuel cell is defined as an electrochemical device which directly converts chemical energy into electrical power. Continuous operation as long as fuel is supplied could also be added to the definition with a few exceptions to distinguish from batteries. This definition nicely contrasts to combustion which employs the following path to electricity: chemical energy→heat→mechanical work→conversion to power. The main component of a fuel cell is its membrane/electrolyte combination. The electrolyte defines the ion used in the reaction, appropriate operating temperatures, choice of catalyst, and the name of the fuel cell. The operating temperature also defines if internal fuel reforming can be adapted. A summary of these properties can be found in Table A-1. Everything else is built around these specifications. The most common fuel cells are:

- PEMFC—Proton Exchange Membrane Fuel Cell.
- DMFC—Direct Methanol Fuel Cell. This is rather an exception when a fuel cell is named after the fuel it utilizes; in reality, it is a modification of PEMFC.
- AFC—Alkaline Fuel Cell.
- PAFC—Phosphoric Acid Fuel Cell.
- MCFC—Molten Carbonate Fuel Cell.
- SOFC—Solid Oxide Fuel Cell.

AFC has been extensively used in space exploration; however due to certain limitations it is being superseded by more advanced PEMFC which is becoming commercially available. Based on PEMFC, DMFC promises to resolve the conundrum of hydrogen storage for mobile applications. The hydrogen energy stored in methanol in liquid form is far greater than any high-pressure hydrogen storage of comparable volume. However, this is still a developing technology (and in liquid form, not very interesting for a combustion course) with very slow anode kinetics. In addition, description of fuel cell operational principles is convenient with PEMFC and will be detailed below.

PAFC is the most commercially developed technology with a range up to 250 kW per unit. Hundreds of units are installed around the world. It performs reliably and with a good variety of fuels, which are reformed externally within the fuel cell unit. PAFC has relatively low efficiency and most likely will be replaced on the market by MCFC and SOFC. The latter two cells operate at high enough temperatures that internal fuel reforming becomes available as an option in addition to high grade heat exhaust that can be harnessed in combined heat and power applications. MCFC presents an excellent example of high temperature reacting thermodynamics related to combustion and also will be detailed in the paper. Many processes considered for MCFC are very similar in SOFC that operates at even higher temperatures; however, coverage of this material will become redundant or can be done very briefly and is not addressed here.

Both combustion and electrochemical reactions follow the principles of thermodynamics. For a system which undergoes a process at constant temperature and pressure, the second law requires

that the Gibbs function defined by Eq 1 decreased for an irreversible process or remained constant for a reversible one, Eq 2.

$$G = H - TS \quad 1$$

$$(dG)_{P,T} \leq 0 \quad 2$$

The chemical reaction given by Eq 3 is valid for combustion as well as for a fuel cell.



The change in the Gibbs energy for this reaction can be expressed by Eq 4.

$$\Delta G = \Delta G^0 + R_u T \ln \left(\frac{P_{C,n}^c P_{D,n}^d}{P_{A,n}^a P_{B,n}^b} \right) \quad 4$$

The subscripts in partial pressures e and n refer to equilibrium and non-equilibrium conditions, respectively. In the case of chemical equilibrium in combustion, the system arrives to such a state that the temperature and pressure are uniform throughout the system and any fluctuation is so minute that it constitutes a reversible process and the Gibbs energy cannot change and is minimized.

$$\Delta G = 0 \quad 5$$

Thus from Eq 4 the change in the standard Gibbs energy should be the negative of the logarithmic term that contains the partial pressures of the reactants in equilibrium.

$$\frac{\Delta G^0}{R_u T} = -\ln K_p = -\ln \left(\frac{P_{C,e}^c P_{D,e}^d}{P_{A,e}^a P_{B,e}^b} \right) \quad 6$$

Returning to fuel cells, the maximum electrical work of an electrochemical reaction can be shown to be the negative of the Gibbs energy change.

$$W_{el} = -\Delta G = nFE \quad 7$$

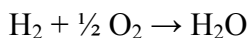
where n is the number of electrons (or protons) transferred in the reaction, F is Faraday's constant — the charge carried by one mole of electrons (96,487 coulombs/g-mole electron), and E is the open circuit potential developed across the cell. Expressing the voltage and substituting Eq 4 for the change in the Gibbs energy results in the following:

$$E = \frac{-\Delta G}{nF} = E^0 - \frac{R_u T}{nF} \ln \left(\frac{P_{C,n}^c P_{D,n}^d}{P_{A,n}^a P_{B,n}^b} \right) \quad 8$$

where E^0 is the ideal or reversible voltage, which plays an important role in defining fuel cell performance and is explored below for a few reactions.

$$E^0 = \frac{-\Delta G^0}{nF} = \frac{-(c\bar{g}_C^0 + d\bar{g}_D^0 - a\bar{g}_A^0 - b\bar{g}_B^0)}{nF} \quad 9$$

For a simple reaction of hydrogen and oxygen the ideal voltage can be calculated:



$$E^0 = \frac{-\Delta G^0}{nF} = \frac{-(1 \cdot \bar{g}_{H_2O}^0 - 1 \cdot \bar{g}_{H_2}^0 - \frac{1}{2} \cdot \bar{g}_{O_2}^0)}{nF} = \frac{-(-228,608) \text{ kJ} / \text{ kmol}}{2 \cdot 96,487 \text{ coulombs} / \text{ gmol}} = 1.18 \text{ V} \quad 10$$

for the case of water remaining in vapor state $E^0 = 1.23 \text{ V}$. The values for this and following calculations are conveniently obtained from a combustion textbook²!

The second and the third reactions given in Table 1 could be present in MCFC fuel cells. MCFC operates by transporting the oxygen ion to fuel rather than proton to oxygen. It attaches O^- to CO_2 forming CO_3^- which is carried across an electrolyte of molten lithium- and potassium or lithium- and sodium carbonate salts. Therefore, the expression in the second equation includes the cathode and anode CO_2 as part of the reaction. In general, the concentrations at the anode and cathode can be different, but in calculating the ideal voltage given in the table, the reaction that is CO_2 neutral and CO_2 Gibbs energies cancel; the net reaction ideal voltage is identical to the reaction in PEMFC. The form of the third equation is given as it appears in SOFC. For MCFC the cathode CO_2 should be added to emphasize the need for the presence of CO_2 at the cathode to maintain proper levels of CO_3^- in the electrolyte. However, this reaction is relatively marginal in MCFC due to slow kinetics.

Table 1. Fuel cell reactions, Nernst equation and developed potentials at various temperatures.

Reaction and Fuel Cell	Nernst Equation	E^0 at 400K (127°C), V	E^0 at 923 K (650 °C), V
$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$, PEMFC	$E = E^0 - \frac{R_u T}{n F} \ln \left(\frac{P_{H_2O,n}^1}{P_{H_2,n}^1 P_{O_2,n}^{1/2}} \right)$	1.16	1.02
$H_2 + \frac{1}{2} O_2 + CO_{2(cathode)} \rightarrow H_2O + CO_{2(anode)}$, MCFC	$E = E^0 - \frac{R_u T}{n F} \ln \left(\frac{P_{H_2O,n}^1 P_{CO_2(cathode),n}^1}{P_{H_2,n}^1 P_{O_2,n}^{1/2} P_{CO_2(anode),n}^1} \right)$	1.16	1.02
$CO + \frac{1}{2} O_2 \rightarrow CO_2$, MCFC and SOFC	$E = E^0 - \frac{R_u T}{n F} \ln \left(\frac{P_{CO_2,n}^1}{P_{CO,n}^1 P_{O_2,n}^{1/2}} \right)$	1.29	1.05

The ideal maximum efficiency of a fuel cell is classically defined as work produced per energy exerted.

$$\eta = \frac{W_{el}}{HHV} = \frac{-\Delta G^0}{HHV} = \frac{-\Delta G^0}{LHV + \Delta \bar{h}_{fg}} = \frac{-228,608 \text{ J} / \text{ gmol}}{(-241,845 - 44,010) \text{ J} / \text{ gmol}} \times 100\% = 83\% \quad 11$$

The efficiency falls with temperature to 62% at 1000° C following the trend set by the Gibbs energy. Even though the theoretical efficiency drops with the temperature so do the irreversible losses, thus rather raising the observed efficiency at high temperatures. This is discussed later in the paper. There are many other definitions of efficiency related to fuel cells. However, they fall out of the scope of this paper.

Fuel cell operation based on PEMFC

Fuel is supplied on the anode side in the passages formed by a bipolar plate, see Fig 1. Hydrogen enters the gas diffusion layer where it reacts on the catalyst splitting into protons and electrons. Protons flow through the membrane to the cathode side. Electrons are rejected by the membrane and flow into the bipolar plate and further to the external circuit. The proton-exchange membrane is sulphonated fluoroethylene (a modification of Teflon) and forms a hydrofolic structure which contains clusters of moisture through which protons hop to the cathode side of the membrane.

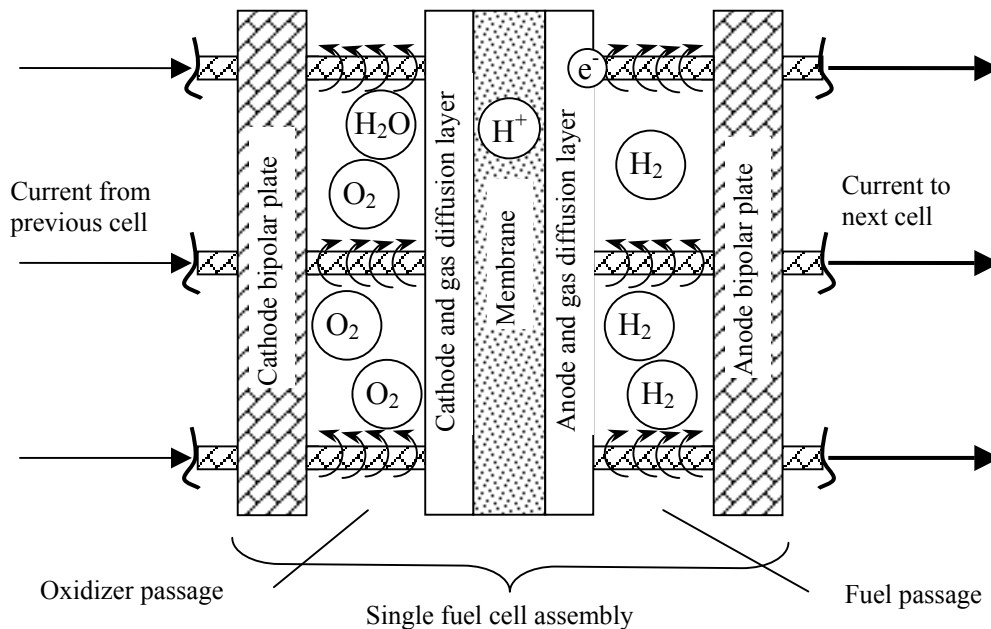


Figure 1. Schematic of PEMFC operation with major component layout and reactants flow. Connection in series is also shown.

On the cathode side pure oxygen, or oxygen contained in the air, also flows in the bipolar plate but on the opposite side of the membrane. It enters the cathode diffusion layer and dissociates on the catalyst. The liberated oxygen ion quickly finds two protons forming a molecule of water. The potential developed across a single cell and the current produced over the cross-sectional area are extremely sensitive and depend on a multitude of factors. For example, water produced in the reaction needs to be removed, and yet a certain amount should remain in the membrane for proton exchange. This presents a delicate balance to maintain and limits the operational temperatures to a traditional setting of 80 °C. Thus not only the moisture but also the heat generated should be controlled to prevent flooding or over drying of the membrane. Higher temperatures are favored, even though they slightly reduce the ideal voltage. The gains are in greater reaction rates and a reduced amount of catalyst. Such low temperatures of operations require a platinum catalyst as opposed to a nickel catalyst in higher temperature types of fuel cells. However, nowadays, due to the advances in technology, the amount of catalyst employed does not significantly contribute to the pricing.

The gas diffusion layer is located between the membrane and the bipolar plate and basically is a carbon paper or cloth. It serves as a connector from catalyst to bipolar plate, diffuses gases trying to reach the catalyst, carries away product water and is a protective barrier for the membrane. The catalyst is located on the boundary of the gas diffusion layer and the electrolyte/membrane, see Fig 2. The catalyst is formed by attaching tiny platinum particles to the powdered carbon which is applied by proprietary methods to the membrane.

A special description of the bipolar plate is required as it performs a myriad of functions and comprises about 80% of the fuel cell mass. Its main function is to distribute the flow of fuel on one side and the oxidizer on the other so it is sometimes called a flow field plate. The air in the oxidizer stream can also provide a cooling function if running more air than needed for the reaction, but most designs include additional passages purely dedicated to cooling, which further adds complexity to the fuel cell design but affords more precise cooling control without drying out the membrane. The intricacy of a bipolar design is represented by Fig 3. Channels are set up to provide minimum pressure losses and uniform concentration distribution. Temperature control is an especially sensitive issue in automotive designs where larger than traditional heat exchangers are called for to compensate for lower temperature gradients generated by PEMFC.

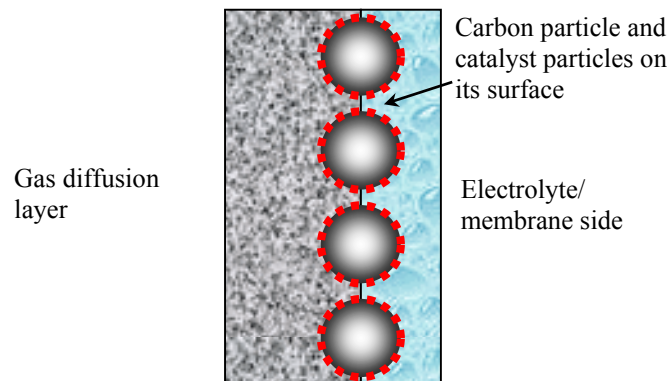


Figure 2. Schematic representation of the boundary formed by the gas diffusion layer

The bipolar plate name comes from connecting fuel cells in series forming a fuel cell stack. As shown above, fuel cell voltage is about one volt, so to obtain a meaningful voltage individual cells should be wired from the anode of one cell to the cathode of the next and so on. However, this would create long routes for electrons and increase ohmic losses. On the other hand, the bipolar plate accomplishes the same effect by simply connecting through its structure the electrodes (usually the carbon powder with catalyst) dispersed in the gas diffusion layer of one anode to the same of the opposing cathode of the next cell as shown in Fig 1. Both flow distribution and electricity conduction compete for contact surface with the membrane presenting another optimization challenge, all meanwhile assuring low pumping losses and higher reactant concentrations.

Before considering fuel cell losses, let us mention the basics of chemical kinetics in combustion. It will reveal additional similarities between the two subjects. Topics of combustion kinetics are quite complex but help to explain a multitude of phenomena encountered in fuel cells.

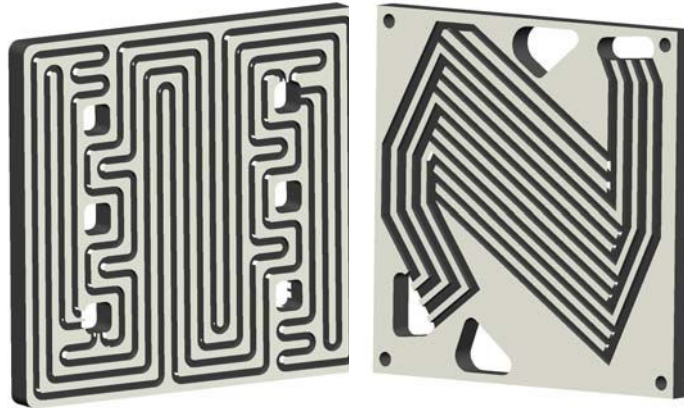


Figure 3. Two bipolar plate renderings modeled after designs by Ballard Power Systems. Intricate designs for flow distribution are revealed. Renderings were performed in Pro/Engineer by J. Jiran and J. Smit in a freshman CAD course.

The traditional coverage of chemical kinetics in an introductory combustion course builds up on the multi-reaction reality of combustion introduced in the combustion equilibrium theory. But now the reaction exists in real time: consuming, producing, waiting for and competing for various species. Each elementary reaction can be represented through its reaction constant and the species involved in the reaction. Depending on how many species are involved in the reaction, they are subdivided into unimolecular, bimolecular and termolecular. Temperature, total pressure and concentrations lead to various paths/mechanisms of reactions as classically shown in H_2-O_2 system where outcomes can be slow reactions or explosions. The four-reaction Zeldovich mechanism of NO formation is an example of uncovering how NO pollution is formed in combustion systems and in what conditions. Several hundred elementary reactions and fifty or so of species are involved in the combustion of hydrocarbons. All of those are superimposed on fluid flow and heat transfer considerations. Modeling such a process is a daunting task even for supercomputers. Practical engineering applications rely on one- or two-step global reaction mechanisms developed from more involved models. Let us consider a one-step global reaction between a fuel and its oxidizer.



A global mechanism can be constructed for the fuel reaction rate corresponding to the reaction expressed in Eq 12.

$$\frac{[F]}{dt} = -k_G [F]^\alpha [Ox]^\beta \quad 13$$

Equation 13 effectively encompasses the consumption rate of the product of the reaction as a function of conditions present in the combustion system (temperature, pressure and reactor arrangement) and concentration of fuel and oxidizer participating in the reaction, where α and β are empirical or derived powers. Equation 12 also specifies that per one mole of fuel consumed b moles of product are generated. The same applies to the rate at which product is generated however positive in magnitude.

The global reaction constant Eq 14 introduced in Eq 13 combines the many effects of the collision theory in one group.

$$k_G = Ap^x T^y \exp(-E_A / R_u T) \quad 14$$

The global reaction constant is traditionally stated in the Arrhenius form, where the exponential term expresses the fraction of the collisions which are energetic enough to overcome the activation energy E_A barrier and A is the pre-exponential constant which is empirical or comes from the collision theory. The effects of pressure and temperature are taken into account by p^x and T^y . However, in many cases of specified temperature and pressure ranges x and y may be taken to be zero. Raising the temperature of the reactants leads to higher reaction rates as the molecules are more energized and are able to overcome the activation energy. This effect is also extremely profound, as will be shown later, on the performance and the design of fuel cells.

Fuel Cell Losses

The operation of a fuel cell unfortunately is not ideal and several irreversibilities exist. All of them lead to the reduction of the voltage produced as a function of the current. Among them are activation, concentration, mass transport, ohmic and fuel crossover losses, see Fig 4. The former three can be related to the Nernst equation and chemical kinetics thus paralleling combustion theory. The latter two have purely electrical origins and will be considered first.

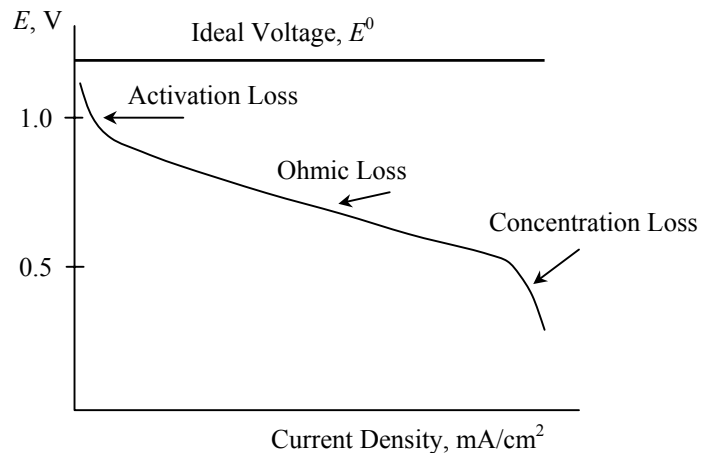


Figure 4. Losses in operational voltage as a function of current density drawn from the cell.

The ohmic losses are the easiest to understand and come from the resistance of the electrolyte to the flow of ions and of structural elements to the flow of current. On Fig 4 this losses appear as a linear function represented by the equation below.

$$\Delta E_{ohmic} = i \cdot R \quad 15$$

The fuel crossover loss happens in fuel cells when fuel is able to cross the electrolyte without giving up electrons for the external circuit. This is usually considered a minor loss with the exception of lower temperature fuel cells where the associated voltage drop will be 0.2 V, which is an appreciable amount for the ideal voltage of 1.2 V.

The activation loss has several names: polarization, overvoltage, etc. All refer to the voltage drop due to overcoming the reaction potential on the anode and cathode electrodes. The anode activation loss is usually much less than the voltage drop observed on the cathode. Initially Tafel documented this behavior, and with later theoretical considerations the activation voltage on the cathode can be expressed as

$$\Delta E_{act} = \frac{RT}{2\gamma F} \ln\left(\frac{i}{i_0}\right) \quad 16$$

The coefficient γ is called the charge transfer coefficient which relates to the portion of electrical energy transferred in oxidation or reduction reactions. Its value can vary from 1 to 0. For the hydrogen oxidation reaction the value is taken as 0.5. As it might seem from Eq. 16, the effect of the increasing temperature would be to raise the activation losses. However, this is not observed. A more sensitive function of temperature is i_0 , the exchange current density, which incorporates the chemical kinetic part of the more general electro-chemical reaction¹¹. Indeed, as seen from Eq-s 13-14, there are two terms sensitive to temperature. The first is the global reaction coefficient which increases with temperature giving the reactants more energy to overcome the activation barrier (alternatively better catalysts can be used reducing the activation energy; platinum in PEMFC is already the best, however). The second (a weaker effect) is “faster” diffusion coefficients supplying more reactants to the catalysis zones. This issue will be considered further in the next section. Thus raising the temperature from room conditions to 800 °C increases i_0 by a hundred times¹². As shown in Table 1, the ideal voltage E^0 drops with increased temperature, but the activation loss potential becomes smaller thus overall giving similar or slightly higher initial operating voltage ($E^0 - \Delta E_{act}$) to the high temperature MCFC and SOFC as compared to PEMFC and PAFC.

Gas- or mass-transport losses generally refer to the voltage losses occurring at relatively high currents. Drawing the larger currents implies the higher reactants’ consumption; however, the environment in a fuel cell is not of a well-stirred reactor but rather is diffusion controlled. Thus as the reactants are consumed at the electrodes, the products and inert species should be removed and reactants refreshed. As discussed above, elevating the temperature helps to increase the diffusion/transport coefficients, but drawing more current introduces the loss again. This is particularly a concern on the cathode side of PEMFC where, if oxygen is supplied in the air, nitrogen tends to occupy the regions around the catalyst. In addition, large amounts of water are generated, and if air circulation is insufficient or the gas diffusion layer is not transporting moisture away, a reduction in fuel cell performance can occur. On the anode side, if hydrogen is supplied as part of the reformed gas, the inert components in the stream can also block the reaction zones from hydrogen, similarly to nitrogen on the cathode side.

Another concentration loss is attributed to spending the fuel and oxidizer as they flow along a fuel cell. To demonstrate this effect let us consider the Nernst equation of hydrogen oxidation given in Table 1.

$$E = E^0 - \frac{R_u T}{n F} \ln\left(\frac{P_{H_2O,n}^1}{P_{H_2,n}^1 P_{O_2,n}^{1/2}}\right) \quad 17$$

As hydrogen and oxygen proceed through the fuel cell, their corresponding partial pressures drop, while the partial pressure of water goes up. Therefore, the logarithmic term in Eq 17 increases, lowering the voltage developed in the fuel cell. This leads to three very important constraints in fuel cell design. First is the design of the bipolar plate which must be optimized to provide the highest concentrations possible over the larger area of the membrane. This has been a hot topic among fuel cell manufacturers and a large variety of options has been explored. Second is that a fuel cell does not benefit from economy of scale, as a matter of fact making it larger adds less efficient regions with low voltage because reactants deplete. Thus, overall, cells remain relatively small in size, where megawatt power plants are assembled from smaller units. This is rather a positive conclusion: smaller cells are just as efficient as larger units making fuel cells adaptable to a large degree of applications. Third is that at the exit stream there will be a sizeable amount of unreacted fuel present that requires recirculation or burning in the fuel reforming process. Details, temperature dependence, and fuel utilization in the logarithmic term in the Nernst equation will be presented later.

Fuel Reforming

Well developed for other needs, the technology of fuel reforming is seemingly a stand-alone topic of chemical engineering, and yet it is intimately interwoven in fuel cell technology. On the other hand, many processes of fuel reforming are very similar in their nature to combustion, making fuel reforming an attractive topic for consideration in combustion applications especially in connection to fuel cells.

The four types of fuel reforming are steam reforming, partial oxidation (POX), autoreforming and thermal decomposition. All are targeting the production of hydrogen from hydrocarbons. These are mature technologies due to the widespread usage of hydrogen in various applications. Synthesis gas has been widely used in the production of plastics or making synthetic diesel. Pure hydrogen is used in binding atmospheric nitrogen to produce fertilizers, in petroleum refining applications, and as a fuel for space exploration. Put in perspective the yearly production of hydrogen in the US would last only two days if all transportation were to switch to hydrogen. This clarifies the necessity to build a hydrogen distribution infrastructure if we are to have fuel cell powered vehicles. Fuel reforming, despite of its advances, is not commercially ready. Current systems are too large to reform gasoline on board of a practical vehicle. The mobile systems also are unable to follow the changing loads in vehicle operation while providing ultra-clean stream of hydrogen: even minute quantities of CO (more than a few ppm) will permanently poison PEMFC. However, hydrogen fueling stations could provide the necessary quality of fuel.

Hydrogen production by steam reforming is accomplished in two steps: steam reforming (endothermic) and the water-gas shift reaction (exothermic), Eq-s 18-19 respectively.



Thus, in steam reforming of alkanes, $3n+1$ moles of hydrogen are created per n moles of CO_2 . This is $2n$ moles of hydrogen more than in direct combustion. But the steam reforming part is an endothermic reaction, and heat provision environmental expenses should be counted in as well. The steam reforming reaction of methane is usually catalyzed by nickel in the 750-1000 °C temperature range. Water-gas shift reaction is accomplished with a mixture of iron and

chromium oxides as catalysts in the 400-550 °C temperature range¹¹. In this sense steam reforming of methanol has advantage of being processed at much lower temperatures of 200-300 °C with copper catalyst.

Partial oxidation is a traditional approach in using higher order hydrocarbons for hydrogen production:



A hydrocarbon is burnt in rich fuel conditions; thus, fuel oxidation is mostly partial to CO and H₂ rather than to CO₂ and water. While the process is relatively straightforward, many drawbacks have been identified in this method of producing syngas in relation to fuel cells. They are the lower outcome of hydrogen in comparison to steam reforming; introduction of a large amount of nitrogen with the atmospheric air used for oxidation, which decreases partial pressure of hydrogen in the feed; and, presence of sulfur, ash and soot to be dealt with. Thus direct POX is abandoned for its catalytic counterpart, which is developed for methanol as in Johnson Matthey Hot Spot™ reactor.

The water-gas shift reaction is introduced in a combustion textbook² in an extensive example of full vs. simplified water-gas equilibrium calculations. Especially interesting is that this example focuses on combustion of propane in rich conditions and then considers the water-gas equilibrium reaction in the formed products. Even though this example does not add water, it is somewhat similar to the third method of hydrogen production from hydrocarbons—direct autoreforming. In this method fuel is partially oxidized and then water is introduced boosting the hydrogen outcome. Not only more hydrogen is produced, but it also takes advantage of combining exothermic oxidation and endothermic steam reforming without the need for complex supply or removal of heat. This process can be represented by Eq-s 18 through 20 working simultaneously to equilibrium.

Thermal decomposition of lighter hydrocarbons directly into hydrogen and carbon is also considered as the hydrogen stream produced is relatively pure. However, the need for carbon removal, for example by oxidation, is inevitable, making the hydrogen supply intermittent. Even though this method is actively investigated for some fuel cells, current progress is limited.

In most of the fuel reforming processes formation of carbon monoxide is inevitable and concentrations of a few percent are possible. Higher temperature fuel cells can tolerate such amounts in their feed, but PEMFC and PAFC will get poisoned if CO is present in quantities higher than a few ppm and 2%, respectively. Further well-developed CO removal techniques are used. For example, palladium/platinum membranes or pressure swing absorption, which are able to purify the feed from CO.

Electrolysis, an electrochemical approach to producing hydrogen, is being omitted from consideration in this paper because it has little connection to combustion topics and is essentially a fuel cell run backwards.

Molten Carbonate Fuel Cell

With respect to fuel reforming, MCFC offers a great deal of possibilities of connecting fuel cells and combustion. MCFC operates at 650 °C, temperatures high enough for species to react not only on the catalyst but also with each other. The general diagram of a MCFC fuel cell is given below, Fig 5. Also note that the bipolar plates have somewhat less intricate design than in PEMFC.

The cathode, membrane and anode are ceramic and are able to withstand high temperatures and aggressive environment (Li doped NiO, LiAlO₂, and Ni-Al, respectively). The electrolyte is a mixture of lithium carbonate (Li₂CO₃) and potassium carbonate (K₂CO₃) and some amounts of sodium carbonate (Na₂CO₃), which melt at about 500 °C, hence the name molten-carbonate. In liquid form CO₃⁼ ion is available to carry the charge across the electrolyte (in PEMFC the charge is carried by proton). The reaction at the cathode is



The reaction at the anode is



The complete reaction is presented on the second line of Table 1.

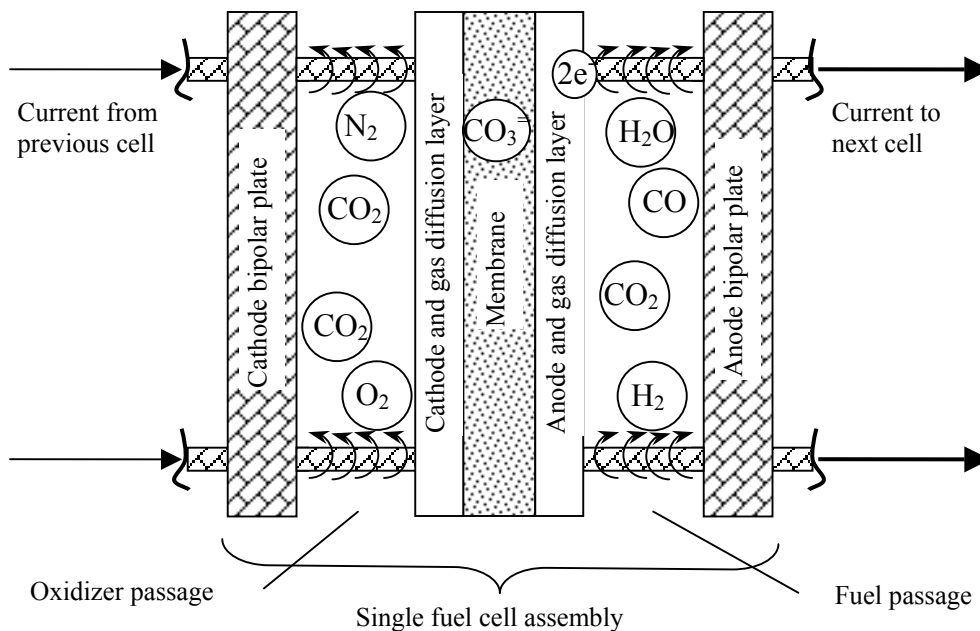


Figure 5. Schematic of MCFC operation with major component layout and reactants flow. Connection in series is also shown. Flow field plate design is less intricate than in PEMFC.

To maintain the balance of CO₃⁼ the cathode should have a plentiful supply of CO₂ as it is bound on the cathode and carried to the anode side. This is usually accomplished by burning and mixing some of the spent anode gas with incoming air. The spent cathode gas is used to preheat the incoming water and fuel.

MCFC can utilize two approaches to its fueling: external and internal. Internal fuel reforming allows direct flow of natural gas into the fuel cell where high temperature and Ni catalyst will provide sufficient conversion to fuel. First, the internal reforming proceeds as the steam reforming reaction given by Eq 18. Later as the fuel cell operates and water is produced, hydrogen is procured in the water-gas shift reaction, Eq 19. Even though Table 1 specifies the reaction where CO could directly participate in electrochemical oxidation, this reaction is very slow in comparison to Ni catalyzed water-gas shift reaction, which takes precedence. This effect will be considered later. Internal reforming allows very high fuel conversion and utilization, making for a very efficient approach. Internal reforming is somewhat more complicated in the design stage of a fuel cell, but overall reduces the complexity of the power plant, and it is very likely that it will be utilized in most of the MCFCs run on lighter hydrocarbons including biogas and landfill gasses. Higher hydrocarbons have a disadvantage of slower kinetics and residual coking in the system. Currently Fuel Cell Energy produces Direct Fuel Cell™ based on this technology. GVSU has access to this technology through its Alternative and Renewable Energy Center where such a cell is installed. From a combustion course adaptation point of view, internal fuel reforming is complex, involves chemical kinetics and finite times the fuel is flowing through the cell and may not be reasonable for adaptation. However, considering an external fuel reforming applied to MCFC creates a nice opportunity to further develop or refresh student knowledge of chemical equilibrium and analytical skills.

If external fuel reforming is employed, the canonical high-energy composition of the anode gas is 80% H₂, 20% CO and H₂O, which content corresponds to saturated vapor at 25 °C. A great variety of reformed feed combinations exists¹³. The anode fuel gas is specified at standard conditions. However, all four components of the anode gas can react at higher temperatures when reactions of dissociation and water-shift become appreciable. Therefore, equilibrium calculation is required to determine the actual gas composition. The cathode gas is 30% O₂, 60% CO₂ and 10% N₂.

$$E = E^0 - \frac{R_u T}{n F} \ln \left(\frac{P_{H_2O,n}^1 P_{CO_2(cathode),n}^1}{P_{H_2,n}^1 P_{O_2,n}^{1/2} P_{CO_2(anode),n}^1} \right) \quad 23$$

The changes in gas composition as a function of temperature at 1 atm are shown in the Appendix. The equilibrium calculations were performed using a chemical equilibrium software¹⁴. However, the system of three elements and four species can be assigned to be programmed manually by students, if a more advanced project is desired. Availability of the gas composition allows to investigate the entry open circuit voltage (OCV) as a function of temperature.

Figure 6 shows the ideal voltage and the total OCV which is higher than E^0 due to the positive contribution of the logarithmic term in Eq 23. The falling value of E^0 originates from increasing values of the Gibbs free energy with increasing temperature, see Eq 9. However, OCV falls slower, demonstrating the positive response of the logarithmic term mainly due to the increase in temperature. MCFC operating temperature as high as 800-900 °C would provide better efficiency; however, temperature of 650 °C is traditionally chosen from a corrosion and long-term performance point of view.

As fuel and oxidizer flow through the cell, they deplete. Equations 24 and 25 represent fuel and oxidizer utilization, respectively, and are based on the moles flowing in and out of the system per unit of time.

$$u_f = \frac{(N_{H_2} + N_{CO})_{in} - (N_{H_2} + N_{CO})_{out}}{(N_{H_2} + N_{CO})_{in}} = \frac{(P_{H_2} + P_{CO})_{in} N_{tot,in} - (P_{H_2} + P_{CO})_{out} N_{tot,out}}{(P_{H_2} + P_{CO})_{in} N_{tot,in}} \quad 24$$

$$u_{ox} = \frac{(N_{CO_2})_{in} - (N_{CO_2})_{out}}{(N_{CO_2})_{in}} = \frac{(P_{CO_2})_{in} N_{tot,in} - (P_{CO_2})_{out} N_{tot,out}}{(P_{CO_2})_{in} N_{tot,in}} \quad 25$$

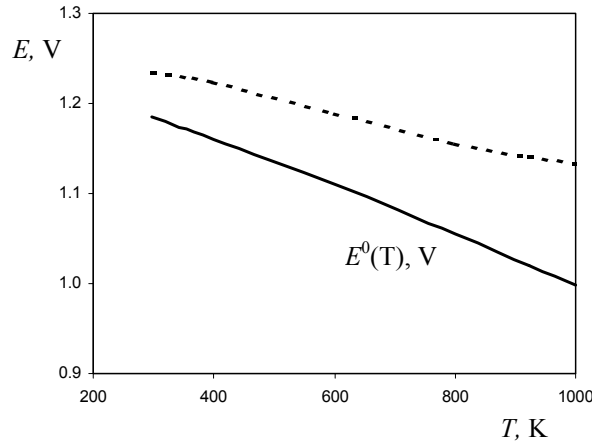


Figure 6. The open circuit voltage in MCFC as a function of temperature. The ideal voltage E^0 is also shown to contrast the contribution of the initial non-equilibrium concentrations of reactants.

Fuel utilization contains both H_2 and CO terms in it as both represent the fuel. In reality, H_2 and CO oxidations produce the same net electrochemical effect. In addition, CO prefers to react in a kinetically fast water-gas shift reaction rather than in a direct oxidation on the anode, producing extra hydrogen. The oxidant utilization is based on a limiting component— O_2 or CO_2 . In practical systems, it is most likely to be the latter.

The effect of fuel and oxidant depletion is shown in Fig 7. The calculations are performed with the same gas composition as previously introduced but with the equilibrium composition specified at $650\text{ }^\circ\text{C}$ and 1 atm. However, the initial partial pressures are converted to moles, and the oxidant moles are taken to satisfy stoichiometry. As the reaction proceeds, the mole count is performed on both cathode and anode sides. The composition changes are accompanied by a net mass transfer from the cathode to the anode in the form of O_2 and CO_2 . Per one mole of H_2 consumed (negative), one mole of H_2O is formed and one mole CO_2 is liberated (both positive). A similar procedure is performed on the cathode side. The corresponding partial pressures are recalculated with thermal equilibrium at the anode. The partial pressures at the cathode are just based on the mole balance. Given partial pressures of all species in the system, OCV and fuel utilization are obtained on the next step. Full details for these calculations are shown in the Appendix. The changes in OCV are driven by the constantly changing composition of the mixture at the cathode and anode due to the reactions given by Eq-s 21 and 22. The horizontal

line $E^0=1.02$ V clearly shows that at first non-equilibrium overall reaction composition adds potential to the reversible value, but after 35% of fuel consumption the composition pulls the conversion performance under that value. Once again, it demonstrates that increasing the fuel cell size will not considerably add to the overall power output. The curve somewhat resembles a negative cubic function relation. There is a tendency for rapid fall in the first 20% and after 60%. Somewhere between these two values a saddle shape is formed. This is due to the reduction in H_2 partial pressure as it is spent creating room for the gas shift reaction which replenishes some of the hydrogen, somewhat slowing down the reduction in potential. However, later both H_2 and CO become depleted plummeting OCV into a sharp fall again. When the circuit is closed, the higher current density drawn, the higher the utilization rate.

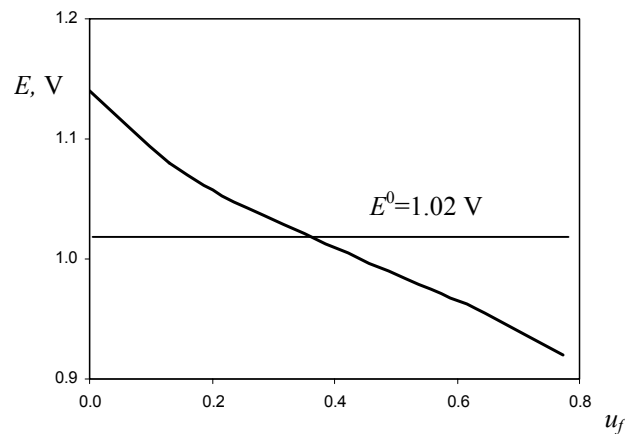


Figure 7. The open circuit voltage in MCFC as a function of utilization. The ideal voltage E^0 is also shown to demonstrate the contribution of the reactant concentrations. It is at first positive increasing voltage and then becomes negative as reactants deplete.

Fuel reforming and fuel utilization show in great detail the basics of fuel cell performance. This concludes the introduction of fuel cell technology in a combustion course.

Conclusions

Both fuel cells and combustion are going to co-exist in the near future requiring engineers well versed in both subjects. This paper demonstrates an approach to including fuel cell topics in a combustion course showing students an alternative technology to combustion while reinforcing chemical equilibrium and kinetics concepts learned in combustion. It also prepares students for more advanced studies of fuel cells. While the topic of fuel cells is too broad to be covered in a limited time, this material takes advantage of the general theory already present in combustion and encompasses the most important founding principles of fuel cell operation at low and high temperature ranges. Clear connections are made between fuel cell performance and equilibrium/kinetic behaviors of reacting combustion systems. The topics included are fuel cell basics, PEMFC and MCFC design and performance; fuel cell operational losses; external and internal techniques of fuel reforming; and fuel utilization aspects in MCFC.

Sample calculations and the material placed in the appendix suggest the types of homework or projects which might be assigned to reinforce the material covered.

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Appendix

Table A - 1. Major types of fuel cells and their main characteristics.

Fuel Cell	Electrolyte	Ion	Operating Temperature, °C	Catalyst	Fuel Reforming
PEMFC	Nafion + H ₂ O	H ⁺	80	Pt	External
AFC (Orbiter)	KOH	OH ⁻	83	Pt/Pd/Au	External
PAFC	H ₃ PO ₄	H ⁺	180-200	Pt	External
MCFC	Li ₂ CO ₃ , K ₂ CO ₃ Na ₂ CO ₃	CO ₃ ⁼	650	Ni/NiO	Internal/Extrenal
SOFC	Ytria-stabilized zirconia	O ⁼	850-1000	Not required	Internal/External

Fuel Reforming and Open Circuit Potential

Let us consider an example where an externally reformed gas is supplied to a fuel cell. The gas mixture will preheat according to the operational temperature of the fuel cell. Determine the gas composition of the fuel at the entrance of the cell and the expected open circuit potential.

A good selection of fuels is possible. Let us consider the canonical high-energy composition of the anode gas given at standard condition of 1 atm and 25 °C as 80% H₂, 20% CO and H₂O content is defined as saturated vapor. The partial pressure of water vapor at 25 ° is 0.0319 bar. The equilibrium calculations were performed using Grashoff gas equilibrium¹⁴ software at a series of temperatures. The results are displayed in Table A - 2 and Fig A - 1.

Table A - 2. The equilibrium cathode gas composition at various temperatures.

T,K	298	400	600	800	923	1000
P, H ₂	0.775	0.773	0.728	0.671	0.647	0.636
P, CO ₂	0.194	0.191	0.146	0.089	0.065	0.054
P, H ₂ O	0.031	0.034	0.078	0.135	0.159	0.170
P, CO	0.000	0.003	0.048	0.105	0.129	0.140

Table A - 3. Open circuit potential for fresh fuel entering a fuel cell operating at various temperatures.

T,K	298	400	600	800	923	1000
ΔG^0 , J/mole	-228,608	-223,929	-214,049	-203,550	-196,879	-192,652
E^0 , V	1.185	1.160	1.109	1.055	1.020	0.998
$RT/nF \ln(Q)$, V	0.048	0.063	0.079	0.100	0.120	0.134
$E=E^0+RT/nF \ln(Q)$, V	1.233	1.224	1.188	1.155	1.140	1.133

Table A - 3 presents the ideal voltage for the water oxidation reaction and the OCV at various temperatures based on Eq 23. These results are also plotted in Fig 6. The cathode gas composition used in these calculations was 30% O₂, 60% CO₂ and 10% N₂. Q in Table A - 3 is defined as

$$Q = \frac{P_{H_2O,n}^1 P_{CO_2(cathode),n}^1}{P_{H_2,n}^1 P_{O_2,n}^{1/2} P_{CO_2(anode),n}^1}$$

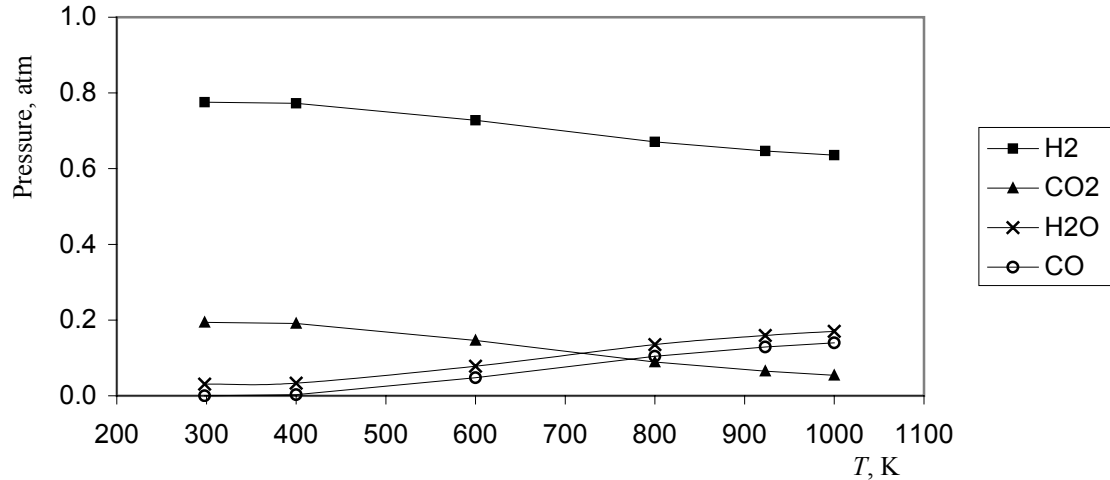


Figure A - 1. Anode gas composition as a function of temperature in the specified mixture at 1 atm.

Fuel Utilization in MCFC

Fuel utilization in a fuel cell presents another fine problem for students to practice their chemical equilibrium skills as well as to learn about one of the more important features in fuel cell performance and design. The cathode and anode gases' composition is the same as used in the previous example and is taken at 650 °C to simulate an MCFC environment.

Equation 22 presents the anode reaction. The net result of this reaction is that, per each mole of H₂ reacted, a mole of CO₂ and H₂O each is formed. This is reflected in Table A - 4. These calculations were started with the rate of moles flowing through the fuel cell equal to the partial pressure times a hundred. For example, 64.672 moles of H₂ were entering the system per unit of time. The changing number of moles due to the influx of CO₂ from the cathode is also calculated.

The values from Table A - 4 were entered in the equilibrium software, and the partial pressures of species were obtained, see Table A - 5. This is a relatively simple calculation which can be set up as a set of few conservation equations and the equilibrium constant of the reactants.

$$K_p = \frac{P_{H_2,e} P_{CO_2,e}}{P_{H_2O,e} P_{CO,e}} \approx 2 \text{ at } 650^\circ\text{C}$$

Then this problem might be presented to students as a medium level project refreshing their equilibrium calculations background.

Table A - 4. Molar composition of the anode gas as it flows through the cell.

H ₂ moles consumed	0	10	20	40	50	60
H ₂ , mol	64.672	54.672	44.672	24.672	14.672	4.672
CO ₂ , mol	6.515	16.515	26.515	46.515	56.515	66.515
H ₂ O, mol	15.942	25.942	35.942	55.942	65.942	75.942
CO, mol	12.871	12.871	12.871	12.871	12.871	12.871
N _{tot} , mol	100	110	120	140	150	160

Table A - 5. Anode gas composition as it flows through the cell.

H ₂ moles consumed	0	10	20	40	50	60
P _{H₂} , atm	0.647	4.84E-01	3.61E-01	1.87E-01	1.24E-01	7.22E-02
P _{CO₂} , atm	0.065	1.37E-01	2.10E-01	3.43E-01	4.03E-01	4.59E-01
P _{H₂O} , atm	0.159	2.49E-01	3.11E-01	3.88E-01	4.13E-01	4.32E-01
P _{CO} , atm	0.129	1.30E-01	1.19E-01	8.07E-02	5.92E-02	3.74E-02

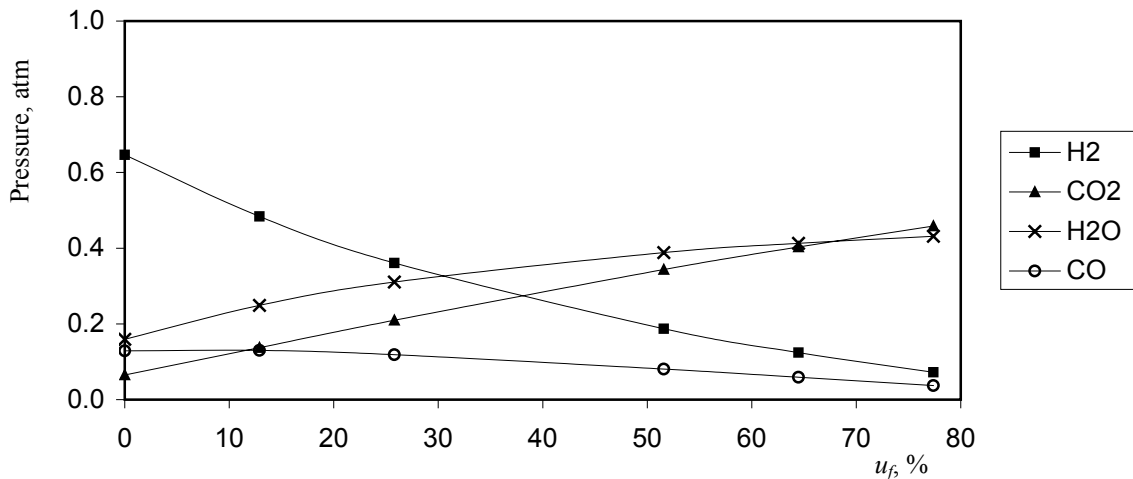


Figure A - 2. Anode gas composition as a function of fuel utilization in MCFC at 650 °C and 1 atm.

The cathode side is set up with the gas composition of 30% O₂, 60% CO₂ and 10% N₂. A stoichiometric number of moles is chosen for the given mixture of fuel, which corresponds to 40 moles of oxygen. The reaction at the cathode proceeds according to Eq 21. Once again, per one mole of H₂ reacted, the cathode side loses half a mole of O₂ and one mole of CO₂, see Table A - 6. The partial pressure calculation is performed only based on the total number of moles, see Table A - 7. Any dissociation reactions for these species are marginal at this temperature.

The total number of moles at the anode and cathode continuously change as the reactions proceed. At the anode the net mass flow rate increases and the opposite occurs on the cathode side. This presents another design factor. If the channels remain the same, the speed at the anode will pick up and at the cathode decelerate.

Once the partial pressures of the fuel and oxidant mixture are known, the OCV for the fuel cell can be calculated. In addition, the utilization of fuel is calculated based on Eq 24. The OCV as a function of the fuel utilization is plotted in Fig 7 and the anode mixture composition as a function of utilization is given in Fig A - 2.

Table A - 6. Molar composition of the cathode gas as it flows through the cell.

H ₂ moles consumed	0	10	20	40	50	60
O ₂ , mol	40.000	35.000	30.000	20.000	15.000	10.000
CO ₂ , mol	80.000	70.000	60.000	40.000	30.000	20.000
N ₂ , mol	13.333	13.333	13.333	13.333	13.333	13.333
N _{tot} , mol	133.33	118.33	103.33	73.33	58.33	43.33

Table A - 7. Cathode gas composition as it flows through the cell.

H ₂ moles consumed	0	10	20	40	50	60
P, O ₂	0.300	0.296	0.290	0.273	0.257	0.231
P, CO ₂	0.600	0.592	0.581	0.545	0.514	0.462
P, N ₂	0.100	0.113	0.129	0.182	0.229	0.308

Table A - 8. Fuel utilization and the corresponding open circuit potential in MCFC.

H ₂ moles consumed	0	10	20	40	50	60
Fuel utilization, %	0.0	12.9	25.8	51.6	64.5	77.4
RT/nF ln(Q), V	0.120	0.060	0.022	-0.036	-0.065	-0.100
$E=E^0+RT/nF \ln(Q)$, V	1.140	1.081	1.042	0.984	0.955	0.920