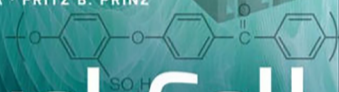


RYAN O'HAYRE · SUK-WON CHA

WHITNEY COLELLA · FRITZ B. PRINZ



# Fuel Cell

# Fundamentals

Third Edition

(fixed gas)

Air or  
(fixed gas)

WILEY

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# FUEL CELL FUNDAMENTALS

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Third Edition

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*To the parents who nurtured us.*

*To the teachers who inspired us.*

# CONTENTS

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<b>PREFACE</b>	<b>xi</b>
<b>ACKNOWLEDGMENTS</b>	<b>xiii</b>
<b>NOMENCLATURE</b>	<b>xvii</b>
<b>I FUEL CELL PRINCIPLES</b>	
<b>1 Introduction</b>	<b>3</b>
1.1 What Is a Fuel Cell? / 3	
1.2 A Simple Fuel Cell / 6	
1.3 Fuel Cell Advantages / 8	
1.4 Fuel Cell Disadvantages / 11	
1.5 Fuel Cell Types / 12	
1.6 Basic Fuel Cell Operation / 14	
1.7 Fuel Cell Performance / 18	
1.8 Characterization and Modeling / 20	
1.9 Fuel Cell Technology / 21	
1.10 Fuel Cells and the Environment / 21	
1.11 Chapter Summary / 22	
Chapter Exercises / 23	

<b>2</b>	<b>Fuel Cell Thermodynamics</b>	<b>25</b>
2.1	Thermodynamics Review / 25	
2.2	Heat Potential of a Fuel: Enthalpy of Reaction / 34	
2.3	Work Potential of a Fuel: Gibbs Free Energy / 37	
2.4	Predicting Reversible Voltage of a Fuel Cell under Non-Standard-State Conditions / 47	
2.5	Fuel Cell Efficiency / 60	
2.6	Thermal and Mass Balances in Fuel Cells / 65	
2.7	Thermodynamics of Reversible Fuel Cells / 67	
2.8	Chapter Summary / 71 Chapter Exercises / 72	
<b>3</b>	<b>Fuel Cell Reaction Kinetics</b>	<b>77</b>
3.1	Introduction to Electrode Kinetics / 77	
3.2	Why Charge Transfer Reactions Have an Activation Energy / 82	
3.3	Activation Energy Determines Reaction Rate / 84	
3.4	Calculating Net Rate of a Reaction / 85	
3.5	Rate of Reaction at Equilibrium: Exchange Current Density / 86	
3.6	Potential of a Reaction at Equilibrium: Galvani Potential / 87	
3.7	Potential and Rate: Butler–Volmer Equation / 89	
3.8	Exchange Currents and Electrocatalysis: How to Improve Kinetic Performance / 94	
3.9	Simplified Activation Kinetics: Tafel Equation / 97	
3.10	Different Fuel Cell Reactions Produce Different Kinetics / 100	
3.11	Catalyst–Electrode Design / 103	
3.12	Quantum Mechanics: Framework for Understanding Catalysis in Fuel Cells / 104	
3.13	The Sabatier Principle for Catalyst Selection / 107	
3.14	Connecting the Butler–Volmer and Nernst Equations (Optional) / 108	
3.15	Chapter Summary / 112 Chapter Exercises / 113	
<b>4</b>	<b>Fuel Cell Charge Transport</b>	<b>117</b>
4.1	Charges Move in Response to Forces / 117	
4.2	Charge Transport Results in a Voltage Loss / 121	
4.3	Characteristics of Fuel Cell Charge Transport Resistance / 124	
4.4	Physical Meaning of Conductivity / 128	
4.5	Review of Fuel Cell Electrolyte Classes / 132	

4.6	More on Diffusivity and Conductivity (Optional) / 153	
4.7	Why Electrical Driving Forces Dominate Charge Transport (Optional) / 160	
4.8	Quantum Mechanics–Based Simulation of Ion Conduction in Oxide Electrolytes (Optional) / 161	
4.9	Chapter Summary / 163	
	Chapter Exercises / 164	
<b>5</b>	<b>Fuel Cell Mass Transport</b>	<b>167</b>
5.1	Transport in Electrode versus Flow Structure / 168	
5.2	Transport in Electrode: Diffusive Transport / 170	
5.3	Transport in Flow Structures: Convective Transport / 183	
5.4	Chapter Summary / 199	
	Chapter Exercises / 200	
<b>6</b>	<b>Fuel Cell Modeling</b>	<b>203</b>
6.1	Putting It All Together: A Basic Fuel Cell Model / 203	
6.2	A 1D Fuel Cell Model / 206	
6.3	Fuel Cell Models Based on Computational Fluid Dynamics (Optional) / 227	
6.4	Chapter Summary / 230	
	Chapter Exercises / 231	
<b>7</b>	<b>Fuel Cell Characterization</b>	<b>237</b>
7.1	What Do We Want to Characterize? / 238	
7.2	Overview of Characterization Techniques / 239	
7.3	In Situ Electrochemical Characterization Techniques / 240	
7.4	Ex Situ Characterization Techniques / 265	
7.5	Chapter Summary / 268	
	Chapter Exercises / 269	
<b>II FUEL CELL TECHNOLOGY</b>		
<b>8</b>	<b>Overview of Fuel Cell Types</b>	<b>273</b>
8.1	Introduction / 273	
8.2	Phosphoric Acid Fuel Cell / 274	
8.3	Polymer Electrolyte Membrane Fuel Cell / 275	
8.4	Alkaline Fuel Cell / 278	
8.5	Molten Carbonate Fuel Cell / 280	

8.6	Solid-Oxide Fuel Cell / 282	
8.7	Other Fuel Cells / 284	
8.8	Summary Comparison / 298	
8.9	Chapter Summary / 299	
	Chapter Exercises / 301	
<b>9</b>	<b>PEMFC and SOFC Materials</b>	<b>303</b>
9.1	PEMFC Electrolyte Materials / 304	
9.2	PEMFC Electrode/Catalyst Materials / 308	
9.3	SOFC Electrolyte Materials / 317	
9.4	SOFC Electrode/Catalyst Materials / 326	
9.5	Material Stability, Durability, and Lifetime / 336	
9.6	Chapter Summary / 340	
	Chapter Exercises / 342	
<b>10</b>	<b>Overview of Fuel Cell Systems</b>	<b>347</b>
10.1	Fuel Cell Subsystem / 348	
10.2	Thermal Management Subsystem / 353	
10.3	Fuel Delivery/Processing Subsystem / 357	
10.4	Power Electronics Subsystem / 364	
10.5	Case Study of Fuel Cell System Design: Stationary Combined Heat and Power Systems / 369	
10.6	Case Study of Fuel Cell System Design: Sizing a Portable Fuel Cell / 383	
10.7	Chapter Summary / 387	
	Chapter Exercises / 389	
<b>11</b>	<b>Fuel Processing Subsystem Design</b>	<b>393</b>
11.1	Fuel Reforming Overview / 394	
11.2	Water Gas Shift Reactors / 409	
11.3	Carbon Monoxide Clean-Up / 411	
11.4	Reformer and Processor Efficiency Losses / 414	
11.5	Reactor Design for Fuel Reformers and Processors / 416	
11.6	Chapter Summary / 417	
	Chapter Exercises / 419	



<b>12 Thermal Management Subsystem Design</b>	<b>423</b>
12.1 Overview of Pinch Point Analysis Steps / 424	
12.2 Chapter Summary / 440	
Chapter Exercises / 441	
<b>13 Fuel Cell System Design</b>	<b>447</b>
13.1 Fuel Cell Design Via Computational Fluid Dynamics / 447	
13.2 Fuel Cell System Design: A Case Study / 462	
13.3 Chapter Summary / 476	
Chapter Exercises / 477	
<b>14 Environmental Impact of Fuel Cells</b>	<b>481</b>
14.1 Life Cycle Assessment / 481	
14.2 Important Emissions for LCA / 490	
14.3 Emissions Related to Global Warming / 490	
14.4 Emissions Related to Air Pollution / 502	
14.5 Analyzing Entire Scenarios with LCA / 507	
14.6 Chapter Summary / 510	
Chapter Exercises / 511	
<b>A Constants and Conversions</b>	<b>517</b>
<b>B Thermodynamic Data</b>	<b>519</b>
<b>C Standard Electrode Potentials at 25°C</b>	<b>529</b>
<b>D Quantum Mechanics</b>	<b>531</b>
D.1 Atomic Orbitals / 533	
D.2 Postulates of Quantum Mechanics / 534	
D.3 One-Dimensional Electron Gas / 536	
D.4 Analogy to Column Buckling / 537	
D.5 Hydrogen Atom / 538	
D.6 Multielectron Systems / 540	
D.7 Density Functional Theory / 540	

<b>E</b>	<b>Periodic Table of the Elements</b>	<b>543</b>
<b>F</b>	<b>Suggested Further Reading</b>	<b>545</b>
<b>G</b>	<b>Important Equations</b>	<b>547</b>
<b>H</b>	<b>Answers to Selected Chapter Exercises</b>	<b>551</b>
	<b>BIBLIOGRAPHY</b>	<b>555</b>
	<b>INDEX</b>	<b>565</b>

# PREFACE

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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](mailto: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	$\text{cm}^2$
$A_c$	Catalyst area coefficient	Dimensionless
$a$	Activity	Dimensionless
ASR	Area specific resistance	$\Omega \cdot \text{cm}^2$
$C$	Capacitance	F
$C_{\text{dl}}$	Double-layer capacitance	F
$c^*$	Concentration at reaction surface	$\text{mol}/\text{cm}^2$
$c$	Concentration	$\text{mol}/\text{m}^3$
$c$	Constant describing how mass transport affects concentration losses	V
$c_p$	Heat capacity	$\text{J}/\text{mol} \cdot \text{K}$
$D$	Diffusivity	$\text{cm}^2/\text{s}$
$E$	Electric field	$\text{V}/\text{cm}$
$E$	Thermodynamic ideal voltage	V
$E_{\text{thermo}}$	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	$\text{Hz}, \text{s}^{-1}$
$f$	Friction factor	Dimensionless



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

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	cm <sup>2</sup> /V · s
$\bar{u}$	Mean flow velocity	cm/s, m/s
$V$	Voltage	V
$V$	Volume	L, cm <sup>3</sup>
$V$	Reaction rate per unit area	mol/cm <sup>2</sup> · s
$v$	Velocity	cm/s
$v$	Hopping rate	s <sup>-1</sup> , Hz
$v$	Molar flow rate	mol/s, mol/min
$W$	Work	J, J/mol
$X$	Parasitic power load	W
$x$	Mole fraction	Dimensionless
$x_v$	Vacancy fraction	mol vacancies/mol sites
$y_x$	Yield of element $X$	Dimensionless
$Z$	Impedance	$\Omega$
$z$	Height	cm

## Greek Symbols

Symbol	Meaning	Common Units
$\alpha$	Charge transfer coefficient	Dimensionless
$\alpha$	Coefficient for CO <sub>2</sub> equivalent	Dimensionless
$\alpha^*$	Channel aspect ratio	Dimensionless
$\beta$	Coefficient for CO <sub>2</sub> equivalent	Dimensionless
$\gamma$	Activity coefficient	Dimensionless
$\Delta$	Denotes change in quantity	Dimensionless
$\delta$	Diffusion layer thickness	m, cm
$\epsilon$	Efficiency	Dimensionless
$\epsilon_{FP}$	Efficiency of fuel processor	Dimensionless
$\epsilon_{FR}$	Efficiency of fuel reformer	Dimensionless
$\epsilon_H$	Efficiency of heat recovery	Dimensionless
$\epsilon_O$	Efficiency overall	Dimensionless
$\epsilon_R$	Efficiency, electrical	Dimensionless
$\epsilon$	Porosity	Dimensionless
$\dot{\epsilon}$	Strain rate	s <sup>-1</sup>

Symbol	Meaning	Common Units
$\eta$	Overtoltage	V
$\eta_{\text{act}}$	Activation overtoltage	V
$\eta_{\text{conc}}$	Concentration overtoltage	V
$\eta_{\text{ohmic}}$	Ohmic overtoltage	V
$\lambda$	Stoichiometric coefficient	Dimensionless
$\lambda$	Water content	Dimensionless
$\mu$	Viscosity	kg · m/s
$\mu$	Chemical potential	J, J/mol
$\tilde{\mu}$	Electrochemical potential	J, J/mol
$\rho$	Resistivity	$\Omega \text{ cm}$
$\rho$	Density	kg/cm <sup>3</sup> , kg/m <sup>3</sup>
$\sigma$	Conductivity	S/cm, ( $\Omega \cdot \text{cm}$ ) <sup>-1</sup>
$\sigma$	Warburg coefficient	$\Omega/\text{s}^{0.5}$
$\tau$	Mean free time	s
$\tau$	Shear stress	Pa
$\varphi$	Electrical potential	V
$\varphi$	Phase factor	Dimensionless
$\omega$	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
$E, e, \text{elec}$	Electrical (e.g., $P_e, W_{\text{elec}}$ )
$f$	Quantity of formation (e.g., $\Delta H_f$ )
(HHV)	Higher heating value
(LHV)	Lower heating value
$i$	Species $i$
$P$	Product
$P$	Parasitic
$R$	Reactant
rxn	Change in a reaction (e.g., $\Delta H_{\text{rxn}}$ )
SK	Stack
SYS	System

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# PART I

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## FUEL CELL PRINCIPLES

---

# CHAPTER 1

---

## INTRODUCTION

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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:

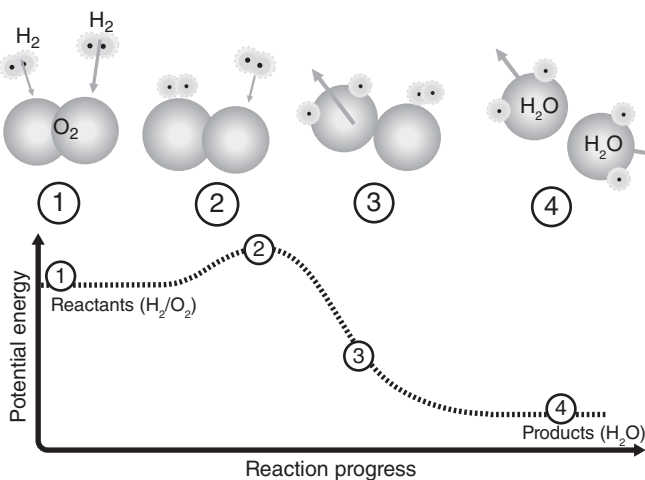




**Figure 1.1.** General concept of a ( $\text{H}_2\text{-O}_2$ ) fuel cell.

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  $\text{H}_2\text{-O}_2$  combustion reaction. (Arrows indicate the relative motion of the molecules participating in the reaction.) Starting with the reactant  $\text{H}_2\text{-O}_2$  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).

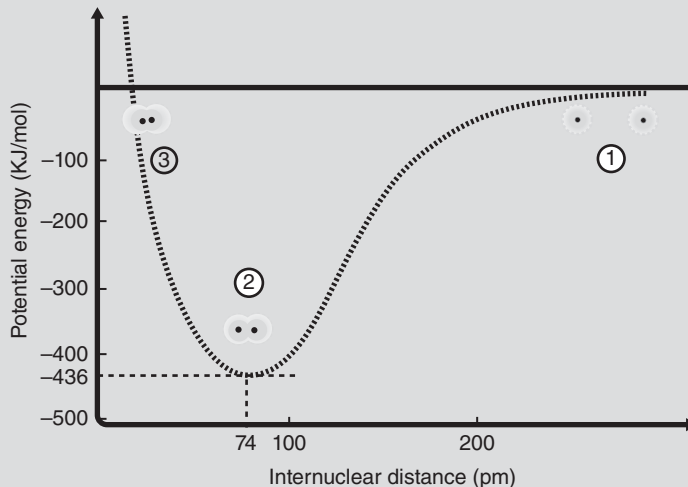
to low-energy product bonds. In fact, this is exactly what a fuel cell does. But the question is, how do we harness electrons that reconfigure in picoseconds at subatomic length scales? The answer is to spatially separate the hydrogen and oxygen reactants so that the electron transfer necessary to complete 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.

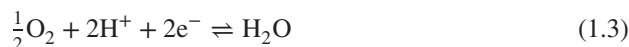
For a reaction to result in a net release of energy, the energy released by the formation of the product bonds must be more than the energy absorbed to break the reactant bonds.



**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

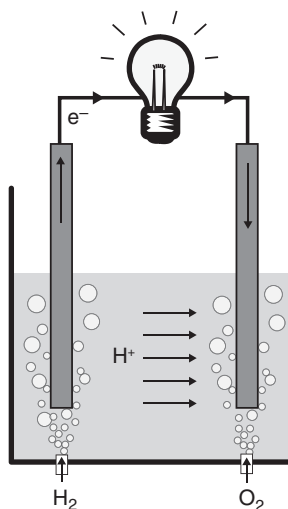
In a fuel cell, the hydrogen *combustion* reaction is split into two *electrochemical* half reactions:



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  $\text{H}_2$ – $\text{O}_2$  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 ( $\text{H}^+$ ) and electrons following Equation 1.2. The protons can flow through the electrolyte (the sulfuric acid is like a “sea” of  $\text{H}^+$ ), 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 ( $1 \text{ W} = 1 \text{ J/s}$ ).

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

$$\text{Energy} = \text{power} \times \text{time} \quad (1.4)$$

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:

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

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  $\text{W}/\text{cm}^3$  or  $\text{kW}/\text{m}^3$ .

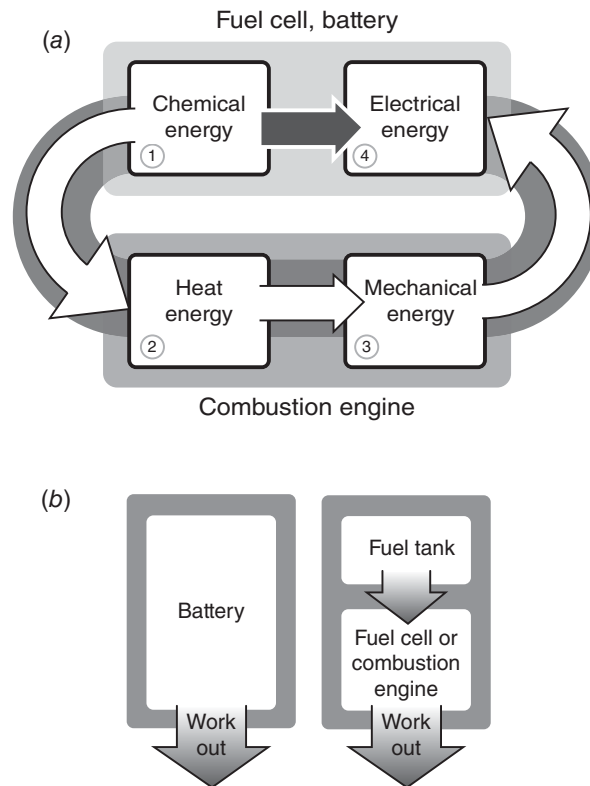
*Gravimetric power density (or specific power)* is the amount of power that can be supplied by a device per unit mass. Typical units are  $\text{W}/\text{g}$  or  $\text{kW}/\text{kg}$ .

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

*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  $\text{NO}_x$ ,  $\text{SO}_x$ , and particulate emissions are virtually zero.

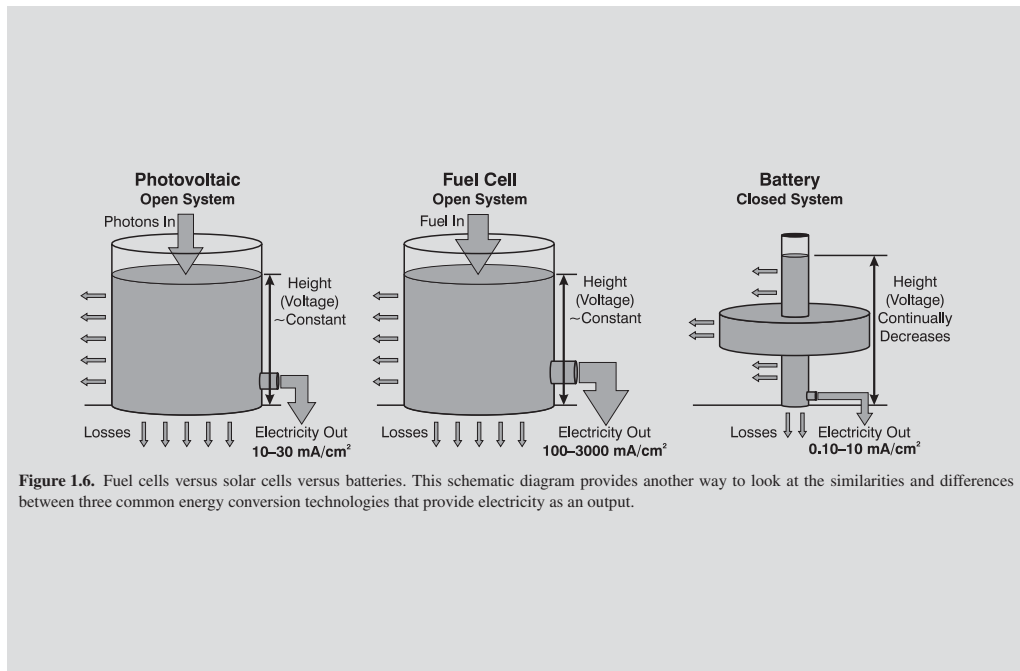
Unlike batteries, fuel cells allow easy independent scaling between power (determined by the fuel cell size) and capacity (determined by the fuel reservoir size). In batteries, power and capacity are often convoluted. Batteries scale poorly at large sizes, whereas fuel cells scale well from the 1-W range (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.”



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

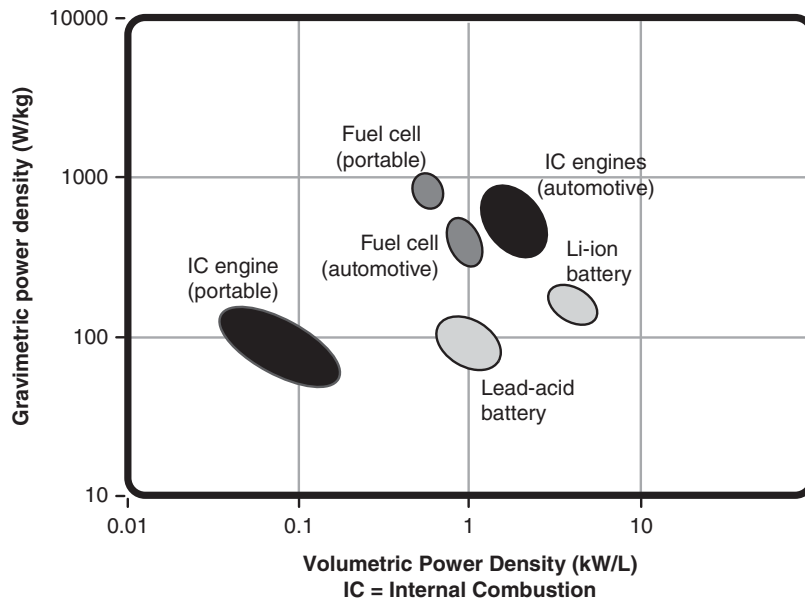
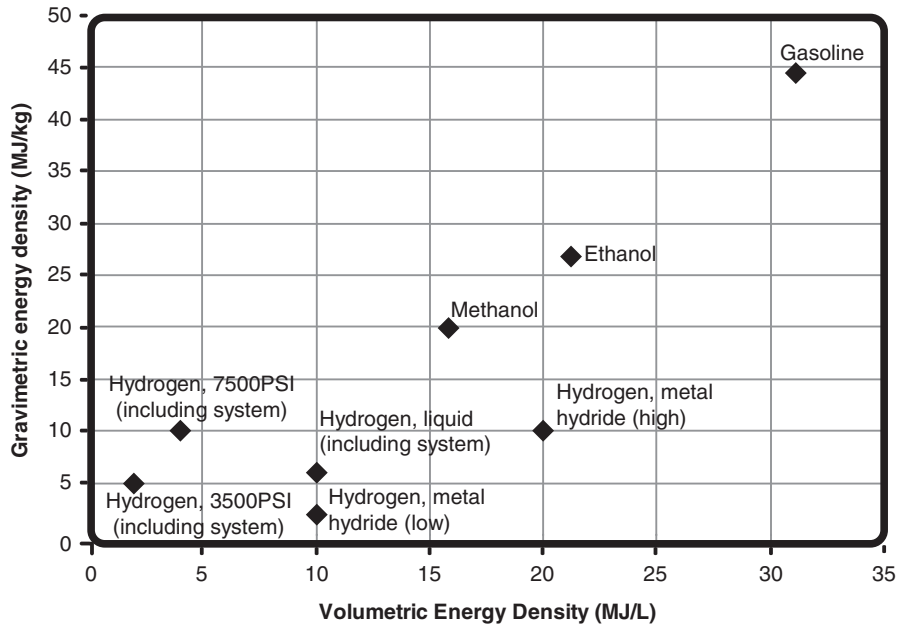


Figure 1.7. Power density comparison of selected technologies (approximate ranges).



**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)