CHAPTER 5.3
BATTERIES AND FUEL CELLS*

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BATTERIES

A battery is a device that converts the chemical energy contained in its active materials directly into electric energy by means of an oxidation-reduction electrochemical reaction. This type of reaction involves the transfer of electrons from one material to another. In a nonelectrochemical reaction this transfer of electrons occurs directly, and only heat is involved. In a battery (Fig. 5.3.1) the negative electrode or anode is the component capable of giving up electrons, being oxidized during the discharge reaction. It is separated from the oxidizing material, which is the positive electrode or cathode, the component capable of accepting electrons. The transfer of electrons takes place in the external electric circuit connecting the two materials and in the electrolyte, which serves to complete the electric circuit in the battery by providing an ionic medium for the electron transfer.

Components of Batteries

The basic unit of the battery is the cell. A battery consists of one or more cells, connected in series or parallel, depending on the desired output voltage or capacity. The cell consists of three major components: the anode (the reducing material or fuel), the cathode or oxidizing agent, and the electrolyte, which provides the necessary internal ionic conductivity. Electrolytes are usually liquid, but some batteries employ solid electrolytes that are ionic conductors at their operating temperatures. In addition, practical cell design requires a separator material, which serves to separate the anode and cathode electrodes mechanically. Electrically conducting grid structures or materials are often added to each electrode to reduce internal resistance. The containers are of many types, depending on the application and its environment.

Theoretical Cell Voltage and Capacity

The theoretical energy delivered by a battery is determined by its active materials; the maximum electric energy (watt-hours) corresponds to the free-energy change of the reaction. The theoretical voltage and ampere-hour capacities of a number of electrochemical systems are given in Table 5.3.1. The voltage is determined by the active materials selected; the ampere-hour capacity is determined by the amount (weight) of available reactants. One gram-equivalent weight of material will supply 96,500 C, or 26.8 Ah, of electric energy.

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*Material for this chapter has been abstracted from the "Handbook of Batteries," 3rd ed., D. Linden and T. B. Reddy, (eds.), McGraw-Hill, 2001.
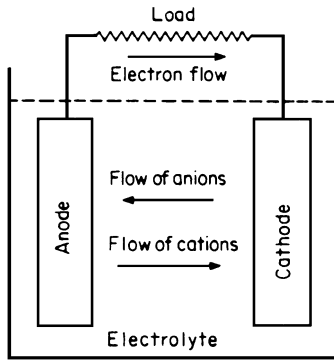
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FIGURE 5.3.1   Electrochemical operation of a cell or battery during discharge.
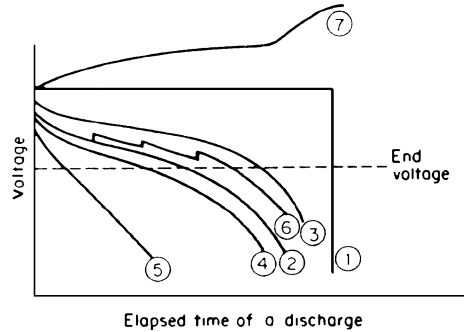

FIGURE 5.3.2   Battery discharge characteristics.

Factors Influencing Battery Voltage and Capacity

In actual practice, only a small fraction of the theoretical capacity is realized. This is a result not only of the presence of nonreactive components (containers, separators, electrolyte) that add to the weight and size of the battery but also of many other factors that prevent the battery from performing at its theoretical level. Factors influencing the voltage and capacity of a battery are as follows.

Voltage Level.   When a battery is discharged in use, its voltage is lower than the theoretical voltage. The difference is caused by *IR* losses because of cell resistance and polarization of the active materials during discharge. This is illustrated in Fig. 5.3.2. The theoretical discharge curve of a battery is shown as curve 1. In this case, the discharge of the battery proceeds at the theoretical voltage until the active materials are consumed and the capacity fully utilized. The voltage then drops to zero. Under load conditions, the discharge curve is similar to curve 2. The initial voltage is lower than theoretical, and it drops off as the discharge progresses.

Current Drain of the Discharge.   As the current drain of the battery is increased, the *IR* loss increases, the discharge is at a lower voltage, and the service life of the battery is reduced (curve 5). At extremely low current drains it is possible to approach the theoretical capacities (in the direction of curve 3). In a very long discharge period, chemical self-deterioration during the discharge becomes a factor and causes a reduction of capacity.

Voltage Regulation.   The voltage regulation required by the equipment is most important. As is apparent by the curves in Fig 5.3.2 design of equipment to operate to the lowest possible end voltage results in the highest capacity and longest service life. Similarly, the upper voltage limit of the equipment should be established to take full advantage of the battery characteristics. In some applications, where only a narrow voltage range can be tolerated, voltage regulators may have to be employed to take full advantage of the battery's capacity. If a storage battery is used in conjunction with another energy source, which is permanently connected in the operating circuit, allowances must be made for the voltage required to charge the battery, as illustrated in curve 7, Fig. 5.3.2. The voltage of the charging source must just exceed the maximum voltage on charge.

Type of Discharge (Continuous, Intermittent, and so Forth).   When a battery stands idle after a discharge, certain chemical and physical changes take place, which can result in voltage recovery. Thus the voltage of a battery that has dropped during a heavy discharge will rise after rest period, giving a sawtooth discharge. Curve 6 of Fig. 5.3.2 shows the characteristic of a battery discharged intermittently at the same drain in curve 2. The improvement resulting from the intermittent discharge depends on the current drain, length of the recovery period, discharge temperature, end voltage, and the particular battery system and design employed. Some battery systems, during inactive stand, develop a protective film on the active-material surface. These batteries, instead of showing a recovery voltage, may momentarily demonstrate a lower voltage after stand until this film is broken by the discharge. This is known as a *voltage delay*.

TABLE 5.3.1 Voltage, Capacity, and Specific Energy of Major Battery and Several Fuel Cell Systems—Theoretical and Practical Values

Battery type	Anode	Cathode	Reaction mechanism	Theoretical values[†]				Practical battery[‡]		
				V	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	$Zn + 2MnO_2 \rightarrow ZnO \cdot Mn_2O_3$	1.6	4.46	224	358	1.5	85[4]	165[4]
Magnesium	Mg	MnO_2	$Mg + 2MnO_2 + H_2O \rightarrow Mn_2O_3 + Mg(OH)_2$	2.8	3.69	271	759	1.7	100[4]	195[4]
Alkaline MnO_2	Zn	MnO_2	$Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3$	1.5	4.46	224	358	1.5	145[4]	400[4]
Mercury	Zn	HgO	$Zn + HgO \rightarrow ZnO + Hg$	1.34	5.27	190	255	1.35	100[6]	470[6]
Mercad	Cd	HgO	$Cd + HgO + H_2O \rightarrow Cd(OH)_2 + Hg$	0.91	6.15	163	148	0.9	55[6]	230[6]
Silver oxide	Zn	Ag_2O	$Zn + Ag_2O + H_2O \rightarrow Zn(OH)_2 + 2Ag$	1.6	5.55	180	288	1.6	135[6]	525[6]
$Zinc/O_2$	Zn	O_2	$Zn + 1/2 O_2 \rightarrow ZnO$	1.65	1.52	658	1085	—	—	—
Zinc/air	Zn	Ambient air	$Zn + (1/2 O_2) \rightarrow ZnO$	1.65	1.22	820	1353	1.5	370[6]	1300[6]
$Li/SOCl_2$	Li	$SOCl_2$	$4Li + 2SOCl_2 \rightarrow 4LiCl + S + SO_2$	3.65	3.25	403	1471	3.6	590[4]	1100[4]
Li/SO_2	Li	SO_2	$2Li + 2SO_2 \rightarrow Li_2S_2O_4$	3.1	2.64	379	1175	3.0	260[5]	415[5]
$LiMnO_2$	Li	MnO_2	$Li + Mn^{IV}O_3 \rightarrow Mn^{III}O_2(Li^+)$	3.5	3.50	286	1001	3.0	230[5]	535[5]
Li/FeS_2	Li	FeS_2	$4Li + FeS_2 \rightarrow 2Li_2S + Fe$	1.8	1.38	726	1307	1.5	260[5]	500[5]
$Li/(CF)_n$	Li	$(CF)_n$	$nLi + (CF)_n \rightarrow nLiF + nC$	3.1	1.42	706	2189	3.0	250[5]	635[5]
$Li/I_2^{(3)}$	Li	$I_2(P2VP)$	$Li + 1/2 I_2 \rightarrow LiI$	2.8	4.99	200	560	2.8	245	900
Reserve batteries										
Cuprous chloride	Mg	CuCl	$Mg + Cu_2Cl_2 \rightarrow MgCl_2 + 2Cu$	1.6	4.14	241	386	1.3	60[7]	80[7]
Zinc/silver oxide	Zn	AgO	$Zn + AgO + H_2O \rightarrow Zn(OH)_2 + Hg$	1.81	3.53	283	512	1.5	30[8]	75[8]
Thermal	Li	FeS_2		2.1–1.6	1.38	726	1307	2.1–1.6	40[9]	100[9]
Secondary batteries										
Lead-acid	Pb	PbO_2	$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$	2.1	8.32	120	252	2.0	35	70[10]
Edison	Fe	Ni oxide	$Fe + 2NiOOH + 2H_2O \rightarrow 2Ni(OH)_2 + Fe(OH)_2$	1.4	4.46	224	314	1.2	30	55[10]
Nickel-cadmium	Cd	Ni oxide	$Cd + 2NiOOH + 2H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2$	1.35	5.52	181	244	1.2	35	100[5]
Nickel-zinc	Zn	Ni oxide	$Zn + 2NiOOH + 2H_2O \rightarrow 2Ni(OH)_2 + Zn(OH)_2$	1.73	4.64	215	372	1.6	60	120
Nickel-hydrogen	H_2	Ni oxide	$H_2 + 2NiOOH \rightarrow 2Ni(OH)_2$	1.5	3.46	289	434	1.2	55	60
Nickel-metal hydride	$MH^{(1)}$	Ni oxide	$MH + NiOOH \rightarrow M + Ni(OH)_2$	1.35	5.63	178	240	1.2	75	240[5]
Silver-zinc	Zn	AgO	$Zn + AgO + H_2O \rightarrow Zn(OH)_2 + Ag$	1.85	3.53	283	524	1.5	105	180[10]
Silver-cadmium	Cd	AgO	$Cd + AgO + H_2O \rightarrow Cd(OH)_2 + Ag$	1.4	4.41	227	318	1.1	70	120[10]

(Continued)

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TABLE 5.3.1 Voltage, Capacity, and Specific Energy of Major Battery and Several Full Cell Systems—Theoretical and Practical Values (*Continued*)

Battery type	Anode	Cathode	Reaction mechanism	Theoretical values[†]				Practical battery[‡]		
				V	g/Ah	Ah/kg	Specific energy Wh/kg	Nominal voltage V	Specific energy Wh/kg	Energy density Wh/L
Zinc/chlorine	Zn	Cl_2	$Zn + Cl_2 \rightarrow ZnCl_2$	2.12	2.54	394	835	—	—	—
Zinc/bromine	Zn	Br_2	$Zn + Br_2 \rightarrow ZnBr_2$	1.85	4.17	309	572	1.6	70	60
Lithium-ion	Li_xC_6	$Li_{(i-x)}CoO_2$	$Li_xC_6 + Li_{(i-x)}CoO_2 \rightarrow LiCoO_2 + C_6$	4.1	9.98	100	410	4.1	150	400[5]
Lithium/ manganese dioxide	Li	MnO_2	$Li + Mn^{IV}O_2 \rightarrow Mn^{IV}O_2(Li^+)$	3.5	3.50	286	1001	3.0	120	265
Lithium/ iron disulfide[2]	Li(Al)	FeS_2	$2Li(Al) + FeS_2 \rightarrow Li_2FeS_2 + 2Al$	1.73	3.50	285	493	1.7	180[11]	350[11]
Lithium/ iron monosulfide[2]	Li(Al)	FeS	$2Li(Al) + FeS \rightarrow Li_2S + Fe + 2Al$	1.33	2.90	345	459	1.3	130[11]	220[11]
Sodium/ sulfur[2]	Na	S	$2Na + 3S \rightarrow Na_2S_3$	2.1	2.65	377	792	2.0	170[11]	345[11]
Sodium/ nickel chloride[2]	Na	$NiCl_2$	$2Na + NiCl_2 \rightarrow 2NaCl + Ni$	2.58	3.28	305	787	2.6	115[11]	190[11]
Fuel cells										
H_2/O_2	H_2	O_2	$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$	1.23	0.336	2975	3660	—	—	—
H_2/air	H_2	Ambient air	$H_2 + (\tfrac{1}{2}O_2) \rightarrow H_2O$	1.23	0.037	26587	32702	—	—	—
Methanol/O_2	CH_3OH	O_2	$CH_3OH + \tfrac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$	1.24	0.50	2000	2480	—	—	—
Methanol/air	CH_3OH	Ambient air	$CH_3OH + (\tfrac{3}{2}O_2) \rightarrow CO_2 + 2H_2O$	1.24	0.20	5020	6225	—	—	—

[†]Based on active anode and cathode materials only, including O_2 but not air (electrolyte not included).
[‡]These values are for single cell batteries based on identified design and at discharge rates optimized for energy density, using midpoint voltage.
(1) MH = metal hydride, data based on 1.7 percent hydrogen storage (by weight).
(2) High temperature batteries.
(3) Solid electrolyte battery (Li/I_2 (P2VP)).
(4) Cylindrical bobbin-type batteries.
(5) Cylindrical spiral-wound batteries.
(6) Button type batteries.
(7) Water-activated.
(8) Automatically activated 2- to 10-min rate.
(9) With lithium anodes.
(10) Prismatic batteries.
(11) Value based on cell performance.
Source: D. Linden and T. B. Reddy (eds.), "Handbook of Batteries," 3rd ed., McGraw-Hill, 2001.

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Temperature During Discharge.   The temperature at which the battery is discharged has a pronounced effect on its service and voltage characteristics. This is because of the reduction in chemical activity and the increase in battery internal resistance at lower temperatures. Curves 3, 2, 4, and 5 of Fig. 5.3.2, can also represent discharges at the same current drawn but at progressively reduced temperatures. The specific characteristics vary for each battery system and discharge rate, but generally best performance is obtained between 20 and 40°C. At higher temperatures, chemical deterioration may be rapid enough during discharge to cause a loss in capacity.

Size.   Battery size influences the voltage characteristics by its effect on current density. A given current drain may be a severe load on a small battery, giving a discharge similar to curve 4 or 5 (Fig. 5.3.2), but be a mild load to a larger battery and give a discharge similar to curve 3. It is often possible to obtain more than a proportional increase in the service life by increasing the size of the battery. The absolute value of current, therefore, is not the key influence, although its relation to the size of the battery, i.e., the current density, is important.

Age and Storage Condition.   Batteries are a perishable product and deteriorate as a result of chemical action that proceeds during storage. The type of battery, design, temperature, and length of storage period are factors that affect the shelf life of the battery. Since shelf-discharge proceeds at a lower rate at reduced temperatures, refrigerated storage extends the shelf life. Refrigerated batteries should be warmed before discharge to obtain maximum capacity.

General Characteristics

The many and varied requirements for battery power and the multitude of environmental and electrical conditions under which they must operate necessitate the use of a number of different battery types and designs, each having superior performance under certain discharge conditions. In addition to the theoretical values, the practical performance characteristics of the major primary and secondary batteries are listed in Table 5.3.1. A comparison of the performance of some typical batteries is given in Fig. 5.3.3.
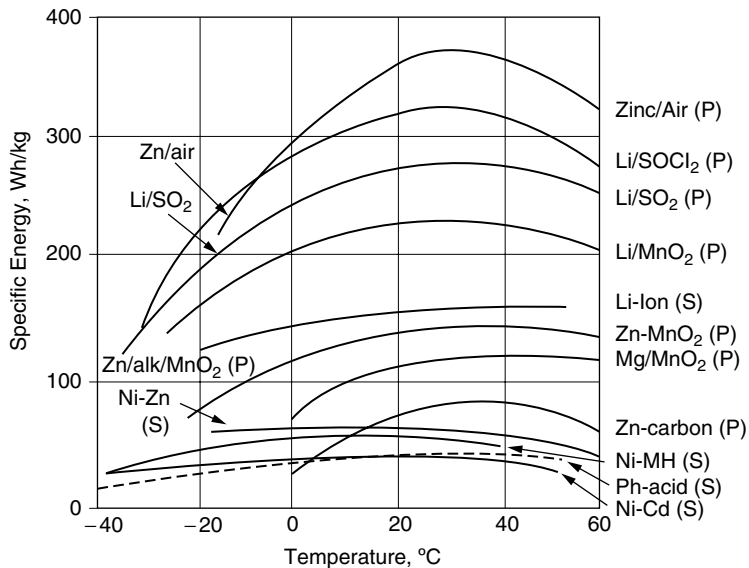
FIGURE 5.3.3   Comparative performance of battery system; primary (P), secondary (S).
Source: D. Linden and T. B. Reddy (eds.), "Handbook of Batteries," 3rd ed. McGraw-Hill, 2001.

TYPES OF BATTERIES

Batteries are generally identified as primary or secondary.

Primary batteries are not capable of being easily recharged electrically and hence are used or discharged a single time and discarded. Many of the primary batteries, in which the electrolyte is contained by absorbent or separator materials (i.e., there is no free or liquid electrolyte), are termed *dry cells*.

Secondary or rechargeable batteries are those that are capable of being recharged electrically, after discharge, to their original condition by passing current through them in the opposite direction to that of the discharge current. They are electric-energy storage devices and are also known as storage batteries or accumulators.

Reserve batteries are primary types in which a key component is separated from the rest of the battery. In the inert condition, the battery is capable of long-term storage. Usually, the electrolyte is the component that is isolated. The battery is activated by introducing this component into the cell structure. In other systems, such as the thermal battery, the battery is inactive until it is heated, melting a solid electrolyte, which then becomes conductive.

PRIMARY BATTERIES

The general advantages of primary batteries are reasonably good shelf life; high energy densities at low to moderate rates; little, if any, maintenance; and ease of use. Typical theoretical and practical characteristics of these batteries are shown in Table 5.3.1 and applications in Table 5.3.2.

Leclanché Battery (Zn/MnO$_2$)

The Leclanché dry cell, known for over 100 years, is still one of the more widely used worldwide but has given way to the popular alkaline cell in the United States and Europe.

The most common construction uses a cylindrical zinc container as the negative electrode and manganese dioxide as the positive element, with electrical connection through a carbon electrode. A paste or paper separator separates the two electrodes. Another common design is the flat cell, used only in multicell batteries, which offers better volume utilization. The Leclanché cell is fabricated in a number of sizes of varying diameter (or cross section) and height.

The capacity varies with different discharge conditions (higher capacities are available at lower current or power densities) to the point where shelf deterioration during the long discharge causes a loss of capacity. Performance is usually better under intermittent discharge, as the cell is given an opportunity to recover. This effect is particularly noticeable at the heavier discharge loads.

Leclanché cells operate best at normal temperatures (20°C). The energy output of the cell increases with higher operating temperatures, but prolonged exposure to high temperatures (50°C) will cause rapid deterioration. The capacity of the Leclanché cell falls off rapidly with decreasing temperature and is essentially zero below −20°C. The effects are more pronounced at heavier current drains. For best operation at low ambient temperatures, the Leclanché cell should be kept warm by some appropriate means. On the other hand there is an advantage in storing batteries at low temperatures for preserving their capacity.

Zinc Chloride Battery

A modification of the Leclanché battery is the zinc chloride battery. The construction is similar to the conventional carbon-zinc cell but the electrolyte contains only zinc chloride, without the saturated solution of ammonium chloride. The zinc chloride battery is a high-performance battery with improved high-rate and low-temperature performance and a reduced incidence of leakage.

TABLE 5.3.2 Major Characteristics and Applications of Primary Batteries

System	Characteristics	Applications
Zinc-carbon (Leclanché) Zinc/MnO$_2$	Common, low-cost primary battery, available in a variety of sizes	Flashlight, portable radios, toys, novelties, instruments
Magnesium (Mg/MnO$_2$)	High-capacity primary battery, long shelf life	Military receiver-transmitters, aircraft emergency transmitters
Mercury (Zn/HgO)	Highest capacity (by volume) of conventional types, flat discharge, good shelf life	Hearing aids, medical devices (pacemakers), photography, detectors, military equipment but in limited use due to environmental hazard of mercury
Mercad (Cd/HgO)	Long shelf life, good low- and high-temperature performance, low energy density	Special applications requiring operation under extreme temperature conditions and long life, in limited use
Alkaline (Zn/alkaline/MnO$_2$)	Most popular general-purpose premium battery, good low-temperature and high-rate performance, moderate cost	Most popular primary-battery, used in a variety of portable battery operated equipments
Silver/zinc (Zn/Ag$_2$O)	Highest capacity (by weight) of conventional types, flat discharge, good shelf life, costly	Hearing aids, photography, electric watches, missiles, underwater, and space application (larger sizes)
Zinc/air (Zn/O$_2$)	Highest energy density, low cost, not independent of environmental conditions	Special applications, hearing aids, pagers, medical devices, portable electronics
Lithium/soluble cathode	High energy density, long shelf life, good performance over wide temperature range	Wide range of applications (capacity from 1 to 10,000 Ah) requiring high energy density, long shelf life, e.g., from utility meters to military power applications
Lithium/solid cathode	High energy density, good rate capability and low-temperature performance, long shelf life, competitive cost	Replacement for conventional button and cylindrical cell applications
Lithium/solid electrolyte	Extremely long shelf life, low-power battery	Medical electronics, memory circuits, fusing

Source: D. Linden and T. B. Reddy (eds.) "Handbook of Batteries," 3rd ed., McGraw-Hill, 2001.

Magnesium Primary Batteries (Mg/MnO$_2$)

The magnesium battery was developed for military use and has two principal advantages over the zinc dry cell: (1) it has twice the capacity or service life of an equivalently sized zinc cell, and (2) it can retain this capacity during storage in an undischarged condition. The construction of the magnesium dry cell is similar to that of the cylindrical zinc cell, except that a magnesium can is used instead of the zinc container. The magnesium cell has a mechanical vent for the escape of hydrogen gas, which forms as a result of a parasitic reaction during the discharge of the battery. Magnesium batteries have not been fabricated successfully in flat-cell designs.

The good shelf life of the magnesium battery results from a film that forms on the inside of the magnesium can, preventing corrosion. This film, however, is responsible for a delay in the battery's ability to deliver full output voltage after it is placed under load. Nevertheless, there has been little commercial interest in this battery because of the generation of hydrogen and the relatively poor storageability of a partially discharged cell.

Zinc/Mercuric Oxide Battery (Zn/HgO)

The zinc/mercuric oxide battery was another important zinc anode primary system. This battery was developed during World War II for military communication applications because of its good shelf life and high volumetric energy density. In the postwar period, it was used in small button, flat, or cylindrical configurations as the power source in electronic watches, calculators, hearing aids, photographic equipment, and similar applications requiring a reliable long-life miniature power source. In the past decade, the use of the mercuric oxide battery has about ended mainly because of environmental problems associated with mercury and with its replacement by other battery systems, such as the zinc/air and lithium batteries, which have superior performance for many applications.

Alkaline-MnO$_2$ Cell (Zn/MnO$_2$)

In the past decade, an increasing portion of the primary battery market has shifted to the Zn/alkaline/MnO$_2$ battery. This system has become the battery of choice because of its superior performance at the higher current drains and low temperatures and its better shelf life. While more expensive than the Leclanché battery on a unit basis, it is more cost-effective for those applications requiring the high-rate or low-temperature capability, where the alkaline battery can outperform the Leclanché battery by a factor of 2 to 10. In addition, because of the advantageous shelf life of the alkaline cell, it is often selected for applications in which the battery is used intermittently and exposed to uncontrolled storage conditions (such as consumer flashlights and smoke alarms), but must perform dependably when required. Most recent advances have been the design of batteries providing improved high rate performance for use in cameras and other consumer electronics requiring this high power capability.

Cadmium/Mercuric Oxide Battery (Cd/HgO)

The substitution of cadmium for the zinc anode (the cadmium/mercuric oxide cell) results in a lower-voltage but very stable system, with a shelf life of up to 10 years as well as performance at high and low temperatures. Because of the lower voltage, the watt-hour capacity of this battery is about 60 percent of the zinc/mercuric oxide battery capacity. Again, because of the hazardous characteristics of mercury and cadmium, the use of this battery is limited.

Zinc/Silver Oxide Battery (Zn/AgO)

The primary zinc/silver oxide battery is similar in design to the small zinc/mercuric oxide button cell, but it has a higher energy density (on a weight basis) and performs better at low temperatures. These characteristics make this battery system desirable for use in hearing aids, photographic applications, and electronic watches. However, because of its high cost and the development of other battery systems, the use of this battery system, as a primary battery, has been limited mainly to small button battery applications where the higher cost is justified.

Lithium Primary Batteries

The lithium battery is the most recent development with a number of advantages over other primary-battery systems. Lithium is an attractive anode because of its reactivity, light weight, and high voltage; cell voltages range between 2 and 3.6 V, depending on the cathode material.

The advantages of the lithium battery include high energy density (see Fig. 5.3.3), high power density, flat discharge characteristics; excellent service over a wide temperature range, down to –40°C or below. Excellent shelf life of 5 to 10 years at normal room temperatures is expected.

Nonaqueous solvents must be used as the electrolyte because of the solubility of lithium in aqueous solutions. Organic solvents, such as acetonitrile and propylene carbonate, and inorganic solvents, such as thionyl chloride, are typical. A compatible solute is added to provide the necessary electrolyte conductivity. A number of different materials (sulfur dioxide, carbon mono-fluoride, vanadium pentoxide, copper sulfide) are used as the active cathode material. Hence the name lithium battery refers to a family of battery systems, ranging in size from 100 mAh to 10,000 Ah; they all use lithium as the anode but differ widely in design and chemical action.

The lithium primary batteries can be classified into three categories. The smallest are the low-power solid-state batteries with excellent shelf life, and are used in applications such as cardiac pacemakers and battery backup for volatile computer memory, where reliability and long shelf life are paramount requirements. In the second category are the solid-cathode batteries, which are designed in coin or small cylindrical configurations. These batteries have replaced the conventional primary batteries in watches, calculators, memory circuits, photographic equipment, communication devices, and other such applications where its high energy density and long shelf life are critical. The soluble-cathode batteries (using gases or liquid cathode materials) constitute the third category. These batteries are typically constructed in a cylindrical configuration, as flat disks, or in prismatic containers using flat plates. These batteries, up to about 35 Ah in size, are used in military and industrial applications, lighting products, and other devices where small size, low weight, and operation over a wide temperature range are important. The larger batteries have been used in special military applications or as standby emergency power sources.

Air Depolarized Batteries

These batteries, particularly the zinc/air battery system, are noted for their high energy density, but they had been used only in large low-power batteries for signaling and navigational-aid applications. With the development of improved air electrodes, the high-rate capability of the system was improved and small button-type batteries are now used widely in hearing aids, electronics, and similar applications. These batteries have a very high energy density as no active cathode material is needed. Wider use of this system and the development of larger batteries have been slow because of some of their performance limitations (sensitivity to extreme temperatures, humidity and other environmental factors, as well as poor activated shelf life and low power density). Nevertheless, because of their attractive energy density, zinc/air and other metal/air batteries are now being seriously considered for a number of applications from portable consumer electronics and eventually for larger devices such as electric vehicles, possibly in a reserve or mechanically rechargeable configuration.

Solid Electrolyte Batteries

Most batteries depend on the ionic conductivity of liquid electrolytes for their operation. The solid electrolyte batteries depend on the ionic conductivity of an electronically nonconductive salt in the solid state, for example, Li^+ ion mobility in lithium iodide. Cells using these solid electrolytes are low-power (microwatt) devices but have an extremely long shelf life and can operate over a wide temperature range. The absence of liquid eliminates corrosion and gassing and permits the use of a hermetically sealed cell. The solid electrolyte batteries are used in medical electronics (in devices such as heart pacemakers), for memory circuits, and other such applications requiring a long-life, low-power battery.

SECONDARY (STORAGE) BATTERIES

Secondary batteries are characterized, in addition to their ability to be recharged, by high-power density, high discharge rate, flat discharge curves, and good low-temperature performance. Their energy densities are usually lower than those of primary batteries. Tables 5.3.1 and 5.3.3 list the characteristics and applications of secondary batteries.

The applications of secondary batteries fall into two major categories: (1) applications where the secondary battery is used essentially as a primary battery but recharged after use; secondary batteries are used in this manner for convenience (as in portable electronic devices), for cost savings (as they can be recharged rather than

TABLE 5.3.3   Major Characteristics and Applications of Secondary Batteries

System	Characteristics	Applications
Lead-acid:		
Automotive	Popular, low-cost secondary battery, moderate specific-energy, high-rate, and low-temperature performance, maintenance-free designs	Automotive SLI, golf carts, lawn mowers, tractors, aircraft, marine
Traction (motive power)	Designed for deep 6–9 h discharge, cycling service	Industrial trucks, materials handling, electric and hybrid electric vehicles, special types for submarine power
Stationary	Designed for standby float service, long life, VRLA designs	Emergency power, utilities, telephone, UPS, load leveling, energy storage, emergency lighting
Portable	Sealed, maintenance-free, low cost, good float capability, moderate cycle life	Portable tools, small appliances and devices, TV and portable electronic equipment
Nickel-cadmium:		
Industrial and FNC	Good high-rate, low-temperature capability, flat voltage, excellent cycle life	Aircraft batteries, industrial and emergency power applications, communication equipment
Portable	Sealed, maintenance-free, good high-rate low-temperature performance, excellent cycle life	Railroad equipment, consumer electronics, portable tools, pagers, appliances, and photographic equipment, standby power, memory backup
Nickel-metal hydride	Sealed, maintenance-free, higher capacity than nickel-cadmium batteries	Consumer electronics and other portable applications, electric and hybrid electric vehicles
Nickel-iron	Durable, rugged construction, long life, low specific energy	Materials handling, stationary applications, railroad cars
Nickel-zinc	High specific energy, extended cycle life and rate capability	Bicycles, scooters, trolling motors
Silver-zinc	Highest specific energy, very good high-rate capability, low cycle life, high cost	Lightweight portable electronic and other equipment, training targets, drones, submarines, other military equipment, launch vehicles and space probes
Silver-cadmium	High specific energy, good charge retention, moderate cycle life, high cost	Portable equipment requiring a lightweight, high-capacity battery, space satellites
Nickel-hydrogen	Long cycle life under shallow discharge, long life	Primarily for aerospace applications such as LEO and GEO satellites
Ambient-temperature rechargeable "primary" types [Zn/MnO_2]	Low cost, good capacity retention, sealed and maintenance-free, limited cycle life and rate capability	Cylindrical cell applications, rechargeable replacement for zinc-carbon and alkaline primary batteries, consumer electronics (ambient-temperature systems)
Lithium ion	High specific energy and energy density, long cycle life	Portable and consumer electronic equipment, electric vehicles, and space applications

Source: D. Linden and T. B. Reddy (eds.), "Handbook of Batteries," 3rd ed., McGraw-Hill, 2001.

replaced), or for power drains beyond the level of primary batteries; (2) applications where the secondary battery is used as an energy-storage device, being charged by primary energy source and delivering its energy to the load on demand. Examples are automotive and aircraft systems, emergency and standby power sources, and hybrid electric vehicles.

Lead-Acid Batteries

This is the most widely used and economical secondary battery. It uses sponge lead for the negative electrode, lead oxide for the positive, and a sulfuric acid solution for the electrolyte. As the cell discharges, the active materials are converted into lead sulfate and the sulfuric acid solution is diluted; i.e., its specific gravity decreases. On charge the reverse actions take place. A key factor is its low cost, good performance, and cycle life.

The lead-acid battery is designed in many configurations, from small sealed cells with a capacity of 1 Ah to large cells, up to 12,000 Ah. The automotive SLI battery is by far the most popular and the one in widest use. Most significant of the advances in SLI battery design are the use of lighter-weight plastic containers, the improvement in shelf life, the "dry-charge" process, and the "maintenance-free" design. The latter, using calcium-lead or low-antimony grids, has greatly reduced water loss during charging (minimizing the need to add water) and has reduced the self-discharge rate so that batteries can be shipped or stored in a wet, charged state for relatively long periods.

The lead-acid industrial storage batteries are generally larger than the SLI batteries, with a stronger, higher-quality construction. Applications of the industrial batteries fall in several categories. The motive power traction types are used in materials-handling trucks, tractors, mining vehicles, and, to a limited extent, golf carts and personnel carriers, although the majority in use are automotive-type batteries. A second category is diesel locomotive engine starting and the rapid-transit batteries, replacing the nickel-iron battery in the latter application. Significant advances are the use of lighter-weight plastic containers in place of the hard-rubber containers, better seals, and changes in the tubular positive-plate designs. Another category is stationary service: telecommunications systems, electric utilities for operating power distribution controls, emergency and standby power systems, uninterruptible power systems (UPS), and in railroads, signaling and car power systems.

The industrial batteries use three different types of positive plates: tubular and pasted flat plates for motive power, diesel engine cranking, and stationary applications, and Planté designs, forming the active materials from pure lead, mainly in the stationary batteries. The flat-plate batteries use either lead-antimony or lead-calcium grid alloys. A relatively recent development for the telephone industry has been the "round cell," designed for trouble-free long-life service. This battery uses plates, conical in shape with pure lead grids, which are stacked one above the other in a cylindrical cell container, rather than the normal prismatic structure with flat, parallel plates.

An important development in lead-acid battery technology is the valve-regulated lead-acid (VRLA) battery. These batteries operate on the principle of oxygen recombination, using a "starved" or immobilized electrolyte. The oxygen generated at the positive electrode during charge can, in these battery designs, diffuse to the negative electrode, where it can react, in the presence of sulfuric acid, with the freshly formed lead. The VRLA design reduces gas emission by over 95 percent as the generation of hydrogen is also suppressed. Oxygen recombination is facilitated by the use of a pressure-relief valve, which is closed during normal operation. When pressure builds up, the valve opens at a predetermined value, venting the gases. The valve reseals before the cell pressure decreases to atmospheric pressure. The VRLA battery is now used in about 70 percent of the telecommunication batteries and in about 80 percent of the uninterrupted power source (UPS) applications.

Smaller sealed lead-acid cells are used in emergency lighting and similar devices requiring backup power in the event of a utility power failure, portable instruments and tools, and various consumer-type applications. These small sealed lead-acid batteries are constructed in two configurations, prismatic cells with parallel plates, ranging in capacity from 1 to 30 Ah, and cylindrical cells similar in appearance to the popular primary alkaline cells and ranging in capacity up to 25 Ah. The acid electrolyte in these cells is either gelled or absorbed in the plates and in highly porous separators so they can be operated virtually in any position without the danger of leakage. The grids generally are of lead-calcium-tin alloy; some use grids of pure lead or a lead-tin alloy. The cells also include the features for oxygen recombination and are considered to be VRLA batteries.

Lead-acid batteries also are used in other types of applications, such as in submarine service, for reserve power in marine applications, and in areas where engine-generators cannot be used, such as indoors and in mining equipment. New applications, to take advantage of the cost-effectiveness of this battery, include load leveling for utilities and solar photovoltaic systems. These applications will require improvements in the energy and power density of the lead-acid battery.

A lead-acid battery can be charged at any rate that does not produce excessive gassing or high temperatures. The most common practice for recharging a fully discharged battery is to start the charge at the $C/5$ rate (amperes, corresponding to one-fifth the rated capacity of the battery) for 5 h, which will return about 80 to 85 percent of the battery's capacity. The charging current is then tapered to about one-half to complete the charge. In an emergency, fast or boost charging is used. In this type of charge, the current should not exceed the C rate or the battery can suffer damage.

The battery can also be *float-* or *trickle-*charged when it is continuously connected to an electrical system. The current should be regulated at a low level to maintain the battery in a charged condition (sufficient just to replace capacity loss because of stand) and to prevent overcharging. The battery manufacturers can supply detailed charging instructions.

Alkaline Secondary Batteries

Most of the other conventional types of secondary batteries use an aqueous alkaline solution (KOH or NaOH) as the electrolyte. Electrode materials are less reactive with alkaline electrolytes than with acid electrolytes. Furthermore, the charge-discharge mechanism in the alkaline electrolyte involves only the transport of oxygen or hydroxyl ions from one electrode to the other; hence the composition or concentration of the electrolyte does not change during charge and discharge.

Nickel-Cadmium Batteries.   The nickel-cadmium secondary battery is the most popular alkaline secondary battery and is available in several cell designs and in a wide range of sizes. The original cell design used the pocket-plate construction. The vented pocket-type cells are very rugged and can withstand both electrical and mechanical abuse. They have very long lives and require little maintenance beyond occasional topping with water. This type of battery is used in heavy-duty industrial applications such as materials-handling trucks, mining vehicles, railway signaling, emergency or standby power, and diesel engine starting. The sintered-plate construction is a more recent development, having higher energy density. It gives better performance than the pocket-plate type at high discharge rates and low temperatures but is more expensive. It is used in applications, such as aircraft engine starting and communications and electronics equipment, where the lighter weight and superior performance are required. Higher energy and power densities can be obtained by using nickel foam, nickel fiber, or plastic-bonded (pressed-plate) electrodes. The sealed cell is a third design. It uses an oxygen-recombination feature similar to the one used in sealed lead-acid batteries to prevent the buildup of pressure caused by gassing during charge. Sealed cells are available in prismatic, button, and cylindrical configurations and are used in consumer and small industrial applications.

Nickel-Iron Batteries.   The nickel-iron battery was important from its introduction in 1908 until the 1970s, when it lost its market share to the industrial lead-acid battery. It was used in materials-handling trucks, mining and underground vehicles, railroad and rapid-transit cars, and in stationary applications. The main advantages of the nickel-iron battery, with major cell components of nickel-plated steel, are extremely rugged construction, long life, and durability. Its limitations, namely, low specific energy, poor charge retention, and poor low-temperature performance, and its high cost of manufacture compared with the lead-acid battery led to a decline in usage.

Silver Oxide Batteries.   The silver-zinc (zinc/silver oxide) battery is noted for its high energy density, low internal resistance desirable for high-rate discharge, and a flat second discharge plateau. This battery system is useful in applications where high energy density is a prime requisite, such as electronic news gathering equipment, submarine and training target propulsion, and other military and space uses. It is not employed for general storage battery applications because its cost is high, its cycle life and activated life are limited, and its performance at low temperatures falls off more markedly than with other secondary battery systems.

The silver-cadmium (cadmium/silver oxide) battery has significantly longer cycle life and better low-temperature performance than the silver-zinc battery but is inferior in these characteristics compared with the

nickel-cadmium battery. Its energy density, too, is between that of the nickel-cadmium and the silver-zinc batteries. The battery is also very expensive, using two of the more costly electrode materials. As a result, the silver-cadmium battery was never developed commercially but is used in special applications, such as nonmagnetic batteries and space applications. Other silver battery systems, such as silver-hydrogen and silver-metal hydride couples, have been the subject of development activity but have not reached commercial viability.

Nickel-Zinc Batteries.   The nickel-zinc (zinc/nickel oxide) battery has characteristics midway between those of the nickel-cadmium and the silver-zinc battery systems. Its energy density is about twice that of the nickel-cadmium battery, but the cycle life previously has been limited because of the tendency of the zinc electrode toward shape change, which reduces capacity and dendrite formations, which cause internal short-circuiting.

Recent development work has extended the cycle life of nickel-zinc batteries through the use of additives in the negative electrode in conjunction with the use of a reduced concentration of KOH to repress zinc solubility in the electrolyte. Both of these modifications have extended the cycle life of this system so that it is now being marketed for use in electric bicycles, scooters, and trolling motors in the United States and Asia.

Hydrogen Electrode Batteries.   Another secondary battery system uses hydrogen for the active negative material (with a fuel-cell-type electrode) and a conventional positive electrode such as nickel oxide. These batteries are being used exclusively for the aerospace programs, which require long cycle life at low depth of discharge. The high cost of these batteries is a disadvantage, which limits their application. A further extension is the sealed nickel/metal hydride battery where the hydrogen is absorbed, during charge, by a metal alloy forming a metal hydride. This metal alloy is capable of undergoing a reversible hydrogen absorption-desorption reaction as the battery is charged and discharged, respectively. The advantage of this battery is that its specific energy and energy density are significantly higher than that of the nickel-cadmium battery. The sealed nickel-metal hydride battery, manufactured in small prismatic and cylindrical cells, is being used for portable electronic applications and are being employed for other applications including hybrid electric vehicles. Larger sizes are finding use in electric vehicles.

Zinc/Manganese Dioxide Batteries.   Several of the conventional primary battery systems have been manufactured as rechargeable batteries, but the only one currently being manufactured is the cylindrical cell using the zinc/alkaline-manganese dioxide chemistry. Its major advantage is a higher capacity than the conventional secondary batteries and a lower initial cost, but its cycle life and rate capability are limited.

Advanced Secondary Batteries

A number of battery systems are being studied for such applications as electric vehicles and utility power which require a high specific energy (in the order of 200 Wh/kg), high power density and low cost. These include: (1) high temperature systems using molten salt electrolytes, (2) high temperature systems using ceramic or glass electrolytes, (3) aqueous zinc halogen batteries. Some of this work, particularly for electric vehicles, has been deemphasized in favor of lithium-ion and other conventional batteries operating at ambient temperatures, which are now demonstrating energy and power capabilities approaching those of high temperature batteries.

Rechargeable Lithium Batteries

Rechargeable lithium batteries operating at room temperature offer several advantages compared to conventional aqueous technologies, including: (1) Higher energy density (up to 150 Wh/kg, 300 Wh/L), (2) Higher cell voltage (up to about 4 V per cell), and (3) Longer charge retention or shelf life (up to 5 to 10 years).

These advantageous characteristics result in part from the high standard potential and low electrochemical equivalent weight of lithium.

Ambient-temperature lithium rechargeable batteries, on the other hand, do not have the high-rate capability (because of the relatively poor conductivity of the aprotic organic or inorganic electrolytes that must be used because of the reactivity of lithium in aqueous electrolytes) nor, in some instances, the cycle life of conventional rechargeable batteries. In addition, the rechargeable lithium cells that use lithium metal as the negative electrode present potential safety problems, which are more challenging than those with primary lithium batteries.

This is because of a three- to fivefold excess of lithium that is required for these types of cells in order to obtain a reasonable cycle life and to the reactivity of the porous high surface area lithium that is formed during cycling with the electrolyte. For these reasons, these types of batteries have had little commercial success except for small, low energy coin batteries where an aluminum lithium alloy is generally used.

Another type of rechargeable lithium battery that has been recently developed and is achieving commercial success, is the "lithium-ion" battery. This battery does not use metallic lithium and thus should minimize the safety concerns. The lithium-ion battery uses lithium intercalation compounds as the positive and negative materials. As the battery is cycled, lithium ions exchange between the positive and negative electrodes. The negative electrode material is typically a graphite carbon, a layered material. The positive material is typically a metal oxide, also with a layered structure, such as lithium cobalt oxide or lithium manganese dioxide. In the charge/discharge process, lithium ions are inserted or extracted from the interstitial space between atomic layers within the active material. Liquid electrolytes, using lithium salts in organic solvents, are the most common electrolytes. There is increasing interest and activity with polymer electrolytes as these allow for a greater flexibility in cell design and better safety characteristics.

Lithium-ion batteries are presently manufactured in a variety of designs in sizes as small as 0.1 Ah to large units of about 100 Ah but with the major emphasis on consumer electronic applications such as laptop computers, camcorders, and cell phones. Various cell designs have been developed including cylindrical, wound prismatic, and flat plate prismatic configurations. The lithium-ion batteries have a number of advantages, including a high cell voltage, a high specific energy and energy density, a competitive specific power, long cycle life, and a broad operating temperature range. Lithium-ion batteries should not be overcharged nor overdischarged. Electronic management circuits or mechanical disconnect devices are usually used with lithium-ion batteries to provide protection from overcharge, overdischarge, and over temperature conditions.

It is expected that the market share enjoyed by the lithium rechargeable battery will increase significantly during the next decade because of its high energy density and its ability to meet consumer demands for lighter weight and longer service more adequately than the conventional aqueous rechargeable batteries. Larger cells also are being considered for a number of military and commercial applications, including underwater propulsion and electric vehicles.

RESERVE BATTERIES

Batteries that use highly active component materials to obtain the required high energy, high power, and/or low-temperature performance, are often designed in a reserve construction to withstand deterioration in storage and to eliminate self-discharge prior to use. These batteries are used primarily to deliver high power for relatively short periods of time after activation in such applications as radiosondes, fuzes, missiles, torpedoes, and other weapon systems. The reserve design also is used for batteries required to meet extremely long or environmentally severe storage requirements.

In the reserve structure, one of the key components of the cells is separated from the remainder of the cell until activation. In this inert condition, chemical reaction between the cell components (self-discharge) is prevented, and the battery is capable of long-term storage. The electrolyte is the component that is usually isolated, although in some water-activated batteries the electrolyte solute is contained in the cell and only water is added.

The reserve batteries can be classified by the type of activating medium or mechanism that is involved in the activation:

Water-activated batteries: Activation by fresh or seawater.

Electrolyte-activated batteries: Activation by the complete electrolyte or with the electrolyte solvent. The electrolyte solute is contained in or formed in the cell.

Gas-activated batteries: Activation by introducing a gas into the cell. The gas can be either the active cathode material or part of the electrolyte.

Heat-activated batteries: A solid salt electrolyte is heated to the molten condition and becomes ionically conductive, thus activating the cell. These are known as thermal batteries.

Activation of the reserve battery is accomplished by adding the missing component just prior to use. In the simplest designs, this is done by manually pouring or adding the electrolyte into the cell or placing the battery in the electrolyte (as in the case of seawater-activated batteries). In more sophisticated applications the electrolyte storage and the activation mechanism are contained within the overall battery structure, and the electrolyte is brought automatically to the active electrochemical components by remotely activating the activation mechanism. Thermal batteries are activated by igniting a heat source that is contained within the battery.

FUEL CELLS

Fuel cells, such as 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 not an integral part of the device (as in a battery), but are fed into the fuel cell from an external source when power is desired. The fuel cell differs from a battery in that it has the capability of producing electrical energy as long as the active materials are fed to the electrodes (assuming the electrodes do not fail). The battery will cease to produce electrical energy when the limiting reactant stored within the battery is consumed.

The electrode materials of the fuel cell are inert in that they are not consumed during the cell reaction, but have catalytic properties that enhance the electroreduction or electrooxidation of the reactants (the active materials).

The anode active materials used in fuel cells are generally gaseous or liquid (compared with the metal anodes generally used in most batteries) and are fed into the anode side of the fuel cell. As these materials are more like the conventional fuels used in heat engines, the term "fuel cell" has become popular to describe these devices. Oxygen or air is the predominant oxidant and is fed into the cathode side of the fuel cell.

TABLE 5.3.4 Types of Fuel Cells

1. Solid Oxide (SOFC): These cells use a solid oxygen-ion-conducting metal oxide electrolyte. They operate at about 1000°C, with an efficiency of up to 60 percent. They are slow to start up, but once running, provide high grade waste heat that can be used to heat buildings. They may find application in industrial and large-scale applications.

2. Molten Carbonate (MCFC): These cells use a mixed alkali-carbonate molten salt electrolyte and operate at about 600°C. They are being developed for continuously operating facilities, and can use coal-based or marine diesel fuels.

3. Phosphoric Acid (PAFC): This is the most commonly used type of fuel cell for stationary commercial sites such as hospitals, hotels, and office buildings. The electrolyte is concentrated phosphoric acid. The fuel cell operates at about 200°C. It is highly efficient and can generate energy at up to 85 percent (40 percent as electricity and another 45 percent if the heat given off is also used).

4. Alkaline (AFC): These are used by NASA on the manned space missions, and operate well at about 200°C. They use alkaline potassium hydroxide as the electrolyte and can generate electricity up to 70 percent efficiency. A disadvantage of this system is that it is restricted to fuels and oxidants that do not contain carbon dioxide.

5. Proton Exchange Membrane (PEM): These cells use a perfluorinated ionomer polymer membrane electrolyte that passes protons from the anode to the cathode. They operate at a relatively low temperature (70 to 85°C), and are especially notable for their rapid start-up time. These are being developed for use in transportation applications and for portable and small fuel cells.

6. Direct Methanol (DMFC): These fuel cells directly convert liquid methanol (methyl alcohol) in an aqueous solution that is oxidized at the anode. Like PEMs, these also use a membrane electrolyte, and operate at similar temperatures. This fuel cell is still in the development stage.

7. Regenerative (RFC): These are closed-loop generators. A powered electrolyzer separates water into hydrogen and oxygen, which are then used by the fuel cell to produce electricity and exhaust (water). That water can then be recycled into the powered electrolyzer for another cycle.

Sources: (1) Connecticut Academy of Science and Engineering Reports, Vol. 15, No. 2000.
             (2) D. Linden and T. B. Reddy (eds.), "Handbook of Batteries," 3rd ed. McGraw-Hill, 2001.

Fuel cells have been of interest for over 150 years as a potentially more efficient and less polluting means for converting hydrogen and carbonaceous or fossil fuels to electricity compared to conventional engines. A well-known application of the fuel cell has been the use of the hydrogen/oxygen fuel cell, using cryogenic fuels, in space vehicles for over 40 years. Use of the fuel cell in terrestrial applications has been developing slowly, but recent advances has revitalized interest in air-breathing systems for a variety of applications, including utility power, load leveling, dispersed or on-site electric generators and electric vehicles.

Fuel cell technology can be classified into two categories:

1. Direct systems where fuels, such as hydrogen, methanol and hydrazine, can react directly in the fuel cell

2. Indirect systems in which the fuel, such as natural gas or other fossil fuel, is first converted by reforming to a hydrogen-rich gas that is then fed into the fuel cell

Fuel cell systems can take a number of configurations depending on the combinations of fuel and oxidant, the type of electrolyte, the temperature of operation, and the application, and so forth. Table 5.3.4 lists the various types of fuel cells distinguished by the electrolyte and operating temperature.

More recently, fuel cell technology has moved toward portable applications, historically the domain of batteries, with power levels from less than 1 to about 100 W, blurring the distinction between batteries and fuel cells. Metal/air batteries, particularly those in which the metal is periodically replaced, can be considered a "fuel cell" with the metal being the fuel. Similarly, small fuel cells, now under development, which are "refueled" by replacing an ampule of fuel can be considered a "battery."

Table 5.3.1 gives both theoretical and practical values of voltage, capacity, and specific energy for several fuel cell systems.

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