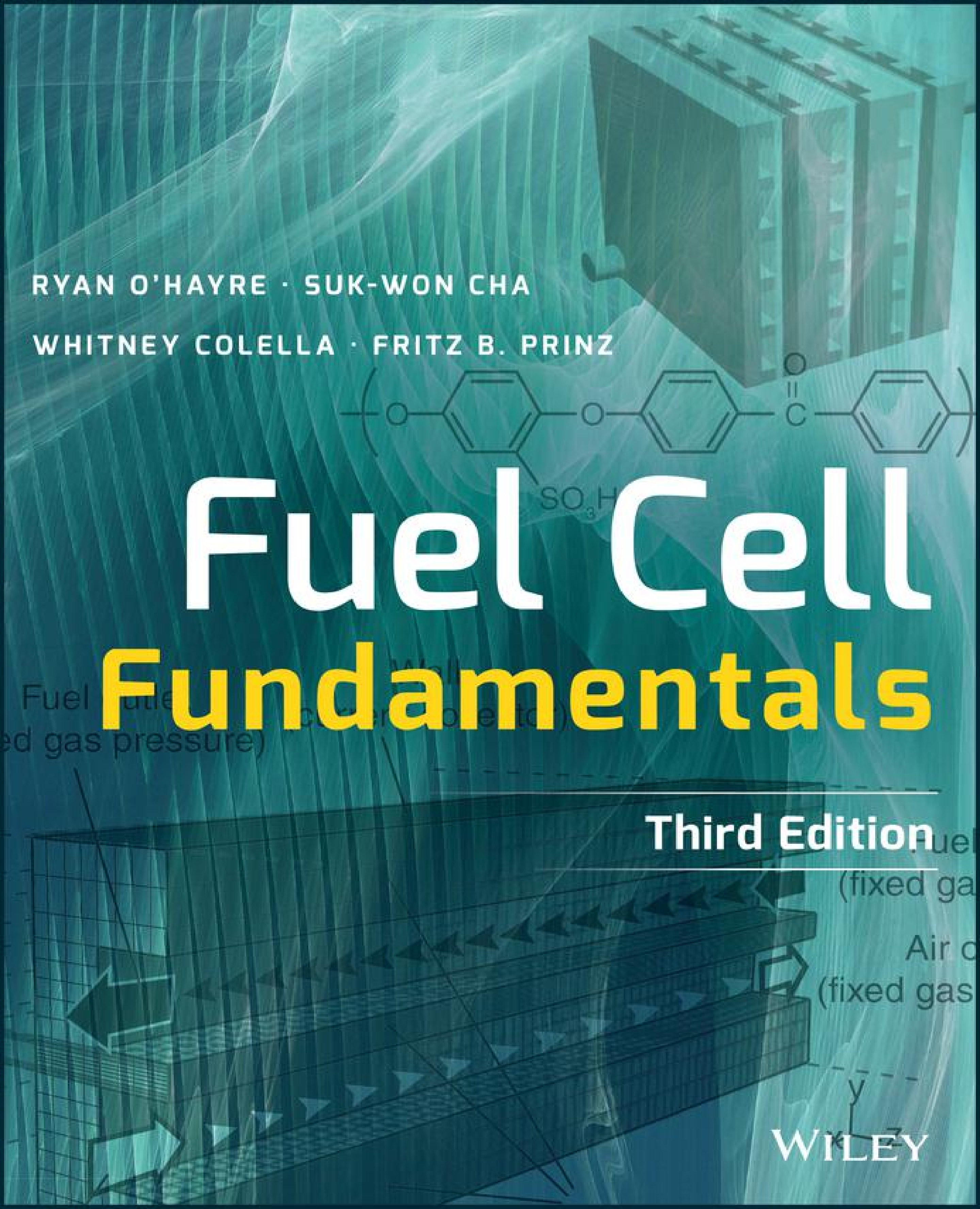

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Fuel Cell Fundamentals

Third Edition

WILEY

FUEL CELL FUNDAMENTALS

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To the parents who nurtured us.
To the teachers who inspired us.

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PREFACE

Imagine driving home in a fuel cell car with nothing but pure water dripping from the tailpipe. Imagine a laptop computer that runs for 30 hours on a single charge. Imagine a world where air pollution emissions are a fraction of that from present-day automobiles and power plants. These dreams motivate today's fuel cell research. While some dreams (like cities chock-full of ultra-low-emission fuel cell cars) may be distant, others (like a 30-hour fuel cell laptop) may be closer than you think.

By taking fuel cells from the dream world to the real world, this book teaches you the *science* behind the technology. This book focuses on the questions "*how*" and "*why*." Inside you will find straightforward descriptions of *how* fuel cells work, *why* they offer the potential for high efficiency, and *how* their unique advantages can best be used. Emphasis is placed on the fundamental scientific principles that govern fuel cell operation. These principles remain constant and universally applicable, regardless of fuel cell type or technology.

Following this philosophy, the first part, "Fuel Cell Principles," is devoted to basic fuel cell physics. Illustrated diagrams, examples, text boxes, and homework questions are all designed to impart a unified, *intuitive* understanding of fuel cells. Of course, no treatment of fuel cells is complete without at least a brief discussion of the practical aspects of fuel cell technology. This is the aim of the second part of the book, "Fuel Cell Technology." Informative diagrams, tables, and examples provide an engaging review of the major fuel cell technologies. In this half of the book, you will learn how to select the right fuel cell for a given application and how to design a complete system. Finally, you will learn how to assess the potential environmental impact of fuel cell technology.

Comments or questions? Suggestions for improving the book? Found a typo, think our explanations could be improved, want to make a suggestion about other important concepts to discuss, or have we got it all wrong? Please send us your feedback by emailing us at fcf3@yahoogroups.com. We will take your suggestions into consideration for the next edition. Our website http://groups.yahoo.com/group/fcf3 posts these discussions, fliers for the book, and additional educational materials. Thank you.

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NOMENCLATURE

Symbol	Meaning	Common Units
A	Area	cm^2
A_c	Catalyst area coefficient	Dimensionless
a	Activity	Dimensionless
ASR	Area specific resistance	$\Omega \cdot \mathrm{cm}^2$
C	Capacitance	F
C_{dl}	Double-layer capacitance	F
c^*	Concentration at reaction surface	$\mathrm{mol/cm}^2$
c	Concentration	$\mathrm{mol/m}^3$
c	Constant describing how mass transport affects concentration losses	V
c_p	Heat capacity	$\mathrm{J/mol \cdot K}$
D	Diffusivity	cm^2/s
E	Electric field	V/cm
E	Thermodynamic ideal voltage	V
E_{thermo}	Thermodynamic ideal voltage	V
E_T	Temperature-dependent thermodynamic voltage at reference concentration	V
F	Helmholtz free energy	J, J/mol
F	Faraday constant	96,485 C/mol
F_k	Generalized force	N
f	Reaction rate constant	Hz, s^{-1}
f	Friction factor	Dimensionless

Symbol	Meaning	Common Units
G, g	Gibbs free energy	J, J/mol
g	Acceleration due to gravity	$\mathrm{m/s^2}$
$\Delta G^{\ddagger}$	Activation energy barrier	J/mol, J
ΔG_{act}	Activation energy barrier	J/mol, J
H	Heat	J
H, h	Enthalpy	J, J/mol
H_C	Gas channel thickness	cm
H_E	Diffusion layer thickness	cm
h	Planck's constant	$6.63 \times 10^{-34}\ \mathrm{J \cdot s}$
$\hbar$	Reduced Planck constant, $h/2\pi$	$1.05 \times 10^{-34}\ \mathrm{J \cdot s}$
h_m	Mass transfer convection coefficient	m/s
i	Current	A
J	Molar flux, molar reaction rate	$\mathrm{mol/cm^2 \cdot s}$
$\hat{J}$	Mass flux	$\mathrm{g/cm^2 \cdot s}$, $\mathrm{kg/m^2 \cdot s}$
J_C	Convective mass flux	$\mathrm{kg/m^2 \cdot s}$
j	Current density	$\mathrm{A/cm^2}$
j_0	Exchange current density	$\mathrm{A/cm^2}$
j_0^0	Exchange current density at reference concentration	$\mathrm{A/cm^2}$
j_L	Limiting current density	$\mathrm{A/cm^2}$
j_{leak}	Fuel leakage current	$\mathrm{A/cm^2}$
k	Boltzmann's constant	$1.38 \times 10^{-23}\ \mathrm{J/K}$
L	Length	m
M	Molar mass	g/mol, kg/mol
M	Mass flow rate	kg/s
M_{ik}	Generalized coupling coefficient between force and flux	Varies
m	Mass	kg
mc_p	Heat capacity flow rate	$\mathrm{kW/kg \cdot {}^{\circ}C}$
N	Number of moles	Dimensionless
N_A	Avogadro's number	$6.02 \times 10^{23}\ \mathrm{mol^{-1}}$
n	Number of electrons transferred in the reaction	Dimensionless
n_g	Number of moles of gas	Dimensionless
P	Power or power density	W or $\mathrm{W/cm^2}$
P	Pressure	bar, atm, Pa
Q	Heat	J, J/mol
Q	Charge	C
Q_h	Adsorption charge	$\mathrm{C/cm^2}$
Q_m	Adsorption charge for smooth catalyst surface	$\mathrm{C/cm^2}$
q	Fundamental charge	$1.60 \times 10^{-19}\ \mathrm{C}$
R	Ideal gas constant	$8.314\ \mathrm{J/mol \cdot K}$
R	Resistance	Ω
R_f	Faradaic resistance	Ω

Symbol	Meaning	Common Units
Re	Reynolds number	Dimensionless
S, s	Entropy	J/K, J/mol · K
S/C	Steam-to-carbon ratio	Dimensionless
Sh	Sherwood number	Dimensionless
T	Temperature	K, °C
t	Thickness	cm
U	Internal energy	J, J/mol
u	Mobility	$\text{cm}^2/\text{V} \cdot \text{s}$
$\bar{u}$	Mean flow velocity	cm/s, m/s
V	Voltage	V
V	Volume	L, cm^3
V	Reaction rate per unit area	$\text{mol}/\text{cm}^2 \cdot \text{s}$
υ	Velocity	cm/s
υ	Hopping rate	s^{-1}, Hz
υ	Molar flow rate	mol/s, mol/min
W	Work	J, J/mol
X	Parasitic power load	W
x	Mole fraction	Dimensionless
x_υ	Vacancy fraction	mol vacancies/mol sites
y_x	Yield of element X	Dimensionless
Z	Impedance	Ω
z	Height	cm

Greek Symbols

Symbol	Meaning	Common Units
α	Charge transfer coefficient	Dimensionless
α	Coefficient for CO_2 equivalent	Dimensionless
α^*	Channel aspect ratio	Dimensionless
β	Coefficient for CO_2 equivalent	Dimensionless
γ	Activity coefficient	Dimensionless
Δ	Denotes change in quantity	Dimensionless
δ	Diffusion layer thickness	m, cm
ε	Efficiency	Dimensionless
ε_{FP}	Efficiency of fuel processor	Dimensionless
ε_{FR}	Efficiency of fuel reformer	Dimensionless
ε_{H}	Efficiency of heat recovery	Dimensionless
ε_{O}	Efficiency overall	Dimensionless
ε_{R}	Efficiency, electrical	Dimensionless
ε	Porosity	Dimensionless
$\dot{\varepsilon}$	Strain rate	s^{-1}

Symbol	Meaning	Common Units
η	Overvoltage	V
η_{act}	Activation overvoltage	V
η_{conc}	Concentration overvoltage	V
η_{ohmic}	Ohmic overvoltage	V
λ	Stoichiometric coefficient	Dimensionless
λ	Water content	Dimensionless
μ	Viscosity	kg · m/s
μ	Chemical potential	J, J/mol
$\tilde{\mu}$	Electrochemical potential	J, J/mol
ρ	Resistivity	Ω cm
ρ	Density	kg/cm^3, kg/m^3
σ	Conductivity	S/cm, $(\Omega \cdot \text{cm})^{-1}$
σ	Warburg coefficient	$\Omega/\text{s}^{0.5}$
τ	Mean free time	s
τ	Shear stress	Pa
φ	Electrical potential	V
φ	Phase factor	Dimensionless
ω	Angular frequency ($\omega = 2\pi f$)	rad/s

Superscripts

Symbol	Meaning
0	Denotes standard or reference state
eff	Effective property

Subscripts

Symbol	Meaning
diff	Diffusion
E, e, elec	Electrical (e.g., P_e, W_{elec})
f	Quantity of formation (e.g., ΔH_f)
(HHV)	Higher heating value
(LHV)	Lower heating value
i	Species i
P	Product
P	Parasitic
R	Reactant
rxn	Change in a reaction (e.g., ΔH_{rxn})
SK	Stack
SYS	System

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PART I

FUEL CELL PRINCIPLES

CHAPTER 1

INTRODUCTION

You are about to embark on a journey into the world of fuel cells and electrochemistry. This chapter will act as a roadmap for your travels, setting the stage for the rest of the book. In broad terms, this chapter will acquaint you with fuel cells: what they are, how they work, and what significant advantages and disadvantages they present. From this starting point, the subsequent chapters will lead you onward in your journey as you acquire a fundamental understanding of fuel cell principles.

1.1 WHAT IS A FUEL CELL?

You can think of a fuel cell as a "factory" that takes fuel as input and produces electricity as output. (See Figure 1.1.) Like a factory, a fuel cell will continue to churn out product (electricity) as long as raw material (fuel) is supplied. This is the key difference between a fuel cell and a battery. While both rely on electrochemistry to work their magic, a fuel cell is not consumed when it produces electricity. It is really a factory, a *shell*, which transforms the chemical energy stored in a fuel into electrical energy.

Viewed this way, combustion engines are also "chemical factories." Combustion engines also take the chemical energy stored in a fuel and transform it into useful mechanical or electrical energy. So what is the difference between a combustion engine and a fuel cell?

In a conventional combustion engine, fuel is burned, releasing heat. Consider the simplest example, the combustion of hydrogen:

$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O \tag{1.1}$$

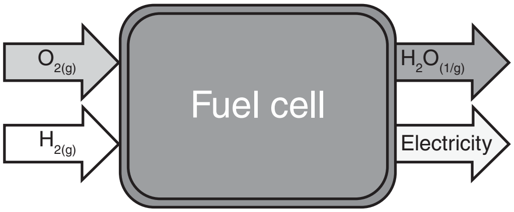

Figure 1.1. General concept of a (H_2–O_2) fuel cell.

On the molecular scale, collisions between hydrogen molecules and oxygen molecules result in a reaction. The hydrogen molecules are oxidized, producing water and releasing heat. Specifically, at the atomic scale, in a matter of picoseconds, hydrogen–hydrogen bonds and oxygen–oxygen bonds are broken, while hydrogen–oxygen bonds are formed. These bonds are broken and formed by the transfer of electrons between the molecules. The energy of the product water bonding configuration is lower than the bonding configurations of the initial hydrogen and oxygen gases. This energy difference is released as heat. Although the energy difference between the initial and final states occurs by a reconfiguration of electrons as they move from one bonding state to another, this energy is recoverable only as heat because the bonding reconfiguration occurs in picoseconds at an intimate, subatomic scale. (See Figure 1.2.) To produce electricity, this heat energy must be converted into mechanical energy, and then the mechanical energy must be converted into electrical energy. Going through all these steps is potentially complex and inefficient.

Consider an alternative solution: to produce electricity directly from the chemical reaction by somehow harnessing the electrons as they move from high-energy reactant bonds

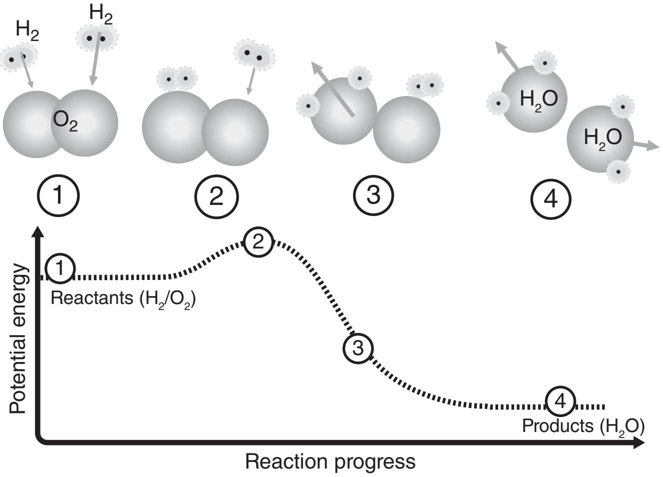

Figure 1.2. Schematic of H_2–O_2 combustion reaction. (Arrows indicate the relative motion of the molecules participating in the reaction.) Starting with the reactant H_2–O_2 gases (1), hydrogen–hydrogen and oxygen–oxygen bonds must first be broken, requiring energy input (2) before hydrogen–oxygen bonds are formed, leading to energy output (3, 4).

to low-energy product bonds. In fact, this is exactly what a fuel cell does. But the question is, how do we harness electrons that reconfigure in picoseconds at subatomic length scales? The answer is to spatially separate the hydrogen and oxygen reactants so that the electron transfer necessary to complete the bonding reconfiguration occurs over a greatly extended length scale. Then, as the electrons move from the fuel species to the oxidant species, they can be harnessed as an electrical current.

BONDS AND ENERGY

Atoms are social creatures. They almost always prefer to be together instead of alone. When atoms come together, they form bonds, lowering their total energy. Figure 1.3 shows a typical energy–distance curve for a hydrogen–hydrogen bond. When the hydrogen atoms are far apart from one another (1), no bond exists and the system has high energy. As the hydrogen atoms approach one another, the system energy is lowered until the most stable bonding configuration (2) is reached. Further overlap between the atoms is energetically unfavorable because the repulsive forces between the nuclei begin to dominate (3). Remember:

- Energy is released when a bond is formed.
- Energy is absorbed when a bond is broken.

For a reaction to result in a net release of energy, the energy released by the formation of the product bonds must be more than the energy absorbed to break the reactant bonds.

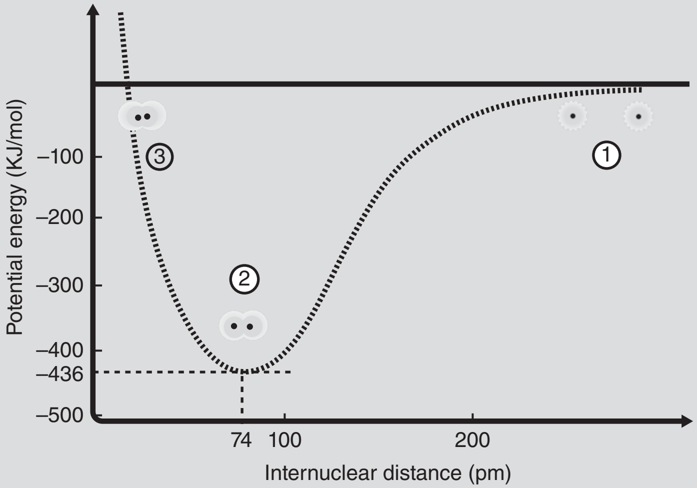

Figure 1.3. Bonding energy versus internuclear separation for hydrogen–hydrogen bond: (1) no bond exists; (2) most stable bonding configuration; (3) further overlap unfavorable due to internuclear repulsion.

1.2 A SIMPLE FUEL CELL

In a fuel cell, the hydrogen *combustion* reaction is split into two *electrochemical* half reactions:

$$H_2 \rightleftharpoons 2H^+ + 2e^- \quad (1.2)$$

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O \quad (1.3)$$

By spatially separating these reactions, the electrons transferred from the fuel are forced to flow through an external circuit (thus constituting an electric current) and do useful work before they can complete the reaction.

Spatial separation is accomplished by employing an electrolyte. An electrolyte is a material that allows ions (charged atoms) to flow but not electrons. At a minimum, a fuel cell must possess two electrodes, where the two electrochemical half reactions occur, separated by an electrolyte.

Figure 1.4 shows an example of an extremely simple H_2–O_2 fuel cell. This fuel cell consists of two platinum electrodes dipped into sulfuric acid (an aqueous acid electrolyte). Hydrogen gas, bubbled across the left electrode, is split into protons (H^+) and electrons following Equation 1.2. The protons can flow through the electrolyte (the sulfuric acid is like a "sea" of H^+), but the electrons cannot. Instead, the electrons flow from left to right through a piece of wire that connects the two platinum electrodes. Note that the resulting current, as it is traditionally defined, is in the opposite direction. When the electrons reach the right electrode, they recombine with protons and bubbling oxygen gas to produce water following Equation 1.3. If a load (e.g., a light bulb) is introduced along the path of the electrons, the flowing electrons will provide power to the load, causing the light bulb to glow. Our fuel cell

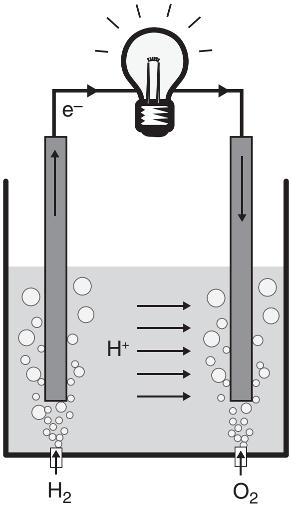

Figure 1.4. A simple fuel cell.

is producing electricity! The first fuel cell, invented by William Grove in 1839, probably looked a lot like the one discussed here.

ENERGY, POWER, ENERGY DENSITY, AND POWER DENSITY

To understand how a fuel cell compares to a combustion engine or a battery, several quantitative metrics, or *figures of merit*, are required. The most common figures of merit used to compare energy conversion systems are *power density* and *energy density*.

To understand energy density and power density, you first need to understand the difference between energy and power:

Energy is defined as the ability to do work. Energy is usually measured in joules (J) or calories (cal).

Power is defined as the rate at which energy is expended or produced. In other words, power represents the *intensity* of energy use or production. Power is a rate. The typical unit of power, the watt (W), represents the amount of energy used or produced per second (1 W = 1 J/s).

From the above discussion, it is obvious that energy is the product of power and time:

$$\text{Energy} = \text{power} \times \text{time} \tag{1.4}$$

Although the International System of Units (SI) uses the joule as the unit of energy, you will often see energy expressed in terms of watt-hours (Wh) or kilowatt-hours (kWh). These units arise when the units of power (e.g., watts) are multiplied by a length of time (e.g., hours) as in Equation 1.4. Obviously, watt-hours can be converted to joules or vice versa using simple arithmetic:

$$1\,\text{Wh} \times 3600\,\text{s/h} \times 1\,(\text{J/s})/\text{W} = 3600\,\text{J} \tag{1.5}$$

Refer to Appendix A for a list of some of the more common unit conversions for energy and power. For portable fuel cells and other mobile energy conversion devices, power density and energy density are more important than power and energy because they provide information about *how big* a system needs to be to deliver a certain amount of energy or power. Power density refers to the amount of power that can be produced by a device per unit mass or volume. Energy density refers to the total energy capacity available to the system per unit mass or volume.

Volumetric power density is the amount of power that can be supplied by a device per unit volume. Typical units are W/cm^3 or kW/m^3.

Gravimetric power density (or specific power) is the amount of power that can be supplied by a device per unit mass. Typical units are W/g or kW/kg.

Volumetric energy density is the amount of energy that is available to a device per unit volume. Typical units are Wh/cm^3 or kWh/m^3.

Gravimetric energy density (or specific energy) is the amount of energy that is available to a device per unit mass. Typical units are Wh/g or kWh/kg.

1.3 FUEL CELL ADVANTAGES

Because fuel cells are "factories" that produce electricity as long as they are supplied with fuel, they share some characteristics in common with combustion engines. Because fuel

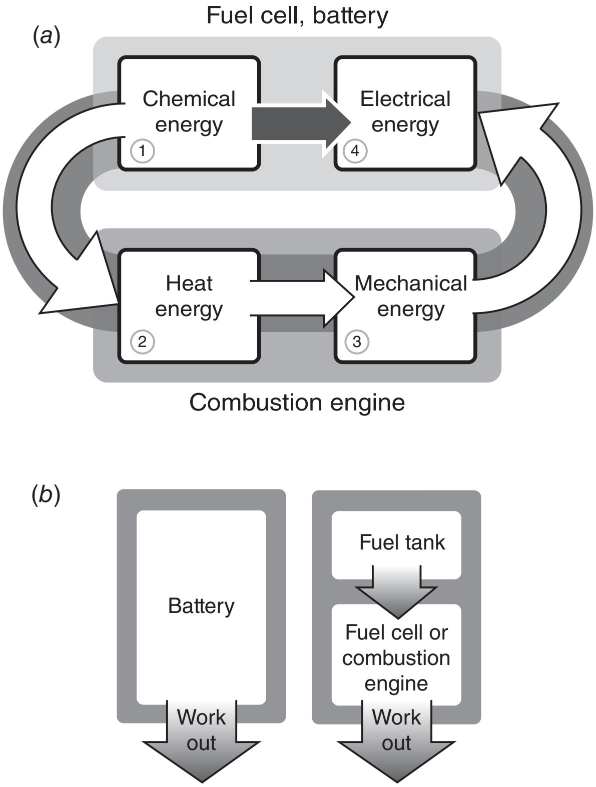

Figure 1.5. Schematic comparison of fuel cells, batteries, and combustion engines. (*a*) Fuel cells and batteries produce electricity directly from chemical energy. In contrast, combustion engines first convert chemical energy into heat, then mechanical energy, and finally electricity (alternatively, the mechanical energy can sometimes be used directly). (*b*) In batteries, power and capacity are typically intertwined—the battery is both the energy storage and the energy conversion device. In contrast, fuel cells and combustion engines allow independent scaling between power (determined by the fuel cell or engine size) and capacity (determined by the fuel tank size).

cells are electrochemical energy conversion devices that rely on electrochemistry to work their magic, they share some characteristics in common with primary batteries. In fact, fuel cells combine many of the advantages of both engines and batteries.

Since fuel cells produce electricity directly from chemical energy, they are often far more efficient than combustion engines. Fuel cells can be all solid state and mechanically ideal, meaning no moving parts. This yields the potential for highly reliable and long-lasting systems. A lack of moving parts also means that fuel cells are silent. Also, undesirable products such as NO_x, SO_x, and particulate emissions are virtually zero.

Unlike batteries, fuel cells allow easy independent scaling between power (determined by the fuel cell size) and capacity (determined by the fuel reservoir size). In batteries, power and capacity are often convoluted. Batteries scale poorly at large sizes, whereas fuel cells scale well from the 1-W range (cell phone) to the megawatt range (power plant). Fuel cells offer potentially higher energy densities than batteries and can be quickly recharged by refueling, whereas batteries must be thrown away or plugged in for a time-consuming recharge. Figure 1.5 schematically illustrates the similarities and differences between fuel cells, batteries, and combustion engines.

FUEL CELLS VERSUS SOLAR CELLS VERSUS BATTERIES

Fuel cells, solar cells, and batteries all produce electrical power by converting either chemical energy (fuel cells, batteries) or solar energy (solar cells) to a direct-current (DC) flow of electricity. The key features of these three devices are compared in Figure 1.6 using the analogy of buckets filled with water. In all three devices, the electrical output power is determined by the operating voltage (the height of water in the bucket) and current density (the amount of water flowing out the spigot at the bottom of the bucket).

Fuel cells and solar cells can be viewed as "open" thermodynamic systems that operate at a thermodynamic steady state. In other words, the operating voltage of a fuel cell (or a solar cell) remains constant in time so long as it is continually supplied with fuel (or photons) from an external source. In Figure 1.6, this is shown by the fact that the water in the fuel cell and solar cell buckets is continually replenished from the top at the same rate that it flows out the spigot in the bottom, resulting in a constant water level (constant operating voltage).

In contrast, most batteries are closed thermodynamic systems that contain a finite and exhaustible internal supply of chemical energy (reactants). As these reactants deplete, the voltage of the battery generally decreases over time. In Figure 1.6, this is shown by the fact that the water in the battery bucket is not replenished, resulting in a decreasing water level (decreasing operating voltage) with time as the battery is discharged. It is important to point out that battery voltage does not decrease linearly during discharge. During discharge, batteries pass through voltage plateaus where the voltage remains more or less constant for a significant part of the discharge cycle. This phenomenon is captured by the strange shape of the battery "bucket."

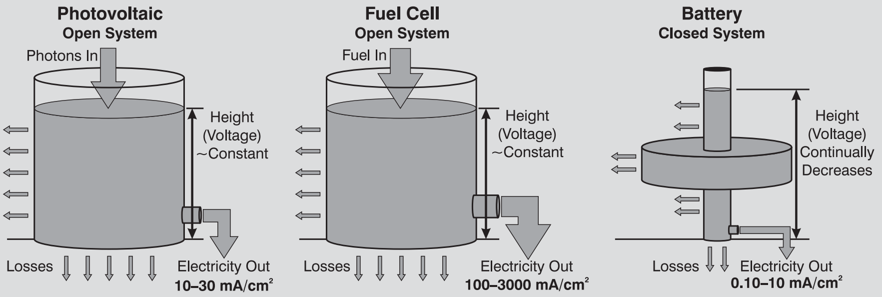

Figure 1.6. Fuel cells versus solar cells versus batteries. This schematic diagram provides another way to look at the similarities and differences between three common energy conversion technologies that provide electricity as an output.

In addition to the thermodynamic operating differences between fuel cells, solar cells, and batteries, Figure 1.6 also shows that fuel cells typically operate at much higher current densities than solar cells or batteries. This characteristic places great importance on using low-resistance materials in fuel cells to minimize ohmic ("*IR*") losses. We will learn more about minimizing ohmic losses in Chapter 4 of this textbook!

1.4 FUEL CELL DISADVANTAGES

While fuel cells present intriguing advantages, they also possess some serious disadvantages. Cost represents a major barrier to fuel cell implementation. Because of prohibitive costs, fuel cell technology is currently only economically competitive in a few highly specialized applications (e.g., onboard the Space Shuttle orbiter). Power density is another significant limitation. Power density expresses how much power a fuel cell can produce per unit volume (volumetric power density) or per unit mass (gravimetric power density). Although fuel cell power densities have improved dramatically over the past decades, further improvements are required if fuel cells are to compete in portable and automotive applications. Combustion engines and batteries generally outperform fuel cells on a volumetric power density basis; on a gravimetric power density basis, the race is much closer. (See Figure 1.7.)

Fuel availability and storage pose further problems. Fuel cells work best on hydrogen gas, a fuel that is not widely available, has a low volumetric energy density, and is difficult

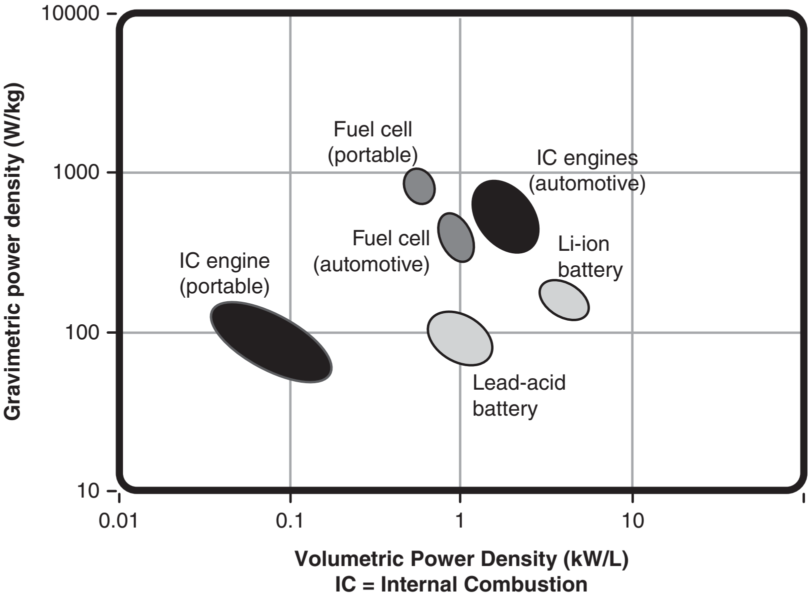

Figure 1.7. Power density comparison of selected technologies (approximate ranges).

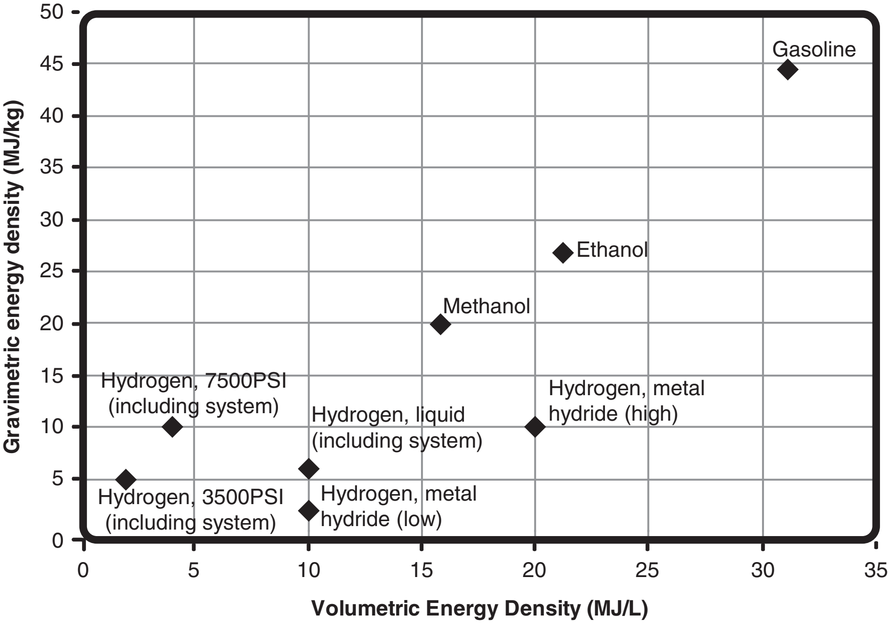

Figure 1.8. Energy density comparison of selected fuels (lower heating value).

to store. (See Figure 1.8.) Alternative fuels (e.g., gasoline, methanol, formic acid) are difficult to use directly and usually require reforming. These problems can reduce fuel cell performance and increase the requirements for ancillary equipment. Thus, although gasoline looks like an attractive fuel from an energy density standpoint, it is not well suited to fuel cell use.

Additional fuel cell limitations include operational temperature compatibility concerns, susceptibility to environmental poisons, and durability under start–stop cycling. These significant disadvantages will not be easy to overcome. Fuel cell adoption will be severely limited unless technological solutions can be developed to hurdle these barriers.

1.5 FUEL CELL TYPES

There are five major types of fuel cells, differentiated from one another by their electrolyte:

1. Phosphoric acid fuel cell (PAFC)
2. Polymer electrolyte membrane fuel cell (PEMFC)
3. Alkaline fuel cell (AFC)
4. Molten carbonate fuel cell (MCFC)
5. Solid-oxide fuel cell (SOFC)

TABLE 1.1. Description of Major Fuel Cell Types

	PEMFC	PAFC	AFC	MCFC	SOFC
Electrolyte	Polymer membrane	Liquid H_3PO_4 (immobilized)	Liquid KOH (immobilized)	Molten carbonate	Ceramic
Charge carrier	H^+	H^+	OH^-	CO_3^{2-}	O^{2-}
Operating temperature	80°C	200°C	60–220°C	650°C	600–1000°C
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskites (ceramic)
Cell components	Carbon based	Carbon based	Carbon based	Stainless based	Ceramic based
Fuel compatibility	H_2, methanol	H_2	H_2	H_2, CH_4	H_2, CH_4, CO

While all five fuel cell types are based on the same underlying electrochemical principles, they all operate at different temperature regimens, incorporate different materials, and often differ in their fuel tolerance and performance characteristics, as shown in Table 1.1. Most of the examples in this book focus on PEMFCs or SOFCs. We will briefly contrast these two fuel cell types.

- PEMFCs employ a thin *polymer* membrane as an electrolyte (the membrane looks and feels a lot like plastic wrap). The most common PEMFC electrolyte is a membrane material called Nafion$^{\text{TM}}$. Protons are the ionic charge carrier in a PEMFC membrane. As we have already seen, the electrochemical half reactions in an H_2–O_2 PEMFC are

$$\begin{aligned} H_2 &\rightarrow 2H^+ + 2e^- \\ \tfrac{1}{2}O_2 + 2H^+ + 2e^- &\rightarrow H_2O \end{aligned} \tag{1.6}$$

  PEMFCs are attractive for many applications because they operate at low temperature and have high power density.

- SOFCs employ a thin *ceramic* membrane as an electrolyte. Oxygen ions (O^{2-}) are the ionic charge carrier in an SOFC membrane. The most common SOFC electrolyte is an oxide material called yttria-stabilized zirconia (YSZ). In an H_2–O_2 SOFC, the electrochemical half reactions are

$$\begin{aligned} H_2 + O^{2-} &\rightarrow H_2O + 2e^- \\ \tfrac{1}{2}O_2 + 2e^- &\rightarrow O^{2-} \end{aligned} \tag{1.7}$$

  To function properly, SOFCs must operate at high temperatures (>600°C). They are attractive for stationary applications because they are highly efficient and fuel flexible.

Note how changing the mobile charge carrier dramatically changes the fuel cell reaction chemistry. In a PEMFC, the half reactions are mediated by the movement of protons (H^+), and water is produced at the cathode. In a SOFC, the half reactions are mediated by the motion of oxygen ions (O^{2-}), and water is produced at the anode. Note in Table 1.1 how other fuel cell types use OH^- or CO_3^{2-} as ionic charge carriers. These fuel cell types will also exhibit different reaction chemistries, leading to unique advantages and disadvantages.

Part I of this book introduces the basic underlying principles that govern all fuel cell devices. What you learn here will be equally applicable to a PEMFC, a SOFC, or any other fuel cell for that matter. Part II discusses the materials and technology-specific aspects of the five major fuel cell types, while also delving into fuel cell system issues such as stacking, fuel processing, control, and environmental impact.

1.6 BASIC FUEL CELL OPERATION

The current (electricity) produced by a fuel cell scales with the size of the reaction area where the reactants, the electrode, and the electrolyte meet. In other words, doubling a fuel cell's area approximately doubles the amount of current produced.

Although this trend seems intuitive, the explanation comes from a deeper understanding of the fundamental principles involved in the electrochemical generation of electricity. As we have discussed, fuel cells produce electricity by converting a primary energy source (a fuel) into a flow of electrons. This conversion necessarily involves an energy transfer step, where the energy from the fuel source is passed along to the electrons constituting

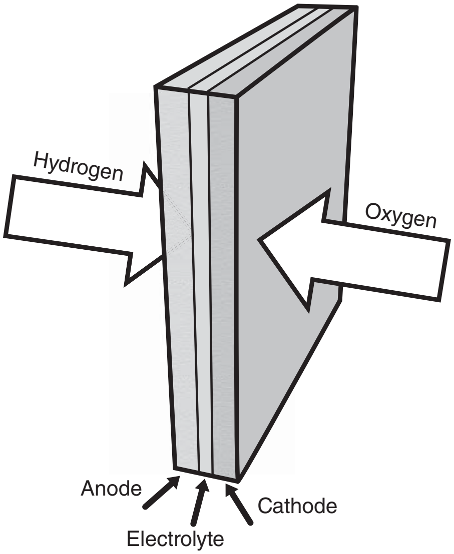

Figure 1.9. Simplified planar anode–electrolyte–cathode structure of a fuel cell.

the electric current. This transfer has a finite rate and must occur at an interface or reaction surface. Thus, the amount of electricity produced scales with the amount of reaction surface area or interfacial area available for the energy transfer. Larger surface areas translate into larger currents.

To provide large reaction surfaces that maximize surface-to-volume ratios, fuel cells are usually made into thin, planar structures, as shown in Figure 1.9. The electrodes are highly porous to further increase the reaction surface area and ensure good gas access. One side of the planar structure is provisioned with fuel (the anode electrode), while the other side is provisioned with oxidant (the cathode electrode). A thin electrolyte layer spatially separates the fuel and oxidant electrodes and ensures that the two individual half reactions occur in isolation from one another. Compare this planar fuel cell structure with the simple fuel cell discussed earlier in Figure 1.4. While the two devices look quite different, noticeable similarities exist between them.

ANODE = OXIDATION; CATHODE = REDUCTION

To understand any discussion of electrochemistry, it is essential to have a clear concept of the terms *oxidation, reduction, anode*, and *cathode*.

Oxidation and Reduction

- Oxidation refers to a process in which electrons are *removed* from a species. Electrons are *liberated* by the reaction.
- Reduction refers to a process in which electrons are *added* to a species. Electrons are *consumed* by the reaction.

For example, consider the electrochemical half reactions that occur in an H_2–O_2 fuel cell:

$$H_2 \rightarrow 2H^+ + 2e^- \tag{1.8}$$

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{1.9}$$

The hydrogen reaction is an oxidation reaction because electrons are being liberated by the reaction. The oxygen reaction is a reduction reaction because electrons are being consumed by the reaction. The preceding electrochemical half reactions are therefore known as the *hydrogen oxidation reaction* (*HOR*) and the *oxygen reduction reaction* (*ORR*).

Anode and Cathode

- Anode refers to an electrode where oxidation is taking place. More generally, the anode of any two-port device, such as a diode or resistor, is the electrode where electrons *flow out*.
- Cathode refers to an electrode where reduction is taking place. More generally, the cathode is the electrode where electrons *flow in*.

For a hydrogen–oxygen fuel cell:

- The anode is the electrode where the HOR takes place.
- The cathode is the electrode where the ORR takes place.

Note that the above definitions have nothing to do with which electrode is the positive electrode or which electrode is the negative electrode. *Be careful!* Anodes and cathodes can be either positive or negative. For a *galvanic cell* (a cell that *produces* electricity, like a fuel cell), the anode is the negative electrode and the cathode is the positive electrode. For an *electrolytic cell* (a cell that *consumes* electricity), the anode is the positive electrode and the cathode is the negative electrode.

Just remember anode = oxidation, cathode = reduction, and you will always be right!

Figure 1.10 shows a detailed, *cross-sectional view* of a planar fuel cell. Using this figure as a map, we will now embark on a brief journey through the major steps involved in producing electricity in a fuel cell. Sequentially, as numbered on the drawing, these steps are as follows:

1. Reactant delivery (transport) into the fuel cell
2. Electrochemical reaction
3. Ionic conduction through the electrolyte and electronic conduction through the external circuit
4. Product removal from the fuel cell

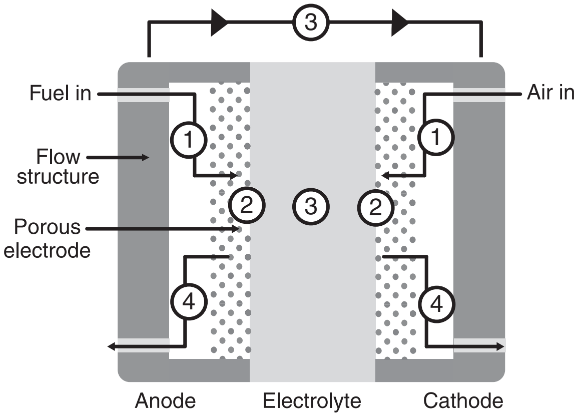

Figure 1.10. Cross section of fuel cell illustrating major steps in electrochemical generation of electricity: (1) reactant transport, (2) electrochemical reaction, (3) ionic and electronic conduction, (4) product removal.

By the end of this book, you will understand the physics behind each of these steps in detail. For now, however, we'll just take a quick tour.

Step 1: Reactant Transport. For a fuel cell to produce electricity, it must be continually supplied with fuel and oxidant. This seemingly simple task can be quite complicated. When a fuel cell is operated at high current, its demand for reactants is voracious. If the reactants are not supplied to the fuel cell quickly enough, the device will "starve." Efficient delivery of reactants is most effectively accomplished by using *flow field plates* in combination with porous electrode structures. Flow field plates contain many fine channels or grooves to carry the gas flow and distribute it over the surface of the fuel cell. The shape, size, and pattern of flow channels can significantly affect the performance of the fuel cell. Understanding how flow structures and porous electrode geometries influence fuel cell performance is an exercise in mass transport, diffusion, and fluid mechanics. The materials aspects of flow structures and electrodes are equally important. Components are held to stringent materials property constraints that include very specific electrical, thermal, mechanical, and corrosion requirements. The details of reactant transport and flow field design are covered in Chapter 5.

Step 2: Electrochemical Reaction. Once the reactants are delivered to the electrodes, they must undergo electrochemical reaction. The current generated by the fuel cell is directly related to how fast the electrochemical reactions proceed. Fast electrochemical reactions result in a high current output from the fuel cell. Sluggish reactions result in low current output. Obviously, high current output is desirable. Therefore, catalysts are generally used to increase the speed and efficiency of the electrochemical reactions. Fuel cell performance critically depends on choosing the right catalyst and carefully designing the reaction zones. Often, the kinetics of the electrochemical reactions represent the single greatest limitation to fuel cell performance. The details of electrochemical reaction kinetics are covered in Chapter 3.

Step 3: Ionic (and Electronic) Conduction. The electrochemical reactions occurring in step 2 either produce or consume ions and electrons. Ions produced at one electrode must be consumed at the other electrode. The same holds for electrons. To maintain charge balance, these ions and electrons must therefore be transported from the locations where they are generated to the locations where they are consumed. For electrons this transport process is rather easy. As long as an electrically conductive path exists, the electrons will be able to flow from one electrode to the other. In the simple fuel cell in Figure 1.4, for example, a wire provides a path for electrons between the two electrodes. For ions, however, transport tends to be more difficult. Fundamentally, this is because ions are much larger and more massive than electrons. An electrolyte must be used to provide a pathway for the ions to flow. In many electrolytes, ions move via "hopping" mechanisms. Compared to electron transport, this process is far less efficient. Therefore, ionic transport can represent a significant resistance loss, reducing fuel cell performance. To combat this effect, the electrolytes in technological fuel cells are made as thin as possible to minimize the distance over which ionic conduction must occur. The details of ionic conduction are covered in Chapter 4.

Step 4: Product Removal. In addition to electricity, all fuel cell reactions will generate at least one product species. The H_2–O_2 fuel cell generates water. Hydrocarbon fuel cells will typically generate water and carbon dioxide (CO_2). If these products are not removed from the fuel cell, they will build up over time and eventually "strangle" the fuel cell, preventing new fuel and oxidant from being able to react. Fortunately, the act of delivering reactants *into* the fuel cell often assists the removal of product species *out of* the fuel cell. The same mass transport, diffusion, and fluid mechanics issues that are important in optimizing reactant delivery (step 1) can be applied to product removal. Often, product removal is not a significant problem and is frequently overlooked. However, for certain fuel cells (e.g., PEMFC) "flooding" byproduct water can be a major issue. Because product removal depends on the same physical principles and processes that govern reactant transport, it is also treated in Chapter 5.

1.7 FUEL CELL PERFORMANCE

The performance of a fuel cell device can be summarized with a graph of its current–voltage characteristics. This graph, called a current–voltage (*i*–*V*) curve, shows the voltage output of the fuel cell for a given current output. An example of a typical *i*–*V* curve for a PEMFC is shown in Figure 1.11. Note that the current has been normalized by the area of the fuel cell, giving a current density (in amperes per square centimeter). Because a larger fuel cell

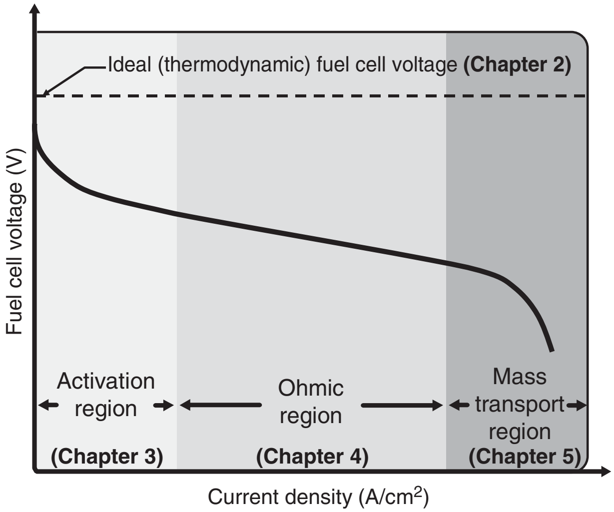

Figure 1.11. Schematic of fuel cell *i*–*V* curve. In contrast to the ideal, thermodynamically predicted voltage of a fuel cell (dashed line), the real voltage of a fuel cell is lower (solid line) due to unavoidable losses. Three major losses influence the shape of this *i*–*V* curve; they will be described in Chapters 3–5.

can produce more electricity than a smaller fuel cell, *i–V* curves are normalized by fuel cell area to make results comparable.

An ideal fuel cell would supply any amount of current (as long as it is supplied with sufficient fuel), while maintaining a constant voltage determined by thermodynamics. In practice, however, the actual voltage output of a real fuel cell is less than the ideal thermodynamically predicted voltage. Furthermore, the more current that is drawn from a real fuel cell, the lower the voltage output of the cell, limiting the total power that can be delivered. The power (P) delivered by a fuel cell is given by the product of current and voltage:

$$P = iV \tag{1.10}$$

A fuel cell *power density curve*, which gives the power density delivered by a fuel cell as a function of the current density, can be constructed from the information in a fuel cell *i–V* curve. The power density curve is produced by multiplying the voltage at each point on the *i–V* curve by the corresponding current density. An example of combined fuel cell *i–V* and power density curves is provided in Figure 1.12. Fuel cell voltage is given on the left-hand y-axis, while power density is given on the right-hand y-axis.

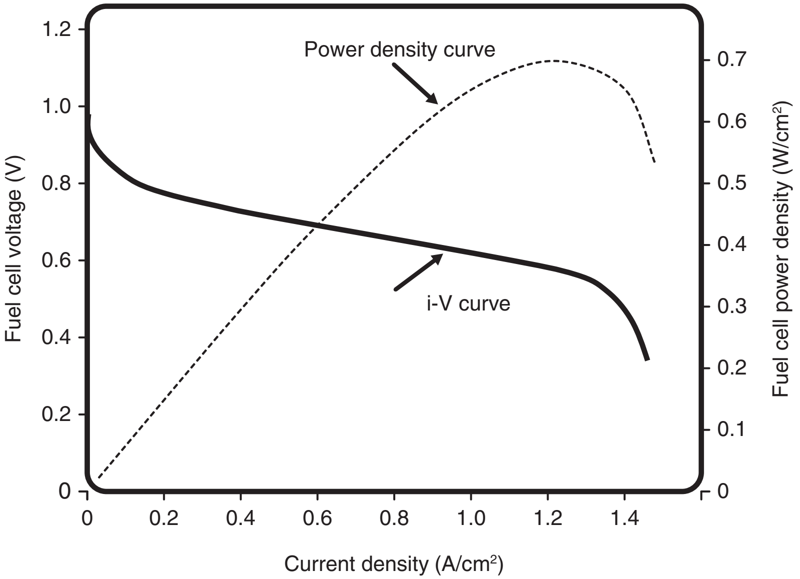

Figure 1.12. Combined fuel cell *i–V* and power density curves. The power density curve is constructed from the *i–V* curve by multiplying the voltage at each point on the *i–V* curve by the corresponding current density. Fuel cell power density increases with increasing current density, reaches a maximum, and then falls at still higher current densities. Fuel cells are designed to operate at or below the power density maximum. At current densities below the power density maximum, voltage efficiency improves but power density falls. At current densities above the power density maximum, both voltage efficiency and power density fall.

The current supplied by a fuel cell is directly proportional to the amount of fuel consumed (each mole of fuel provides n moles of electrons). Therefore, as fuel cell voltage decreases, the electric power produced *per unit of fuel* also decreases. In this way, fuel cell voltage can be seen as a measure of fuel cell efficiency. In other words, you can think of the fuel cell voltage axis as an "efficiency axis." Maintaining high fuel cell voltage, even under high current loads, is therefore critical to the successful implementation of the technology.

Unfortunately, it is hard to maintain a high fuel cell voltage under the current load. The voltage output of a real fuel cell is less than the thermodynamically predicted voltage output due to irreversible losses. The more current that is drawn from the cell, the greater these losses. There are three major types of fuel cell losses, which give a fuel cell i–V curve its characteristic shape. Each of these losses is associated with one of the basic fuel cell steps discussed in the previous section:

1. Activation losses (losses due to electrochemical reaction)
2. Ohmic losses (losses due to ionic and electronic conduction)
3. Concentration losses (losses due to mass transport)

The real voltage output for a fuel cell can thus be written by starting with the thermodynamically predicted voltage output of the fuel cell and then subtracting the voltage drops due to the various losses:

$$V = E_{\text{thermo}} - \eta_{\text{act}} - \eta_{\text{ohmic}} - \eta_{\text{conc}} \tag{1.11}$$

where

V = real output voltage of fuel cell

E_{thermo} = thermodynamically predicted fuel cell voltage output; this will be the subject of Chapter 2

η_{act} = activation losses due to reaction kinetics; this will be the subject of Chapter 3

η_{ohmic} = ohmic losses from ionic and electronic conduction; this will be the subject of Chapter 4

η_{conc} = concentration losses due to mass transport; this will be the subject of Chapter 5

The three major losses each contribute to the characteristic shape of the fuel cell i–V curve. As shown in Figure 1.11, the activation losses mostly affect the initial part of the curve, the ohmic losses are most apparent in the middle section of the curve, and the concentration losses are most significant in the tail of the i–V curve.

Equation 1.11 sets the stage for the next six chapters of this book. As you progress through these chapters, you will be armed with the tools needed to understand the major losses in fuel cell devices. Using Equation 1.11 as a starting point, you will eventually be able to characterize and model the performance of real fuel cell devices.

1.8 CHARACTERIZATION AND MODELING

Characterization and modeling are pivotal to the development and advancement of fuel cell technology. By assimilating theory and experiment, careful characterization and modeling studies allow us to better understand how fuel cells work, often paving the way toward further improvements.

Because these subjects provide great insight, each has been given a chapter in this book. Fuel cell modeling is covered in Chapter 6. Fuel cell characterization techniques are covered in Chapter 7. These chapters will yield a practical understanding of how fuel cells are tested, how to diagnose their performance, and how to develop simple mathematical models to predict fuel cell behavior.

1.9 FUEL CELL TECHNOLOGY

The first half of this book is devoted to understanding the fundamental principles underlying fuel cells. However, no treatment of fuel cells is complete without a discussion of the practical aspects of fuel cell technology. This is the aim of the second part of this book. A series of chapters will introduce the major considerations for fuel cell stacking and system design, as well as specific technological aspects related to each of the five major fuel cell types. You will gain insight into the state of the art in fuel cell materials and fuel cell design as well as a historical perspective on the development of practical fuel cell technology.

1.10 FUEL CELLS AND THE ENVIRONMENT

If employed correctly, fuel cells are environmentally friendly. In fact, this may be their single greatest advantage over other energy conversion technologies. However, the environmental impact of fuel cells depends strongly on the context of their use. If they are not deployed wisely, fuel cells may be no better than our current fossil energy conversion system! In the final chapter of this book, you will learn to evaluate possible fuel cell deployment scenarios. Using a technique known as process chain analysis, you will be able to identify promising fuel cell futures.

One such future, referred to as the “hydrogen economy,” is illustrated in Figure 1.13. In this figure, H_2 fuel cells are coupled with electrolyzers and renewable energy conversion technologies (such as wind and solar power) to provide a completely closed-loop, pollution-free energy economy. In such a system, fuel cells would play a prominent role, with a primary benefit being their dispatchability. When the sun is shining or the wind is blowing, the electricity produced from solar and wind energy can be used to power cities directly, while producing extra hydrogen on the side via electrolysis. Anytime the wind stops or night falls, however, the fuel cells can be dispatched to provide on-demand power by converting the stored hydrogen into electricity. In such a system, fossil fuels are completely eliminated.

Currently, it is unclear when, if ever, the hydrogen economy will become a reality. Various studies have examined the technical and economic hurdles that stand in the way of the hydrogen economy. While many of these studies differ on the details, it is clear that the transition to a hydrogen economy would be difficult, costly, and lengthy. Do not count on it happening anytime soon. In the meantime, we have a fossil fuel world. Even in a fossil fuel world, however, it is important to realize that fuel cells can provide increased

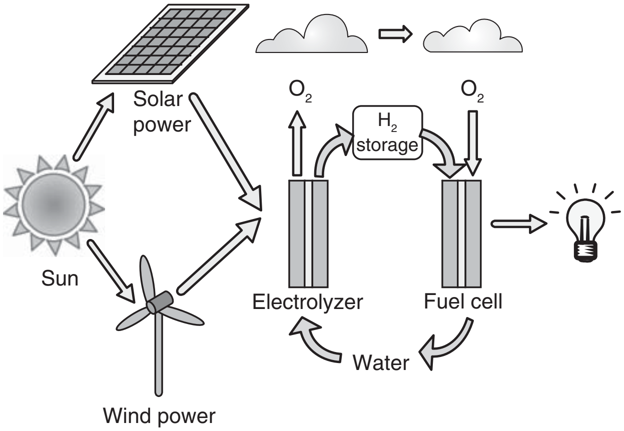

Figure 1.13. Schematic of hydrogen economy dream.

efficiency, greater scaling flexibility, reduced emissions, and other advantages compared to conventional power technologies. Fuel cells have found, and will continue to find, niche applications. These applications should continue to drive forward progress for decades to come, with or without the hydrogen economy dream.

1.11 CHAPTER SUMMARY

The purpose of this chapter was to set the stage for learning about fuel cells and to give a broad overview of fuel cell technology.

- A fuel cell is a direct electrochemical energy conversion device. It directly converts energy from one form (chemical energy) into another form (electrical energy) through electrochemistry.
- Unlike a battery, a fuel cell cannot be depleted. It is a “factory” that will continue to generate electricity as long as fuel is supplied.
- At a minimum, a fuel cell must contain two electrodes (an anode and a cathode) separated by an electrolyte.
- Fuel cell power is determined by fuel cell size. Fuel cell capacity (energy capacity) is determined by the fuel reservoir size.
- There are five major fuel cell types, differentiated by their electrolyte.
- Electrochemical systems must contain two coupled half reactions: an oxidation reaction and a reduction reaction. An oxidation reaction liberates electrons. A reduction reaction consumes electrons.
- Oxidation occurs at the anode electrode. Reduction occurs at the cathode electrode.
- The four major steps in the generation of electricity in a fuel cell are (1) reactant transport, (2) electrochemical reaction, (3) ionic (and electronic) conduction, and (4) product removal.

- Fuel cell performance can be assessed by current–voltage curves. Current–voltage curves show the voltage output of a fuel cell for a given current load.
- Ideal fuel cell performance is dictated by thermodynamics.
- Real fuel cell performance is always less than ideal fuel cell performance due to losses. The major types of loss are (1) activation loss, (2) ohmic loss, and (3) concentration loss.

CHAPTER EXERCISES

Review Questions

1.1 List three major advantages and three major disadvantages of fuel cells compared to other power conversion devices. Discuss at least two potential applications where the unique attributes of fuel cells make them attractive.

1.2 In general, do you think a portable fuel cell would be better for an application requiring low power but high capacity (long run time) or high power but small capacity (short run time)? Explain.

1.3 Label the following reactions as oxidation or reduction reactions:

(a) $Cu \rightarrow Cu^{2+} + 2e^-$
(b) $2H^+ + 2e^- \rightarrow H_2$
(c) $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$
(d) $CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-$
(e) $O^{2-} + CO \rightarrow CO_2 + 2e^-$
(f) $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$
(g) $H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$

1.4 From the reactions listed in problem 1.3 (or their reverse), write three complete and balanced pairs of electrochemical half reactions. For each pair of reactions, identify which reaction is the cathode reaction and which reaction is the anode reaction.

1.5 Consider the relative volumetric and gravimetric energy densities of 7500 psi compressed H_2 versus liquid H_2. Which would probably be the better candidate for a fuel cell bus? *Hint:* Bus efficiency strongly depends on gross vehicle weight.

1.6 Describe the four major steps in the generation of electricity within a fuel cell. Describe the potential reasons for loss in fuel cell performance for each step.

Calculations

1.7 Energy is released when hydrogen and oxygen react to produce water. This energy comes from the fact that the final hydrogen–oxygen bonds represent a lower total energy state than the original hydrogen–hydrogen and oxygen–oxygen bonds. Calculate how much energy (in kilojoules per mole of product) is released by the reaction

$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O \qquad (1.12)$$

at constant pressure and given the following standard bond enthalpies. Standard bond enthalpies denote the enthalpy *absorbed* when bonds are *broken* at standard temperature and pressure (298 K and 1 atm).

Standard Bond Enthalpies
H–H = 432 kJ/mol O = O = 494 kJ/mol H–O = 460 kJ/mol

1.8 Consider a fuel cell vehicle. The vehicle draws 30 kW of power at 60 mph and is 40% efficient at rated power. (It converts 40% of the energy stored in the hydrogen fuel to electric power.) You are asked to size the fuel cell system so that a driver can go at least 300 miles at 60 mph before refueling. Specify the minimum volume and mass requirements for the fuel cell system (fuel cell + fuel tank) given the following information:

- Fuel cell power density: 1 kW/L, 500 W/kg
- Fuel tank energy density (compressed hydrogen): 4 MJ/L, 8 MJ/kg

1.9 For the fuel cell *i–V* curve shown in Figure 1.11, sketch the approximate corresponding current density–power density curve.

1.10 A cylindrical metal hydride container measures 9 cm in diameter, is 42.5 cm in length, and has a mass of 7 kg. The metal hydride container has a capacity of 900 normal liters of hydrogen. Using the lower heating value of hydrogen (244 kJ/mol), determine the energy density.

(a) 3.6 kWh/L
(b) 3.6 MWh/ L
(c) 1.0 Wh/ L
(d) 1.0 kWh/ L

CHAPTER 2

FUEL CELL THERMODYNAMICS

Thermodynamics is the study of energetics; the study of the transformation of energy from one form to another. Since fuel cells are energy conversion devices, fuel cell thermodynamics is key to understanding the conversion of chemical energy into electrical energy. For fuel cells, thermodynamics can predict whether a candidate fuel cell reaction is energetically spontaneous. Furthermore, thermodynamics places upper bound limits on the maximum electrical potential that can be generated in a reaction. Thus, thermodynamics yields the theoretical boundaries of what is possible with a fuel cell; it gives the "ideal case."

Any real fuel cell will perform at or below its thermodynamic limit. Understanding real fuel cell performance requires a knowledge of kinetics in addition to thermodynamics. This chapter covers the thermodynamics of fuel cells. Subsequent chapters will cover the major kinetic limitations on fuel cell performance, defining practical performance.

2.1 THERMODYNAMICS REVIEW

This section presents a brief review of the main tenets of thermodynamics. These basic theories are typically taught in an introductory thermodynamics course. Next, these concepts are extended to include parameters that are needed to understand fuel cell behavior. Readers are advised to consult a thermodynamics book if additional review is required.

2.1.1 What Is Thermodynamics?

It is no secret that no one really understands the meaning of popular thermodynamic quantities. For example, Nobel Prize–winning physicist Richard Feynman wrote in his *Lectures* *on Physics*: "It is important to realize that in modern physics today, we have no knowledge of what energy is" [1]. We have even less intuition about terms such as *enthalpy* and *free energy*. The fundamental assumptions of thermodynamics are based on human experience. Assumptions are the best we can do. We *assume* that energy can never be created or destroyed (first law of thermodynamics) only because it fits with everything experienced in human existence. Nevertheless, no one knows why it should be so.

If we accept a few of these fundamental assumptions, however, we can develop a self-consistent mathematical description that tells us how important quantities such as energy, temperature, pressure, and volume are related. This is really all that thermodynamics is; it is an elaborate bookkeeping scheme that allows us to track the properties of systems in a self-consistent manner, starting from a few basic assumptions or "laws."

2.1.2 Internal Energy

A fuel cell converts energy stored within a fuel into other, more useful forms of energy. The total intrinsic energy of a fuel (or of any substance) is quantified by a property known as internal energy (*U*). Internal energy is the energy associated with microscopic movement and interaction between particles on the atomic and molecular scales. It is separated in scale from the macroscopic ordered energy associated with moving objects. For example, a tank of H_2 gas sitting on a table has no apparent energy. However, the H_2 gas actually has significant internal energy (see Figure 2.1); on the microscopic scale it is a whirlwind of molecules traveling hundreds of meters per second. Internal energy is also associated with the *chemical bonds* between the hydrogen atoms. A fuel cell can convert *only a portion* of the internal energy associated with a tank of H_2 gas into electrical energy. The limits on

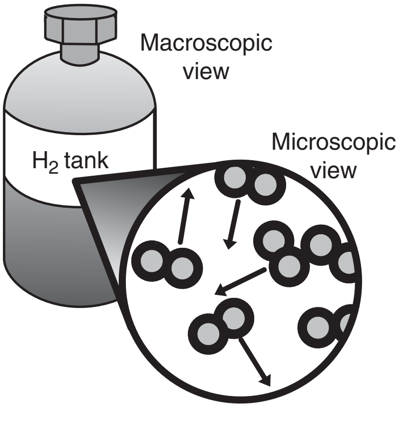

Figure 2.1. Although this tank of H_2 gas has no apparent macroscopic energy, it has significant internal energy. Internal energy is associated with microscopic movement (kinetic energy) and interactions between particles (chemical/potential energy) on the atomic scale.

how much of the internal energy of the H_2 gas can be transformed into electrical energy are established by the first and second laws of thermodynamics.

2.1.3 First Law

The first law of thermodynamics is also known as the law of conservation of energy—energy can never be created or destroyed—as expressed by the equation

$$d(\text{Energy})_{\text{univ}} = d(\text{Energy})_{\text{system}} + d(\text{Energy})_{\text{surroundings}} = 0 \tag{2.1}$$

Viewed another way, this equation states that any change in the energy of a system must be fully accounted for by energy transfer to the surroundings:

$$d(\text{Energy})_{\text{system}} = -d(\text{Energy})_{\text{surroundings}} \tag{2.2}$$

There are two ways that energy can be transferred between a closed system and its surroundings: via *heat* (Q) or *work* (W). This allows us to write the first law in its more familiar form:

$$dU = dQ - dW \tag{2.3}$$

This expression states that the change in the internal energy of a closed system (dU) must be equal to the heat transferred to the system (dQ) minus the work done by the system (dW). To develop this expression from Equation 2.2, we have substituted dU for $d(\text{Energy})_{\text{system}}$; if we choose the proper reference frame, then all energy changes in a system are manifested as internal energy changes. Note that we define positive work as work done *by* the system on the surroundings.

For now, we will assume that only mechanical work is done by a system. Mechanical work is accomplished by the expansion of a system against a pressure. It is given by

$$(dW)_{\text{mech}} = p\,dV \tag{2.4}$$

where p is the pressure and dV is the volume change. Later, when we talk about fuel cell thermodynamics, we will consider the electrical work done by a system. For now, however, we ignore electrical work. Considering only mechanical work, we can rewrite the expression for the internal energy change of a system as

$$dU = dQ - p\,dV \tag{2.5}$$

2.1.4 Second Law

The second law of thermodynamics introduces the concept of *entropy*. Entropy is determined by the number of possible microstates accessible to a system, or, in other words, the number of possible ways of configuring a system. For this reason, entropy can be thought of as a measure of "disorder," since an increasing entropy indicates an increasing number of ways of configuring a system. For an isolated system (the simplest case)

$$S = k \log \Omega \tag{2.6}$$

where S is the total entropy of the system, k is Boltzmann's constant, and Ω denotes the number of possible microstates accessible to the system.

WORK AND HEAT

In contrast to internal energy, work and heat are not properties of matter or of any particular system (e.g., substance or body). They represent *energy in transit*, in other words, energy that is transferred between substances or bodies.

In the case of work, this transfer of energy is accomplished by the application of a force over a distance. Heat, on the other hand, is transferred between substances whenever they have different thermal energies, as manifested by differences in their temperature.

Due to repercussions of the second law (which we will discuss momentarily), work is often called the most "noble" form of energy; it is the universal donor. Energy, in the form of work, can be converted into any other form of energy at 100% theoretical efficiency. In contrast, heat is the most "ignoble" form of energy; it is the universal acceptor. Any form of energy can eventually be 100% dissipated to the environment as heat, but heat can never be 100% converted back to more noble forms of energy such as work.

The nobility of work versus heat illustrates one of the central differences between fuel cells and combustion engines. A combustion engine burns fuel to produce heat and then converts some of this heat into work. Because it first converts energy into heat, the combustion engine destroys some of the work potential of the fuel. This unfortunate destruction of work potential is called the "thermal bottleneck." Because a fuel cell bypasses the heat step, it avoids the thermal bottleneck.

Microstates can best be understood with an example. Consider the "perfect" system of 100 identical atoms shown in Figure 2.2*a*. There is only one possible microstate, or *configuration*, for this system. This is because the 100 atoms are exactly identical and indistinguishable from one another. If we were to "switch" the first and the second atoms, the system would look exactly the same. The entropy of this perfect 100-atom crystal is therefore zero ($S = k \log 1 = 0$). Now consider Figure 2.2*b*, where three atoms have been removed from their original locations and placed on the surface of the crystal. Any three atoms could have been removed from the crystal, and depending on which atoms were removed, the final configuration of the system would be different. In this case, there are many microstates available to the system. (Figure 2.2*b* represents just one of them.) We can calculate the number of microstates available to the system by evaluating the number of possible ways there are to take N atoms from a total of Z atoms:

$$\Omega \equiv \frac{Z(Z-1)(Z-2)\cdots(Z-N+1)}{N!} = \frac{Z!}{(Z-N)!(N!)} \tag{2.7}$$

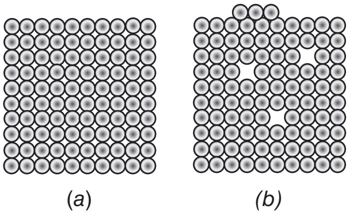

Figure 2.2. (*a*) The entropy of this 100-atom perfect crystal is zero because there is only one possible way to arrange the atoms to produce this configuration. (*b*) When three atoms are removed from the crystal and placed on the surface, the entropy increases. This is because there are many possible ways to configure a system of 100 atoms where 3 have been removed.

In Figure 2.2*b*, there are 100 atoms. The number of ways to take 3 atoms from 100 is

$$\Omega = \frac{100!}{97!3!} == 1.62 \times 10^5 \tag{2.8}$$

This yields $S = 7.19 \times 10^{-23}$ J/K.

Except for extremely simple systems like the one in this example, it is impossible to calculate entropy exactly. Instead, a system's entropy is usually *inferred* based on how heat transfer causes the entropy of the system to change. For a reversible transfer of heat at constant pressure, the entropy of a system will change as

$$dS = \frac{dQ_{\text{rev}}}{T} \tag{2.9}$$

where dS is the entropy change in the system associated with a reversible transfer of heat (dQ_{rev}) at a constant temperature (T). In other words, "dumping" energy, including heat, into a system causes its entropy to increase. Essentially, by providing additional energy to the system, we enable it to access additional microstates, causing its entropy to increase. For an irreversible transfer of heat, the entropy increase will be even larger than that dictated by Equation 2.9. This is a key statement of the second law of thermodynamics.

The most widely known form of the second law acknowledges that the entropy of a system and its surroundings must increase or at least remain zero for any process:

$$dS_{\text{univ}} \geq 0 \tag{2.10}$$

This inequality, when combined with the first law of thermodynamics, allows us to separate thermodynamically "spontaneous" processes from "nonspontaneous" processes.

2.1.5 Thermodynamic Potentials

Based on the first and second laws of thermodynamics, we can write down "rules" to specify how energy can be transferred from one form to another. These rules are called *thermodynamic potentials*. You are already familiar with one thermodynamic potential: the internal energy of a system. We can combine results from the first and the second laws of thermodynamics (Equations 2.3 and 2.9) to arrive at an equation for internal energy that is based on the variation of two independent variables, entropy S and volume V:

$$dU = T\,dS - p\,dV \tag{2.11}$$

Remember, $T\ dS$ represents the reversible heat transfer and $p\ dV$ is the mechanical work. As mentioned above, from this equation we can conclude that U, the internal energy of a system, is a function of entropy and volume:

$$U = U(S, V) \tag{2.12}$$

We can also derive the following useful relations, which show how the *dependent* variables T and p are related to variations in the *independent* variables (S and V):

$$\left(\frac{dU}{dS}\right)_V = T \tag{2.13}$$

$$\left(\frac{dU}{dV}\right)_S = -p \tag{2.14}$$

Unfortunately, S and V are not easily measurable in most experiments. (There is no such thing as an "entropy meter.") Therefore, a new thermodynamic potential is needed equivalent to U but depending on quantities that are more readily measured than S and V. Temperature T and pressure p fall into this category. Happily, there is a simple mathematical way to accomplish this conversion using a *Legendre transform*. A step-by-step transformation of U begins by defining a new thermodynamic potential $G(T,\ p)$ as follows:

$$G = U - \left(\frac{dU}{dS}\right)_V S - \left(\frac{dU}{dV}\right)_S V \tag{2.15}$$

Since we know that $(dU/dS)_V = T$ and $(dU/dV)_S = -p$, we obtain

$$G = U - TS + pV \tag{2.16}$$

This function is called the Gibbs free energy. Let us show that G is indeed a function of the temperature and the pressure. The variation of G (mathematically dG) results in

$$dG = dU - T\,dS - S\,dT + p\,dV + V\,dp \tag{2.17}$$

Since we know that $dU = T\ dS - p\ dV$, we can see that

$$dG = -S\,dT + V\,dp \tag{2.18}$$

So, the Gibbs free energy is nothing more than a thermodynamic description of a system that depends on T and p instead of S and V.

What if we want a potential that depends on S and p? No problem! Remember that U is a function of S and V. To get a thermodynamic potential that is a function of S and p, we need only to transform U with respect to V this time. Analogously to Equation 2.15, we define this new thermodynamic potential H as

$$H = U - \left(\frac{dU}{dV}\right)_S V \tag{2.19}$$

Again, since $(dU/dV)_S = -p$, we obtain

$$H = U + pV \tag{2.20}$$

where H is called enthalpy. Through differentiation, we can show that H is a function of S and p:

$$dH = dU + p\,dV + V\,dp \tag{2.21}$$

Again, $dU = T\,dS - p\,dV$; so

$$dH = T\,dS + V\,dp \tag{2.22}$$

Thus far, we have defined three thermodynamic potentials: $U(S,\ V)$, $H(S,\ p)$, and $G(T,\ p)$. Defining a fourth and final thermodynamic potential that depends on temperature and volume, $F(T,\ V)$, completes the symmetry:

$$F = U - TS \tag{2.23}$$

where F is the Helmholtz free energy. We leave it to the reader to show that

$$dF = -S\,dT - p\,dV \tag{2.24}$$

A summary of these four thermodynamic potentials is provided in Figure 2.3. This mnemonic diagram, originally suggested by Schroeder [2], can help you keep track of the relationships between the thermodynamic potentials. Loosely, the four potentials are defined as follows:

- *Internal Energy* (U). The energy needed to create a system in the absence of changes in temperature or volume.
- *Enthalpy* (H). The energy needed to create a system plus the work needed to make room for it (from zero volume).
- *Helmholtz Free Energy* (F). The energy needed to create a system minus the energy that you can get from the system's environment due to spontaneous heat transfer (at constant temperature).
- *Gibbs Free Energy* (G). The energy needed to create a system and make room for it minus the energy that you can get from the environment due to heat transfer. In other words, G represents the net energy cost for a system created at a constant environmental temperature T from a negligible initial volume after subtracting what the environment automatically supplied.

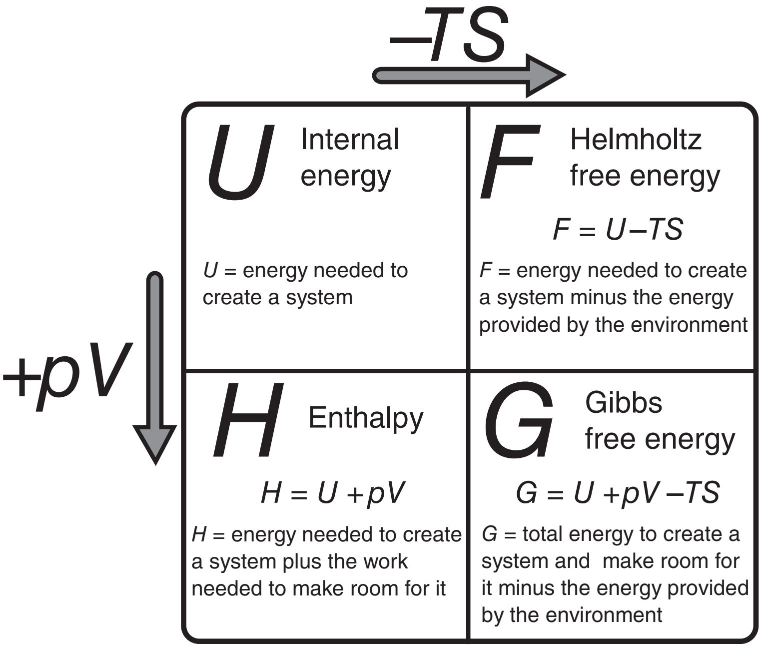

Figure 2.3. Pictorial summary of the four thermodynamic potentials. They relate to one another by offsets of the "energy from the environment" term *TS* and the "expansion work" term *pV*. Use this diagram to help remember the relationships. Copyright © 2000 by Addison Wesley Longman. Reprinted by permission of Pearson Education, Inc. (Figure 5.2, p. 151, from *An Introduction to Thermal Physics* by Daniele V. Schroeder [2]).

2.1.6 Molar Quantities

Typical notation distinguishes between intrinsic and extrinsic variables. Intrinsic quantities such as temperature and pressure do not scale with the system size; extrinsic quantities such as internal energy and entropy do scale with system size. For example, if the size of a box of gas molecules is doubled and the number of molecules in the box doubles, then the internal energy and entropy double, while the temperature and pressure remain constant. It is conventional to denote intrinsic quantities with a lowercase letter (p) and extrinsic quantities with an uppercase letter (U).

Molar quantities such as $\hat{u}$, the internal energy per mole of gas (units of kilojoules per mole), are intrinsic. It is often useful to calculate energy changes due to a reaction on a per-mole basis:

$$\Delta\hat{g}_{\text{rxn}}, \Delta\hat{s}_{\text{rxn}}, \Delta\hat{v}_{\text{rxn}}$$

The Δ symbol denotes a change during a thermodynamic process (such as a reaction), calculated as final state–initial state. Therefore, a negative energy change means energy is released during a process: A negative volume change means the volume decreases during a process. For example, the overall reaction in a H_2–O_2 fuel cell,

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \tag{2.25}$$

has $\Delta\hat{g}_{\text{rxn}} = -237\ \text{kJ/mol}\ H_2$ at room temperature and pressure. For every mole of H_2 gas consumed (or every 1/2 mol of O_2 gas consumed or mole of H_2O produced), the Gibbs free-energy change is –237 kJ. If 5 mol of O_2 gas is reacted, the extrinsic Gibbs free-energy change (ΔG_{rxn}) would be

$$5\ \text{mol}\ O_2 \times \left(\frac{1\ \text{mol}\ H_2}{(1/2)\ \text{mol}\ O_2}\right) \times \left(\frac{-237\ \text{kJ}}{\text{mol}\ H_2}\right) = -2370\ \text{kJ} \tag{2.26}$$

Of course the *intrinsic* (per-mole) Gibbs free energy of this reaction is still $\Delta\hat{g}_{\text{rxn}} = -237\,\text{kJ/mol}\ H_2$.

2.1.7 Standard State

Because most thermodynamic quantities depend on temperature and pressure, it is convenient to reference everything to a standard set of conditions. This set of conditions is called the standard state. There are two common types of standard conditions:

The thermodynamic standard state describes the standard set of conditions under which reference values of thermodynamic quantities are typically given. Standard-state conditions specify that all reactant and product species are present in their pure, most stable forms at unit activity. (Activity is discussed in Section 2.4.3.) Standard-state conditions are designated by a superscript zero. For example, $\Delta\hat{h}^0$ represents an enthalpy change under standard-state thermodynamic conditions. Importantly, there is no "standard temperature" in the definition of thermodynamic standard-state conditions. However, since most tables list standard-state thermodynamic quantities at 25°C (298.15 K), this temperature is usually implied. At temperatures other than 25°C, it is sometimes necessary to apply temperature corrections to $\Delta\hat{h}^0$ and $\Delta\hat{s}^0$ values obtained at 25°C, although it is frequently approximated that these values change only slightly with temperature, and hence this issue can be ignored. For temperatures far from 25°C, however, this approximation should not be made. You will have the opportunity to explore this issue in Example 2.1 and problem 2.9.

It should be noted that $\Delta\hat{g}^0$ changes much more strongly with temperature (as shown in Equation 2.39) and therefore $\Delta\hat{g}^0$ values should always be adjusted by temperature using at least the linear dependence predicted by Equation 2.39. The use of this linear temperature dependence is shown in Example 2.2.

Standard temperature and pressure, or STP, is the standard condition most typically associated with gas law calculations. STP conditions are taken as room temperature (298.15 K) and atmospheric pressure. (Standard-state pressure is actually defined as 1 bar = 100 kPa. Atmospheric pressure is taken as 1 atm = 101.325 kPa. These slight differences are usually ignored.)