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FIFTH EDITION

LINDEN'S

HANDBOOK OF

BATTERIES



**Mc
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KIRBY W. BEARD

CHAPTER 1

ELECTRICITY, ELECTROCHEMISTRY, AND BATTERIES: PROLOGUE AND EXPOSITION

David Linden, Thomas B. Reddy, Kirby W. Beard

1.0 OVERVIEW

To best describe any field of human endeavor is to reveal the collective wisdom behind the creation and continued viability of the enterprise. The field of electrochemical cells and battery systems has at its core the ability to store chemical energy and then provide electrical energy derived from chemical processes. The battery industry is based on unique electrochemical energy transformations where the electrons, which are normally obscured by chemical reactions, are now separated from the reactants, collected by a current-carrying circuit and delivered, as a unit of commerce, to electronic equipment or an energy conversion device. Specifically, special types of oxidation-reduction (redox) reactions, or in some cases, charge separation processes, both involving electron transfer, are present, whereby the electrons are diverted through an external electrical circuit to do useful work. The force and volume of electron transfer from the high-potential to the low-potential electrode are proportional to the type and magnitude of the redox reactions. Ion flux and/or accumulation provide the other essential mechanism to achieve a practical working electrochemical energy source.

1.1 HANDBOOK CONTENT AND ORGANIZATION

The first several editions of *Linden's Handbook of Batteries* were an assembly of chapters targeted to summarize the large and growing body of work on various electrochemical systems developed up through the mid-1980s. Many new systems had been identified in preceding decades, and some were making inroads into commercial markets. David Linden's initial editions brought organization and clarity to a diversity of technologies. With the addition of Thomas Reddy to the editorial staff, sections on more modern systems (e.g., lithium primary cells) were expanded and the first series of battery application chapters were introduced.

This new 5th edition preserves the basics of the prior compendium while streamlining the content to allow coverage of the many innovations that have proliferated over the past 10 years. The Handbook is based on a process flow concept. The first two technical chapters are new additions that highlight battery raw materials (Chap. 2) and manufactured battery components (Chap. 3). Chapters 4 to 8 revisit the electroanalytical techniques, described in the prior edition, necessary for understanding the building blocks of batteries. Chapters 9 to 22 are updated chapter versions, also from the prior edition, that provide specific discussion of both new and traditional electrochemical systems. Battery applications, covering the evolving marketplace, are updated and

supplemented with new content in Chaps. 23 to 29. The Handbook concludes with three new chapters intended to provide an added perspective on the battery industry as a whole:

Chapter 30: Manufacturing (a summary of current battery industry production concepts)

Chapter 31: Charging (a general review of charging strategies and related electronics)

Chapter 32: Ancillary and supporting services (a collection of discussions from an array of sources that contribute to the viability of the industry as a whole)

Figure 1.1 provides a schematic flow diagram of the 5th edition's organization. The organization of these topics/chapters will, ideally, provide two main benefits for this new edition. First, by reading through the entire text in order, one can gain a good overview of what makes the battery industry a unique and compelling field of study. But second, a reader who is interested in just a single or a few topics will be able to easily locate and quickly focus on the chapter(s) of interest.

The Handbook does not, however, provide a detailed, comprehensive treatment of the various specific electrochemical cells. Entire textbooks have been and can be written on each of these separate chapters. This Handbook is simply intended to provide a survey of the battery field and background knowledge for pursuing further investigation of any specific technology, market application, or strategic action plan. This introductory chapter provides an overview of the “battery basics.” Further details for these various items are reviewed in Parts 1 to 4, as noted in Fig. 1.1.

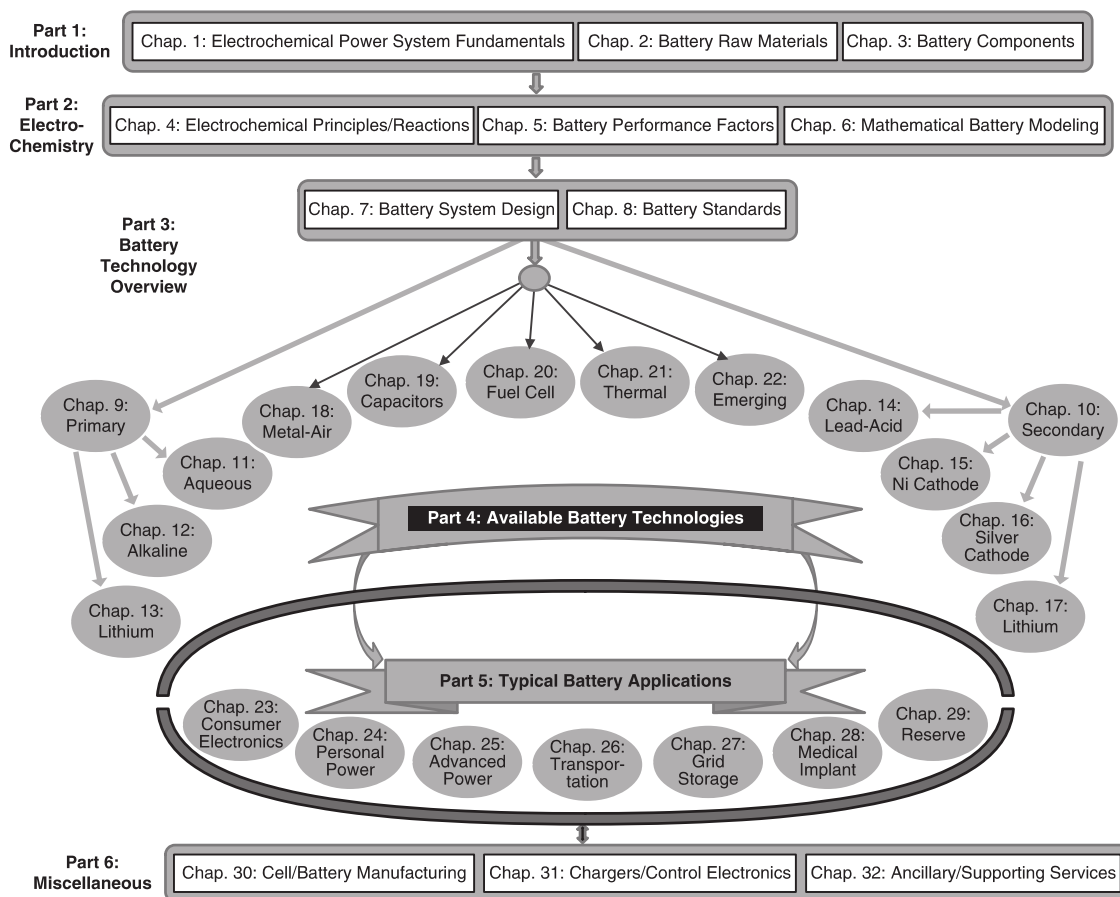


FIGURE 1.1 Handbook content and organization.

1.2 THE AGE OF ELECTROCHEMISTRY

The invention of the electrochemical cell did not come easy. First, electricity needed to be better understood. In the 18th century, various electrical phenomena were known: lightning, Leyden jar static electricity (a type of capacitor), and Galvani's "animal electricity" discovery. Benjamin Franklin (Fig. 1.2) was the most prominent proponent for setting the record straight. He deduced that lightning was electricity and coined the term "battery," based on the resemblance of aligned, connected glass plates (or Leyden jars) to an artillery battery.



FIGURE 1.2 Franklin's burial site, Christ Church, Philadelphia, PA. (Image courtesy of Kirby W. Beard.)

However, it was Alessandro Volta (see Fig. 1.3) who actually built and documented the first functioning battery. Volta surmised that Galvani misunderstood the cause for movement in a frog's leg created by contact with a metal probe. Volta realized that the chemical reaction of the metal probe in the saline environment of the animal tissue was actually a corrosion reaction (now known as galvanic corrosion) that created the electrical stimulus. By interleaving metal plates between layers of cloth soaked in brine solution, the voltaic pile was invented.

Equally important to the invention of the battery was the ability to document the findings. Without a communication network (letters to The Royal Society, London), the scientific musings and experimentations of these early electrochemistry pioneers might have been lost for another century. But, it still took another 50 to 100 years before many practical batteries with useful applications succeeded. Communication through battery textbooks/e-books, web pages, conferences, and sponsored research reports are critical to continued advancements in the field.

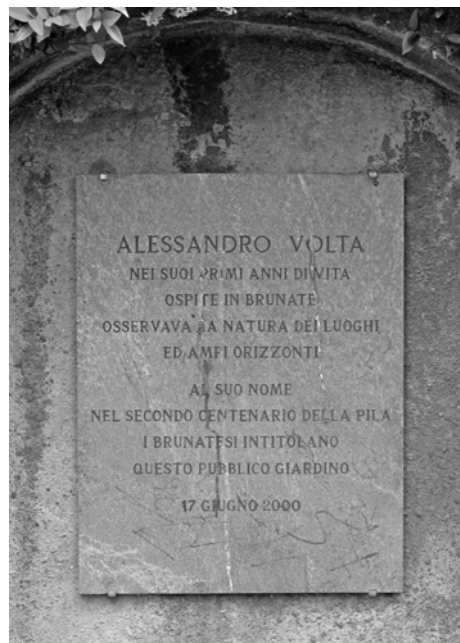


FIGURE 1.3 Volta Memorial Plaque, Como, Italy. (Image courtesy of Kirby W. Beard.)

1.3 BATTERY FUNCTIONING

Batteries convert the chemical energy contained in materials directly into electric energy by means of electrochemical oxidation-reduction (redox) reactions between two or more “ingredients.” Primary cells have full capacity, as built, but in rechargeable systems, the battery must be recharged by a reversal of the process. The transfer of electrons from one material to another through an electric circuit differs from nonelectrochemical redox reaction, such as rusting or burning, where the transfer of electrons occurs directly between the reactants, producing thermal energy only and no electrical power. As the battery electrochemically converts chemical energy into electricity, it is not subjected, as are combustion or heat engines, to the limitations of the Carnot cycle dictated by the second law of thermodynamics.

Batteries, therefore, represent a revolutionary invention, capable of having higher energy conversion efficiencies than prior engines of the industrial revolution (i.e., steam, internal combustion, gas turbines, etc.). It is especially noteworthy to state, as noted in the Preface, that elimination of combustion and heat engines is key to solving society needs for energy supply. While environmental concerns are an important consideration, it is the thermodynamic inefficiency of the combustion or oxidation process that is the real culprit. A fuel cell can convert hydrocarbons to electrical energy with nearly an order of magnitude less wasted energy than a gasoline-powered engine. Energy efficiency (or waste heat) should be the prime metric to use in any energy study.

1.4 BATTERY TERMINOLOGY

While the term “battery” is often used interchangeably with “cell,” the basic electrochemical unit is the “cell,” and a battery consists of one or more connected cells. Cells may be connected in series or parallel, or both, depending on the desired output voltage and capacity. A *cell* consists of an assembly of electrodes, separators, electrolyte, container, and terminals. A *battery* consists of cells and any control circuitry and other ancillary components (e.g., fuses, diodes), case, terminals, etc. Popular usage considers the “battery” to be the product that is sold or provided to the “user.” While the term “cell” may often be used for the single electrochemical unit and “battery” for the finished product, the chapters of this book may use the terms differently depending on the preferences of the chapter writers. Performance characteristics will also vary between single cells and battery packs that must be noted in comparing data.

1.5 BATTERY COMPONENTS

The cell consists of three major components:

1. *The anode or negative electrode:* the reducing or fuel electrode, which gives up electrons to the external circuit and is oxidized during the electrochemical reaction.
2. *The cathode or positive electrode:* the oxidizing electrode, which accepts electrons from the external circuit and is reduced during the electrochemical reaction.
3. *The electrolyte:* the ionic conductor, which provides the medium for transfer of charged species (ions) inside the cell between electrodes.

The electrolyte is typically a liquid, such as water or other solvents, with dissolved salts, acids, or alkalis to impart ionic conductivity. Some batteries use ionically conductive solids or gel-type polymers. The most advantageous combinations of anode and cathode materials are those that will be lightest and give a high cell voltage and capacity. Such combinations may not always be practical, however, due to reactivity with other cell components, kinetic limitations, processing issues, high cost, and other deficiencies.

Anodes are selected for efficiency as a reducing agent, coulombic output (Ah/g), conductivity (mS/cm), stability, ease of fabrication, and cost. Hydrogen is an exceptional anode material but requires containment vessels or absorption materials (see Chap. 15). Metals are a major category of anode materials. Zinc and lithium have been

dominant in primary cells (Chaps. 11–13) because of favorable properties. Lithium, the lightest metal, with a high value of electrochemical equivalence, is a very attractive anode but requires electrolytes and cell designs to accommodate its high reducing potential. Lithium ion anodes have been developed that use lithiated carbons to temper the reactivity of lithium metal (see Chap. 17). The cathode must be an efficient oxidizing agent, stable in contact with the electrolyte, and should have sufficient working voltage. Oxygen is a good cathode material that can be extracted from air for use in zinc/air or similar batteries (Chap. 18). However, most of the common cathode materials are metallic oxides (see Chap. 3A). Other cathode materials, such as the halogens and the oxyhalides, and sulfur and its oxides, are also used for special battery systems.

The electrolyte must have good ionic conductivity but not be electronically conductive, as this would cause internal short-circuiting. Other important characteristics are electrode compatibility, tolerance to temperature variations, safety, and low cost. Traditional electrolytes are aqueous solutions, but thermal and lithium anode batteries use nonaqueous electrolytes due to reactivity of water with the anodes. Anode and cathode electrodes are electronically isolated in the cell to prevent internal short-circuiting. The electrodes are immersed in electrolyte with a permeable, ionically conductive separator material typically used to mechanically separate the electrodes. Various alternative designs do exist and are discussed in individual chapters. Examples include certain liquids that serve as both cathode and electrolyte and, hence, allow direct contact of the active materials.

The cell designs include many variations:

1. Cell shape—cylindrical, button, flat, and prismatic
2. Electrode configurations—series or parallel arrays, bipolar plates, etc.
3. Component modifications tailored to fit cell design or applications
4. Electrically conductive grid structures or additives that reduce internal resistance

The cells are sealed in a variety of ways to prevent leakage and dry-out. Some cells are provided with venting devices or other means to allow accumulated gases to escape. Suitable cases or containers, means for terminal connection, and labeling are added to complete the fabrication of the cell and battery.

1.6 CLASSIFICATION OF CELLS AND BATTERIES

Electrochemical cells and batteries are identified as primary (nonrechargeable) or secondary (rechargeable), depending on their capability of being electrically recharged. However, other classifications or subcategories may apply based on particular structures or designs and user preferences.

Also, while batteries and fuel cells both employ redox reactions, capacitors represent another type of electrochemical device, but not one that typically involves chemical reactions. These include electrostatic capacitors (such as the Leyden jar), which are not detailed in this Handbook, as well as electrolytic systems, where ions flow within the electrolyte and accumulate at the electrodes but do not participate in redox reactions. A new type of capacitor, referenced as a hybrid, does have a change in valence state at one of the electrodes but does not undergo permanent oxidation or reduction (see Chap. 20, including discussions on ultra- or super-capacitors).

1.6.1 Primary Cells or Batteries

While all electrochemical cells may conceptually be capable of charging after being depleted, there are practical limitations to recharge: activation energy, deleterious side reactions, safety issues, energy efficiency, costs, etc. Hence, batteries that are not suitable for recharge are discharged once and discarded.

The primary battery is a convenient, usually inexpensive, lightweight source of packaged energy for portable electronic and electromechanical devices and a myriad of other applications. The general advantages of primary batteries are good shelf life, high energy density at low to moderate discharge rates, little, if any, maintenance, and ease of use. Although large high-capacity primary batteries are used in military applications, signaling, and standby power, the vast majority of primary batteries are small, single-cell cylindrical cans (AAA–D size), flat button batteries or multicell stacks of these components (9–V transistor radio battery).

1.6.2 Secondary or Rechargeable Cells or Batteries

Secondary batteries can be recharged electrically, after discharge, to nearly original condition by passing current through the electrodes in the opposite direction of the discharge. They are storage devices for electric energy and are also known as “storage batteries” or “accumulators.” In some cases, though, such as lead acid and lithium-ion cells, the batteries are manufactured in a depleted state and must actually be charged (called formation) before being able to function.

The applications of secondary batteries fall into two main categories:

1. *Energy storage for backup power or occasional use.* Batteries are electrically connected to and kept charged by a prime energy source, delivering energy to the load to supplement the main power system. Examples are automotive (Chap. 14), aircraft (Chap. 25B), emergency and standby power (uninterrupted power supply [UPS]), hybrid electric vehicles (HEVs; Chap. 26A), and electrical grid reserve energy storage systems (Chap. 27).
2. *Primary energy supply.* The secondary battery is used or discharged essentially as a primary battery, but recharged after use rather than being discarded. Examples include portable consumer electronics (Chap. 23), power tools/hand-held equipment (Chap. 24), etc., where life cycle costs are favorable compared to primary cells or where power drains exceed primary battery capabilities. Electric vehicles (EVs), plug-in hybrid electric vehicles (PHEVs; Chap. 26A), and light EVs (Chap. 25A) also fall into this category.

Secondary batteries are often characterized by high-power density/discharge rate, stable voltage levels, and good low-temperature performance. Compared to primary cells, most secondary cells have lower energy density and poorer charge retention. A few special-purpose batteries can be “mechanically” recharged by replacement of the discharged or depleted electrode, usually the metal anode or a liquid/gaseous fuel (see Chaps. 18 and 19).

1.6.3 Reserve Batteries

These special-purpose primary cells isolate the active materials or electrolyte from contact until power is needed. Self-discharge is essentially eliminated, and the battery is capable of long-term storage. Thermal batteries store the electrolyte in a frozen state (i.e., a solidified salt) until needed, whereupon, the salt melts and becomes conductive.

The reserve battery designs replace both primary and secondary cells where extreme environments or prolonged storage are encountered, such as in missiles, torpedoes, and other weapon systems (see Chap. 29).

1.6.4 Fuel Cells

Fuel cells, like batteries, are electrochemical galvanic cells that convert chemical energy directly into electrical energy and are not subject to the Carnot cycle limitations of heat engines. Fuel cells are similar to batteries except that the active materials are fed into the device from an external source when power is desired. The fuel cell produces electrical energy as long as the active materials are fed to the electrodes.

The electrode materials of the fuel cell do not react during cell operation but function as catalysts in the redox reactions of the active materials. Most fuel cells have gaseous or liquid anode materials (compared to most batteries with metal or solid anodes). The anode materials are more like the conventional fuels used in heat engines; hence, the term “fuel cell” is used. Oxygen or air is the predominant oxidant and is fed into the cathode side of the fuel cell.

Fuel cells have been known for almost two centuries and continue to be of interest as a more efficient and less polluting means for converting hydrogen and carbonaceous or fossil fuels to electricity compared to internal combustion engines. Hydrogen/oxygen fuel cells, using cryogenic fuels, have been used in spacecraft for about 70 years (see Chap. 15F). Fuel cell designs can vary but include two basic types: directly fueled and hydrogen fueled via chemical conversion of hydrocarbons. Fuel cell configurations vary from small portable devices to large power plants. The designs and electrolytes vary (i.e., direct methanol fuel cells, molten carbonate, proton exchange membrane, etc.) and can even include metal air systems where the anodes are replenished regularly. Applications include utility power, load leveling, remote electric generators, EVs, and potential replacements for batteries in consumer electronics (see Chap. 19).

1.7 OPERATION OF A CELL

1.7.1 Discharge

A generic discharge reaction is shown schematically in Fig. 1.4. Under electrical load, electrons flow from the anode, which is oxidized, through the external circuit to the cathode, which is reduced. The electric current flow is balanced by the flow of anions (negative ions) and cations (positive ions) to the anode and cathode, respectively, in the electrolyte.

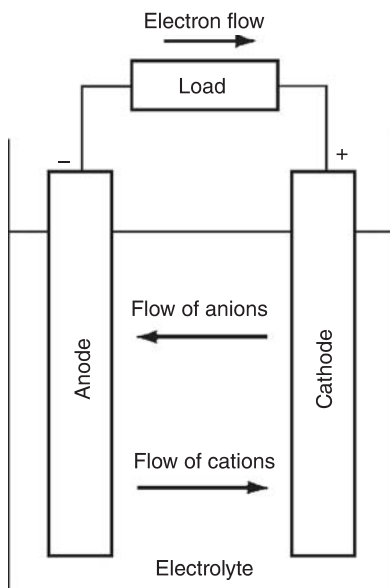


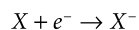
FIGURE 1.4 Electrochemical operation of a cell (discharge).

The discharge reaction can be generically written as follows:

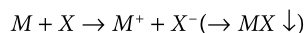
Negative electrode: anodic reaction (oxidation, loss of electrons)



Positive electrode: cathodic reaction (reduction, gain of electrons)



Overall reaction (discharge):



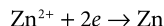
where M is typically a metal and X is an oxidant, such as an oxide or a halogen, which react to form ions and may be a solid compound as shown.

1.7.2 Charge

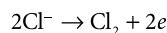
During the recharge, the current flow is reversed and oxidation takes place at the positive electrode and reduction at the negative electrode. By definition, the oxidizing electrode is the anode and the reducing one, the cathode. Hence, the positive electrode is now the anode and the negative the cathode. (Note: To avoid confusion, battery practitioners typically do not switch the electrode names during recharge.)

In an example where zinc and chlorine have reacted to form ZnCl_2 discharge product, the reaction on charge of the solvated ions can be written as follows:

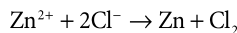
Negative electrode: cathodic reaction (reduction, gain of electrons)



Positive electrode: anodic reaction (oxidation, loss of electrons)

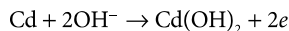


Overall reaction (charge):

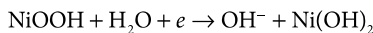


1.7.3 Specific Example (Nickel-Cadmium)

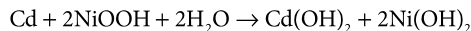
The chemical electrode reactions that create electron flow can be illustrated using the nickel-cadmium (NiCd) cell. At the anode (negative electrode), the discharge reaction is the oxidation of cadmium metal to cadmium hydroxide with the release of two electrons:



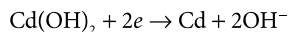
At the cathode, nickel oxide (or more accurately, nickel oxyhydroxide) is reduced to nickel hydroxide with the acceptance of an electron:



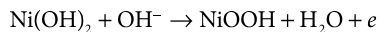
When these two “half-cell” reactions occur (via electron flow between electrodes through the external electrical circuit), the overall cell reaction converts cadmium to cadmium hydroxide at the anode and nickel oxyhydroxide to nickel hydroxide at the cathode:



In primary nonrechargeable cells, the device would be discarded at the end of discharge, but in secondary (rechargeable) system, such as the NiCd cells, the reactions are reversed by electrical recharge. At the negative electrode, the reaction is:



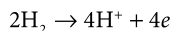
At the positive electrode, the reaction is:



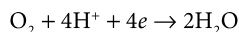
Each electrochemical couple has its own unique discharge/charge reactions and characteristics. The chapters in Part 4 detail a variety of these variations.

1.7.4 Fuel Cell

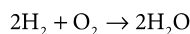
One of the most basic electrochemical systems is the hydrogen/oxygen fuel cell. Hydrogen is oxidized at the anode and oxygen is reduced at the cathode, both electrocatalyzed with platinum or platinum alloys. The simplified anodic reaction is:



while the cathodic reaction is:



The overall reaction is the oxidation of hydrogen by oxygen, with water as the reaction product:



This system can then be electrically (charged) or mechanically (replacement of the gases) reactivated (i.e., recharged).

1.8 THEORETICAL ELECTROCHEMISTRY FUNDAMENTALS

The theoretical voltage (i.e., the half-cell potentials) and capacity (i.e., the coulombs) of a cell are a function of the anode and cathode materials. Key concepts are introduced next (see Chap. 4 for details).

1.8.1 Free Energy

Gibbs free energy is known throughout science as a measure of the spontaneity of a reaction. Whenever a reaction occurs, there is a decrease in the free energy of the system, which is expressed as:

$$\Delta G^0 = -nFE^0$$

where F = constant known as the Faraday ($\approx 96,500$ C or 26.8 Ah)
 n = number of electrons involved in stoichiometric reaction
 E^0 = standard potential, V

Electrochemical systems may be analyzed by the use of this equation.

1.8.2 Theoretical Voltage

The standard potential (or theoretical voltage) of the cell is determined by the type of active materials and is calculated from free-energy data or obtained experimentally. A listing of electrode potentials (reduction potentials) under standard conditions is given in Table 1.1. A more complete list is presented in App. B.

TABLE 1.1 Characteristics of Typical Electrode Materials*

| Material | Atomic or molecular weight, g | Standard reduction potential at 25°C, V | Valence change | Melting point, °C | Density, g/cm ³ | Electrochemical equivalents | | |
|---|-------------------------------|---|----------------|-------------------|----------------------------|-----------------------------|-------|--------------------|
| | | | | | | Ah/g | g/Ah | Ah/cm ³ |
| Anode materials | | | | | | | | |
| H ₂ | 2.01 | 0 −0.83 [†] | 2 | — | — | 26.59 | 0.037 | — |
| Li | 6.94 | −3.01 | 1 | 180 | 0.54 | 3.86 | 0.259 | 2.06 |
| Na | 23.0 | −2.71 | 1 | 98 | 0.97 | 1.16 | 0.858 | 1.14 |
| Mg | 24.3 | −2.38 −2.69 [†] | 2 | 650 | 1.74 | 2.20 | 0.454 | 3.8 |
| Al | 26.9 | −1.66 | 3 | 659 | 2.69 | 2.98 | 0.335 | 8.1 |
| Ca | 40.1 | −2.84 −2.35 [†] | 2 | 851 | 1.54 | 1.34 | 0.748 | 2.06 |
| Fe | 55.8 | −0.44 −0.88 [†] | 2 | 1528 | 7.85 | 0.96 | 1.04 | 7.5 |
| Zn | 65.4 | −0.76 −1.25 [†] | 2 | 419 | 7.14 | 0.82 | 1.22 | 5.8 |
| Cd | 112.4 | −0.40 −0.81 [†] | 2 | 321 | 8.65 | 0.48 | 2.10 | 4.1 |
| Pb | 207.2 | −0.13 | 2 | 327 | 11.34 | 0.26 | 3.87 | 2.9 |
| (Li)C ₆ [§] | 72.06 | ~−2.8 | 1 | — | 2.25 | 0.372 | 2.69 | 0.837 |
| MH [†] | | −0.83 [†] | 2 | — | — | 0.305 | 3.28 | — |
| CH ₃ OH | 32.04 | — | 6 | — | — | 5.02 | 0.20 | — |
| Cathode materials | | | | | | | | |
| CuF ₂ | 101.5 | 3.55 | 2 | | | 0.528 | 1.89 | |
| O ₂ | 32.0 | 1.23 0.40 [†] | 4 | — | — | 3.35 | 0.30 | |
| Cl ₂ | 71.0 | 1.36 | 2 | — | — | 0.756 | 1.32 | |
| SO ₂ | 64.0 | — | 1 | — | — | 0.419 | 2.38 | |
| MnO ₂ | 86.9 | 1.28 [‡] | 1 | — | 5.0 | 0.308 | 3.24 | 1.54 |
| NiOOH | 91.7 | 0.49 | 1 | — | 7.4 | 0.292 | 3.42 | 2.16 |
| CuCl | 99.0 | 0.14 | 1 | — | 3.5 | 0.270 | 3.69 | 0.95 |
| FeS ₂ | 119.9 | — | 4 | — | — | 0.89 | 1.12 | 4.35 |
| AgO | 123.8 | 0.57 [†] | 2 | — | 7.4 | 0.432 | 2.31 | 3.20 |
| Br ₂ | 159.8 | 1.07 | 2 | — | — | 0.335 | 2.98 | |
| HgO | 216.6 | 0.10 [†] | 2 | — | 11.1 | 0.247 | 4.05 | 2.74 |
| Ag ₂ O | 231.7 | 0.35 [†] | 2 | — | 7.1 | 0.231 | 4.33 | 1.64 |
| PbO ₂ | 239.2 | 1.69 | 2 | — | 9.4 | 0.224 | 4.45 | 2.11 |
| LiFePO ₄ | 163.8 | ~0.42 | 1 | — | 3.44 | 0.160 | 6.25 | 0.554 |
| LiMn ₂ O ₄ (spinel) | 148.8 | ~1.2 | 1 | — | 4.1 | 0.120 | 8.33 | 0.492 |
| Li _x CoO ₂ | 98 | ~1.25 | 0.5 | — | 5.05 | 0.155 | 6.45 | 0.782 |
| I ₂ | 253.8 | 0.54 | 2 | — | 4.94 | 0.211 | 4.73 | 1.04 |

*See also Apps. B and C.

[†]Basic electrolyte; all others, aqueous acid or nonaqueous electrolytes.[‡]Based on density values shown.[§]Calculations based only on weight of carbon.[†]Based on type AB₃ alloy.

The standard potential of a cell can be calculated from the standard electrode potentials as follows (the oxidation potential is the negative value of the reduction potential):

$$\text{Anode (oxidation potential)} + \text{cathode (reduction potential)} = \text{standard cell potential}$$

For example, in the reaction $\text{Zn} + \text{Cl}_2 \rightarrow \text{ZnCl}_2$, the standard cell potential is:

$$\begin{array}{rcl} \text{Zn} \rightarrow \text{Zn}^{2+} + 2e & -(-0.76 \text{ V}) & \\ \text{Cl}_2 \rightarrow 2\text{Cl}^- - 2e & \underline{1.36 \text{ V}} & \\ E^\circ = & 2.12 \text{ V} & \end{array}$$

The cell voltage is also dependent on other factors, including concentration and temperature, as expressed by the Nernst equation (also see Chap. 4).

1.8.3 Theoretical Capacity (Coulombs of Stored/Generated Electricity)

The theoretical capacity of a cell is determined by the type and amount of active materials in the cell and is expressed in coulombs or ampere-hours (Ah) as the total quantity of electricity derived from the electrochemical reactions. Battery capacity is based on the ability of one (1) gram-equivalent weight of material to deliver 96,487 C or 26.8 Ah of electricity for each valence state change. (Gram-equivalent weight is the atomic or molecular weight of the active material in grams divided by the number of electrons, valence changes, involved in the reaction.) Electrochemical equivalence values are listed in Table 1.1 and App. C.

The theoretical capacity of an electrochemical cell, based only on the active materials participating in the electrochemical reaction, is calculated from the equivalent weight of the reactants. Hence, the theoretical capacity of the Zn/Cl₂ cell is 0.394 Ah/g, as follows:

$$\begin{array}{rcl} \text{Zn} & + & \text{Cl}_2 \longrightarrow \text{ZnCl}_2 \\ (0.82 \text{ Ah/g}) & (0.76 \text{ Ah/g}) & \\ 1.22 \text{ g/Ah} & + & 1.32 \text{ g/Ah} = 2.54 \text{ g/Ah or } 0.394 \text{ Ah/g} \end{array}$$

Similarly, the ampere-hour capacity on a volume basis can be calculated using the appropriate data for ampere-hours per cubic centimeter as listed in Table 1.1.

The theoretical voltages and capacities of a number of the major electrochemical systems are given in Table 1.2. These theoretical values are based on active anode and cathode materials only. Water, electrolyte, or any other materials that may be involved in the cell reaction are not included in the calculation.

1.8.4 Theoretical Energy^a

Cell output can also be considered on an energy (i.e., watt-hour) basis by factoring in the voltage level at which a quantity of electricity is provided as follows:

$$\text{Watt-hour (Wh)} = \text{voltage (V)} \times \text{ampere-hour (Ah)}$$

^aThe energy output of a cell or battery is often expressed as a ratio of its weight or size. The preferred terminology for this ratio on a weight basis, e.g., watt-hours/kilogram (Wh/kg), is "specific energy." On a volume basis, e.g., watt-hours/liter (Wh/L), it is "energy density." Commonly, the term "energy density" may be used to refer to either ratio but should still specify a weight or volume basis.

TABLE 1.2 Voltage, Capacity, and Specific Energy of Major Battery Systems—Theoretical and Practical Values

| Battery type | Anode | Cathode | Reaction mechanism | V | Theoretical values ^a | | | Practical battery ^b | | |
|--------------------------------|-----------------|-----------------------|--|---------|---------------------------------|-------|-----------------------|--------------------------------|-----------------------|---------------------|
| | | | | | g/Ah | Ah/kg | Specific energy Wh/kg | Nominal voltage V | Specific energy Wh/kg | Energy density Wh/L |
| Primary batteries | | | | | | | | | | |
| Leclanché | Zn | MnO ₂ | Zn + 2MnO ₂ → ZnO · Mn ₂ O ₃ | 1.6 | 4.46 | 224 | 358 | 1.5 | 85 ^f | 165 ^f |
| Magnesium | Mg | MnO ₂ | Mg + 2MnO ₂ + H ₂ O → Mn ₂ O ₃ + Mg(OH) ₂ | 2.8 | 3.69 | 271 | 759 | 1.7 | 100 ^f | 195 ^f |
| Alkaline MnO ₂ | Zn | MnO ₂ | Zn + 2MnO ₂ → ZnO + Mn ₂ O ₃ | 1.5 | 4.46 | 224 | 358 | 1.5 | 154 ^f | 461 ^f |
| Mercury | Zn | HgO | Zn + HgO → ZnO + Hg | 1.34 | 5.27 | 190 | 255 | 1.35 | 100 ^h | 470 ^h |
| Mercad | Cd | HgO | Cd + HgO + H ₂ O → Cd(OH) ₂ + Hg | 0.91 | 6.15 | 163 | 148 | 0.9 | 55 ^h | 230 ^h |
| Silver oxide | Zn | Ag ₂ O | Zn + Ag ₂ O + H ₂ O → Zn(OH) ₂ + 2Ag | 1.6 | 5.55 | 180 | 288 | 1.6 | 135 ^h | 525 ^h |
| Zinc/O ₂ | Zn | O ₂ | Zn + ½O ₂ → ZnO | 1.65 | 1.52 | 658 | 1085 | — | — | — |
| Zinc/air | Zn | Ambient air | Zn + (½ O ₂) → ZnO | 1.65 | 1.22 | 820 | 1353 | 1.5 | 415 ^h | 1350 ^h |
| Li/SOCl ₂ | Li | SOCl ₂ | 4Li + 2SOCl ₂ → 4LiCl + S + SO ₂ | 3.65 | 3.25 | 403 | 1471 | 3.6 | 590 ^f | 1100 ^f |
| Li/SO ₂ | Li | SO ₂ | 2Li + 2SO ₂ → Li ₂ S ₂ O ₄ | 3.1 | 2.64 | 379 | 1175 | 3.0 | 260 ^g | 415 ^g |
| LiMnO ₂ | Li | MnO ₂ | Li + Mn ^{IV} O ₂ → Mn ^{IV} O ₂ (Li ⁺) | 3.5 | 3.50 | 286 | 1001 | 3.0 | 260 ^g | 546 ^g |
| Li/FeS ₂ | Li | FeS ₂ | 4Li + FeS ₂ → 2Li ₂ S + Fe | 1.8 | 1.38 | 726 | 1307 | 1.5 | 310 ^g | 560 ^g |
| Li/CF _x | Li | CF _x | xLi + CF _x → xLiF + xC | 3.1 | 1.42 | 706 | 2189 | 3.0 | 360 ^g | 540 ^g |
| Li/I ₂ ^e | Li | I ₂ (P2VP) | Li + ½I ₂ → LiI | 2.8 | 4.99 | 200 | 560 | 2.8 | 245 | 900 |
| Reserve batteries | | | | | | | | | | |
| Cuprous chloride | Mg | CuCl | Mg + Cu ₂ Cl ₂ → MgCl ₂ + 2Cu | 1.6 | 4.14 | 241 | 386 | 1.3 | 60 ⁱ | 80 ⁱ |
| Zinc/silver oxide | Zn | AgO | Zn + AgO + H ₂ O → Zn(OH) ₂ + Hg | 1.81 | 3.53 | 283 | 512 | 1.5 | 30 ^j | 75 ^j |
| Thermal ^d | Li | FeS ₂ | See Section 36.3.1 | 2.1–1.6 | 1.38 | 726 | 1307 | 2.1–1.6 | 40 ^k | 100 ^k |
| Secondary batteries | | | | | | | | | | |
| Lead-acid | Pb | PbO ₂ | Pb + PbO ₂ + 2H ₂ SO ₄ → 2PbSO ₄ + 2H ₂ O | 2.1 | 8.32 | 120 | 252 | 2.0 | 35 | 70 ^l |
| Edison | Fe | Ni oxide | Fe + 2NiOOH + 2H ₂ O → 2Ni(OH) ₂ + Fe(OH) ₂ | 1.4 | 4.46 | 224 | 314 | 1.2 | 30 | 55 ^l |
| Nickel-cadmium | Cd | Ni oxide | Cd + 2NiOOH + 2H ₂ O → 2Ni(OH) ₂ + Cd(OH) ₂ | 1.35 | 5.52 | 181 | 244 | 1.2 | 40 | 135 ^g |
| Nickel-zinc | Zn | Ni oxide | Zn + 2NiOOH + 2H ₂ O → 2Ni(OH) ₂ + Zn(OH) ₂ | 1.73 | 4.64 | 215 | 372 | 1.6 | 90 | 185 |
| Nickel-hydrogen | H ₂ | Ni oxide | H ₂ + 2NiOOH → 2Ni(OH) ₂ | 1.5 | 3.46 | 289 | 434 | 1.2 | 55 | 60 |
| Nickel-metal hydride | MH ^c | Ni oxide | MH + NiOOH → M + Ni(OH) ₂ | 1.35 | 5.63 | 178 | 240 | 1.2 | 100 | 235 ^g |

| | | | | | | | | | | |
|-------------------------------------|--------------------------------|--------------------------------------|--|------|-------|--------|--------|-----|------------------|------------------|
| Silver-zinc | Zn | AgO | $\text{Zn} + \text{AgO} + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 + \text{Ag}$ | 1.85 | 3.53 | 283 | 524 | 1.5 | 105 | 180 ^j |
| Silver-cadmium | Cd | AgO | $\text{Cd} + \text{AgO} + \text{H}_2\text{O} \rightarrow \text{Cd(OH)}_2 + \text{Ag}$ | 1.4 | 4.41 | 227 | 318 | 1.1 | 70 | 120 ^j |
| Zinc/chlorine | Zn | Cl ₂ | $\text{Zn} + \text{Cl}_2 \rightarrow \text{ZnCl}_2$ | 2.12 | 2.54 | 394 | 835 | — | — | — |
| Zinc/bromine | Zn | Br ₂ | $\text{Zn} + \text{Br}_2 \rightarrow \text{ZnBr}_2$ | 1.85 | 4.17 | 309 | 572 | 1.6 | 70 | 60 |
| Lithium-ion | Li _x C ₆ | Li _(1-x) CoO ₂ | $\text{Li}_x\text{C}_6 + \text{Li}_{(1-x)}\text{CoO}_2 \rightarrow \text{LiCoO}_2 + \text{C}_6$ | 4.1 | 9.14 | 109 | 448 | 3.8 | 200 | 570 ^g |
| Lithium/manganese dioxide | Li | MnO ₂ | $\text{Li} + \text{Mn}^{\text{IV}}\text{O}_2 \rightarrow \text{Mn}^{\text{IV}}\text{O}_2(\text{Li}^+)$ | 3.5 | 3.50 | 286 | 1001 | 3.0 | 120 | 265 |
| Lithium/iron disulfide ^d | Li(Al) | FeS ₂ | $2\text{Li(Al)} + \text{FeS}_2 \rightarrow \text{Li}_2\text{FeS}_2 + 2\text{Al}$ | 1.73 | 3.50 | 285 | 493 | 1.7 | 180 ^m | 350 ^m |
| Sodium/sulfur ^d | Na | S | $2\text{Na} + 3\text{S} \rightarrow \text{Na}_2\text{S}_3$ | 2.1 | 2.65 | 377 | 792 | 2.0 | 170 ^m | 345 ^m |
| Sodium/nickel chloride ^d | Na | NiCl ₂ | $2\text{Na} + \text{NiCl}_2 \rightarrow 2\text{NaCl} + \text{Ni}$ | 2.58 | 3.28 | 305 | 787 | 2.6 | 115 ^m | 190 ^m |
| Fuel cells | | | | | | | | | | |
| H ₂ /O ₂ | H ₂ | O ₂ | $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ | 1.23 | 0.336 | 2975 | 3660 | | | |
| H ₂ /air | H ₂ | Ambient air | $\text{H}_2 + (\frac{1}{2}\text{O}_2) \rightarrow \text{H}_2\text{O}$ | 1.23 | 0.037 | 26,587 | 32,702 | | | |
| Methanol/O ₂ | CH ₃ OH | O ₂ | $\text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ | 1.24 | 0.50 | 2000 | 2480 | — | — | — |
| Methanol/air | CH ₃ OH | Ambient air | $\text{CH}_3\text{OH} + (\frac{3}{2}\text{O}_2) \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ | 1.24 | 0.20 | 5020 | 6225 | — | — | — |

^aBased on active anode and cathode materials only, including O₂ but not air (electrolyte not included).

^bThese values are for single-cell batteries based on identified design and at discharge rates optimized for energy density, using midpoint voltage. More specific values are given in chapters on each battery system.

^cMH = metal hydride, data based on type AB₃ alloy.

^dHigh temperature batteries.

^eSolid electrolyte battery (Li/I₂ [P2VP]).

^fCylindrical bobbin-type batteries.

^gCylindrical spiral-wound batteries.

^hButton type batteries.

ⁱWater-activated.

^jAutomatically activated 2- to 10-min rate.

^kWith lithium anodes.

^lPrismatic batteries.

^mValue based on cell performance, see appropriate chapter for details.

This energy value is the maximum that can be delivered by a specific electrochemical system since it is based on theoretical voltages, which are always greater than actual discharge voltages. In the Zn/Cl₂ cell example, if the standard potential is taken as 2.12 V, the theoretical watt-hour capacity per gram of active material (theoretical gravimetric specific energy or theoretical gravimetric energy density) is

$$\text{Specific energy (watt-hours/gram)} = 2.12 \text{ V} \times 0.394 \text{ Ah/g} = 0.835 \text{ Wh/g or } 835 \text{ Wh/kg}$$

Table 1.2 also lists the theoretical specific energy of various electrochemical systems.

1.9 SPECIFIC ENERGY AND ENERGY DENSITY OF PRACTICAL BATTERIES

In summary, the maximum energy that can be delivered by an electrochemical system is based on the composition of active materials that are used, which determines voltage, and on the amount of the active materials that are used, which further determines ampere-hour capacity. In practice, only a fraction of the theoretical energy of the battery is realized, and this output is further diluted on an energy density basis by electrolyte and nonreactive components (containers, separators, electrodes), as illustrated in Fig. 1.5. This figure, which was modeled after an assumed (i.e., nonexistent) lithium-ion cell design, shows that active materials consume a relatively small fraction of the total battery and do not even contribute to the majority of cell costs. Clearly, then, cell designs are dominated by the peripheral parts, which decrease specific energy and increase costs. Also, the average cell discharge voltage is less than theoretical and a cell is never, practically, discharged to zero. Active materials in a practical battery are usually not stoichiometrically balanced, creating an excess amount of one of the active materials, which further impacts the delivered specific energy/energy density.

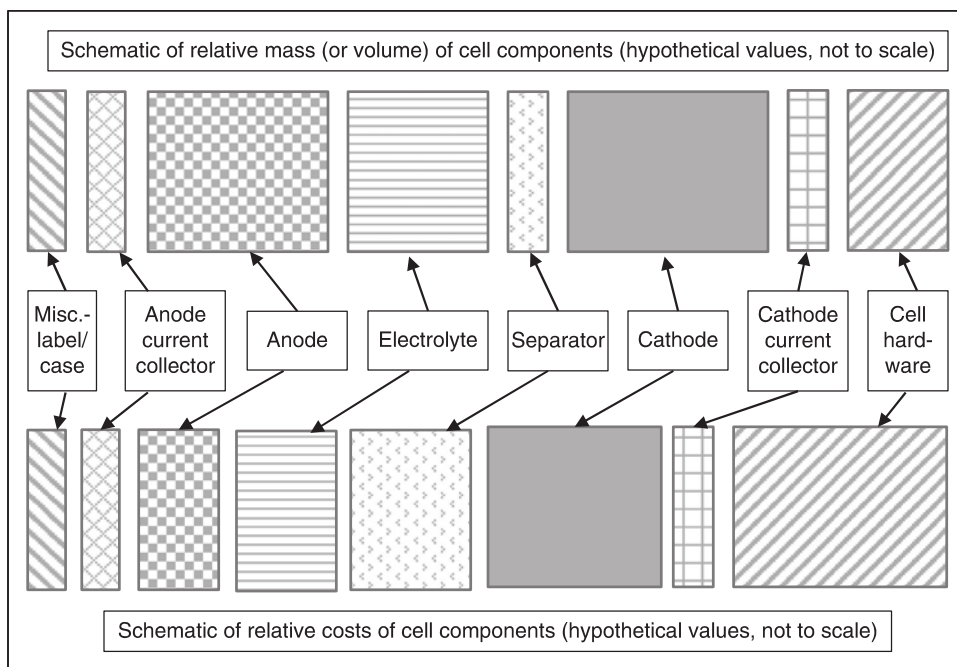


FIGURE 1.5 Illustrative example of cell component building blocks.

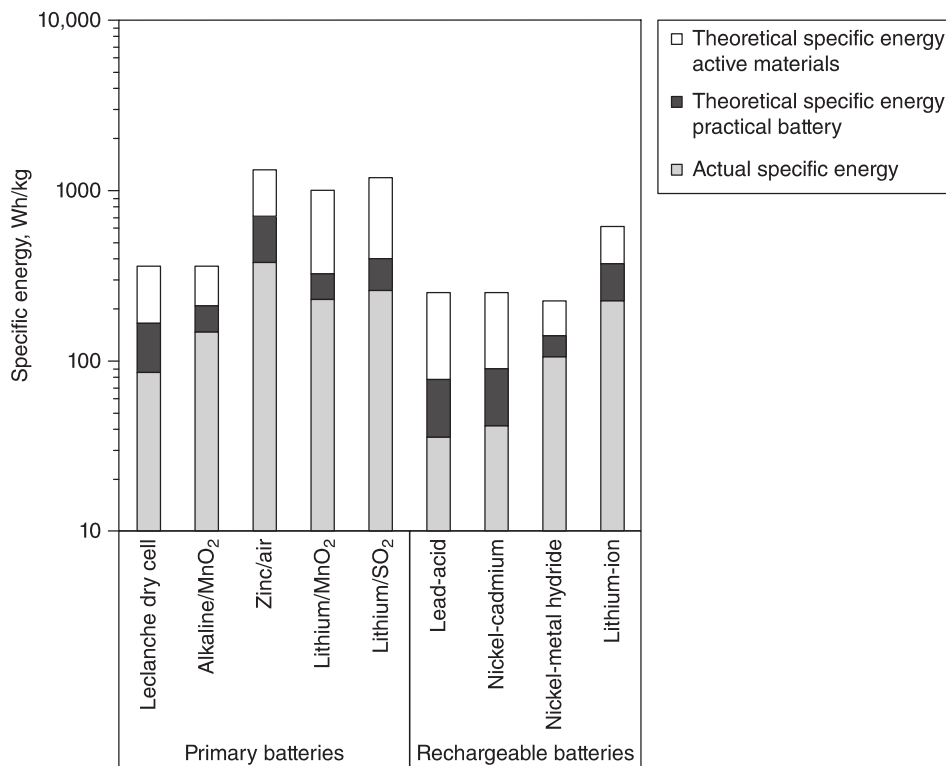


FIGURE 1.6 Theoretical and actual specific energy of battery systems.

In Fig. 1.6, rating factors, as follows, are plotted for various batteries:

1. The theoretical specific energy (based on the active anode and cathode materials only)
2. The theoretical specific energy of a practical battery (accounting for the electrolyte and nonreactive components)
3. The actual specific energy of these batteries when discharged at 20°C under optimal discharge conditions

These data show the following energy density deratings:

- A 50% reduction due to materials of construction
- A 50 to 75% reduction due to actual cell test inefficiencies (even under ideal conditions)

Thus, the actual energy that is available from a battery under even benign discharge conditions is only about 25 to 35% of the theoretical energy of the active materials. Chapter 5 covers the performance of batteries when used under more stringent conditions.

Table 1.2 summarizes these data along with the characteristics and performance of practical batteries. The specific energy (Wh/kg) and energy density (Wh/L) delivered by the major battery systems are also plotted in Fig. 1.7a for primary batteries and 1.7b for rechargeable batteries. In these figures, the energy storage capability is shown as a field, rather than as a single optimum value, to illustrate the spread in performance of that battery system under different conditions of use.

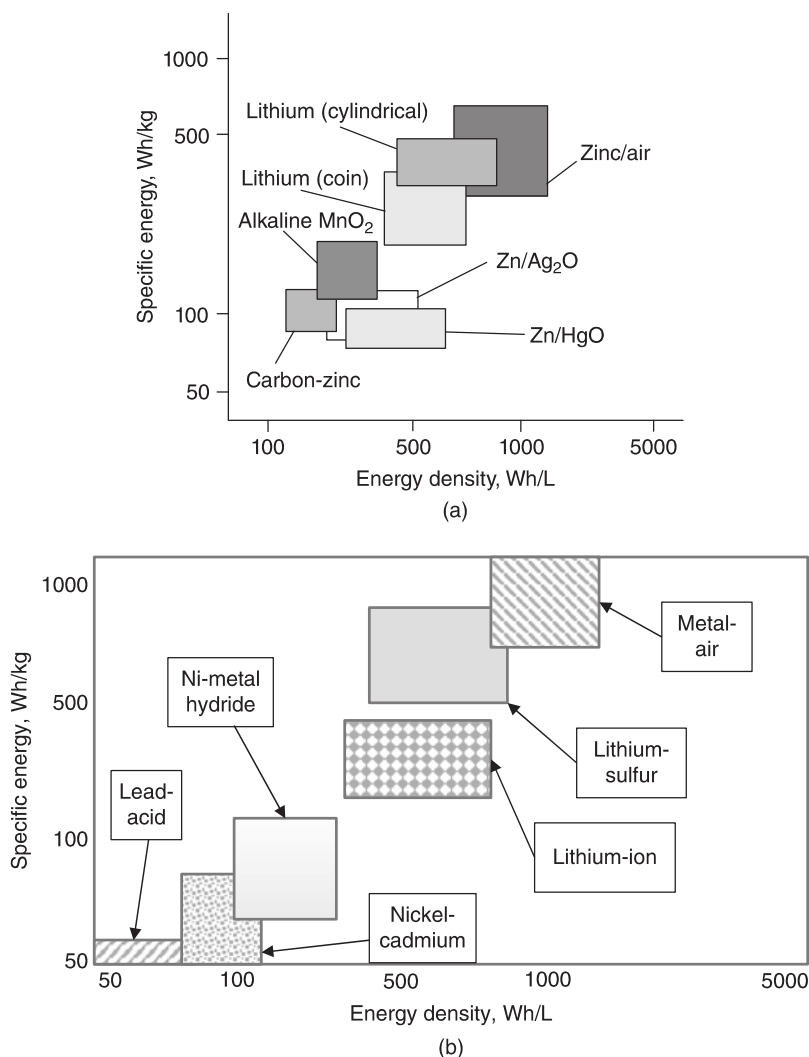


FIGURE 1.7 Comparison of the energy storage capability of various battery systems: (a) primary batteries, (b) secondary batteries.

1.10 LIMITS OF SPECIFIC ENERGY AND ENERGY DENSITY

Many advances have been made in battery technology over the years, as illustrated in Fig. 1.8, both through continued improvement of a specific electrochemical system and through the development and introduction of new battery chemistries. However, batteries, unlike electronic devices, consume materials when delivering electrical energy and, as discussed in Secs. 1.8 and 1.9, there are theoretical limits to the amount of electrical energy that can be delivered electrochemically by the available materials.

As shown in Table 1.2, except for some of the ambient air-breathing systems and the hydrogen/oxygen fuel cell, where the weight of the cathode active material is not included in the calculation, the values for the

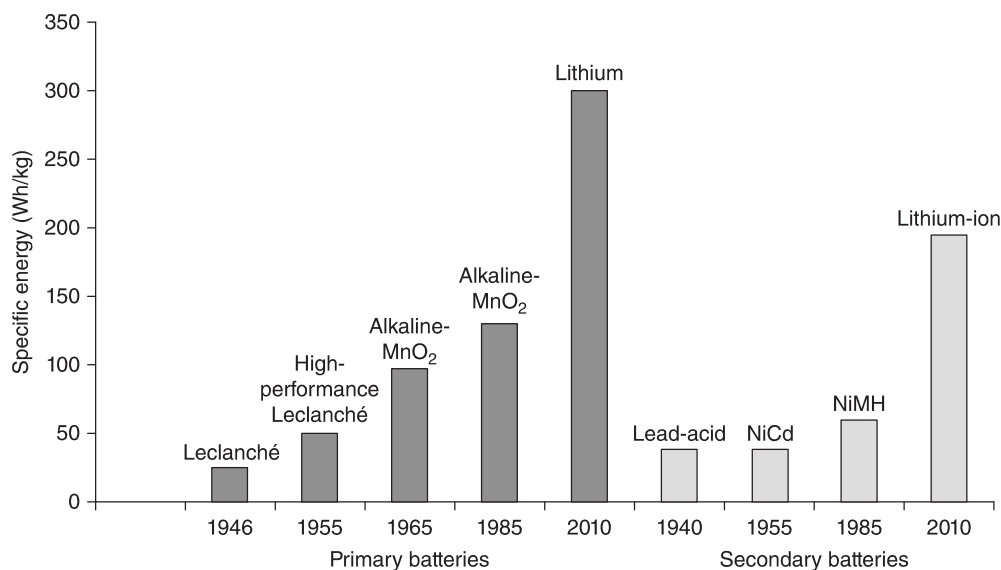


FIGURE 1.8 Advances in battery performance for portable applications.

theoretical energy density do not exceed 1500 Wh/kg. Even the values for hydrogen/air and liquid fuel cells are impacted since the weight and volume of suitable containers for these fuels must be included.

The data in Table 1.2 also show that the specific energy delivered by these batteries, based on the actual performance when discharged under optimum conditions, does not exceed 600 Wh/kg or 1300 Wh/L energy density. Rechargeable systems are more negatively impacted than primary batteries, due in part to a more limited selection of materials that can be recharged practically and the need for designs to facilitate recharging and cycle life.

1.11 MARKET TRENDS

The size and diversity of the battery industry are massive and growing. The supply of energy by conventional sources is simply inadequate to meet consumer expectations. The evolving statistics for specific electrochemical systems will be addressed in other chapters of this Handbook, but Table 1.3 presents an overview of the markets as a whole, based on recent analyses by The Freedonia Group.

TABLE 1.3 Battery Supply and Demand (million dollars)*

| Item | 2005 | 2010 | 2015 | 2020 | 2025 |
|---------------------------------|--------|--------|--------|--------|--------|
| Gross domestic product (bil \$) | 13,094 | 14,964 | 18,037 | 22,200 | 27,500 |
| \$ batteries/000\$ GDP | 0.66 | 0.77 | 0.79 | 0.80 | 0.79 |
| Battery demand | 8590 | 11,450 | 14,200 | 17,650 | 21,750 |
| Single-use | 2895 | 3300 | 3250 | 3500 | 3750 |
| Rechargeable | 5695 | 8150 | 10,950 | 14,150 | 18,000 |
| –Net imports | –1185 | –950 | –1350 | –1000 | –250 |
| Battery shipments | 7405 | 10,500 | 12,850 | 16,650 | 21,500 |
| Price deflator (2009 = 100) | 76.8 | 102.6 | 107.0 | 116.3 | 126.2 |
| Battery shipments (mil 2009\$) | 9642 | 10,234 | 12,009 | 14,316 | 17,036 |

*Table III-1, Battery Markets in the U.S. by Application and End User, published December 2016 by The Freedonia Group.

Table 1.3 reveals that batteries will have grown from less than 0.066% of the U.S. economy 15 years ago to nearly 0.08% of the gross domestic product (GDP) within 10 years—a remarkable increase, considering that rapid growth in other parts of the economy dilutes the growth of batteries. GDP nearly doubles over this 20-year period while batteries grow $2\frac{1}{2}$ times with secondary batteries increasing threefold. Two other key facts are that primary cells are basically flat and that imported batteries are projected to nearly disappear (down >80% from a 2015 peak).

1.12 CASE STUDY: BATTERY-POWERED RIVER BARGE FOR HAULING COAL

As an example of the perspectives necessary to search out and implement new battery technologies in this new era of heightened energy awareness, a case study warrants consideration. Specifically, the development and commissioning of a battery-powered river barge was recently announced in China.^b The use of electricity, rather than diesel fuel, to deliver cargo is an accomplishment that is certainly commendable and seemingly worthy of implementation. However, one critical circumstance is that the barge will be used to ship coal from the mine to the power plant down river. Examining this situation based on thermodynamic calculations brings up a major potential issue: What is the overall efficiency of this battery power barge system, as opposed to the alternative options? Locating the power plant at the mine is a typical practice, but one that is not always possible. Certainly, solar, wind, or even river currents would be more efficient (i.e., preferable) energy sources, but they are not very reliable. Other critics might say it is best to eliminate coal-fired power plants altogether and switch to solar or hydroelectric power. These options are certainly desirable, but not always practical.

Hence, assuming coal-fired power plants are still necessary to generate electricity in the near term, what is the best method for shipping coal? A complete thermodynamic efficiency analysis should compare the use of diesel engines (or diesel-electric power) to the use of batteries. There are two basic areas to consider in this analysis of the use of batteries:

1. The use of resources to produce the barge batteries (ideally prorated over battery life)
2. The use of electricity to recharge the batteries each trip

In the first category, electricity and other forms of energy, including human power, are used to mine the battery materials, construct the battery factory, and build each battery module and all related equipment. Additionally, energy is also expended to mine and ship the coal that is used to generate the electricity to produce the batteries. How this energy is derived and where it is used are not trivial issues. The energy consumed and the efficiencies (i.e., waste heat) for this entire portfolio of equipment, operating over the full battery product life cycle, deserve proper thermodynamic analyses (and comparison to fossil fuels) if the correct decision on barge power is to be made.

For instance, if not for the pollution, would it perhaps be preferable (more energy efficient) to simply use a coal-fired steam boiler on the barge? The coal mine then provides all the power needed to ship the coal. No resources to build the battery are consumed, no battery electrical storage is required, and no electrical energy generation is needed for either of these two tasks.

However, the heat (i.e., combustion) engine is, as a whole, the most inefficient power source available. Therefore, a complete analysis of energy efficiency of all potential power sources for the river barge is the only truly viable approach to making the proper selection. These analyses will ideally include current technologies as well as new or evolving power systems. Battery power may or may not be the right solution for this application. Once the thermodynamic calculations are completed and after other peripheral issues are considered (capital costs, operating costs, pollution, performance capabilities, etc.), then (and only then) can an informed decision be made.

Ultimately, though, the best choice for this situation (i.e., coal shipment from the mine to the power plant) seems fairly logical: Use fuel cells (or redox flow cells) based on new technology that can accept pulverized coal slurries as the fuel and air as the oxidant. Such electrochemical systems could have extremely high thermodynamic efficiencies and zero emissions (no particulates, no sulfurous or nitrous compounds, and no carbon dioxide). A fuel cell system can be engineered for long life with minimal use of strategic materials. The by-products, ash and CO₂, would be contained and easily redirected to other useful applications.

^b<https://cleantechnica.com/2017/12/02/china-launches-worlds-first-electric-cargo-ship-will-use-haul-coal/> (extracted from web 12/2/2017).

1.13 A SYSTEM OF SYSTEMS

New battery systems with significantly higher energy output and lower costs will be increasingly difficult to engineer and commercialize at this nexus of market forces and technical and financial barriers. The major goals for the near term will likely center on materials availability, cost, safety, and environmental acceptability.

Perfecting the use of lithium metal- or silicon-based anodes, enhancing cathode capabilities to match the anodes, improving the ratio of active to inactive components, increasing conversion efficiency and recharging ability, maximizing performance under more stringent operating conditions, and enhancing safety will be subjects of much R&D in the future. Alternative electrochemistry and components, such as fuel cells, redox flow cells, solid-state and hybrid electrolytes, wireless charging, etc., also offer opportunities for improving the state-of-the-art technology.

However, beyond such technical issues, attention needs to be paid to business models for battery development and equipment deployment. Intellectual property issues, supply chain complexities (including the need for recycling), and manufacturing strategies will play a major role in the future of the world's energy supply. Clearly, batteries are a system of systems, in which overall success will stem from unprecedented levels of cooperation and communication, just as was the case with Franklin and Volta at the dawn of the era of electrochemistry.

ACKNOWLEDGMENT

Table 1.3 is provided by The Freedonia Group.

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