PRINCIPLES OF OPERATION

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CHAPTER 1 BASIC CONCEPTS

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1.1 COMPONENTS OF CELLS AND BATTERIES

A battery is a device that converts the chemical energy contained in its active materials directly into electric energy by means of an electrochemical oxidation-reduction (redox) reaction. In the case of a rechargeable system, the battery is recharged by a reversal of the process. This type of reaction involves the transfer of electrons from one material to another through an electric circuit. In a nonelectrochemical redox reaction, such as rusting or burning, the transfer of electrons occurs directly and only heat is involved. As the battery electrochemically converts chemical energy into electric energy, it is not subject, as are combustion or heat engines, to the limitations of the Carnot cycle dictated by the second law of thermodynamics. Batteries, therefore, are capable of having higher energy conversion efficiencies.

While the term "battery" is often used, the basic electrochemical unit being referred to is the "cell." A battery consists of one or more of these cells, connected in series or parallel, or both, depending on the desired output voltage and capacity.*

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.

^{*}Cell vs. Battery: A *cell* is the basic electrochemical unit providing a source of electrical energy by direct conversion of chemical energy. The cell consists of an assembly of electrodes, separators, electrolyte, container and terminals. A *battery* consists of one or more electrochemical cells, electrically connected in an appropriate series/parallel arrangement to provide the required operating voltage and current levels, including, if any, monitors, controls and other ancillary components (e.g. fuses, diodes), case, terminals and markings. (Although much less popular, in some publications, the term "battery" is considered to contain two or more cells.)

Popular usage considers the "battery" and not the "cell" to be the product that is sold or provided to the "user." In this 3rd Edition, the term "cell" will be used when describing the cell component of the battery and its chemistry. The term "battery" will be used when presenting performance characteristics, etc. of the product. Most often, the electrical data is presented on the basis of a single-cell battery. The performance of a multicell battery will usually be different than the performance of the individual cells or a single-cell battery (see Section 3.2.13).

3. The electrolyte—the ionic conductor—which provides the medium for transfer of charge, as ions, inside the cell between the anode and cathode. 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 solid electrolytes, which are ionic conductors at the operating temperature of the cell.

The most advantageous combinations of anode and cathode materials are those that will be lightest and give a high cell voltage and capacity (see Sec. 1.4). Such combinations may not always be practical, however, due to reactivity with other cell components, polarization, difficulty in handling, high cost, and other deficiencies.

In a practical system, the anode is selected with the following properties in mind: efficiency as a reducing agent, high coulombic output (Ah/g), good conductivity, stability, ease of fabrication, and low cost. Hydrogen is attractive as an anode material, but obviously, must be contained by some means, which effectively reduces its electrochemical equivalence. Practically, metals are mainly used as the anode material. Zinc has been a predominant anode because it has these favorable properties. Lithium, the lightest metal, with a high value of electrochemical equivalence, has become a very attractive anode as suitable and compatible electrolytes and cell designs have been developed to control its activity.

The cathode must be an efficient oxidizing agent, be stable when in contact with the electrolyte, and have a useful working voltage. Oxygen can be used directly from ambient air being drawn into the cell, as in the zinc/air battery. However, most of the common cathode materials are metallic oxides. Other cathode materials, such as the halogens and the oxyhalides, sulfur and its oxides, are 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 nonreactivity with the electrode materials, little change in properties with change in temperature, safety in handling, and low cost. Most electrolytes are aqueous solutions, but there are important exceptions as, for example, in thermal and lithium anode batteries, where molten salt and other nonaqueous electrolytes are used to avoid the reaction of the anode with the electrolyte.

Physically the anode and cathode electrodes are electronically isolated in the cell to prevent internal short-circuiting, but are surrounded by the electrolyte. In practical cell designs a separator material is used to separate the anode and cathode electrodes mechanically. The separator, however, is permeable to the electrolyte in order to maintain the desired ionic conductivity. In some cases the electrolyte is immobilized for a nonspill design. Electrically conducting grid structures or materials may also be added to the electrodes to reduce internal resistance.

The cell itself can be built in many shapes and configurations—cylindrical, button, flat, and prismatic—and the cell components are designed to accommodate the particular cell shape. 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.

1.2 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. Within this classification, other classifications are used to identify particular structures or designs. The classification used in this handbook for the different types of electrochemical cells and batteries is described in this section.

1.2.1 Primary Cells or Batteries

These batteries are not capable of being easily or effectively recharged electrically and, hence, are discharged once and discarded. Many primary cells in which the electrolyte is contained by an absorbent or separator material (there is no free or liquid electrolyte) are termed "dry cells."

The primary battery is a convenient, usually inexpensive, lightweight source of packaged power for portable electronic and electric devices, lighting, photographic equipment, toys, memory backup, and a host of other applications, giving freedom from utility power. 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 highcapacity primary batteries are used in military applications, signaling, standby power, and so on, the vast majority of primary batteries are the familiar single cell cylindrical and flat button batteries or multicell batteries using these component cells.

1.2.2 Secondary or Rechargeable Cells or Batteries

These batteries can be 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 storage devices for electric energy and are known also as "storage batteries" or "accumulators."

The applications of secondary batteries fall into two main categories:

- 1. Those applications in which the secondary battery is used as an energy-storage device, generally being electrically connected to and charged by a prime energy source and delivering its energy to the load on demand. Examples are automotive and aircraft systems, emergency no-fail and standby (UPS) power sources, hybrid electric vehicles and stationary energy storage (SES) systems for electric utility load leveling.
- **2.** Those applications in which the secondary battery is used or discharged essentially as a primary battery, but recharged after use rather than being discarded. Secondary batteries are used in this manner as, for example, in portable consumer electronics, power tools, electric vehicles, etc., for cost savings (as they can be recharged rather than replaced), and in applications requiring power drains beyond the capability of primary 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 generally lower than those of primary batteries. Their charge retention also is poorer than that of most primary batteries, although the capacity of the secondary battery that is lost on standing can be restored by recharging.

Some batteries, known as "mechanically rechargeable types," are "recharged" by replacement of the discharged or depleted electrode, usually the metal anode, with a fresh one. Some of the metal/air batteries (Chap. 38) are representative of this type of battery.

1.2.3 Reserve Batteries

In these primary types, a key component is separated from the rest of the battery prior to activation. In this condition, chemical deterioration or self-discharge is essentially eliminated, and the battery is capable of long-term storage. Usually the electrolyte is the component that is isolated. In other systems, such as the thermal battery, the battery is inactive until it is heated, melting a solid electrolyte, which then becomes conductive.

The reserve battery design is used to meet extremely long or environmentally severe storage requirements that cannot be met with an "active" battery designed for the same performance characteristics. These batteries are used, for example, to deliver high power for relatively short periods of time, in missiles, torpedoes, and other weapon systems.

1.2.4 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 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 which enhance the electroreduction or electro-oxidation 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.

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 which 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, etc.

More recently, fuel cell technology has moved towards portable applications, historically the domain of batteries, with power levels from less than 1 to about 100 watts, blurring the distinction between batteries and fuel cells. Metal/air batteries (see Chap. 38), 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 "refueld" by replacing an ampule of fuel can be considered a "battery."

Fuel cells were not included in the 2nd Edition of this Handbook as the technical scope and applications at that time differed from that of the battery. Now that small to medium size fuel cells may become competitive with batteries for portable electronic and other applications, these portable devices are covered in Chap. 42. Information on the larger fuel cells for electric vehicles, utility power, etc can be obtained from the references listed in Appendix F "Bibliography."

1.3 OPERATION OF A CELL

1.3.1 Discharge

The operation of a cell during discharge is also shown schematically in Fig. 1.1. When the cell is connected to an external load, electrons flow from the anode, which is oxidized, through the external load to the cathode, where the electrons are accepted and the cathode material is reduced. The electric circuit is completed in the electrolyte by the flow of anions (negative ions) and cations (positive ions) to the anode and cathode, respectively.



FIGURE 1.1 Electrochemical operation of a cell (discharge).

The discharge reaction can be written, assuming a metal as the anode material and a cathode material such as chlorine (Cl_2) , as follows:

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

$$Zn \rightarrow Zn^{2+} + 2e$$

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

$$Cl_2 + 2e \rightarrow 2Cl^-$$

Overall reaction (discharge):

$$Zn + Cl_2 \rightarrow Zn^{2+} + 2Cl^{-}(ZnCl_2)$$

1.3.2 Charge

During the recharge of a rechargeable or storage cell, the current flow is reversed and oxidation takes place at the positive electrode and reduction at the negative electrode, as shown in Fig. 1.2. As the anode is, by definition, the electrode at which oxidation occurs and the cathode the one where reduction takes place, the positive electrode is now the anode and the negative the cathode.

In the example of the Zn/Cl_2 cell, the reaction on charge can be written as follows:

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

$$Zn^{2+} + 2e \rightarrow Zn$$

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

$$2Cl^- \rightarrow Cl_2 + 2e$$

Overall reaction (charge):

$$Zn^{2+} + 2Cl^{-} \rightarrow Zn + Cl_{2}$$



FIGURE 1.2 Electrochemical operation of a cell (charge).

1.3.3 Specific Example: Nickel-Cadmium Cell

The processes that produce electricity in a cell are chemical reactions which either release or consume electrons as the electrode reaction proceeds to completion. This can be illustrated with the specific example of the reactions of the nickel-cadmium cell. At the anode (negative electrode), the discharge reaction is the oxidation of cadmium metal to cadmium hydroxide with the release of two electrons,

$$Cd + 2OH^{-} \rightarrow Cd(OH)_{2} + 2e$$

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

 $NiOOH + H_2O + e \rightarrow OH^- + Ni(OH)_2$

When these two "half-cell" reactions occur (by connection of the electrodes to an external discharge circuit), the overall cell reaction converts cadmium to cadmium hydroxide at the anode and nickel oxyhydroxide to nickel hydroxide at the cathode,

$$Cd + 2NiOOH + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$$

This is the discharge process. If this were a primary non-rechargeable cell, at the end of discharge, it would be exhausted and discarded. The nickel-cadmium battery system is, however, a secondary (rechargeable) system, and on recharge the reactions are reversed. At the negative electrode the reaction is:

$$Cd(OH)_2 + 2e \rightarrow Cd + 2OH^2$$

At the positive electrode the reaction is:

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e$$

After recharge, the secondary battery reverts to its original chemical state and is ready for further discharge. These are the fundamental principles involved in the charge–discharge mechanisms of a typical secondary battery.

1.3.4 Fuel Cell

A typical fuel cell reaction is illustrated by the hydrogen/oxygen fuel cell. In this device, hydrogen is oxidized at the anode, electrocatalyzed by platinum or platinum alloys, while at the cathode oxygen is reduced, again with platinum or platinum alloys as electrocatalysts. The simplified anodic reaction is

 $2H_2 \rightarrow 4H^+ + 4e$

while the cathodic reaction is

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O$$

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

$$2H_2 + O_2 \rightarrow 2H_2O$$

1.4 THEORETICAL CELL VOLTAGE, CAPACITY, AND ENERGY

The theoretical voltage and capacity of a cell are a function of the anode and cathode materials. (See Chap. 2 for detailed electrochemical theory.)

1.4.1 Free Energy

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 Faraday ($\approx 96,500 \text{ C}$ or 26.8 Ah) n = number of electrons involved in stoichiometric reaction

 E^0 = standard potential, V

1.4.2 Theoretical Voltage

The standard potential of the cell is determined by the type of active materials contained in the cell. It can be 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 Appendix B.

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):

Anode (oxidation potential) + cathode (reduction potential) = standard cell potential.

For example, in the reaction $Zn + Cl_2 \rightarrow ZnCl_2$, the standard cell potential is:

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

The cell voltage is also dependent on other factors, including concentration and temperature, as expressed by the Nernst equation (covered in detail in Chap. 2).

1.4.3 Theoretical Capacity (Coulombic)

The theoretical capacity of a cell is determined by the amount of active materials in the cell. It is expressed as the total quantity of electricity involved in the electrochemical reaction and is defined in terms of coulombs or ampere-hours. The "ampere-hour capacity" of a battery is directly associated with the quantity of electricity obtained from the active materials. Theoretically 1 gram-equivalent weight of material will deliver 96,487 C or 26.8 Ah. (A gram-equivalent weight is the atomic or molecular weight of the active material in grams divided by the number of electrons involved in the reaction.)

The electrochemical equivalence of typical materials is listed in Table 1.1 and Appendix 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/Cl_2 cell is 0.394 Ah/g, that is,

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

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 the 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.

	Atomic or	Standard reduction potential at 25°C, V	Valence change	Melting point, °C	Density, g/cm ³	Electrochemical equivalents			
Material	molecular weight, g					Ah/g	g/Ah	Ah/cm ³ ‡	
			Anod	e materials					
H ₂	2.01	$0 \\ -0.83^{\dagger}$	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	
$(Li)C_{6}^{(1)}$	72.06	~ -2.8	1		2.25	0.37	2.68	0.84	
MH ⁽²⁾	116.2	-0.83^{+}	2	—	—	0.45	2.21		
CH ₃ OH	32.04	—	6	_		5.02	0.20		
			Cathoo	de materials					
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	
AgÕ	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	
Li _x CoO ₂ ⁽³⁾	98	~2.7	0.5	_		0.137	7.29		
1 ₂	253.8	0.54	2	_	4.94	0.211	4.73	1.04	

TABLE 1.1 Characteristics of Electrode Materials*

*See also Appendixes B and C.

†Basic electrolyte: all others, aqueous acid electrolyte.

(1) Calculations based only on weight of carbon.

(2) Based on 1.7% H_2 storage by weight.

(3) Based on x = 0.5; higher valves may be obtained in practice.

[‡]Based on density values shown.

TABLE 1.2 Voltage, Capacity and Specific Energy of	Major Battery Systems-Theoretical and Practical Values
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					Theoretical values [†]				Practical battery‡		
Battery type	Anode	Cathode	Reaction mechanism	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	$ \begin{array}{l} Zn + 2MnO_2 \rightarrow ZnO \cdot Mn_2O_3 \\ Mg + 2MnO_2 + H_2O \rightarrow Mn_2O_3 + Mg(OH)_2 \end{array} $	1.6	4.46	224	358	1.5	85 ⁽⁴⁾	165 ⁽⁴⁾	
Magnesium	Mg	MnO ₂		2.8	3.69	271	759	1.7	100 ⁽⁴⁾	195 ⁽⁴⁾	
Alkaline MnO ₂	Zn	MnO ₂	$\begin{array}{l} Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3 \\ Zn + HgO \rightarrow ZnO + Hg \\ Cd + HgO + H_2O \rightarrow Cd(OH)_2 + Hg \end{array}$	1.5	4.46	224	358	1.5	145 ⁽⁴⁾	400 ⁽⁴⁾	
Mercury	Zn	HgO		1.34	5.27	190	255	1.35	100 ⁽⁶⁾	470 ⁽⁶⁾	
Mercad	Cd	HgO		0.91	6.15	163	148	0.9	55 ⁽⁶⁾	230 ⁽⁶⁾	
Silver oxide	Zn	Ag_2O	$\begin{array}{l} Zn + Ag_2O + H_2O \rightarrow Zn(OH)_2 + 2Ag \\ Zn + \frac{1}{2}O_2 \rightarrow ZnO \\ Zn + (\frac{1}{2}O_2) \rightarrow ZnO \end{array}$	1.6	5.55	180	288	1.6	135 ⁽⁶⁾	525 ⁽⁶⁾	
Zinc/O ₂	Zn	O_2		1.65	1.52	658	1085				
Zinc/air	Zn	Ambient air		1.65	1.22	820	1353	1.5	370 ⁽⁶⁾	1300 ⁽⁶⁾	
Li/SOCl ₂	Li	$SOCl_2$	$4\text{Li} + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{S} + \text{SO}_2$	3.65	3.25	403	1471	3.6	590 ⁽⁴⁾	$1100^{(4)} \\ 415^{(5)} \\ 535^{(5)} \\ 500^{(5)} \\ 635^{(5)} $	
Li/SO ₂	Li	SO_2	$2\text{Li} + 2\text{SO}_2 \rightarrow \text{Li}_2\text{S}_2\text{O}_4$	3.1	2.64	379	1175	3.0	260 ⁽⁵⁾		
LiMnO ₂	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	230 ⁽⁵⁾		
Li/FeS ₂	Li	FeS_2	$4\text{Li} + \text{FeS}_2 \rightarrow 2\text{Li}_2\text{S} + \text{Fe}$	1.8	1.38	726	1307	1.5	260 ⁽⁵⁾		
Li/(CF)	Li	(CF)	$\text{nLi} + (\text{CF}) \rightarrow \text{nLiF} + nC$	3.1	1.42	706	2189	3.0	250 ⁽⁵⁾		
$Li/I_2^{(3)}$	Li	$I_2(P2VP)$	$Li + \frac{1}{2}I_2 \rightarrow LiI$	2.8	4.99	200	560	2.8	245	900	
			Reserve batteries								
Cuprous chloride	Mg	CuCl	$\begin{array}{l} Mg + Cu_2 Cl_2 \rightarrow Mg Cl_2 + 2Cu \\ Zn + AgO + H_2O \rightarrow Zn(OH)_2 + Hg \\ See \ Section \ 21.3.1 \end{array}$	1.6	4.14	241	386	1.3	60 ⁽⁷⁾	80 ⁽⁷⁾	
Zinc/silver oxide	Zn	AgO		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 Edison	Pb Fe	PbO ₂ Ni oxide	$\begin{array}{l} Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \\ Fe + 2NiOOH + 2H_2O \rightarrow 2Ni(OH)_2 + Fe(OH)_2 \end{array}$	2.1 1.4	8.32 4.46	120 224	252 314	2.0 1.2	35 30	70 ⁽¹⁰⁾ 55 ⁽¹⁰⁾
Nickel-cadmium Nickel-zinc Nickel-hydrogen Nickel-metal hydride	$\begin{array}{c} Cd \\ Zn \\ H_2 \\ MH^{(1)} \end{array}$	Ni oxide Ni oxide Ni oxide Ni oxide	$\begin{array}{l} Cd + 2NiOOH + 2H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2 \\ Zn + 2NiOOH + 2H_2O \rightarrow 2Ni(OH)_2 + Zn(OH)_2 \\ H_2 + 2NiOOH \rightarrow 2Ni(OH)_2 \\ MH + NiOOH \rightarrow M + Ni(OH)_2 \end{array}$	1.35 1.73 1.5 1.35	5.52 4.64 3.46 5.63	181 215 289 178	244 372 434 240	1.2 1.6 1.2 1.2	35 60 55 75	$100^{(5)}$ 120 60 240^{(5)}
Silver-zinc Silver-cadmium	Zn Cd	AgO AgO	$\begin{array}{l} Zn \ + \ AgO \ + \ H_2O \ \rightarrow \ Zn(OH)_2 \ + \ Ag \\ Cd \ + \ AgO \ + \ H_2O \ \rightarrow \ Cd(OH)_2 \ + \ Ag \end{array}$	1.85 1.4	3.53 4.41	283 227	524 318	1.5 1.1	105 70	$\frac{180^{(10)}}{120^{(10)}}$
Zinc/chlorine Zinc/bromine	Zn Zn	Cl ₂ Br ₂	$\begin{array}{l} \mathrm{Zn}+\mathrm{Cl}_2\to\mathrm{ZnCl}_2\\ \mathrm{Zn}+\mathrm{Br}_2\to\mathrm{ZnBr}_2 \end{array}$	2.12 1.85	2.54 4.17	394 309	835 572	1.6	70	
Lithium-ion Lithium/manganese dioxide	Li _x C ₆ Li	$\begin{array}{l} Li_{(i-x)}CoO_2\\ MnO_2 \end{array}$	$\begin{array}{l} \text{Li}_{x}\text{C}_{6} + \text{Li}_{(i-x)}\text{CoO}_{2} \rightarrow \text{LiCoO}_{2} + \text{C}_{6} \\ \text{Li} + \text{Mn}^{\text{IV}}\text{O}_{2} \rightarrow \text{Mn}^{\text{IV}}\text{O}_{2}(\text{Li}^{+}) \end{array}$	4.1 3.5	9.98 3.50	100 286	410 1001	4.1 3.0	150 120	400 ⁽⁵⁾ 265
Lithium/iron disulfide ⁽²⁾ Lithium/iron monosulfide ⁽²⁾	Li(Al) Li(Al)	FeS_2 FeS	$\begin{array}{l} 2\text{Li}(\text{Al}) + \text{FeS}_2 \rightarrow \text{Li}_2\text{FeS}_2 + 2\text{Al} \\ 2\text{Li}(\text{Al}) + \text{FeS} \rightarrow \text{Li}_2\text{S} + \text{Fe} + 2\text{Al} \end{array}$	1.73 1.33	3.50 2.90	285 345	493 459	1.7 1.3	180 ⁽¹¹⁾ 130 ⁽¹¹⁾	$\frac{350^{(11)}}{220^{(11)}}$
Sodium/sulfur ⁽²⁾ Sodium/nickel chloride ⁽²⁾	Na Na	S NiCl ₂	$\begin{array}{l} 2\mathrm{Na}+3\mathrm{S}\rightarrow\mathrm{Na_2S_3}\\ 2\mathrm{Na}+\mathrm{NiCl_2}\rightarrow\mathrm{2NaCl}+\mathrm{Ni} \end{array}$	2.1 2.58	2.65 3.28	377 305	792 787	2.0 2.6	$\frac{170^{(11)}}{115^{(11)}}$	345 ⁽¹¹⁾ 190 ⁽¹¹⁾
			Fuel cells							
H_2/O_2 H_2/air Methanol/O ₂	Н ₂ Н ₂ СН ₂ ОН	O_2 Ambient air O_2	$H_2 + \frac{1}{2O_2} \rightarrow H_2O$ $H_2 + (\frac{1}{2O_2}) \rightarrow H_2O$ $CH_1OH + \frac{3}{2O_2} \rightarrow CO_2 + 2H_2O$	1.23 1.23 1.24	0.336 0.037 0.50	2975 26587 2000	3660 32702 2480	_		
Methanol/air	CH ₃ OH	Ambient air	$CH_3OH + (\frac{3}{2}O_2) \rightarrow CO_2 + 2H_2O$	1.24	0.20	5020	6225	—	—	

[†]Based on active anode and cathode materials only, including O₂ 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. More specific values are given in chapters on each battery system.

(1)MH = metal hydride, data based on 1.7% hydrogen storage (by weight).

(1) Mil - mean hydride, data obser on 177
(2) High temperature batteries.
(3) Solid electrolyte battery (Li/I₂ (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, see appropriate chapter for details.

1.4.4 Theoretical Energy*

The capacity of a cell can also considered on an energy (watthour) basis by taking both the voltage and the quantity of electricity into consideration. This theoretical energy value is the maximum value that can be delivered by a specific electrochemical system:

Watthour (Wh) = voltage (V) \times ampere-hour (Ah)

In the Zn/Cl_2 cell example, if the standard potential is taken as 2.12 V, the theoretical watthour capacity per gram of active material (theoretical gravimetric specific energy or theoretical gravimetric energy density) is:

Specific Energy (Watthours/gram) = $2.12 \text{ V} \times 0.394 \text{ Ah/g} = 0.835 \text{ Wh/g}$ or 835 Wh/kg

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

1.5 SPECIFIC ENERGY AND ENERGY DENSITY OF PRACTICAL BATTERIES

The theoretical electrical properties of cells and batteries are discussed in Sec. 1.4. In summary, the maximum energy that can be delivered by an electrochemical system is based on the types of active materials that are used (this determines the voltage) and on the amount of the active materials that are used (this determines ampere-hour capacity). In practice, only a fraction of the theoretical energy of the battery is realized. This is due to the need for electrolyte and nonreactive components (containers, separators, electrodes) that add to the weight and volume of the battery, as illustrated in Fig. 1.3. Another contributing factor is that the battery does not discharge at the theoretical voltage (thus lowering the average



FIGURE 1.3 Components of a cell.

^{*}The 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. Watthours/kilogram (Wh/kg), is "specific energy"; on a volume basis, e.g. Watthours/liter (Wh/L), it is "energy density." Quite commonly, however, the term "energy density" is used to refer to either ratio.

voltage), nor is it discharged completely to zero volts (thus reducing the delivered amperehours) (also see Sec. 3.2.1). Further, the active materials in a practical battery are usually not stoichiometrically balanced. This reduces the specific energy because an excess amount of one of the active materials is used.

In Fig. 1.4, the following values for some major batteries are plotted:

- 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 non-reactive components)
- **3.** The actual specific energy of these batteries when discharged at 20°C under optimal discharge conditions

These data show:

- That the weight of the materials of construction reduces the theoretical energy density or of the battery by almost 50 percent, and
- That the actual energy delivered by a practical battery, even when discharged under conditions close to optimum, may only be 50 to 75 percent of that lowered value

Thus, the actual energy that is available from a battery under practical, but close to optimum, discharge conditions is only about 25 to 35 percent of the theoretical energy of the active materials. Chapter 3 covers the performance of batteries when used under more stringent conditions.



FIGURE 1.4 Theoretical and actual specific energy of battery systems.

These data are shown again in Table 1.2 which, in addition to the theoretical values, lists the characteristics of each of these batteries based on the actual performance of a practical battery. Again, these values are based on discharge conditions close to optimum for that battery.

The specific energy (Wh/kg) and energy density (Wh/L) delivered by the major battery systems are also plotted in Fig. 1.5(a) for primary batteries and 1.5(b) for rechargeable batteries. In these figures, the energy storage capability is shown as a field, rather than as a



FIGURE 1.5 Comparison of the energy storage capability of various battery systems (*a*) Primary batteries; (*b*) Rechargeable batteries. (*From Ref 1*)

single optimum value, to illustrate the spread in performance of that battery system under different conditions of use.

In practice, as discussed in detail in Chap. 3, the electrical output of a battery may be reduced even further when it is used under more stringent conditions.

1.6 UPPER LIMITS OF SPECIFIC ENERGY AND ENERGY DENSITY

Many advances have been made in battery technology in recent years as illustrated in Fig. 1.6, both through continued improvement of a specific electrochemical system and through the development and introduction of new battery chemistries. But batteries are not keeping pace with developments in electronics technology, where performance doubles every 18 months, a phenomenon known as Moore's Law. Batteries, unlike electronic devices, consume materials when delivering electrical energy and, as discussed in Secs. 1.4 and 1.5, there are theoretical limits to the amount of electrical energy that can be delivered electrochemically by the available materials. The upper limit is now being reached as most of the materials that are practical for use as active materials in batteries have already been investigated and the list of unexplored materials is being depleted.

As shown in Table 1.2, and the other such tables in the Handbook, 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 theoretical energy density do not exceed 1500 Wh/kg. Most of the values are, in fact, lower. Even the values for the hydrogen/air and the liquid fuel cells have to be lowered to include, at least, the weight and volume of suitable containers for these fuels.

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 450 Wh/kg, even including the air-breathing systems. Similarly, the energy density values do not exceed 1000 Wh/L. It is also noteworthy that the values for the rechargeable systems are lower than those of the 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.



FIGURE 1.6 Advances in battery performance for portable applications.

Recognizing these limitations, while new battery systems will be explored, it will be more difficult to develop a new battery system which will have a significantly higher energy output and still meet the requirements of a successful commercial product, including availability of materials, acceptable cost, safety and environmental acceptability.

Battery research and development will focus on reducing the ratio of inactive to active components to improve energy density, increasing conversion efficiency and rechargability, maximizing performance under the more stringent operating and enhancing safety and environment. The fuel cell is offering opportunities for powering electric vehicles, as a replacement for combustion engines, for use in utility power and possibly for the larger portable applications (see Chap. 42). However, the development of a fuel cell for a small portable applications that will be competitive with batteries presents a formidable challenge.

REFERENCES

 Ralph J. Broad, "Recent Developments in Batteries for Portable Consumer Electronics Applications," *Interface* 8:3, Fall 1999, Electrochemical Society, Pennington, NJ.

CHAPTER 2 ELECTROCHEMICAL PRINCIPLES AND REACTIONS

John Broadhead and Han C. Kuo

2.1 INTRODUCTION

Batteries and fuel cells are electrochemical devices which convert chemical energy into electrical energy by electrochemical oxidation and reduction reactions, which occur at the electrodes. A cell consists of an anode where oxidation takes place during discharge, a cathode where reduction takes place, and an electrolyte which conducts the electrons (*via* ions) within the cell.

The maximum electric energy that can be delivered by the chemicals that are stored within or supplied to the electrodes in the cell depends on the change in free energy ΔG of the electrochemical couple, as shown in Eq. (2.5) and discussed in Sec. 2.2.

It would be desirable if during the discharge all of this energy could be converted to useful electric energy. However, losses due to polarization occur when a load current i passes through the electrodes, accompanying the electrochemical reactions. These losses include: (1) activation polarization, which drives the electrochemical reaction at the electrode surface, and (2) concentration polarization, which arises from the concentration differences of the reactants and products at the electrode surface and in the bulk as a result of mass transfer.

These polarization effects consume part of the energy, which is given off as waste heat, and thus not all of the theoretically available energy stored in electrodes is fully converted into useful electrical energy.

In principle, activation polarization and concentration polarization can be calculated from several theoretical equations, as described in later sections of this chapter, if some electrochemical parameters and the mass-transfer condition are available. However, in practice it is difficult to determine the values for both because of the complicated physical structure of the electrodes. As covered in Sec. 2.5, most battery and fuel cells electrodes are composite bodies made of active material, binder, performance enhancing additives and conductive filler. They usually have a porous structure of finite thickness. It requires complex mathematical modeling with computer calculations to estimate the polarization components.

There is another important factor that strongly affects the performance or rate capability of a cell, the internal impedance of the cell. It causes a voltage drop during operation, which also consumes part of the useful energy as waste heat. The voltage drop due to internal impedance is usually referred to as "ohmic polarization" or *IR* drop and is proportional to the current drawn from the system. The total internal impedance of a cell is the sum of the ionic resistance of the electrolyte (within the separator and the porous electrodes), the electronic resistances of the active mass, the current collectors and electrical tabs of both elec-

trodes, and the contact resistance between the active mass and the current collector. These resistances are ohmic in nature, and follow Ohm's law, with a linear relationship between current and voltage drop.

When connected to an external load R, the cell voltage E can be expressed as

$$E = E_0 - [(\eta_{ct})_a + (\eta_c)_a] - [(\eta_{ct})_c + (\eta_c)_c] - iR_i = iR$$
(2.1)

where E_0 = electromotive force or open-circuit voltage of cell

 $(\eta_{cl})_a, (\eta_{ct})_c$ = activation polarization or charge-transfer overvoltage at anode and cathode $(\eta_c)_a, (\eta_c)_c$ = concentration polarization at anode and cathode

i = operating current of cell on load

 R_i = internal resistance of cell

As shown in Eq. (2.1), the useful voltage delivered by the cell is reduced by polarization and the internal *IR* drop. It is only at very low operating currents, where polarization and the *IR* drop are small, that the cell may operate close to the open-circuit voltage and deliver most of the theoretically available energy. Figure 2.1 shows the relation between cell polarization and discharge current.



FIGURE 2.1 Cell polarization as a function of operating current.

Although the available energy of a battery or fuel cell depends on the basic electrochemical reactions at both electrodes, there are many factors which affect the magnitude of the charge-transfer reaction, diffusion rates, and magnitude of the energy loss. These factors include electrode formulation and design, electrolyte conductivity, and nature of the separators, among others. There exist some essential rules, based on the electrochemical principles, which are important in the design of batteries and fuel cells to achieve a high operating efficiency with minimal loss of energy.

- 1. The conductivity of the electrolyte should be high enough that the *IR* polarization is not excessively large for practical operation. Table 2.1 shows the typical ranges of specific conductivities for various electrolyte systems used in batteries. Batteries are usually designed for specific drain rate applications, ranging from microamperes to several hundred amperes. For a given electrolyte, a cell may be designed to have improved rate capability, with a higher electrode interfacial area and thin separator, to reduce the *IR* drop due to electrolyte resistance. Cells with a spirally wound electrode design are typical examples.
- **2.** Electrolyte salt and solvents should have chemical stability to avoid direct chemical reaction with the anode or cathode materials.

Electrolyte system	Specific conductivity, $\Omega^{-1} \text{ cm}^{-1}$
Aqueous electrolytes	$1-5 \times 10^{-1}$
Molten salt	$\sim 10^{-1}$
Inorganic electrolytes	2×10^{-2} - 10^{-1}
Organic electrolytes	$10^{-3} - 10^{-2}$
Polymer electrolytes	$10^{-7} - 10^{-3}$
Inorganic solid electrolytes	$10^{-8} - 10^{-5}$

TABLE 2.1 Conductivity Ranges of VariousElectrolytes at Ambient Temperature

- **3.** The rate of electrode reaction at both the anode and the cathode should be sufficiently fast so that the activation or charge-transfer polarization is not too high to make the cell inoperable. A common method of minimizing the charge-transfer polarization is to use a porous electrode design. The porous electrode structure provides a high electrode surface area within a given geometric dimension of the electrode and reduces the local current density for a given total operating current.
- **4.** In most battery and fuel cell systems, part or all of the reactants are supplied from the electrode phase and part or all of the reaction products must diffuse or be transported away from the electrode surface. The cell should have adequate electrolyte transport to facilitate the mass transfer to avoid building up excessive concentration polarization. Proper porosity and pore size of the electrode, adequate thickness and structure of the separator, and sufficient concentration of the reactants in the electrolyte are very important to ensure functionality of the cell. Mass-transfer limitations should be avoided for normal operation of the cell.
- 5. The material of the current collector or substrate should be compatible with the electrode material and the electrolyte without causing corrosion problems. The design of the current collector should provide a uniform current distribution and low contact resistance to minimize electrode polarization during operation.
- **6.** For rechargeable cells it is preferable to have the reaction products remain at the electrode surface to facilitate the reversible reactions during charge and discharge. The reaction products should be stable mechanically as well as chemically with the electrolyte.

In general, the principles and various electrochemical techniques described in this chapter can be used to study all the important electrochemical aspects of a battery or fuel cell. These include the rate of electrode reaction, the existence of intermediate reaction steps, the stability of the electrolyte, the current collector, the electrode materials, the mass-transfer conditions, the value of the limiting current, the formation of resistive films on the electrode surface, the impedance characteristics of the electrode or cell, and the existence of the rate-limiting species.

2.4 CHAPTER TWO

2.2 THERMODYNAMIC BACKGROUND

In a cell, reactions essentially take place at two areas or sites in the device. These reaction sites are the electrode interfaces. In generalized terms, the reaction at one electrode (reduction in forward direction) can be represented by

$$aA + ne \rightleftharpoons cC \tag{2.2}$$

where a molecules of A take up n electrons e to form c molecules of C. At the other electrode, the reaction (oxidation in forward direction) can be represented by

$$bB - ne \rightleftharpoons dD$$
 (2.3)

The overall reaction in the cell is given by addition of these two half-cell reactions

$$aA + bB \rightleftharpoons cC + dD \tag{2.4}$$

The change in the standard free energy ΔG^0 of this reaction is expressed as

$$\Delta G^0 = -nFE^0 \tag{2.5}$$

where F = constant known as the Faraday (96,487 coulombs) $E^0 = \text{standard}$ electromotive force

Electrode reaction	E^0 , V	Electrode reaction	<i>E</i> ⁰ , V
$Li^+ + e \rightleftharpoons Li$	-3.01	$Tl^+ + e \rightleftharpoons Tl$	-0.34
$Rb^+ + e \rightleftharpoons Rb$	-2.98	$\mathrm{Co}^{2+} + 2e \rightleftharpoons \mathrm{Co}$	-0.27
$Cs^+ + e \rightleftharpoons Cs$	-2.92	$Ni^{2+} + 2e \rightleftharpoons Ni$	-0.23
$\mathbf{K}^{+} + e \rightleftharpoons \mathbf{K}$	-2.92	$\mathrm{Sn}^{2+} + 2e \rightleftharpoons \mathrm{Sn}$	-0.14
$Ba^{2+} + 2e \rightleftharpoons Ba$	-2.92	$Pb^{2+} + 2e \rightleftharpoons Pb$	-0.13
$\mathrm{Sr}^{2+} + 2e \rightleftharpoons \mathrm{Sr}$	-2.89	$D^+ + e \rightleftharpoons \frac{1}{2}D_2$	-0.003
$Ca^{2+} + 2e \rightleftharpoons Ca$	-2.84	$\mathrm{H}^{+} + e \rightleftharpoons \frac{1}{2}\mathrm{H}_{2}^{2}$	0.000
$Na^+ + e \rightleftharpoons Na$	-2.71	$Cu^{2+} + 2e \rightleftharpoons Cu$	0.34
$Mg^{2+} + 2e \rightleftharpoons Mg$	-2.38	$^{1}/_{2}O_{2} + H_{2}O + 2e \rightleftharpoons 2OH^{-}$	0.40
$Ti^+ + 2e \rightleftharpoons Ti$	-1.75	$Cu^+ + e \rightleftharpoons Cu$	0.52
$Be^{2+} + 2e \rightleftharpoons Be$	-1.70	$Hg^{2+} + 2e \rightleftharpoons 2Hg$	0.80
$Al^{3+} + 3e \rightleftharpoons Al$	-1.66	$Ag^+ + e \rightleftharpoons Ag$	0.80
$Mn^{2+} + 2e \rightleftharpoons Mn$	-1.05	$Pd^{2+} + 2e \rightleftharpoons Pd$	0.83
$Zn^{2+} + 2e \rightleftharpoons Zn$	-0.76	$Ir^{3+} + 3e \rightleftharpoons Ir$	1.00
$Ga^{3+} + 3e \rightleftharpoons Ga$	-0.52	$Br_2 + 2e \rightleftharpoons 2Br^-$	1.07
$\mathrm{Fe}^{2+} + 2e \rightleftharpoons \mathrm{Fe}$	-0.44	$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$	1.23
$Cd^{2+} + 2e \rightleftharpoons Cd$	-0.40	$Cl_2 + 2e \rightleftharpoons 2Cl^-$	1.36
$In^{3+} + 3e \rightleftharpoons In$	-0.34	$F_2 + 2e \rightleftharpoons 2F^-$	2.87

TABLE 2.2 Standard Potentials of Electrode Reactions at 25°C

When conditions are other than in the standard state, the voltage E of a cell is given by the Nernst equation,

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_c^c a_D^d}{a_a^a a_B^b}$$
(2.6)

where a_i = activity of relevant species

R = gas constant

T = absolute temperature

The change in the standard free energy ΔG^0 of a cell reaction is the driving force which enables a battery to deliver electrical energy to an external circuit. The measurement of the electromotive force, incidentally, also makes available data on changes in free energy, entropies and enthalpies together with activity coefficients, equilibrium constants, and solubility products.

Direct measurement of single (absolute) electrode potentials is considered practically impossible.¹ To establish a scale of half-cell or standard potentials, a reference potential "zero" must be established against which single electrode potentials can be measured. By convention, the standard potential of the $H_2/H^+(aq)$ reaction is taken as zero and all standard potentials are referred to this potential. Table 2.2 and Appendix B list the standard potentials of a number of anode and cathode materials.

2.3 ELECTRODE PROCESSES

Reactions at an electrode are characterized by both chemical and electrical changes and are heterogeneous in type. Electrode reactions may be as simple as the reduction of a metal ion and incorporation of the resultant atom onto or into the electrode structure. Despite the apparent simplicity of the reaction, the mechanism of the overall process may be relatively complex and often involves several steps. Electroactive species must be transported to the electrode surface by migration or diffusion prior to the electron transfer step. Adsorption of electroactive material may be involved both prior to and after the electron transfer step. Chemical reactions may also be involved in the overall electrode reaction. As in any reaction, the overall rate of the electrochemical process is determined by the rate of the slowest step in the whole sequence of reactions.

The thermodynamic treatment of electrochemical processes presented in Sec. 2.2 describes the equilibrium condition of a system but does not present information on nonequilibrium conditions such as current flow resulting from electrode polarization (overvoltage) imposed to effect electrochemical reactions. Experimental determination of the currentvoltage characteristics of many electrochemical systems has shown that there is an exponential relation between current and applied voltage. The generalized expression describing this relationship is called the Tafel equation,

$$\eta = a \pm b \log i \tag{2.7}$$

where η = overvoltage

i = current

a, b = constants

Typically, the constant b is referred to as the Tafel slope.

The Tafel relationship holds for a large number of electrochemical systems over a wide range of overpotentials. At low values of overvoltage, however, the relationship breaks down and results in curvature in plots of η versus log *i*. Figure 2.2 is a schematic presentation of a Tafel plot, showing curvature at low values of overvoltage.





FIGURE 2.2 Schematic representation of a Tafel plot showing curvature at low overvoltage and indicating significance of parameters a and b.

FIGURE 2.3 Simplified representation of electroreduction process at an electrode.

Success of the Tafel equation's fit to many experimental systems encouraged the quest for a kinetic theory of electrode processes. Since the range of validity of the Tafel relationship applies to high overvoltages, it is reasonable to assume that the expression does not apply to equilibrium situations but represents the current-voltage relationship of a unidirectional process. In an oxidation process, this means that there is a negligible contribution from reduction processes. Rearranging Eq. (2.7) into exponential form, we have

$$i = \exp\left(\pm \frac{a}{b}\right) \exp\frac{\eta}{b}$$
 (2.8)

To consider a general theory, one must consider both forward and backward reactions of the electroreduction process, shown in simplified form in Fig. 2.3. The reaction is represented by the equation

$$O + ne \rightleftharpoons R \tag{2.9}$$

where O = oxidized species

$$R =$$
 reduced species

n = number of electrons involved in electrode process

The forward and backward reactions can be described by heterogeneous rate constants k_f and k_b , respectively. The rates of the forward and backward reactions are then given by the products of these rate constants and the relevant concentrations which typically are those at the electrode surface. As will be shown later, the concentrations of electroactive species at the electrode surface often are dissimilar from the bulk concentration in solution. The rate of the forward reaction is $k_f C_o$ and that for the backward reaction is $k_b C_R$. For convenience, these rates are usually expressed in terms of currents i_f and i_b , for the forward and backward reactions, respectively,

$$i_f = nFAk_f C_O \tag{2.10}$$

$$i_b = nFAk_bC_R \tag{2.11}$$

where A is the area of the electrode and F the Faraday.

Establishing these expressions is merely the result of applying the law of mass action to the forward and backward electrode processes. The role of electrons in the process is established by assuming that the magnitudes of the rate constants depend on the electrode potential. The dependence is usually described by assuming that a fraction αE of the electrode potential is involved in driving the reduction process, while the fraction $(1 - \alpha)E$ is effective in making the reoxidation process more difficult. Mathematically these potential-dependent rate constants are expressed as

$$k_f = k_f^0 \exp \frac{-\alpha n F E}{RT}$$
(2.12)

$$k_b = k_b^0 \exp \frac{(1 - \alpha)nFE}{RT}$$
(2.13)

where α is the transfer coefficient and *E* the electrode potential relative to a suitable reference potential.

A little more explanation regarding what the transfer coefficient α (or the symmetry factor β , as it is referred to in some texts) means in mechanistic terms is appropriate since this term is not implicit in the kinetic derivation.² The transfer coefficient determines what fraction of the electric energy resulting from the displacement of the potential from the equilibrium value affects the rate of electrochemical transformation. To understand the function of the transfer coefficient α , it is necessary to describe an energy diagram for the reductionoxidation process. Figure 2.4 shows an approximate potential energy curve (Morse curve) for an oxidized species approaching an electrode surface together with the potential energy curve for the resultant reduced species. For convenience, consider the hydrogen ion reduction at a solid electrode as the model for a typical electroreduction. According to Horiuti and Polanyi,³ the potential energy diagram for reduction of the hydrogen ion can be represented by Fig. 2.5 where the oxidized species O is the hydrated hydrogen ion and the reduced species R is a hydrogen atom bonded to the metal (electrode) surface. The effect of changing the electrode potential by a value of E is to raise the potential energy of the Morse curve of the hydrogen ion. The intersection of the two Morse curves forms an energy barrier, the height of which is αE . If the slope of the two Morse curves is approximately constant at the point of intersection, then α is defined by the ratio of the slope of the Morse curves at the point of intersection

$$\alpha = \frac{m_1}{m_1 + m_2}$$
(2.14)

where m_1 and m_2 are the slopes of the potential curves of the hydrated hydrogen ion and the hydrogen atom, respectively.



FIGURE 2.4 Potential energy diagram for reduction-oxidation process taking place at an electrode.



FIGURE 2.5 Potential energy diagram for reduction of a hydrated hydrogen ion at an electrode.

There are inadequacies in the theory of transfer coefficients. It assumes that α is constant and independent of *E*. At present there are no data to prove or disprove this assumption. The other main weakness is that the concept is used to describe processes involving a variety of different species such as (1) redox changes at an inert electrode (Fe²⁺/Fe³⁺ at Hg); (2) reactant and product soluble in different phases [Cd²⁺/Cd(Hg)]; and (3) electrodeposition (Cu²⁺/Cu). Despite these inadequacies, the concept and application of the theory are appropriate in many cases and represent the best understanding and description of electrode processes at the present time. Examples of a few values of α are given in Table 2.3.⁴

TABLE 2.3 Values of Transfer Coefficient α at 25°C⁴

Metal	System	α
Platinum	$\mathrm{Fe}^{3+} + e \rightarrow \mathrm{Fe}^{2+}$	0.58
Platinum	$Ce^{4+} + e \rightarrow Ce^{2+}$	0.75
Mercury	$Ti^{4+} + e \rightarrow Ti^{3+}$	0.42
Mercury	$2H^+ + 2e \rightarrow H_2$	0.50
Nickel	$2H^+ + 2e \rightarrow H_2^2$	0.58
Silver	$Ag^+ + e \rightarrow Ag^-$	0.55

From Eqs. (2.12) and (2.13) we can derive parameters useful for evaluating and describing an electrochemical system. Equations (2.12) and (2.13) are compatible both with the Nernst equation [Eq. (2.6)] for equilibrium conditions and with the Tafel relationships [Eq. (2.7)] for unidirectional processes.

Under equilibrium conditions, no net current flows and

$$i_f = i_b = i_0$$
 (2.15)

where i_0 is the exchange current. From Eqs. (2.10)–(2.13), together with Eq. (2.15), the following relationship is established:

$$C_O k_f^0 \exp \frac{-\alpha n F E_e}{RT} = C_R k_b^0 \exp \frac{(1-\alpha) n F E_e}{RT}$$
(2.16)

where E_{e} is the equilibrium potential.

Rearranging,

$$E_e = \frac{RT}{nF} \ln \frac{k_f^0}{k_b^0} + \frac{RT}{nF} \ln \frac{C_o}{C_R}$$
(2.17)

From this equation we can establish the definition of formal standard potential E_c^0 , where concentrations are used rather than activities,

- 0

$$E_{C}^{0} = \frac{RT}{nF} \ln \frac{k_{f}^{0}}{k_{b}^{0}}$$
(2.18)

For convenience, the formal standard potential is often taken as the reference point of the potential scale in reversible systems.

Combining Eqs. (2.17) and (2.18), we can show consistency with the Nernst equation,

$$E_e = E_C^0 + \frac{RT}{nF} \ln \frac{C_O}{C_R}$$
(2.19)

except that this expression is written in terms of concentrations rather than activities.

From Eqs. (2.10) and (2.12), at equilibrium conditions,

$$i_0 = i_f = nFAC_O k_f^0 \exp \frac{-\alpha nFE_e}{RT}$$
(2.20)

The exchange current as defined in Eq. (2.15) is a parameter of interest to researchers in the battery field. This parameter may be conveniently expressed in terms of the rate constant k by combining Eqs. (2.10), (2.12), (2.17), and (2.20),

$$i_0 = n FAkC_O^{(1-\alpha)}C_R^a \tag{2.21}$$

The exchange current i_0 is a measure of the rate of exchange of charge between oxidized and reduced species at any equilibrium potential without net overall change. The rate constant k, however, has been defined for a particular potential, the formal standard potential of the system. It is not in itself sufficient to characterize the system unless the transfer coefficient is also known. However, Eq. (2.21) can be used in the elucidation of the electrode reaction mechanism. The value of the transfer coefficient can be determined by measuring the exchange current density as a function of the concentration of the reduction or oxidation species at a constant concentration of the oxidation of reduction species, respectively. A schematic representation of the forward and backward currents as a function of overvoltage, $\eta = E - E_e$, is shown in Fig. 2.6, where the net current is the sum of the two components.

For situations where the net current is not zero, that is, where the potential is sufficiently different from the equilibrium potential, the net current approaches the net forward current (or, for anodic overvoltages, the backward current). One can then write

$$i = nFAkC_o \exp \frac{-\alpha nF\eta}{RT}$$
(2.22)

Now when $\eta = 0$, $i = i_0$, then

$$i = i_0 \exp \frac{-\alpha n F \eta}{RT}$$
(2.23)



FIGURE 2.6 Schematic representation of relationship between overvoltage and current.

and

$$\eta = \frac{RT}{\alpha nF} \ln i_0 - \frac{RT}{\alpha nF} \ln i$$
(2.24)

which is the Tafel equation introduced earlier in a generalized form as Eq. (2.7).

It can now be seen that the kinetic treatment here is self-consistent with both the Nernst equation (for equilibrium conditions) and the Tafel relationship (for unidirectional processes). To present the kinetic treatment in its most useful form, a transformation into a net current flow form is appropriate. Using

$$i = i_f - i_b \tag{2.25}$$

substitute Eqs. (2.10), (2.13), and (2.18),

$$i = nFAk \left[C_o \exp \frac{-\alpha nFE_c^0}{RT} - C_R \exp \frac{(1-\alpha)nFE_c^0}{RT} \right]$$
(2.26)

When this equation is applied in practice, it is very important to remember that C_o and C_R are concentrations at the surface of the electrode, or are the effective concentrations. These are not necessarily the same as the bulk concentrations. Concentrations at the interface are often (almost always) modified by differences in electric potential between the surface and the bulk solution. The effects of potential differences that are manifest at the electrode-electrolyte interface are given in the following section.

2.4 ELECTRICAL DOUBLE-LAYER CAPACITY AND IONIC ADSORPTION

When an electrode (metal surface) is immersed in an electrolyte, the electronic charge on the metal attracts ions of opposite charge and orients the solvent dipoles. There exist a layer of charge in the metal and a layer of charge in the electrolyte. This charge separation establishes what is commonly known as the "electrical double layer."⁵

Experimentally, the electrical double-layer affect is manifest in the phenomenon named "electrocapillarity." The phenomenon has been studied for many years, and there exist thermodynamic relationships that relate interfacial surface tension between electrode and electrolyte solution to the structure of the double layer. Typically the metal used for these measurements is mercury since it is the only conveniently available metal that is liquid at room temperature (although some work has been carried out with gallium, Wood's metal, and lead at elevated temperature).

Determinations of the interfacial surface tension between mercury and electrolyte solution can be made with a relatively simple apparatus. All that are needed are (1) a mercury-solution interface which is polarizable, (2) a nonpolarizable interface as reference potential, (3) an external source of variable potential, and (4) an arrangement to measure the surface tension of the mercury-electrolyte interface. An experimental system which will fulfill these requirements is shown in Fig. 2.7. The interfacial surface tension is measured by applying pressure to the mercury-electrolyte interface by raising the mercury "head." At the interface, the forces are balanced, as shown in Fig. 2.8. If the angle of contact at the capillary wall is zero (typically the case for clean surfaces and clean electrolyte), then it is a relatively simple arithmetic exercise to show that the interfacial surface tension is given by

$$\gamma = \frac{h\rho gr}{2} \tag{2.27}$$

where γ = interfacial surface tension

- ρ = density of mercury
- g = force of gravity
- r = radius of capillary
- h = height of mercury column in capillary

The characteristic electrocapillary curve that one would obtain from a typical electrolyte solution is shown in Fig. 2.9. From such measurements and, more accurately, by AC impedance bridge measurements, the structure of the electrical double layer has been determined.⁵



FIGURE 2.7 Experimental arrangement to measure interfacial surface tension at mercury-electrolyte interface.



FIGURE 2.8 Close-up of mercury-electrolyte interface in a capillary immersed in an electrolyte solution



FIGURE 2.9 Generalized representation of an electro-capillary curve.

Consider a negatively charged electrode in an aqueous solution of electrolyte. Assume that at this potential no electrochemical charge transfer takes place. For simplicity and clarity, the different features of the electrical double layer will be described individually.

Orientation of solvent molecules, water for the sake of this discussion, is shown in Fig. 2.10. The water dipoles are oriented, as shown in the figure, so that the majority of the dipoles are oriented with their positive ends (arrow heads) toward the surface of the electrode. This represents a "snapshot" of the structure of the layer of water molecules since the electrical double layer is a dynamic system which is in equilibrium with water in the bulk solution. Since the representation is statistical, not all dipoles are oriented the same way. Some dipoles are more influenced by dipole-dipole interactions than by dipole-electrode interactions.

Next, consider the approach of a cation to the vicinity of the electrical double layer. The majority of cations are strongly solvated by water dipoles and maintain a sheath of water dipoles around them despite the orienting effect of the double layer. With a few exceptions, cations do not approach right up to the electrode surface but remain outside the primary layer of solvent molecules and usually retain their solvation sheaths. Figure 2.11 shows a typical example of a cation in the electrical double layer. The establishment that this is the most likely approach of a typical cation comes partly from experimental AC impedance measurements of mixed electrolytes and mainly from calculations of the free energy of approach of an ion to the electrode surface. In considering water-electrode, ion-electrode, and ion-water interactions, the free energy of approach of a cation to an electrode surface is strongly influenced by the hydration of the cation. The general result is that cations of very large radius (and thus of low hydration) such as Cs^+ can contact/adsorb on the electrode surface, but for the majority of cations the change in free energy on contact absorption is positive and thus is against the mechanism of contact adsorption.⁶ Figure 2.12 gives an example of the ion Cs⁺ contact-adsorbed on the surface of an electrode.

It would be expected that because anions have a negative charge, contact adsorption of anions would not occur. In analyzing the free-energy balance of the anion system, it is found that anion-electrode contact is favored because the net free-energy balance is negative. Both from these calculations and from experimental measurements, anion contact adsorption is found to be relatively common. Figure 2.13 shows the generalized case of anion adsorption



FIGURE 2.10 Orientation of water molecules in electrical double layer at a negatively charged electrode.

double layer.

FIGURE 2.11 Typical cation situated in electrical





FIGURE 2.12 Contact adsorption of Cs^+ on an electrode surface.

FIGURE 2.13 Contact adsorption of anion on an electrode surface.

on an electrode. There are exceptions to this type of adsorption. Calculation of the free energy of contact adsorption of the fluoride ion is positive and unlikely to occur. This is supported by experimental measurement. This property is utilized, as NaF, as a supporting electrolyte* to evaluate adsorption properties of surface-active species devoid of the influence of adsorbed supporting electrolyte.

Extending out into solution from the electrical double layer (or the compact double layer, as it is sometimes known) is a continuous repetition of the layering effect, but with diminishing magnitude. This "extension" of the compact double layer toward the bulk solution is known as the Gouy-Chapman diffuse double layer.⁵ Its effect on electrode kinetics and the concentration of electroactive species at the electrode surface is manifest when supporting electrolyte concentrations are low or zero.

The end result of the establishment of the electrical double-layer effect and the various types of ion contact adsorption, is directly to influence the real (actual) concentration of electroactive species at an electrode surface and indirectly to modify the potential gradient at the site of electron transfer. In this respect it is important to understand the influence of the electrical double layer and allow for it where and when appropriate.

The potential distribution near an electrode is shown schematically in Fig. 2.14. The inner Helmholtz plane corresponds to the plane which contains the contact-adsorbed ions and the innermost layer of water molecules. Its potential is defined as ϕ^i with the zero potential being taken as the potential of the bulk solution. The outer Helmholtz plane is the plane of closest approach of those ions which do not contact-adsorb but approach the electrode with a sheath of solvated water molecules surrounding them. The potential at the outer Helmholtz plane is defined as ϕ^o and is again referred to the potential of the bulk solution. In some texts ϕ^i is defined as ϕ^1 and ϕ^o as ϕ^2 .

^{*}A supporting electrolyte is a salt used in large excess to minimize internal resistance in an electrode chemical cells, but which does not enter into electrode reactions.



FIGURE 2.14 Potential distribution of positively charged electrode.

As mentioned previously, the bulk concentration of an electroactive species is often not the value to be used in kinetic equations. Species which are in the electrical double layer are in a different energy state from those in bulk solution. At equilibrium, the concentration C^e of an ion or species that is about to take part in the charge-transfer process at the electrode is related to the bulk concentration by

$$C^e = C^B \exp \frac{-zF\phi^e}{RT}$$
(2.28)

where z is the charge on the ion and ϕ^e the potential of *closest approach* of the species to the electrode. It will be remembered that the plane of closest approach of many species is the outer Hemholtz plane, and so the value of ϕ^e can often be equated to ϕ^o . However, as noted in a few special cases, the plane of closest approach can be the inner Helmholtz plane, and so the value of ϕ^e in these cases would be the same as ϕ^i . A judgment has to be made as to what value of ϕ^e should be used.

The potential which is effective in driving the electrode reaction is that between the species at its closest approach and the potential of the electrode. If *E* is the potential of the electrode, then the driving force is $E - \phi^e$. Using this relationship together with Eqs. (2.26) and (2.28), we have

$$\frac{i}{nFAk} = C_o \exp \frac{-z_o E \phi^e}{RT} \exp \frac{-\alpha n F (E - \phi^e)}{RT} - C_R \exp \frac{-z_R F \phi^e}{RT} \exp \frac{(1 - \alpha) n F (E - \phi^e)}{RT}$$
(2.29)

where z_o and z_R are the charges (with sign) of the oxidized and reduced species, respectively. Rearranging Eq. (2.28) and using

$$z_o - n = z_R \tag{2.30}$$

yields

$$\frac{i}{nFAk} = \exp\frac{(\alpha n - z_o)F\phi^e}{RT} \left[C_o \exp\frac{-\alpha nFE}{RT} - C_R \exp\frac{(1 - \alpha)nFE}{RT} \right]$$
(2.31)

In experimental determination, the use of Eq. (2.26) will provide an apparent rate constant k_{app} , which does not take into account the effects of the electrical double layer. Taking into account the effects appropriate to the approach of a species to the plane of nearest approach,

$$k_{\rm app} = k \exp \frac{(\alpha n - z_o) F \phi^e}{RT}$$
(2.32)

For the exchange current the same applies,

$$(i_0)_{\rm app} = i_0 \exp \frac{(\alpha n - z_0) F \phi^e}{RT}$$
(2.33)

Corrections to the rate constant and the exchange current are not insignificant. Several calculated examples are given in Bauer.⁷ The differences between apparent and true rate constants can be as great as two orders of magnitude. The magnitude of the correction also is related to the magnitude of the difference in potential between the electrocapillary maximum for the species and the potential at which the electrode reaction occurs; the greater the potential difference, the greater the correction to the exchange current or rate constant.

2.5 MASS TRANSPORT TO THE ELECTRODE SURFACE

We have considered the thermodynamics of electrochemical processes, studied the kinetics of electrode processes, and investigated the effects of the electrical double layer on kinetic parameters. An understanding of these relationships is an important ingredient in the repertoire of the researcher of battery technology. Another very important area of study which has major impact on battery research is the evaluation of mass transport processes to and from electrode surfaces.

Mass transport to or from an electrode can occur by three processes: (1) convection and stirring, (2) electrical migration in an electric potential gradient, and (3) diffusion in a concentration gradient. The first of these processes can be handled relatively easily both mathematically and experimentally. If stirring is required, flow systems can be established, while if complete stagnation is an experimental necessity, this can also be imposed by careful design. In most cases, if stirring and convection are present or imposed, they can be handled mathematically.

The migration component of mass transport can also be handled experimentally (reduced to close to zero or occasionally increased in special cases) and described mathematically, provided certain parameters such as transport number or migration current are known. Migration of electroactive species in an electric potential gradient can be reduced to near zero by addition of an excess of inert "supporting electrolyte," which effectively reduces the potential gradient to zero and thus eliminates the electric field which produces migration. Enhancement of migration is more difficult. This requires that the electric field be increased so that movement of charged species is increased. Electrode geometry design can increase migration slightly by altering electrode curvature. The fields at convex surfaces are greater than those at flat or concave surfaces, and thus migration is enhanced at convex curved surfaces.

The third process, diffusion in a concentration gradient, is the most important of the three processes and is the one which typically is dominant in mass transport in batteries. The analysis of diffusion uses the basic equation due to Fick^8 which defines the flux of material crossing a plane at distance *x* and time *t*. The flux is proportional to the concentration gradient and is represented by the expression:

$$q = D \,\frac{\delta C}{\delta x} \tag{2.34}$$

where q =flux

D = diffusion coefficient

C = concentration

The rate of change of concentration with time is defined by

$$\frac{\delta C}{\delta t} = D \, \frac{\delta^2 C}{\delta x^2} \tag{2.35}$$

This expression is referred to as Fick's second law of diffusion. Solution of Eqs. (2.34) and (2.35) requires that boundary conditions be imposed. These are chosen according to the electrode's expected "discharge" regime dictated by battery performance or boundary conditions imposed by relevant electroanalytical technique.⁹ Several of the electroanalytical techniques are discussed in Sec. 2.6.

For application directly to battery technology, the three modes of mass transport have meaningful significance. Convective and stirring processes can be employed to provide a flow of electroactive species to reaction sites. Examples of the utilization of stirring and flow processes in batteries are the circulating zinc/air system, the vibrating zinc electrode, and the zinc-chlorine hydrate battery. In some types of advanced lead-acid batteries, circulation of acid is provided to improve utilization of the active materials in the battery plates.

Migration effects are in some cases detrimental to battery performance, in particular those caused by enhanced electric fields (potential gradients) around sites of convex curvature. Increased migration at these sites tends to produce dendrite formations which eventually lead to a short-circuit and battery failure.

2.5.1 Concentration Polarization

Diffusion processes are typically the mass-transfer processes operative in the majority of battery systems where the transport of species to and from reaction sites is required for maintenance of current flow. Enhancement and improvement of diffusion processes are an appropriate direction of research to follow to improve battery performance parameters. Equation (2.34) may be written in an approximate, yet more practical, form, remembering that i = nFq, where q is the flux through a plane of unit area. Thus,

$$i = nF \frac{DA(C_B - C_E)}{\delta}$$
(2.36)

where symbols are defined as before, and C_B = bulk concentration of electroactive species, C_E = concentration at electrode, A = electrode area, δ = boundary-layer thickness, that is, the layer at the electrode surface in which the majority of the concentration gradient is concentrated (see Fig. 2.15).

When $C_E = 0$, this expression defines the maximum diffusion current, i_L , that can be sustained in solution under a given set of conditions,

$$i_L = nF \frac{DAC_B}{\delta_L} \tag{2.37}$$

where δ_L is the boundary-layer thickness at the limiting condition. It tells us that to increase i_L , one needs to increase the bulk concentration, the electrode area, or the diffusion coefficient. In the design of a battery, an understanding of the implication of this expression is important. Specific cases can be analyzed quickly by applying Eq. (2.36), and parameters such as discharge rate and likely power densities of new systems may be estimated.



FIGURE 2.15 Boundary-layer thickness at an electrode surface.

Assume that the thickness of the diffusion boundary layer does not change much with concentration. Then $\delta_L = \delta$ and Eq. (2.36) may be rewritten as

$$i = \left(1 - \frac{C_E}{C_B}\right)i_L \tag{2.38}$$

The difference in concentration existing between the electrode surface and the bulk of the electrolyte results in a concentration polarization. According to the Nernst equation, the concentration polarization or overpotential η_c , produced from the change of concentration across the diffusion layer, may be written as

$$\eta_c = \frac{RT}{nF} \ln \frac{C_B}{C_E} \tag{2.39}$$

From Eq. (2.38) we have

$$\eta_c = \frac{RT}{nF} \ln \left(\frac{i_L}{i_L - i} \right) \tag{2.40}$$

This gives the relation of concentration polarization and current for mass transfer by diffusion. Equation (2.40) indicates that as *i* approaches the limiting current i_L , theoretically the overpotential should increase to infinity. However, in a real process the potential will increase only to a point where another electrochemical reaction will occur, as illustrated in Fig. 2.16. Figure 2.17 shows the magnitude of the concentration over-potential as a function of i/i_L with n = 2 at 25°C, based on Eq. (2.40).




FIGURE 2.17 Magnitude of concentration overpotential as a function of i/i_L , with n = 2 at 25°C, based on Eq. (2.40).

2.5.2 Porous Electrodes

Electrochemical reactions are heterogeneous reactions which occur on the electrolyteelectrolyte interface. In fuel cell systems, the reactants are supplied from the electrolyte phase to the catalytic electrode surface. In battery systems, the electrodes are usually composites made of active reactants, binder and conductive filler. In order to minimize the energy loss due to both activation and concentration polarizations at the electrode surface and to increase the electrode efficiency or utilization, it is preferred to have a large electrode surface area. This is accomplished with the use of a porous electrode design. A porous electrode can provide an interfacial area per unit volume several decades higher than that of a planar electrode (such as 10^4 cm^{-1}). A porous electrode consists of porous matrices of solids and void spaces. The electrolyte penetrates the void spaces of the porous matrix. In such an active porous mass, the mass-transfer condition in conjunction with the electrochemical reaction occurring at the interface is very complicated. In a given time during cell operation, the rate of reaction within the pores may vary significantly depending on the location. The distribution of current density within the porous electrode depends on the physical structure (such as tortuosity, pore sizes), the conductivity of the solid matrix and the electrolyte, and the electrochemical kinetic parameters of the electrochemical processes. A detailed treatment of such complex porous electrode systems can be found in Newman.¹⁰

2.6 ELECTROANALYTICAL TECHNIQUES

Many steady-state and impulse electroanalytical techniques are available to the experimentalist to determine electrochemical parameters and assist in both improving existing battery systems and evaluating couples as candidates for new batteries.¹¹ A few of these techniques are described in this section.

2.6.1 Cyclic Voltammetry

Of the electroanalytical techniques, cyclic voltammetry (or linear sweep voltammetry as it is sometimes known) is probably one of the more versatile techniques available to the electrochemist. The derivation of the various forms of cyclic voltammetry can be traced to the initial studies of Matheson and Nicols¹² and Randles.¹³ Essentially the technique applies a linearly changing voltage (ramp voltage) to an electrode. The scan of voltage might be ± 2 V from an appropriate rest potential such that most electrode reactions would be encompassed. Commercially available instrumentation provides voltage scans as wide as ± 5 V.

To describe the principles behind cyclic voltammetry, for convenience let us restate Eq. (2.9), which describes the reversible reduction of an oxidized species O,

$$O + ne \rightleftharpoons R \tag{2.9}$$

In cyclic voltammetry, the initial potential sweep is represented by

$$E = E_i - vt \tag{2.41}$$

where E_i = initial potential

t = time

v = rate of potential change or sweep rate (V/s)

The reverse sweep of the cycle is defined by

$$E = E_i + v't \tag{2.42}$$

where v' is often the same value as v. By combining Eq. (2.42) with the appropriate form of the Nernst equation [Eq. (2.6)] and with Fick's laws of diffusion [Eqs. (2.34) and (2.35)], an expression can be derived which describes the flux of species to the electrode surface. This expression is a complex differential equation and can be solved by the summation of an integral in small successive increments.^{14–16} As the applied voltage approaches that of the reversible potential for the electrode process, a small current flows, the magnitude of which increases rapidly but later becomes limited at a potential slightly beyond the standard potential by the subsequent depletion of reactants. This depletion of reactants establishes concentration profiles which spread out into the solution, as shown in Fig. 2.18. As the concentation profiles extend into solution, the rate of diffusive transport at the electrode surface decreases and with it the observed current. The current is thus seen to pass through a well-defined maximum, as illustrated in Fig. 2.19. The peak current of the reversible reduction [Eq. (2.9)] is defined by

$$i_p = \frac{0.447 \ F^{3/2} \ A n^{3/2} \ D^{1/2} \ C_o \ v^{1/2}}{R^{1/2} \ T^{1/2}}$$
(2.43)

The symbols have the same identity as before while i_p is the peak current and A the electrode area. It may be noted that the value of the constant varies slightly from one text or publication to another. This is because, as mentioned previously, the derivation of peak current height is performed numerically.



FIGURE 2.18 Concentration profiles for reduction of a species in cyclic voltammetry, $t_4 > t_0$.



FIGURE 2.19 Cyclic voltammetry peak current for reversible reduction of an electroactive species.

A word of caution is due regarding the interpretation of the value of the peak current. It will be remembered from the discussion of the effects of the electrical double layer on electrode kinetics that there is a capacitance effect at an electrode-electrolyte interface. Consequently the "true" electrode potential is modified by the capacitance effect as it is also by the ohmic resistance of the solution. Equation (2.41) should really be written in a form which described these two components. Equation (2.44) shows such a modification,

$$E = E_i - vt + r(i_f + i_c)$$
(2.44)

where r = cell resistance

$$i_f$$
 = faradic current

 $i_c = capacity current$

At small values of voltage sweep rate, typically below 1 mV/s, the capacity effects are small and in most cases can be ignored. At greater values of sweep rate, a correction needs to be applied to interpretations of i_p , as described by Nicholson and Shain.¹⁷ With regard to the correction for ohmic drop in solution, typically this can be handled adequately by careful cell design and positive feedback compensation circuitry in the electronic instrumentation.

Cyclic voltammetry provides both qualitative and quantitative information on electrode processes. A reversible, diffusion-controlled reaction such as presented by Eq. (2.9) exhibits an approximately symmetrical pair of current peaks, as shown in Fig. 2.20. The voltage separation ΔE of these peaks is

$$\Delta E = \frac{2.3 \ RT}{nF} \tag{2.45}$$

and the value is independent of the voltage sweep rate. In the case of the electrodeposition of an insoluble film, which can be, subsequently, reversibly reoxidized and which is not governed by diffusion to and from the electrode surface, the value of ΔE is considerably less than that given by Eq. (2.45), as shown in Fig. 2.21. In the ideal case, the value of ΔE for this system is close to zero. For quasi-reversible processes, the current peaks are more separated, and the shape of the peak is less sharp at its summit and is generally more rounded, as shown in Fig. 2.22. The voltage of the current peak is dependent on the voltage sweep rate, and the voltage separation is much greater than that given by Eq. (2.45). A completely





FIGURE 2.20 Cyclic voltammogram of a reversible diffusion-controlled process.

FIGURE 2.21 Cyclic voltammogram of electroreduction and reoxidation of a deposited, insoluble film.



FIGURE 2.22 Cyclic voltammogram of a quasireversible process.

irreversible electrode process produces a single peak, as shown in Fig. 2.23. Again the voltage of the peak current is sweep-rate dependent, and, in the case of an irreversible charge-transfer process for which the back reaction is negligible, the rate constant and transfer coefficient can be determined. With negligible back reaction, the expression for peak current as a function of peak potential is¹⁷

$$i_p = 0.22nFC_O k_{app} \exp\left[-\alpha \frac{nF}{RT} (E_m - E^o)\right]$$
(2.46)

where the symbols are as before and E_m is the potential of the current peak. A plot of E_m versus ln i_p , for different values of concentration, gives a slope which yields the transfer coefficient α and an intercept which yields the apparent rate constant k_{app} . Though both α and k_{app} can be obtained by analyzing E_m as a function of voltage sweep rate v by a reiterative calculation, analysis by Eq. (2.46) (which is independent of v) is much more convenient.

For more complex electrode processes, cyclic voltammetric traces become more complicated to analyze. An example of one such case is the electroreduction of a species controlled by a preceding chemical reaction. The shape of the trace for this process is shown in Fig. 2.24. The species is formed at a constant rate at the electrode surface and, provided the diffusion of the inactive component is more rapid than its transformation to the active form, it cannot be depleted from the electrode surface. The "peak" current is thus independent of potential and resembles a plateau.





FIGURE 2.23 Cyclic voltammogram of an irreversible process.

FIGURE 2.24 Cyclic voltammogram of electroreduction of a species controlled by a preceding chemical reaction.

Cyclic voltammograms of electrochemical systems can often be much more complicated than the traces presented here. It often takes some ingenuity and persistence to determine which peaks belong to which species or processes. Despite these minor drawbacks, the cyclic voltammetric technique is a versatile, and relatively sensitive, electroanalytical method appropriate to the analysis of systems of interest to battery development. The technique will identify reversible couples (desirable for secondary batteries), it provides a method for measuring the rate constant and transfer coefficient of an electrode process (a fast rate constant indicates a process of possible interest for battery development), and it can provide a tool to help unravel complex electrochemical systems.

2.6.2 Chronopotentiometry

Chronopotentiometry involves the study of voltage transients at an electrode upon which is imposed a constant current. It is sometimes alternately known as galvanostatic voltammetry. In this technique, a constant current is applied to an electrode, and its voltage response indicates the changes in electrode processes occurring at its interface. Consider, for example, the reduction of a species O as expressed by Eq. (2.9). As the constant current is passed through the system, the concentration of O in the vicinity of the electrode surface begins to decrease. As a result of this depletion, O diffuses from the bulk solution into the depleted layer, and a concentration gradient grows out from the electrode surface into the solution. As the electrode process continues, the concentration profile extends further into the bulk solution as shown in Fig. 2.25. When the surface concentration of O falls to zero (at time t_6 in Fig. 2.25), the electrode process can no longer be supported by electroreduction of O. An additional cathodic reaction must be brought into play and an abrupt change in potential occurs. The period of time between the commencement of electoreduction and the sudden change in potential is called the transition time τ . The transition time for electroreduction of a species in the presence of excess supporting electrolyte was first quantified by Sand,¹⁸ who showed that the transition time τ was related into the diffusion coefficient of the electroactive species,

$$\tau^{1/2} = \frac{\pi^{1/2} n F C_o D^{1/2}}{2i} \tag{2.47}$$

where D is the diffusion coefficient of species O and the other symbols have their usual meanings.



FIGURE 2.25 Concentration profiles extending into bulk solution during constant-current depletion of species at an electrode surface, $t_6 > t_0$.

Unlike cyclic voltammetry, the solution of Fick's diffusion equations [Eqs. (2.34) and (2.35)] for chronopotentiometry can be obtained as an exact expression by applying appropriate boundary conditions. For a reversible reduction of an electroactive species [Eq. (2.9)], the potential-time relationship has been derived by Delahay¹⁹ for the case where O and R are free to diffuse to and from the electrode surface, including the case where R diffuses into a mercury electrode,

$$E = E_{\tau/4} + \frac{RT}{nF} \ln \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}}$$
(2.48)

In this equation $E_{\tau/4}$ is the potential at the one-quarter transition time (the same as the polarographic half-wave potential in the case of a mercury electrode) and *t* is any time from zero to the transition time. The trace represented by this expression is shown in Fig. 2.26.

The corresponding expression for an irreversible process²⁰ with one rate-determining step is

$$E = \frac{RT}{\alpha n_a F} \ln \frac{n F C_o k_{app}}{i} + \frac{RT}{\alpha n_a F} \ln \left[1 - \left(\frac{t}{\tau}\right)^{1/2} \right]$$
(2.49)

where k_{app} is the apparent rate constant, n_a is the number of electrons involved in the ratedetermining step (often the same as *n*, the overall number of electrons involved in the total reaction), and the other symbols have their usual meanings. A plot of the logarithmic term versus potential yields both the transfer coefficient and the apparent rate constant.

In a practical system, the chronopotentiogram is often less than ideal in the shape of the potential trace. To accommodate variations in chronopotentiometric traces, measurement of the transition time can be assisted by use of a construction technique, as shown in Fig. 2.27. The transition time is measured at the potential of $E_{\tau/4}$.





FIGURE 2.26 Potential curve at constant current for reversible reduction of an electroactive species.

FIGURE 2.27 Construction of transition time τ for a chronopotentiogram.

To analyze two or more independent reactions separated by a potential sufficient to define individual transition times, the situation is slightly more complicated than with cyclic voltammetry. Analysis of the transition time of the reduction of the *n*th species has been derived elsewhere^{21,22} and is

$$(\tau_1 + \tau_2 + \dots + \tau_n)^{1/2} - (\tau_1 + \tau_2 + \dots + \tau_{n-1})^{1/2} = \frac{\pi^{1/2} n F D_n^{1/2} C_n}{2i}$$
(2.50)

As can be seen, this expression is somewhat cumbersome.

An advantage of the technique is that it can be used conveniently to evaluate systems with high resistance. The trace conveniently displays segments due to the *IR* component, the charging of the double layer, and the onset of the faradaic process. Figure 2.28 shows these different features of the chronopotentiogram of solutions with significant resistance. If the solution is also one which does not contain an excess of supporting electrolyte to suppress the migration current, it is possible to describe the transition time of an electroreduction process in terms of the transport number of the electroactive species^{23,24}

$$\tau^{1/2} = \frac{\pi^{1/2} n F C_o D_s^{1/2}}{2i(1 - t_o)} \tag{2.51}$$

where D_s is the diffusion coefficient of the salt (not the ion) and t_o the transport number of the electroactive species. This expression can be useful in battery research since many battery systems do not have supporting electrolyte.



FIGURE 2.28 Chronopotentiogram of a system with significant resistance.

2.6.3 Electrochemical Impedance Spectroscopy (EIS) Methods

The two preceding electroanalytical techniques, one in which the measured value was the current during imposition of a potential scan and the other a potential response under an imposed constant current, owe their electrical response to the change in impedance at the electrode-electrolyte interface. A more direct technique for studying electrode processes is to measure the change in the electrical impedance of an electrode by electrochemical impedance spectroscopy (EIS). To relate the impedance of the electrode-electrolyte interface to electrochemical parameters, it is necessary to establish an equivalent circuit to represent the dynamic characteristics of the interface.

Establishment of equivalent circuits attempting to describe electrode processes dates to the turn of the century with the derivation by Warburg²⁵ of an equation for the faradaic impedance of diffusion-controlled processes at a planar electrode. In fact, the impedance of the diffusion process is often referred to as the "Warburg impedance." In 1903, Krüger²⁶ realized that the double-layer capacity had influence on the impedance of the electrode interface and derived an expression for its effect. Much later the technique was developed and adapted to the study of electrode kinetics,²⁷⁻³¹ with emphasis on the charge-transfer process. The technique has been found to be extremely useful in evaluating several different electrode processes at a planar electrode and has been analyzed by several authors. The charge-transfer step has been considered and analyzed by Randles,²⁸ Grahame,³² Delahay,³³ Baticle and Perdu^{34,35} and Sluyters-Rehbach and Sluyters,³⁶ while Gerischer^{37,38} and Barker³⁹ considered coupled homogeneous and heterogeneous chemical reactions. Adsorption processes can be studied by this technique, and the description of the method used to measure adsorption has been given by Laitinen and Randles,⁴⁰ Llopis et al.,⁴¹ Senda and Delahay,⁴² Sluyters-Rehbach et al.,⁴³ Timmer et al.,⁴⁴ Barker,³⁹ and Holub et al.⁴⁵ An excellent EIS publication has been written by J. R. MacDonald⁴⁶ that analyses the solid/solution interface by equivalent circuitry to calculate the interfacial resistance, capacitance, and inductance and relates these to reaction mechanisms.

The expressions defining the various electrochemical parameters are relatively straightforward to derive but are complex in format, in particular when capacity effects are considered in the presence of strongly adsorbed electroactive species. Derivation of expressions relevant to the previously mentioned processes will not be given here. Only one of the more applicable analyses, and the one which is the most straightforward to handle, will be presented. The problem is that the majority of the processes require a transmission-line analysis to give a closed-system solution for a nonplanar electrode. We shall consider the system without adsorption and without complications of homogeneous series reactions where the impedance can be represented by a circuit diagram as shown in Fig. 2.29. In this analysis, due to Sluyters and coworkers, the electrode process is evaluated by the analytical technique of complex plane analysis. Here the capacitive component $1/\omega C$ is plotted versus the resistive component of the cell. Figure 2.30 shows a typical plot, which displays kinetic control only. The interdependence of the capacitive and resistive components yields a semicircle, with the top yielding the charge-transfer resistance r_{ct} .

$$\omega_m = \frac{1}{r_{\rm ct}C_{\rm nf}} \tag{2.52}$$





FIGURE 2.29 Equivalent circuit for a cell where the cell impedance is kinetically controlled and is localized at the working electrode by using a large, unpolarized countrelectrode. C_{nf} —nonfaradic capacitance; C_s , r_s —faradic components of impedance; r_e —electrolyte resistance.

FIGURE 2.30 Complex plane analysis of cell impedance for a charge-transfer process with kinetic control at a planar electrode.

where $C_{\rm nf}$ is the nonfaradaic capacitance and $r_{\rm ct} = RT/nF(i_{\rm O})_{\rm app}$. The intercept of the semicircle and the abscissa gives the electrolyte resistance r_e and again $r_{\rm ct}$. If the electrode process is governed by both kinetic and diffusion control, a somewhat different plot is observed, as shown in Fig. 2.31. In this plot, the linear portion of the curve corresponds to the process where diffusion control is predominant. From this plot, in addition to the previously mentioned measurement, the extrapolated linear portion gives a somewhat complex expression involving the diffusion coefficients of the oxidized and reduced species,

$$Intercept = r_e + 2S^2 C_{nf}$$
(2.53)

where

$$S = \frac{RTL}{n^2 F^2 \sqrt{2}} \tag{2.54}$$

and

$$L = \frac{1}{C_o \sqrt{D_o}} + \frac{1}{C_R \sqrt{D_R}}$$
(2.55)

 D_o being the diffusion coefficient of the oxidized species and D_R that of the reduced species. Treatment of this system assumes that we can write the equivalent circuit of kinetic and diffusion control as shown in Fig. 2.32, where the diffusion component of the impedance is given by the Warburg impedance W. It should also be noted that the derivation applies to a planar electrode only. Electrodes with more complex geometries such as porous electrodes require a transmission-line analysis.



FIGURE 2.31 Complex plane analysis of cell impedance for a charge-transfer process with both kinetic and diffusion control at a planar electrode.



FIGURE 2.32 Equivalent circuit for an electrode process limited by both charge-transfer kinetics and diffusion processes. The diffusion portion of the impedance is represented by the Warburg impedance, the other circuit components are the same as in Fig. 2.29.

The AC impedance technique coupled to the complex plane method of analysis is a powerful tool to determine a variety of electrochemical parameters. To make the measurements, instrumentation is somewhat more complex than with other techniques. It requires a Wheatstone bridge arrangement with series capacitance and resistance in the comparison arm, a tuned amplifier/detector, and an oscillator with an isolation transformer. A Wagner* ground is required to maintain bridge sensitivity, and a suitably large inductance should be incorporated in the electrode polarization circuit to prevent interference from the low impedance of this ancillary circuitry. Sophisticated measurement instruments or frequency response analyzers with frequency sweep and computer interface are currently available such as the Solartron frequency response analyzers. Data obtained can be analyzed or fitted into proper equivalent circuit using appropriate software.

This technique has found considerable acceptance in measuring fast rate constants, and it has been extended to include faradaic rectification and second-harmonic generation and detection. These advanced techniques extend the range of AC impedance measurements to the evaluation of charge-transfer rate constants with values of 10 cm/s or greater. Unfortunately the description of these techniques is beyond the scope of this chapter, but can be found in advanced texts on electrochemical methods.¹¹ In addition to applications in electrode kinetics, the technique has been used to study the corrosion and passivation of metals,⁴⁷⁻⁴⁹ to characterize battery electrode reactions, as well as for a simple nondestructive check of the state of charge of batteries.⁵⁰⁻⁵³ This method is therefore finding increasing utility in the study of battery systems. EIS is a powerful tool to evaluate battery electrode materials and has recently been shown to describe metal hydride anodes⁵⁴ and lithium intercalation anodes⁶⁵ and provide rate constants for the respective electrode processes.

2.6.4 Polarography

The technique of polarographic analysis is one of the most widely employed and the electroanalytical technique with the longest history of use. Polarography^{56–59} utilizes a dropping mercury electrode (DME) as the sensing electrode to which a slowly changing potential is applied, usually increasing in the negative direction, such that for each mercury drop, the potential remains essentially constant. The output current from the DME is typically displayed on a chart recorder, and the current magnitude is a measure of the concentration of electroactive species in solution. Because of the periodic nature of the DME, the current measuring circuit includes a damping capacitor with a time constant such that the oscillations in current due to the charging current of the DME are minimized. Figure 2.33 shows a typical polarogram of an electroactive species, where i_m is the polarographic mean diffusion current. The expression relating the concentration of electroactive species to the mean diffusion current is given by the Ilkovic equation.^{60,61}

$$I_m = 607nD^{1/2}Cm^{2/3}t_d^{1/6}$$
(2.56)

where i_m = mean diffusion current, μA

- n = number of electrons involved in overall electrode process
- D = diffusion coefficient of electroactive species
- C =concentration of electroactive species, mmol/L
- m = mercury flow rate, mg/s
- t_d = mercury drop time, s

^{*}A Wagner ground maintains a corner of a bridge at ground potential without actually connecting it directly to ground. This helps to eliminate stray capacitances to ground and maintains bridge sensitivity over a wide range of frequencies.



FIGURE 2.33 Polarogram of an electroactive species. i_m —polarographic mean diffusion current.

Analysis of the solutions usually is performed by calibrations with known standards rather than by using Eq. (2.56). Occasionally the polarogram of a solution may show a current spike at the beginning of the current plateau. This effect is due to a streaming phenomenon around the DME and can be suppressed by the addition of a *small* quantity of a surface-active compound such as gelatin or Triton X-100.

Solutions containing several electroactive species can be conveniently analyzed from one polarogram, provided the potential separation, the half-wave potential,* is sufficient to distinguish the current plateaus. Figure 2.34 shows a polarogram of an aqueous solution containing several species in a potassium chloride supporting electrolyte. The polarographic method is often found as a standard instrumental technique in electrochemical laboratories.



FIGURE 2.34 Polarogram of reduction of several electroactive species in a solution of 0.1*M* potassium chloride as supporting electrolyte.

Linden, D., & Reddy, T. (2001). Handbook of batteries. Retrieved from http://ebookcentral.proquest.com Created from uc on 2019-05-28 16:53:43.

^{*}The half-wave potential $(E_{1/2})$ is the electrode potential of the DME at which the value of *i* is one-half of its limiting value (i_m) .

2.6.5 Electrodes

Several electroanalytical techniques have been discussed in the preceding sections, but little was mentioned about electrodes or electrode geometries used in the various measurements. This section deals with electrodes and electrode systems.

A typical electroanalytical cell has an indicator electrode (sometimes called a working electrode), a counter electrode, and, in most cases, a reference electrode. The counter electrode is a large, inert, relatively unpolarized electrode situated a suitable distance from the indicator electrode and sometimes separated from it by a sintered glass disk or some other porous medium which will allow ionic conduction but prevent gross mixing of solutions surrounding the counter and working electrodes. The reference electrode provides an unpolarized reference potential against which the potentials of the indicator electrode can be measured. Reference electrodes are usually constructed in a separate vessel and are connected to the cell via a salt bridge composed of an electrolyte with a common anion or cation with the supporting electrolyte solution in the cell. The concentration of the salt bridge electrolyte is also chosen to be approximately the same as the supporting electrolyte. This minimizes liquid junction potentials which are established between solutions of different composition or concentration. Contamination of the cell solution with material from the salt bridge is minimized by restricting the orifice of the salt bridge by a Luggin capillary. Typical reference electrode systems are Ag/AgCl, Hg/Hg₂Cl₂, and Hg/HgO. For a comprehensive treatise on the subject of reference electrodes, the reader is referred to an excellent text by Ives and Janz.62

Indicator electrodes have been designed and fabricated in many different geometrical shapes to provide various performance characteristics and to accommodate the special requirements of some of the electroanalytical techniques. The simplest of the indicator electrode types is the planar electrode. This can be simply a "flag" electrode, or it can be shielded to provide for linear diffusion during long electrolysis times. Figure 2.35 shows a selection of planar-type indicator electrodes. Included in this selection is a thin-film cell (Fig. 2.35*e*) in which two planar electrodes confine a small quantity of solution within a small gap between the working and counter electrodes. The counter electrode is adjusted by a micrometer drive, and the reference salt bridge is located, as shown, as a radial extension of the cell. This cell has the advantage that only a small quantity of solution is required, and in many cases it can be used as a coulometer to determine n, the overall number of electrons involved in an electrode reaction.

Indicator electrodes not requiring a planar surface can be fabricated in many different geometries. For simplicity and convenience of construction, a wire electrode can be sealed into an appropriate glass support and used with little more than a thorough cleaning. For more symmetrical geometry, a spherical bead electrode can often be formed by fusing a thin wire of metal and shriveling it into a bead. In some cases, is possible to form a single crystal of the metal. Figure 2.36 shows various electrodes with nonplanar electrode-electrolyte interfaces.

Several electroanalytical methods require special electrodes or electrode systems. A classic example is the DME, first used extensively in polarography (Sec. 2.6.4). The DME is established by flowing ultrapure mercury through a precision capillary from a mercury reservoir connected to the capillary by a flexible tube. Mercury flow rates and drop times are adjusted by altering the height of the mercury head so that mercury drops detach every 2 to 7 s, with typical polarographic values being in the range 3 to 5 s. Figure 2.37 shows a schematic representation of a DME system. In addition to use of the DME in polarography, the electrode finds application when a fresh, clean mercury surface is necessary for reproducible electroanalytical determinations. In this respect, the DME can be used as a "stationary" spherical mercury electrode suitably "frozen" in time by a timing circuit initiated by the voltage pulse at the birth of the drop and triggered at a time short of the natural drop time of the DME. With a suitably short transient impulse (voltage, current, and so on) an output response can be obtained from what is essentially a hanging mercury drop electrode.



FIGURE 2.35 Various planar working electrodes, some with shielding to maintain laminar diffusion of electroactive species to surface.

Other special types of electrodes are the rotating disk electrode and the rotating ring-disk electrode. Figure 2.38 shows both rotating disk and ring-disk electrodes. In both cases, rotation of the electrode establishes a flow pattern which maintains a relatively constant diffusion layer thickness during reduction or oxidation of an electroactive species and provides a means of hydrodynamically varying the rate at which electroactive species are brought to the outer surface of the diffusion layer. In the ring-disk electrode, the ring can be used either as a "guard ring" to ensure laminar diffusion to the disk or as an independent working electrode to monitor species generated from the disk electrode or the generation of transient intermediate species. Details of the derivation of current-voltage curves as a function of rotation speed have been given by Riddiford⁶³ for the disk electrode, while more detail is given by Yeager and Kuta⁶⁴ and Pleskov and Filinovski⁶⁵ on the ring-disk electrode, with emphasis being given by the latter authors to the detection of transient species. Details of the current-voltage characteristics are not given here. It is sufficient to say that limiting currents for a fixed potential can be obtained by varying the rotation speed of the electrode from which potential-dependent rate constants can be determined. Ring currents may be determined either at a fixed potential such as to reverse the process leading to the formation of the species of interest or scanning through a range of potentials to detect a variety of species electroactive over a range of potentials. Quantitative measurements with the ring of the ring-disk electrode are difficult to interpret because the capture fraction N of the ring is difficult to evaluate.66





FIGURE 2.37 Dropping mercury electrode complete with polarographic H cell.



Disk electrode. (b) Ring-disk electrode.

REFERENCES

- 1. J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, vol. 2, Plenum, New York, 1970, p. 644.
- 2. H. H. Bauer, J. Electroanal. Chem. 16:419 (1968).
- 3. J. Horiuti and M. Polanyi, Acta Physicochim. U.S.S.R. 2:505 (1935).
- 4. J. O'M. Bockris and A. K. N. Reddy, op. cit., p. 918.
- 5. P. Delahay, Double Layer and Electrode Kinetics, Interscience, New York, 1965.
- 6. J. O'M. Bockris and A. K. N. Reddy, op. cit., p. 742.
- 7. H. H. Bauer, Electrodics, Wiley, New York, 1972, p. 54, table 3.2.
- 8. A. Fick, Ann. Phys. 94:59 (1855).
- 9. P. Delahay, New Instrumental Methods in Electrochemistry, Interscience, New York, 1954.
- 10. J. S. Newman, Electrochemical Systems, 2d ed., Prentice-Hall, Englewood Cliffs, N.J., 1991.
- E. B. Yeager and J. Kuta, "Techniques for the Study of Electrode Processes," in *Physical Chemistry*, vol. IXA: *Electrochemistry*, Academic, New York, 1970, p. 346.
- 12. L. A. Matheson and N. Nichols, J. Electrochem. Soc. 73:193 (1938).
- 13. J. E. B. Randles, Trans. Faraday Soc. 44:327 (1948).
- 14. A. Sevcik, Coll. Czech, Chem. Comm. 13:349 (1948).
- 15. T. Berzins and P. Delahay, J. Am. Chem. Soc. 75:555 (1953).
- 16. P. Delahay, J. Am. Chem. Soc. 75:1190 (1953).
- 17. R. S. Nicholson and I. Shain, Anal. Chem. 36:706 (1964).
- 18. H. J. S. Sand, Phil. Mag. 1:45 (1901).
- 19. P. Delahay, New Instrumental Methods in Electrochemistry, op. cit., p. 180.
- 20. P. Delahay and T. Berzins, J. Am. Chem. Soc. 75:2486 (1953).
- 21. C. N. Reilley, G. W. Everett, and R. H. Johns, Anal. Chem. 27:483 (1955).

- 22. T. Kambara and I. Tachi, J. Phys. Chem. 61:405 (1957).
- 23. M. D. Morris and J. J. Lingane, J. Electroanal. Chem. 6:300 (1963).
- 24. J. Broadhead and G. J. Hills, J. Electroanal. Chem. 13:354 (1967).
- 25. E. Warburg, Ann. Phys. 67:493 (1899).
- 26. F. Krüger, Z. Phys. Chem. 45:1 (1903).
- 27. P. Dolin and B. V. Ershler, Acta Physicochim. U.S.S.R. 13:747 (1940).
- 28. J. E. B. Randles, Disc. Faraday Soc. 1:11 (1947).
- 29. B. V. Ershler, Disc. Faraday Soc. 1:269 (1947).
- 30. B. V. Ershler, Zh. Fiz. Khim. 22:683 (1948).
- 31. K. Rozental and B. V. Ershler, Zh. Fiz. Khim. 22:1344 (1948).
- 32. D. C. Grahame, J. Electrochem. Soc. 99:370C.
- 33. P. Delahay, New Instrumental Methods in Electrochemistry, op. cit., p. 146.
- 34. A. M. Baticle and F. Perdu, J. Electroanal. Chem. 12:15 (1966).
- 35. A. M. Baticle and F. Perdu, J. Electroanal. Chem. 13:364 (1967).
- 36. M. Sluyters-Rehbach and J. H. Sluyters, Rec. Trav. Chim. 82:525, 535 (1963).
- 37. H. Gerischer, Z. Phys. Chem. 198:286 (1951).
- 38. H. Gerischer, Z. Phys. Chem. 201:55 (1952).
- G. C. Barker, in E. B. Yeager (ed.), *Trans. Symp. Electrode Processes* (Philadelphia, 1959), Wiley, New York, p. 325.
- 40. H. A. Laitinen and J. E. B. Randles, Trans. Faraday Soc. 51:54 (1955).
- 41. J. Llopis, J. Fernandez-Biarge, and M. Perez-Fernandez, Electrochim. Acta 1:130 (1959).
- 42. M. Senda and P. Delahay, J. Phys. Chem. 65:1580 (1961).
- 43. M. Sluyters-Rehbach, B. Timmer, and J. H. Sluyters, J. Electroanal. Chem. 15:151 (1967).
- 44. B. Timmer, M. Sluyters-Rehbach, and J. H. Sluyters, J. Electroanal. chem. 15:343 (1967).
- 45. K. Holub, G. Tesari, and P. Delahay, J. Phys. Chem. 71:2612 (1967).
- J. R. MacDonald, Impedance Spectroscopy, Emphasizing Solid Materials and Systems, Wiley, New York, 1987, pp. 154–155.
- 47. F. Mansfeld, Advances in Corrosion Science and Technology, vol. 6, Plenum, New York, p. 163.
- I. Epelboin, C. Gabrielli, M. Keddam, and H. Takenouti, in F. Mansfeld and U. Bertocci (eds.), Proc. ASTM Symp. on Progress in Electrochemical Corrosion Testing (May 1979), p. 150.
- S. Haruyama and T. Tsuru, in R. P. Frankenthal and J. Kruger (eds.), *Passivity of Metals*, Electrochemical Soc., Princeton, New Jersey, p. 564.
- 50. N. A. Hampson, S. A. G. R. Karunathlaka, and R. Leek, J. Appl. Electrochem. 10:3 (1980).
- 51. S. Sathyanarayana, S. Venugopalan, and M. L. Gopikanth, J. Appl. Electrochem. 9:129 (1979).
- S. A. G. R. Karunathlaka, N. A. Hampson, R. Leek, and T. J. Sinclair, J. Appl. Electrochem. 10: 357 (1980).
- 53. M. L. Gopikanth and S. Sathyanarayana, J. Appl. Electrochem. 9:369 (1979).
- C. Wang, "Kinetic Behavior of Metal Hydride Electrode by Means of AC Impedance," J. Electrochem. Soc. 145:1801 (1998).
- M. D. Levi, K. Gamolsky, D. Aurbach, U. Heider, and R. Oesten, "On Electrochemical Impedance Measurements of Li_xCo_{0.2}Ni_{0.8}O₂ and Li_xNiO₂ Intercalation Electrodes," *Electrochem. Acta* 45:1781 (2000).
- 56. I. M. Kolthoff and J. J. Lingane, Polarography, 2d ed., Interscience, New York, 1952.
- J. Heyrovsky and J. Kuta, *Principles of Polarography*, Czechoslovak Academy of Sciences, Prague, 1965.
- 58. L. Meites, Polarographic Techniques, 2d ed., Interscience, New York, 1965.
- 59. G. W. C. Milner, *The Principles and Applications of Polarography and Other Electroanalytical Processes*, Longmans, London, 1957.

- 60. D. Ilkovic, Coll. Czech. Chem. Comm. 6:498 (1934).
- 61. D. Ilkovic, J. Chim. Phys. 35:129 (1938).
- 62. D. J. G. Ives and G. J. Janz, *Reference Electrodes, Theory and Practice.* Academic, New York, 1961.
- 63. A. C. Riddiford, "The Rotating Disc System," in P. Delahay and C. W. Tobias (eds.), Advances in *Electrochemistry and Electrochemical Engineering*, Interscience, New York, 1966, p. 47.
- 64. E. B. Yeager and J. Kuta, op. cit., p. 367.
- 65. Y. V. Pleskov and V. Y. Filinovskii, in H. S. Wroblowa and B. E. Conway (eds.), *The Rotating Disc Electrode*, Consultants Bureau, New York, 1976, chap. 8.
- 66. W. J. Albery and S. Bruckenstein, Trans. Faraday Soc. 62:1920, 1946 (1966).

BIBLIOGRAPHY

General

Bauer, H. H.: Electrodics, Wiley, New York, 1972.

Bockris, J. O'M., and A. K. N. Reddy: *Modern Electrochemistry*, vols. 1 and 2, Plenum, New York, 1970.

Conway, B. E.: Theory and Principles of Electrode Processes, Ronald Press, New York, 1965.

Gileadi, E., E. Kirowa-Eisner, and J. Penciner: *Interfacial Electrochemistry*, Addison-Wesley, Reading, Mass., 1975.

Newman, J. S.: Electrochemical Systems, 2d ed., Prentice-Hall, Englewood Cliffs, N.J., 1991.

Sawyer, D. T., and J. L. Roberts: Experimental Electrochemistry for Chemists, Wiley, New York, 1974.

Transfer Coefficient

Bauer, H. H.: J. Electroanal. Chem. 16:419 (1968).

Electrical Double Layer

Delahay, P.: Double Layer and Electrode Kinetics, Interscience, New York, 1965.

Electroanalytical Techniques

Delahay, P.: *New Instrumental Methods in Electrochemistry*, Interscience, New York, 1954. Yeager, E. B., and J. Kuta: "Techniques for the Study of Electrode Processes," in *Physical Chemistry*, vol. IXA: *Electrochemistry*, Academic, New York, 1970.

Polarography

Heyrovsky, J., and J. Kuta: *Principles of Polarography*, Czechoslovak Academy of Sciences, Prague, 1965.Kolthoff, I. M., and J. J. Lingane: *Polarography*, 2d ed., Interscience, New York, 1952.

Meites, L.: Polarographic Techniques, 2d ed., Interscience, New York, 1965.
 Milner, G. W. C.: The Principles and Applications of Polarography and Other Electroanalytical Processes, Longmans, London, 1957.

Reference Electrodes

Ives, D. J. G., and G. J. Janz: Reference Electrodes, Theory and Practice, Academic, New York, 1961.

Electrochemistry of the Elements

Bard, A. J. (ed.): *Encyclopedia of Electrochemistry of the Elements*, vols. I–XIII, Dekker, New York, 1979.

Organic Electrode Reactions

Meites, L., and P. Zuman: Electrochemical Data, Wiley, New York, 1974.

AC Impedance Techniques

Gabrielli, G.: Identification of Electrochemical Processes by Frequency Response Analysis, Tech. Rep. 004/83, Solartron Instruments, Billerica, Mass., 1984.
Macdonald, J. R. (ed.): Impedance Spectroscopy, Wiley, New York, 1987.

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CHAPTER 3 FACTORS AFFECTING BATTERY PERFORMANCE

David Linden

3.1 GENERAL CHARACTERISTICS

The specific energy of a number of battery systems was listed in Table 1.2 These values are based on optimal designs and discharge conditions. While these values can be helpful to characterize the energy output of each battery system, the performance of the battery may be significantly different under actual conditions of use, particularly if the battery is discharged under more stringent conditions than those under which it was characterized. The performance of the battery under the specific conditions of use should be obtained before any final comparisons or judgments are made.

3.2 FACTORS AFFECTING BATTERY PERFORMANCE

Many factors influence the operational characteristics, capacity, energy output and performance of a battery. The effect of these factors on battery performance is discussed in this section. It should be noted that because of the many possible interactions, these effects can be presented only as generalizations and that the influence of each factor is usually greater under the more stringent operating conditions. For example, the effect of storage is more pronounced not only with high storage temperatures and long storage periods, but also under more severe conditions of discharge following storage. After a given storage period, the observed loss of capacity (compared with a fresh battery) will usually be greater under heavy discharge loads than under light discharge loads. Similarly, the observed loss of capacity at low temperatures (compared with normal temperature discharges) will be greater at heavy than at light or moderate discharge loads. Specifications and standards for batteries usually list the specific test or operational conditions on which the standards are based because of the influence of these conditions on battery performance.

Furthermore it should be noted that even within a given cell or battery design, there will be performance differences from manufacturer to manufacturer and between different versions of the same battery (such as standard, heavy-duty, or premium). There are also performance variables within a production lot, and from production lot to production lot, that are inherent in any manufacturing process. The extent of the variability depends on the process controls as well as on the application and use of the battery. Manufacturers' data should be consulted to obtain specific performance characteristics.

3.2.1 Voltage Level

Different references are made to the voltage of a cell or battery:

- 1. The *theoretical voltage* is a function of the anode and cathode materials, the composition of the electrolyte and the temperature (usually stated at 25°C).
- **2.** The *open-circuit voltage* is the voltage under a no-load condition and is usually a close approximation of the theoretical voltage.
- 3. The closed-circuit voltage is the voltage under a load condition.
- **4.** The *nominal voltage* is one that is generally accepted as typical of the operating voltage of the battery as, for example, 1.5 V for a zinc-manganese dioxide battery.
- 5. The *working voltage* is more representative of the actual operating voltage of the battery under load and will be lower than the open-circuit voltage.
- 6. The *average voltage* is the voltage averaged during the discharge.
- 7. The *midpoint voltage* is the central voltage during the discharge of the cell or battery.
- 8. The *end* or *cut-off voltage* is designated as the end of the discharge. Usually it is the voltage above which most of the capacity of the cell or battery has been delivered. The end voltage may also be dependent on the application requirements.

Using the lead-acid battery as an example, the theoretical and open-circuit voltages are 2.1 V, the nominal voltage is 2.0 V, the working voltage is between 1.8 and 2.0 V, and the end voltage is typically 1.75 V on moderate and low-drain discharges and 1.5 V for engine-cranking loads. On charge, the voltage may range from 2.3 to 2.8 V.

When a cell or battery is discharged its voltage is lower than the theoretical voltage. The difference is caused by *IR* losses due to cell (and battery) resistance and polarization of the active materials during discharge. This is illustrated in Fig. 3.1. In the idealized case, the discharge of the battery proceeds at the theoretical voltage until the active materials are consumed and the capacity is fully utilized. The voltage then drops to zero. Under actual conditions, the discharge curve is similar to the other curves in Fig. 3.1. The initial voltage of the cell under a discharge load is lower than the theoretical value due to the internal cell resistance and the resultant *IR* drop as well as polarization effects at both electrodes. The voltage also drops during discharge as the cell resistance increases due to the accumulation of discharge products, activation and concentration, polarization, and related factors. Curve 2 is similar to curve 1, but represents a cell with a higher internal resistance or a higher discharge rate, or both, compared to the cell represented by curve 1. As the cell resistance or the discharge shows a more sloping profile.



FIGURE 3.1 Characteristic discharge curves.

The specific energy that is delivered by a battery in practice is, therefore, lower than the theoretical specific energy of its active materials, due to:

- **1.** The average voltage during the discharge is lower than the theoretical voltage.
- 2. The battery is not discharged to zero volts and all of the available ampere-hour capacity is not utilized.

As specific energy equals

Watthours/gram = Voltage \times Ampere hours/gram

the delivered specific energy is lower than the theoretical energy as both of the components of the equation are lower.

The shape of the discharge curve can vary depending on the electrochemical system, constructional features, and other discharge conditions. Typical discharge curves are shown in Fig. 3.2. The flat discharge (curve 1) is representative of a discharge where the effect of change in reactants and reaction products is minimal until the active materials are nearly exhausted. The plateau profile (curve 2) is representative of two-step discharge indicating a change in the reaction mechanism and potential of the active material(s). The sloping discharge (curve 3) is typical when the composition of the active materials, reactants, internal resistance, and so on, change during the discharge, affecting the shape of the discharge curve similarly.

Specific examples of these curves and many others are presented in the individual chapters covering each battery system.



Elapsed time of discharge

FIGURE 3.2 Battery discharge characteristics-voltage profiles.

3.2.2 Current Drain of Discharge

As the current drain of the battery is increased, the *IR* losses and polarization effects increase, the discharge is at a lower voltage, and the service life of the battery is reduced. Figure 3.3a shows typical discharge curves as the current drain is changed. At extremely low current drains (curve 2) the discharge can approach the theoretical voltage and theoretical capacity. [However, with very long discharge periods chemical deterioration during the discharge can become a factor and cause a reduction in capacity (Sec. 3.2.12).] With increasing current drain (curves 3–5) the discharge voltage decreases, the slope of the discharge curve becomes more pronounced, and the service life, as well as the delivered ampere-hour or coulombic capacity, are reduced.

If a battery that has reached a particular voltage (such as the cutoff voltage) under a given discharge current is used at a lower discharge rate, its voltage will rise and additional capacity or service life can be obtained until the cutoff voltage is reached at the lighter load. Thus, for example, a battery that has been used to its end-of-life in a flash camera (a high drain



FIGURE 3.3 (*a*) Battery discharge characteristics—voltage levels. (*b*) Discharge characteristics of a battery discharged sequentially from high to lower discharge rates.

application) can subsequently be used successfully in a quartz clock application which operates at a much lower discharge rate. This procedure can also be used for determining the life of a battery under different discharge loads using a single test battery. As shown in Fig. 3.3b, the discharge is first run at the highest discharge rate to the specified end voltage. The discharge rate is then reduced to the next lower rate. The voltage increases and the discharge is continued again to the specified end voltage, and so on. The service life can be determined for each discharge rate, but the complete discharge curve for the lower discharge rates, as shown by the dashed portion of the each curve, obviously is lost. In some instances a time interval is allowed between each discharge for the battery to equilibrate prior to discharge at the progressively lower rates.

"C" Rate.* A common method for indicating the discharge, as well as the charge current of a battery, is the C rate, expressed as

$$I = M \times C_n$$

$$I_t(A) = C_n(Ah)/1(h)$$

where I = is expressed in amperes

 C_n = is the rated capacity declared by the manufacturer in ampere-hours, and

n'' = is the time base in hours for which the rated capacity is declared.

For example, a battery rated at 5 Ah at the 5 hour discharge rate (C_5 (Ah)) and discharged at 0.1 I_t (A) will be discharged at 0.5 A or 500 mA. For this Handbook, the method discussed in the text, and not in this footnote, will be used.

^{*}Traditionally, the manufacturers and users of secondary alkaline cells and batteries have expressed the value of the current used to charge and discharge cells and batteries as a multiple of the capacity. For example, a current of 200 mA used to charge a cell with a rated capacity of 1000 mAh would be expressed as C/5 or 0.2 C (or, in the European convention as C/5 A or 0, 2 CA). This method for designation of current has been criticized as being dimensionally incorrect in that a multiple of the capacity (e.g. ampere-hours) will be in ampere-hours and not, as required for current, in amperes. As a result of these comments, the International Electrotechnical commission (IEC) Sub-committee SC-21A has published a "Guide to the Designation of Current in Alkaline Secondary Cell and Battery Standards (IEC 61434)" which described a new method for so designating this current. In brief, the method states that the current (I) shall be expressed as

where I = discharge current, A

- C = numerical value of rated capacity of the battery, in ampere-hours (Ah)
- n = time, in hours, for which rated capacity is declared

M = multiple or fraction of C

For example, the 0.1C or C/10 discharge rate for a battery rated at 5 Ah is 0.5 A. Conversely, a 250-mAh battery, discharged at 50 mA, is discharged at the 0.2C or C/5 rate, which is calculated as follows:

$$M = \frac{I}{C_n} = \frac{0.050}{0.250} = 0.2$$

To further clarify this nomenclature system the designation for a C/10 discharge rate for a battery rated at 5 Ah at the 5 hour rate is:

 $0.1 C_5$

In this example, the C/10 rate is equal to 0.5 A, or 500 mA.

It is to be noted that the capacity of a battery generally decreases with increasing discharge current. Thus the battery rated at 5 Ah at the C/5 rate (or 1 A) will operate for 5 h when discharged at 1 A. If the battery is discharged at a lower rate, for example the C/10 rate (or 0.5 A), it will run for more than 10 h and deliver more than 5 Ah of capacity. Conversely, when discharged at its C rate (or 5 A), the battery will run for less than 1 h and deliver less than 5 Ah of capacity.

Hourly Rate. Another method for specifying the current is the *hourly rate*. This is the current at which the battery will discharge for a specified number of hours.

"E" Rate. The constant power discharge mode is becoming more popular for batterypowered applications. A method, analogous to the "C rate," can be used to express the discharge or charge rate in terms of power:

$$P = M \times E_n$$

where P = power(W),

- E = numerical value of the rated energy of the battery in watthours (Wh),
- n = time, in hours, at which the battery was rated

M = multiple or fraction of E.

For example, the power level at the $0.5E_5$ or $E_5/2$ rate for a battery rated at 1200 mWh, at the 0.2*E* or *E*/5 rate, is 600 mW.

3.2.3 Mode of Discharge (Constant Current, Constant Load, Constant Power)

The mode of discharge of a battery, among other factors, can have a significant effect on the performance of the battery. For this reason, it is advisable that the mode of discharge used in a test or evaluation program be the same as the one used in the application for which it is being tested.

A battery, when discharged to a specific point (same closed-circuit voltage, at the same discharge current, at the same temperature, etc.) will have delivered the same ampere-hours to a load regardless of the mode of discharge. However, as during the discharge, the discharge current will be different depending on the mode of discharge, the service time or "hours of discharge" delivered to that point (which is the usual measure of battery performance) will, likewise, be different.

Three of the basic modes under which the battery may be discharged are:

- **1.** *Constant Resistance:* The resistance of the load remains constant throughout the discharge (The current decreases during the discharge proportional to the decrease in the battery voltage)
- 2. Constant Current: The current remains constant during the discharge.
- **3.** *Constant Power:* The current increases during the discharge as the battery voltage decreases, thus discharging the battery at constant power level (power = current × voltage).

The effect of the mode of discharge on the performance of the battery is illustrated under three different conditions in Figs. 3.4, 3.5 and 3.6.

Case 1: Discharge loads are the same for each mode of discharge at the start of discharge In Fig. 3.4, the discharge loads are selected so that at the start of the discharge the discharge current and, hence, the power are the same for all three modes. Figure 3.4b is a plot of the voltage during discharge. As the cell voltage drops during the discharge, the current in the case of the constant resistance discharge, reflects the drop in the cell voltage according to Ohm's law:

$$I = V/R$$

This is shown in Fig. 3.4*a*.

In the case of a constant current discharge, the current remains the same throughout the discharge. However, the discharge time or service life is lower than for the constant resistance case because the average current is higher. Finally, in the constant power mode, the current increases with decreasing voltage according to the relationship:

$$I = P/V$$

The average current is now even higher and the discharge time still lower.

Figure 3.4*c* is a plot of the power level for each mode of discharge.

Case 2: "Hours of discharge" is the same for each mode of discharge

Figure 3.5 shows the same relationships but with the respective discharge loads selected so that the discharge time or "hours of service" (to a given end voltage) is the same for all three modes of discharge. As expected, the discharge curves vary depending on the mode of discharge.

Case 3: Power level is the same for each mode of discharge at the end of the discharge

From an application point of view the most realistic case is the assumption that the power under all three modes of operation is the same at the end of the discharge (Fig. 3.6). Electric and electronic devices require a minimum input power to operate at a specified performance level. In each case, the discharge loads are selected so that at the end of the discharge (when the cell reaches the cutoff voltage) the power output is the same for all of the discharge modes and at the level required for acceptable equipment performance. During the discharge, depending on the mode of discharge, the power output equals or exceeds the power required by the equipment until the battery reaches the cutoff voltage.

In the constant-resistance discharge mode, the current during the discharge (Fig. 3.6*b*) follows the drop in the battery voltage (Fig. 3.6*a*). The power, $I \times V$ or V^2/R , drops even more rapidly, following the square of the battery voltage (Fig. 3.6*c*). Under this mode of discharge, to assure that the required power is available at the cutoff voltage, the levels of current and power during the earlier part of the discharge are in excess of the minimum required. The battery discharges at a higher current than needed, draining its capacity rapidly, which will result in a shorter service life.

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FIGURE 3.4 Discharge profiles under different discharge modes; same current and power at start of discharge. (a) Current profile during discharge. (b) Voltage profile during discharge. (c) Power profile during discharge.



(c)

Discharge current

Voltage

Power

Constant current

Discharge time

Constant current

Discharge time

Constant current

Discharge time

(b)

(a)

FIGURE 3.6 Discharge profiles under different discharge modes: same power at end of discharge. (a) current profile during discharge. (b) Voltage profile during discharge. (c) Power profile during discharge.

(c)

(a)

(b)



In the constant-current mode, the current is maintained at a level such that the power output at the cutoff voltage is equal to the level required for acceptable equipment performance. Thus both current and power throughout the discharge are lower than for the constantresistance mode. The average current drain on the battery is lower and the discharge time or service life to the end of the battery life is longer.

In the constant-power mode, the current is lowest at the beginning of the discharge and increases as the battery voltage drops in order to maintain a constant-power output at the level required by the equipment. The average current is lowest under this mode of discharge, and hence, the longest service time is obtained.

It should be noted that the extent of the advantage of the constant-power discharge mode over the other modes of discharge is dependent on the discharge characteristics of the battery. The advantage is higher with battery systems that require a wide voltage range to deliver their full capacity.

3.2.4 Example of Evaluation of Battery Performance Under Different Modes of Discharge

Thus, in evaluating or comparing the performance of batteries, because of the potential difference in performance (service hours) due to the mode of discharge, the mode of discharge used in the evaluation or test should be the same as that in the application. This is illustrated further in Fig. 3.7.

Figure 3.7*a* shows the discharge characteristics of a typical "AA"-size primary battery with the values for the discharge loads for the three modes of discharge selected so that the hours of discharge to a given end voltage (in this case, 1.0 volt) are the same. This is the same condition shown in Fig. 3.5*b*. (This example illustrates the condition when a resistive load, equivalent to the average current, is used, albeit incorrectly, as a "simpler" less-costly test to evaluate a constant current or constant power application.) Although the hours of service to the given end voltage is obviously the same because the loads were pre-selected, the discharge current vs. discharge time and power vs. discharge time curves (see Figs. 3.5*a* and *c* respectively), show significantly different characteristics for the different modes of discharge.

Figure 3.7b shows the same three types of discharge as Fig. 3.7a, but on a battery that has about the same ampere-hour capacity (to a 1.0 volt end voltage) as the battery illustrated in Fig. 3.7a. The battery illustrated in Fig. 3.7b, however, has a lower internal resistance and a higher operating voltage. Note, by comparing the voltage vs. discharge time curves in Fig. 3.7b, that, although the voltage level is higher, the "hours of discharge" obtained on the constant resistance discharge to the 1.0 volt cutoff in Fig. 3.7b is about the same as obtained on Fig. 3.7a. However, the hours of service obtained on the constant current discharge and, particularly, the constant power discharge are significantly higher.

In Fig. 3.7*a*, the discharge loads were deliberately selected to give the same "hours of service" to 1.0 volt at the three modes of discharge. Using these same discharge loads, but with a battery having different characteristics, Fig. 3.7*b* shows that different "hours of service" and performance are obtained with the different modes of discharge. To the specified 1.0 volt end voltage, the longest "hours of service" are obtained with the constant power discharge mode. The shortest service time is obtained with the constant resistance discharge mode and the constant current mode is in the middle position. This clearly illustrates that, on application tests, where performance is measured in "hours of service," erroneous results will be obtained if the mode of discharge used in the test is different from that used in the application.

It is recognized that the performance differences obtained when comparing batteries are directly dependent on the differences in battery design and performance characteristics. With batteries that are significantly different in design and characteristics, the performance obtained on test will be quite different as shown in the comparisons between Figs. 3.7*a* and





3.7*b*. When the batteries are similar, the performance differences obtained on any of the modes of discharge may not be large and may not appear to be significantly different. However, just because the difference in this case are small, it should not lead to the false assumption that testing under a discharge mode different from the application would give accurate results.

This is illustrated in Fig. 3.7*c*, which shows the discharge characteristics of another battery which has a slightly higher capacity and higher internal resistance than the one shown in Fig. 3.7*a*. Although the differences are small, a careful comparison of the Fig. 3.7*a* with Fig. 3.7*c* at the different modes of discharge does show a different behavior in the "hours of discharge" obtained to the specified 1.0 volt end voltage. Under the constant power mode, the "hours of discharge" show a slight decrease comparing Fig. 3.7*c* with Fig. 3.7*a*. While there is a slight increase under the constant current and constant resistance discharge modes.

(Note: The influence of end voltage should be noted. As 1.0 volt was used as the endvoltage in determining the load values for these examples, this end voltage should be used in making comparisons. If discharged to lower end voltages, the service life for the constant resistance mode increases compared to the other modes because of the lower current and power levels. However, these lower values may be inadequate for the specified application).

3.2.5 Temperature of Battery During Discharge

The temperature at which the battery is discharged has a pronounced effect on its service life (capacity) and voltage characteristics. This is due to the reduction in chemical activity and the increase in the internal resistance of the battery at lower temperatures. This is illustrated in Fig. 3.8, which shows discharges at the same current drain but at progressively increasing temperatures of the battery (T_1 to T_4), with T_4 representing a discharge at normal room temperature. Lowering of the discharge temperature will result in a reduction of capacity as well as an increase in the slope of the discharge curve. Both the specific characteristics and the discharge profile vary for each battery system, design, and discharge rate, but generally best performance is obtained between 20 and 40°C. At higher temperatures, the internal resistance decreases, the discharge voltage increases and, as a result, the amperehour capacity and energy output usually increase as well. On the other hand, chemical activity also increases at the higher temperatures and may be rapid enough during the discharge (a phenomenon known as *self-discharge*) to cause a net loss of capacity. Again, the extent is dependent on the battery system, design and temperature.



FIGURE 3.8 Effect of temperature on battery capacity. T_1 to T_4 —increasing temperatures.

Figures 3.9 and 3.10 summarize the effects of temperature and discharge rate on the battery's discharge voltage and capacity. As the discharge rate is increased, the battery voltage (for example, the midpoint voltage) decreases; the rate of decrease is usually more rapid at the lower temperatures. Similarly, the battery's capacity falls off most rapidly with increasing discharge load and decreasing temperature. Again, as noted previously, the more stringent the discharge conditions, the greater the loss of capacity. However, discharging at high rates could cause apparent anomalous effects as the battery may heat up to temperatures much above ambient, showing the effects of the higher temperatures. Curve T_6 in Fig. 3.10 shows the loss of capacity at high temperatures at low discharge rates or long discharge times due to self-discharge or chemical deterioration. It also shows the higher capacity that may be obtained as a result of the battery heating at the high rate discharge.



FIGURE 3.9 Effect of discharge load on battery midpoint voltage at various temperatures, T_1 to T_4 —increasing temperatures; T_4 —normal room temperature



FIGURE 3.10 Effect of discharge load on battery capacity at various temperatures. T_1 to T_6 —increasing temperatures; T_4 —normal room temperature

3.2.6 Service Life

A useful graph employed in this Handbook summarizing the performance of each battery system, presents the service life at various discharge loads and temperatures, normalized for unit weight (amperes per kilogram) and unit volume (amperes per liter). Typical curves are shown in Fig. 3.11. In this type of presentation of data, curves with the sharpest slope represent a better response to increasing discharge loads than those which are flatter or flatten out at the high current drain discharges.



FIGURE 3.11 Battery service life at various discharge loads and temperatures (log–log scale). T_1 to T_4 —increasing temperature.

Data of this type can be used to approximate the service life of a given cell or battery under a particular discharge condition or to estimate the weight or size of a battery required to meet a given service requirement. In view of the linearity of these curves on a log-log plot, mathematical relationships have been developed to estimate the performance of batteries under conditions that are not specifically stated. Peukert's equation,

$$I''t = C$$

$$n \log I + \log t = \log C$$

where I is the discharge rate and t the corresponding discharge time, has been used in this manner to describe the performance of a battery. The value n is the slope of the straight line. The curves are linear on a log-log plot of discharge load versus discharge time but taper off at both ends because of the battery's inability to handle very high rates and the effect of self-discharge at the lower discharge rates. A more detailed explanation of the use of these graphs in a specific example is presented in Fig. 14.13. Other mathematical relationships have been developed to describe battery performance and account for the non-linearity of the curves.¹

Other types of graphs are used to show similar data. A Ragone plot, such as the one illustrated in Fig. 6.3, plots the specific energy or energy density of a battery system against the specific power or power density on a log-log scale. This type of graph effectively shows the influence of the discharge load (in this case, power) on the energy that can be delivered by a battery.

or

3.2.7 Type of Discharge (Continuous, Intermittent, etc.)

When a battery stands idle after a discharge, certain chemical and physical changes take place which can result in a recovery of the battery voltage. Thus the voltage of a battery, which has dropped during a heavy discharge, will rise after a rest period, giving a sawtooth-shaped discharge, as illustrated in Fig. 3.12. This can result in an increase in service life. However, on lengthy discharges, capacity losses may occur due to self-discharge (see Sec. 3.2.12). This improvement, resulting from the intermittent discharge, is generally greater after the higher current drains (as the battery has the opportunity to recover from polarization effects that are more pronounced at the heavier loads). In addition to current drain, the extent of recovery is dependent on many other factors such as the particular battery system and constructional features, discharge temperature, end voltage, and length of recovery period.

The interactive effect on capacity due to the discharge load and the extent of intermittency is shown in Fig. 8.11. It can be seen that the performance of a battery as a function of duty cycle can be significantly different at low and high discharge rates. Similarly, the performance as a function of discharge rate can be different depending on the duty cycle.



FIGURE 3.12 Effect of intermittent discharge on battery capacity.

3.2.8 Duty Cycles (Intermittent and Pulse Discharges)

Another consideration is the response of the battery voltage when the discharge current is changed during the discharge, such as changing loads from receive to transmit in the operation of a radio transceiver. Figure 3.13 illustrates a typical discharge of a radio-transceiver, discharging at a lower current during the receive mode and at a higher current during the transmit mode. Note that the service life of the battery is determined when the cut-off or end voltage is reached under the higher discharge load. The average current cannot be used to determine the service life. Operating at two or more discharge loads is typical of most electronic equipment because of the different functions they must perform during use.

Another example is a higher rate periodic pulse requirement against a lower background current, such as backlighting for an LCD watch application, the audible trouble signal pulse in the operation of a smoke detector, or a high rate pulse during the use of a cell phone or computer. A typical pulse discharge is plotted in Fig. 3.14. The extent of the drop in voltage



FIGURE 3.13 Typical discharge characteristics of a battery cycling between transmit and receive loads.



FIGURE 3.14 Typical discharge characteristics of a battery subjected to a periodic high rate pulse.

depends on the battery design. The drop in voltage for a battery with lower internal resistance and better response to changes in load current will be less than one with higher internal resistance. In Fig. 3.14, note that the voltage spread widens as the battery is discharged due to the increase in internal resistance as the battery is discharged.

The shape of the pulse can vary significantly depending on the characteristics of the pulse and the battery. Figure 3.15 shows the characteristics of 9-volt primary batteries subjected to the 100 millisecond audible trouble signal pulse in a smoke detector. Curve A shows the response of a zinc-carbon battery, the voltage dropping sharply initially and then recovering. Curves B and C are typical of the response of a zinc/alkaline/manganese dioxide battery, the voltage initially falling and either maintaining the lower voltage or dropping slowly as the pulse discharge continues.

The type of response shown in Fig. 3.15*a* is also typical of batteries that have developed a protective or passivating film on an electrode, the voltage recovering as the film is broken during the discharge (see Sec. 3.2.12 on Voltage Delay). The specific characteristics, how-



FIGURE 3.15 Discharge characteristics of a 9-volt battery subjected to a 100 ms pulse (smoke detector pulse tests): (*a*) zinc-carbon battery; (*b*) and (*c*) zinc/alkaline/ manganese dioxide battery.

Linden, D., & Reddy, T. (2001). Handbook of batteries. Retrieved from http://ebookcentral.proquest.com Created from uc on 2019-05-28 16:53:43.

ever, are dependent on the battery chemistry, design, state of discharge, and other factors, related to the battery's internal resistance at the time of the pulse and during the pulse (also see Chap. 2 on internal resistance and polarization).

The performance of a battery under pulse conditions can be characterized by plotting the output power of the pulse against the load voltage, measuring the power delivered to the load by the short term pulse over the range of open circuit to short circuit.² Peak power is delivered to the load when the resistance of the external is equal to the internal resistance of the battery. Figure 3.16 is a power vs. load voltage plot of the pulse characteristics of an undischarged zinc/alkaline/manganese dioxide battery ("AA"-size) at the end of constant voltage pulses of 0.1 and 1 second. The lower values of power for the longer pulse is indicative of the drop in voltage as the pulse length increases. Figure 10.15 shows a similar plot, with the 1-second pulse taken at different depths of battery discharge.



FIGURE 3.16 Power vs. Load voltage at the end of a constant voltage pulses (undischarged zinc/alkaline/ manganese dioxide "AA" size battery. (*From Ref 2.*)

3.2.9 Voltage Regulation

The voltage regulation required by the equipment is most important in influencing the capacity or service life obtainable from a battery. As is apparent from the various discharge curves, design of the equipment to operate to the lowest possible end voltage and widest voltage range result 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.

Figure 3.17 compares two typical battery discharge curves: curve 1 depicts a battery having a flat discharge curve; curve 2 depicts a battery having a sloping discharge curve. In applications where the equipment cannot tolerate the wide voltage spread and is restricted, for example, to the -15% level, the battery with the flat discharge profile gives the longer service. On the other hand, if the batteries can be discharged, to lower cutoff voltages, the service life of the battery with the sloping discharge is extended and could exceed that of the battery with the flat discharge profile.


FIGURE 3.17 Comparison of flat ① and sloping ② discharge curves.

Discharging multicell series-connected batteries to too low an end voltage, however, may result in safety problems. It is possible, in this situation, for the poorest cell to be driven into voltage reversal. With some batteries this could result in venting or rupture.

In applications where only a narrow voltage range can be tolerated, the selection of the battery may be limited to those having a flat discharge profile. An alternative is to use a voltage regulator to convert the varying output voltage of the battery into a constant output voltage consistent with the equipment requirements. In this way, the full capacity of the battery can be used with inefficiency of the voltage regulator the only energy penalty. Figure 3.18 illustrates the voltage and current profiles of the battery and regulator outputs. The input from the battery to the regulator is at a constant power of 1 W, with the current increasing as the battery voltage drops. With an 84% conversion efficiency, the output from the regulator is constant at a predetermined 6 V and 140 mA (constant power = 840 mW).



FIGURE 3.18 Characteristics of a voltage regulator. Battery output—1 W; regular output—840 mW.

3.2.10 Charging Voltage

If a rechargeable battery is used (for example, as a standby power source) in conjunction with another energy source which is permanently connected in the operating circuit, allowance must be made for the battery and equipment to tolerate the voltage of the battery on charge. Figure 3.19 shows the charge and discharge characteristics of such a battery. The specific voltage and the voltage profile on charge depend on such factors such as the battery system, charge rate, temperature, and so on.



FIGURE 3.19 Typical voltage profile on charge and discharge.

If a primary battery is used in a similar circuit (for example, as memory backup battery), it is usually advisable to protect the primary battery from being charged by including an isolating or protective diode in the circuit, as shown in Fig. 3.20. Two diodes provide redundancy in case one fails. The resistor in Fig. 3.20b serves to limit the charging current in case the diode fails.

The charging source must also be designed so that its output current is regulated during the charge to provide the needed charge control for the battery.



FIGURE 3.20 Protective circuits for memory backup applications. (*a*) Using two diodes. (*b*) Using diode and resistor.

3.2.11 Effect of Cell and Battery Design

The constructional features of the cell and battery strongly influence its performance characteristics.

Electrode Design. Cells that are designed, for example, for optimum service life or capacity at relatively low or moderate discharge loads contain maximum quantities of active material. On the other extreme, cells capable of high-rate performance are designed with large electrode or reaction surfaces and features to minimize internal resistance and enhance current density (amperes per area of electrode surface), often at the expense of capacity or service life.

For example, two designs are used in cylindrical cells. One design known as the bobbin construction, is typical for zinc-carbon and alkaline-manganese dioxide cells. Here the electrodes are shaped into two concentric cylinders (Fig. 3.21*a*). This design maximizes the amount of active material that can be placed into the cylindrical can, but at the expense of surface area for the electrochemical reaction.

The second design is the "spirally wound" electrode construction, typically used in sealed portable rechargeable batteries and high-rate primary and rechargeable lithium batteries (Fig. 3.21b). In this design, the electrodes are prepared as thin strips and then rolled, with a separator in between, into a "jelly roll" and placed into the cylindrical can. This design emphasizes surface area to enhance high-rate performance, but at the expense of active material and capacity.

Another popular electrode design in the flat-plate construction, typically used in the leadacid SLI and most larger storage batteries (Fig. 3.21*c*). This construction also provides a large surface area for the electrochemical reaction. As with the other designs, the manufacturer can control the relationship between surface area and active material (for example, by controlling the plate thickness) to obtain the desired performance characteristics.

A modification of this design is the bipolar plate illustrated in Fig. 3.21*d*. Here the anode and cathode are fabricated as layers on opposite sides of an electronically conductive but ion-impermeable material which serves as the intercell connector.

Most battery chemistries can be adapted to the different electrode designs, and some in fact, are manufactured in different configurations. Manufacturers choose chemistries and designs to optimize the performance for the particular applications and markets in which they are interested.

In Fig. 3.22 the performance of a battery designed for high-rate performance is compared with one using the same electrochemical system, but optimized for capacity. The high-rate batteries have a lower capacity but deliver a more constant performance as the discharge rate increases.

Hybrid Designs. "Hybrid" designs, which combine a high energy power source with a high-rate power source, are now becoming popular. These hybrid systems fulfill applications more effectively (e.g. higher total specific energy or energy density), than using a single power source. The high energy power source is the basic source of energy, but also charges a high-rate battery which handles any peak power requirement that cannot be handled efficiently by the main power source. Hybrid designs are being considered in many applications, ranging from combining a high energy, low rate metal/air battery or fuel cell with a high rate rechargeable battery to electric vehicles, using an efficient combustion engine with a rechargeable battery to handle starting, acceleration and other peak power demands (also see Fig. 6.13).



FIGURE 3.21 Cell design; typical internal configurations. (*a*) bobbin construction. (*b*) Spiral wound construction. (*c*) Flat-plate construction. (*d*) Bipolar-plate construction.



FIGURE 3.22 Comparison of performance of batteries designed for high- and low-rate service.

Shape and Configuration. The shape or configuration of the cell will also influence the battery capacity as it affects such factors as internal resistance and heat dissipation. For example, a tall, narrow-shaped cylindrical cell in a bobbin design will generally have a lower internal resistance than a wide, squat-shaped one of the same design and may outperform it, in proportion to its volume, particularly at the higher discharge rates. For example, a thin "AA" size bobbin type cell will have proportionally better high rate performance than a wider diameter "D" size cell. Heat dissipation also will be better from cells with a high surface-to-volume ratio or with internal components that can conduct heat to the outside of the battery.

Volumetric Efficiency versus Energy Density. The size and shape of the cell or battery and the ability to effectively use its internal volume influence the energy output of the cell. The volumetric energy density (watthours per liter) decreases with decreasing battery volume as the percentage of "dead volume" for containers, seals, and so on, increases for the smaller batteries. This relationship is illustrated for several button-type cells in Fig. 3.23. The shape of the cell (such as wide or narrow diameter) may also influence the volumetric efficiency as it relates to the amount of space lost for the seal and other cell construction materials.



FIGURE 3.23 Energy density, in watthours per cubic centimeter, of button batteries as a function of cell volume. (*From Paul Ruetschi, "Alkaline Electrolyte-Lithium Miniature Primary Batteries," J. Power Sources, vol. 7, 1982.*)

Effect of Size on Capacity. The size of the battery 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 profile similar to curve 4 or 5 of Fig. 3.3, but it may be a mild load on a larger battery with a discharge curve similar to curve 2 or 3. Often it is possible to obtain more than a proportional increase in the service life by increasing the size of the battery (for paralleling cells) as the current density is lowered. The absolute value of the discharge current, therefore, is not the key influence, although its relation to the size of the battery, that is, the current density, is significant.

In this connection, the alternative of using a series-connected multicell battery versus a lower voltage battery, with fewer but larger cells and a voltage converter to obtain the required high voltage, should be considered. An important factor is the relative advantage of the potentially more efficient larger battery versus the energy losses of the voltage converter. In addition, the reliability of the system is enhanced by the use of a smaller number of cells. However, all pertinent factors must be considered in this decision because of the influences of cell and battery design, configuration, and so on, as well as the equipment power requirements.

3.2.12 Battery Age and Storage Condition

Batteries are a perishable product and deteriorate as a result of the chemical action that proceeds during storage. The design, electrochemical system, temperature, and length of storage period are factors which affect the shelf life or charge retention of the battery. The type of discharge following the storage period will also influence the shelf life of the battery. Usually the percentage charge retention following storage (comparing performance after and before storage) will be lower the more stringent the discharge condition. The self-discharge characteristics of several battery systems at various temperatures are shown in Fig. 6.7 as well as in the chapters on specific battery chemistries. As self-discharge proceeds at a lower rate at reduced temperatures, refrigerated or low-temperature storage extends the shelf life and is recommended for some battery systems. Refrigerated batteries should be warmed before discharge to obtain maximum capacity.

Self-discharge can also become a factor during discharge, particularly on long-term discharges, and can cause a reduction in capacity. This effect is illustrated in Fig. 3.10 and 3.24. More capacity will be delivered on a discharge at a light load than on a heavy load. However, on an extremely light load over a long discharge period, capacity may be reduced due to self-discharge.



FIGURE 3.24 Effect of self-discharge on battery capacity.

Some battery systems will develop protective or passivating films on one or both electrode surfaces during storage. These films can improve the shelf life of the battery substantially. However, when the battery is placed on discharge after storage, the initial voltage may be low due to the impedance characteristics of the film until it is broken down or depassivated by the electrochemical reaction. This phenomenon is known as "voltage delay" and is illustrated in Fig. 3.25. The extent of the voltage delay is dependent on an increases with increasing storage time and storage temperature. The delay also increases with increasing discharge current and decreasing discharge temperature.

The self-discharge characteristics of a battery that has been or is being discharged can be different from one that has been stored without having been discharged. This is due to a number of factors, such as the discharge rate and temperature, the accumulation of discharge products, the depth of discharge, or the partial destruction or reformation of the protective film. Some batteries, such as the magnesium primary battery (Chapter 9), may lose their good shelf-life qualities after being discharged because of the destruction of the protective film during discharge. Knowledge of the battery's storage and discharge history is needed to predict the battery's performance under these conditions.



3.2.13 Effect of Battery Design

The performance of the cells in a multicell battery will usually be different than the performance of the individual cells. The cells cannot be manufactured identically and, although cells are selected to be "balanced," they each encounter a somewhat different environment in the battery pack.

The specific design of the multicell battery and the hardware that is used (such as packaging techniques, spacing between the cells, container material, insulation, potting compound, fuses and other electronic controls, etc.) will influence the performance as they effect the environment and temperature of the individual cells. Obviously, the battery materials add to its size and weight and the specific energy or energy density if the battery will be lower than that of the component cells. Accordingly, when comparing values such as specific energy, in addition to being aware of the conditions (discharge rate, temperature, etc.) under which these values were determined, it should be ascertained whether the values given are for cells, single cell batteries or multicell batteries. Usually, as is the case in this Handbook, they are on the basis of a single-cell battery unless specified otherwise. A comparison of the performance of single-cell and multicell batteries can be made by reviewing the data in Table 1.2 on single-cell batteries with the data in Table 6.5 on 24-volt multicell batteries.

Battery designs that retain the heat dissipated by the cells can improve the performance at low temperatures. On the other hand, excessive buildup of heat can be injurious to the battery's performance, life and safety. As much as possible, batteries should be designed thermally to maintain a uniform internal temperature and avoid "hot spots."

In the case of rechargeable batteries, cycling could cause the individual cells in a battery peak to become unbalanced and their voltage, capacity or other characteristics could become significantly different. This could result in poor performance or safety problems, and end-of-charge or discharge control may be necessary to prevent this.

The influence of battery design and recommendations for effective battery design are covered in Chap. 5.

REFERENCES

- R. Selim and P. Bro, "Performance Domain Analysis of Primary Batteries," *Electrochemical Technology, J. Electrochem. Soc.* 118(5) 829 (1971).
- D. I. Pomerantz, "The Characterization of High Rate Batteries," *IEEE Transactions Electronics*" 36(4) 954 (1990).

CHAPTER 4 BATTERY STANDARDIZATION

Frank Ciliberti and Steven Wicelinski

4.1 GENERAL

The standardization of batteries started in 1912, when a committee of the American Electrochemical Society recommended standard methods of testing dry cells. This eventually led to the first national publication in 1919 issued as an appendix to a circular from the National Bureau of Standards. It further evolved into the present American National Standards Institute (ANSI) Accredited Standards Committee C18 on Portable Cells and Batteries. Since then, other professional societies have developed battery related standards. Many battery standards were also issued by international, national, military, and federal organizations. Manufacturers' associations, trade associations, and individual manufacturers have published standards as well. Related application standards, published by the Underwriters Laboratories, the International Electrotechnical Commission, and other organizations that cover battery-operated equipment may also be of interest.

Table 4.1*a* to d lists some of the widely known standards for batteries. Standards covering the safety and regulation of batteries are listed in Table 4.11.

4.2 CHAPTER FOUR

Publication	Title	Electrochemical systems
IEC 60086-1, IEC 60086-2	Primary Batteries; Part 1 General, and Part 2, Specification Sheets	Zinc-carbon Zinc/air Alkaline-manganese dioxide Mercuric oxide Silver oxide Lithium/carbon monofluoride Lithium/carbon monofluoride Lithium/copper oxide Lithium/chromium oxide Lithium/chromium oxide
IEC 60086-3	Watch Batteries	Elunum, anonyi emoriae
IEC 60095	Lead-Acid Starter Batteries	Lead-acid
IEC 60254	Lead-Acid Traction Batteries	Lead-acid
IEC 60285	Sealed Nickel-Cadmium Cylindrical Rechargeable Single Cells	Nickel cadmium
IEC 60509	Sealed Nickel-Cadmium Button Rechargeable Single Cells	Nickel-cadmium
IEC 60622	Sealed Nickel-Cadmium Prismatic Rechargeable Single Cells	Nickel-cadmium
IEC 60623	Vented Nickel-Cadmium Prismatic Rechargeable Cells	Nickel-cadmium
IEC 60952	Aircraft Batteries	Nickel-cadmium Lead-acid
IEC 60986	Stationary Lead-Acid Batteries	Lead-acid
IEC 61056	Portable Lead-Acid Cells and Batteries	Lead-acid
IEC 61150	Sealed Nickel-Cadmium Rechargeable Monobloc Batteries in Button Cell Design	Nickel-cadmium
IEC 61436	Sealed Nickel-Metal Hydride Rechargeable Cells	Nickel-metal hydride
IEC 61440	Sealed Nickel-Cadmium Small Prismatic Rechargeable Single Cells	Nickel-cadmium

TABLE 4.1a	International Standard	s (IEC-Inte	ernational Electrote	echnical Commission)
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Note: See Table 4.11a for IEC Safety Standards.

TABLE 4.1b National Standards (ANSI-American National Standards Institute)

Publication	Title	Electrochemical systems
ANSI C18.1M, Part 1	Standard for Portable Primary Cells and Batteries with Aqueous Electrolyte	Zinc-carbon Alkaline-manganese dioxide Silver oxide Zinc/air
ANSI C18.2M, Part 1	Standard for Portable Rechargeable Cells and Batteries	Nickel-cadmium Nickel-metal hydride Lithium-ion
ANSI C18.3M, Part 1	Standard for Portable Lithium Primary Cells and Batteries	Lithium/carbon monofluoride Lithium/manganese dioxide

Note: see Table 4.11a for ANSI Safety Standards.

Publication	Title	Electrochemical systems
MIL-B-18	Batteries Non-Rechargeable	Zinc-carbon, mercury
MIL-B-8565	Aircraft Batteries	Various
MIL-B-11188	Vehicle Batteries	Lead-acid
MIL-B-49030	Batteries, Dry, Alkaline (Non-Rechargeable)	Alkaline-manganese dioxide
MIL-B-55252	Batteries, Magnesium	Magnesium
MIL-B-49430	Batteries, Non-Rechargeable	Lithium/sulfur dioxide
MIL-B-49436	Batteries, Rechargeable, Sealed Nickel-Cadium	Nickel-cadmium
MIL-B-49450	Vented Aircraft Batteries	Nickel-cadmium
MIL-B-49458	Batteries, Non-Rechargeable	Lithium/manganese dioxide
MIL-B-49461	Batteries, Non-Rechargeable	Lithium/thionyl chloride
MIL-B-55130	Batteries, Rechargeable, Sealed Nickel-Cadmium	Nickel-cadmium
MIL-B-81757	Aircraft Batteries	Nickel-cadmium
MIL-PRF-49471	Batteries, Non-Rechargeable, High Performance	Various

TABLE 4.1c U.S. Military Standards (MIL)

TABLE 4.1 *d* Manufacturers' and Professional Associations

Publication	Title	Battery type covered
Society of Automotive Engineers SAE AS 8033 SAE J 537	Aircraft Batteries Storage Batteries	Nickel-cadmium Lead-acid
Battery Council International	Battery Replacement Data Book	Lead-acid

4.2 INTERNATIONAL STANDARDS

International standards are rapidly gaining in importance. This has been further accelerated by the creation of the European Common Market and the 1979 Agreement on Technical Barriers to Trade. The latter requires the use of international standards for world trade purposes.

The International Electrotechnical Commission (IEC) is the designated organization responsible for standardization in the fields of electricity, electronics, and related technologies. Promoting international cooperation on all questions of electrotechnical standardization and related matters is its basic mission. This organization was founded in 1906 and consists of 50 national committees that represent more than 80% of the world's population and 95% of the world's production and consumption of electricity. The International Standards Organization (ISO) is responsible for international standards in fields other than electrical. IEC and ISO are gradually adopting equivalent development and documentation procedures while ever closer ties are being established between these two international organizations.

The American National Standards Institute (ANSI) is the sole U.S. representative of the IEC through the United States National Committee (USNC). This committee coordinates all IEC activities in the United States. It also serves as the U.S. interface with emerging regional standards-developing bodies such as CENELEC, PASC, CANENA, COPANT, ARSO, and other foreign and national groups. ANSI does not itself develop standards; rather it facilitates development by establishing consensus among accredited, qualified groups. These standards are published as U.S. National Standards (see Table 4.1(b)).

To further its overall mission, the objectives of the IEC are to:

- 1. Efficiently meet the requirements of the global marketplace
- 2. Ensure maximum use of its standards and conformity assessment schemes
- 3. Assess and improve the quality of products and services covered by its standards
- 4. Establish conditions for interchangeability
- 5. Increase the efficiency of electrotechnical industrial processes
- 6. Contribute to the improvement of human health and safety
- 7. Work towards protection of the environment

The objectives of the international battery standards are:

- 1. To define a standard of quality and provide guidance for its assessment
- **2.** To ensure the electrical and physical interchangeability of products from different manufacturers
- **3.** To limit the number of battery types
- 4. To provide guidance on matters of safety

The IEC sponsors the development and publication of standard documents. This development is carried out by working groups of experts from participating countries. These experts represent consumer, user, producer, academia, government, and trade and professional interests in the consensus development of these standards. The Groups of Experts in IEC working on battery standards are:

TC 21: Rechargeable Batteries

TC 35: Primary Batteries

The designation for the ANSI Committee on Portable Cells and Batteries is C18.

Table 4.1a lists the IEC standards that pertain to primary and secondary batteries. Many countries utilize these standards either by simply adopting them in toto as their national standards or by harmonizing their national standards to the IEC standards.

Table 4.1b lists the ANSI battery standards. When feasible, the two groups harmonize the requirements in their standards.

4.3 CONCEPTS OF STANDARDIZATION

The objective of battery interchangeability is achieved by specifying the preferred values for the physical aspects of the battery, such as dimensions, polarity, terminals, nomenclature and marketing. In addition, performance characteristics, such as service life or capacity, may be described and specified with test conditions for verification.

It is the inherent nature of batteries, in particular primary batteries, that replacements will at some time be required. A third-party end-user of the equipment typically replaces the battery. It is therefore essential that certain characteristics of the battery be specified by standard values—size, shape, voltage and terminals. Without a reasonable match of at least these parameters there can be no interchangeability. These characteristics are absolute requirements in order to fit the appliance receptacle, to make proper contact, and to provide the proper voltage. In addition to the end-user's need for replacement information, the original equipment manufacturer (OEM) appliance designer must have a reliable source of information about these parameters in order to design a battery compartment and circuits that will accommodate the tolerances on battery products available for purchase by the end-user.

4.4 IEC AND ANSI NOMENCLATURE SYSTEMS

It is unfortunate that the various standards identified in Table 4.1 do not share the same nomenclature system. The independent nomenclature systems of the various battery manufacturers even worsen this situation. Cross-references, however, are generally available from battery manufacturers.

4.4.1 Primary Batteries

The IEC nomenclature system for primary batteries, which became effective in 1992, is based on the electrochemical system and the shape and size of the battery. The letter designations for the electrochemical system and the type of cell remain the same as in the previous IEC system for primary batteries. The new numerical designations are based on a diameter/height number instead of the arbitrary size classification used previously. The first digits specify the diameter of the cell in millimeters and the second the height of the cell (millimeters times 10). An example is shown in Table 4.2*a*. The codes for the shape and electrochemical system are given in Tables 4.2*b* and 4.2*c*, respectively. For reference, the ANSI letter codes for the electrochemical systems are also listed in Table 4.2*c*. The ANSI nomenclature system does not use a code to designate shape.

Nomenclature for existing batteries was grandfathered. Examples of the nomenclature for some of these primary cells and batteries are shown in Table 4.3*a*. Examples of the IEC nomenclature system for primary batteries are shown in Table 4.3*b*.

Nomenclature	Number of cells	System letter (Table 4.2c)	Shape (Table 4.2 <i>b</i>)	Diameter, mm	Height, mm	Example
CR2025	1	С	R	20	2.5	A unit round battery having dimensions shown and electro-chemical system letter C of Table $4.2c$ (Li/MnO ₂)

TABLE 4.2a IEC Nomenclature System for Primary Batteries, Example

TABLE 4.2*b* IEC Nomenclature for Shape, Primary Batteries

Letter designation	Shape
R	Round-Cylindrical
Р	Non-Round
F	Flat (layer built)
S	Square (or Rectangular)

SOP

ANSI	IEC	Negative electrode	Electrolyte	Positive electrode	Nominal voltage (V)
(1)	_	Zinc	Ammonium chloride, Zinc chloride	Manganese dioxide	1.5
	А	Zinc	Ammonium chloride, Zinc chloride	Oxygen (air)	1.4
LB	В	Lithium	Organic	Carbon monofluoride	3
LC	С	Lithium	Organic	Manganese dioxide	3
	Е	Lithium	Non-aqueous inorganic	Thionyl chloride	3.6
LF	F	Lithium	Organic	Iron sulfide	1.5
	G	Lithium	Organic	Copper dioxide	1.5
A ⁽²⁾	L	Zinc	Alkali metal hydroxide	Manganese dioxide	1.5
Z ⁽³⁾	Р	Zinc	Alkali metal hydroxide	Oxygen (air)	1.4
SO ⁽⁴⁾	S	Zinc	Alkali metal hydroxide	Silver oxide	1.55
Notes	:				
(1)	No suffix	Carbon-zinc			
	C	Carbon-zinc indust	rial basyy duty		
	D	Carbon-zinc heavy	duty		
	F	Carbon-zinc, gener	al purpose		
(2)	А	Alkaline	I I I I I I I I I I I I I I I I I I I		
	AC	Alkaline industrial			
	AP	Alkaline photograp	ohic		
(3)	Z	Zinc/air			
(4)	ZD	Zinc/air, heavy du	ty		
(4)	30	Silver Oxide			

TABLE 4.2c Letter Codes Denoting Electrochemical System of Primary Batteries

TABLE 4.3a	IEC Nomenclature	for Typic	al Primary	Round, I	Flat. and	Square	Cells or	Batteries*
	in the internet at an e	101 1,010				Square	00110 01	Datteries

Silver oxide photographic

150		Nominal					
IEC designation	Diameter	Height	Length	Width	Thickness	ANSI designation	Common designation
]	Round batterie	es			
R03	10.5	44.5				24	AAA
R1	12.0	30.2				—	Ν
R6	14.5	50.5				15	AA
R14	26.2	50.0				14	С
R20	34.2	61.5				13	D
R25	32.0	91.0				—	F
			Flat cells				
F22			24	13.5	6.0		
F80			43	43	6.4		
	l	S	Square batterie	es		L	
S4		125.0	57.0	57.0			
S8		200.0	85.0	85.0			

*Chart is not complete—only a sampling of sizes is shown. Dimensions are used for identification only. Complete dimensions can be found in the relevant specification sheets listed in IEC 60086-2 and in Table 4.9a.

Linden, D., & Reddy, T. (2001). Handbook of batteries. Retrieved from http://ebookcentral.proquest.com Created from uc on 2019-05-28 16:53:43.

IEC Nomenclature	Number of cells	System letter (Table 4.2c)	Shape (Table 4.2 <i>b</i>)	Cell (Table 4.3 <i>a</i>)	C, P, S, X, Y	Parallel	Groups in parallel	Example
R20	1	None	R	20	*			A unit round battery using basic R20 type cell and electrochemical system letter (none) of Table 4.2 <i>c</i>
LR20	1	L	R	20	*			Same as above, except using electrochemical system letter L of Table $4.2c$
6F22	6	None	F	22	*			A 6-series multicell battery using flat F22 cells and electrochemical system letter (none) of Table 4.2 <i>c</i>
4LR25-2	4	L	R	25	*		2	A multicell battery consist- ing of two parallel groups, each group having four cells in series of the R25 type and electrochemical system, letter L, of Table $4.2c$
CR17345	1	С	R	see Section 4.4.1				A unit round battery, with a diam. of 17 mm and height of 34.5 mm, and electrochemical system, letter C, of Table 4.2 <i>c</i>

TABLE 4.3b Examples of IEC Nomenclature for Primary Batteries

* If required, letters C, P, or S will indicate different performance characteristics and letters X and Y different terminal arrangements.

4.4.2 Rechargeable Batteries

The documentation for standardization of rechargeable batteries is not as complete as the documentation for primary batteries. Most of the primary batteries are used in a variety of portable applications, using user-replaceable batteries. Hence, the need for primary battery standards to insure interchangeability. Developing such standards have been active projects by both IEC and ANSI for many years.

The early use of rechargeable batteries was mainly with larger batteries, however, usually application specific and multicell. The large majority of rechargeable batteries were lead-acid manufactured for automotive SLI (starting, lighting, ignition) use. Standards for these batteries were developed by the Society for Automotive Engineers (SAE), the Battery Council International (BCI) and the Storage Battery Association of Japan. More recently, rechargeable batteries have been developed for portable applications, in many cases in the same cell and battery sizes as the primary batteries. Starting with the portable-sized nickel-cadmium batteries, IEC and ANSI are developing standards for the nickel-metal hydride and lithium-ion batteries. The currently available standards are listed in Tables 4.1*a* and 4.1*b*.

The IEC has been considering a new nomenclature system, possibly covering both primary and rechargeable batteries but none have yet been published. Table 4.4a lists the letter codes that are being considered by IEC and those adopted by ANSI for secondary or rechargeable batteries. The IEC nomenclature system for nickel-cadmium batteries is shown in Table. 4.4b. In this system, the first letter designates the electrochemical system, a second letter the shape, the first number of the diameter, and a second number the height. In addition, the letters L, M, and H may be used to classify arbitrarily the rate capability as low, medium, or high. The last part of the designation is reserved for two letters which indicate various tab terminal arrangements, such as CF—none, HH—terminal at positive end and positive sidewall, or HB—terminals at positive and negative ends, as shown in Table 4.4b.

ANSI	IEC ⁽¹⁾	Negative electrode	Electrolyte	Positive electrode	Nominal voltage (V)
Н	Н	Hydrogen absorbing alloy	Alkali metal hydroxide	Nickel oxide	1.2
K	Κ	Cadmium	Alkali metal hydroxide	Nickel oxide	1.2
Р	PB	Lead	Sulfuric acid	Lead dioxide	2
Ι	IC	Carbon	Organic	Lithium cobalt oxide	3.6
Ι	IN	Carbon	Organic	Lithium nickel oxide	3.6
Ι	IM	Carbon	Organic	Lithium manganese oxide	3.6

TABLE 4.4a Letter(s) Denoting Electrochemical System of Secondary Batteries

(1) Proposed for portable batteries.

Nomenclature ⁽²⁾	System letter (Table 4.4 <i>a</i>)	Shape (Table 4.2 <i>b</i>)	Diameter, mm	Height, mm	Terminals	Example
KR 15/51 (R6)	К	R	14.5	50.5	CF	A unit round battery of the K system having dimensions shown, with no connecting tabs

TABLE 4.4b IEC Nomenclature System for Rechargeable Nickel-Cadmium Cells and Batteries

⁽²⁾Nomenclature dimensions are shown rounded off. () indicates interchangeable with a primary battery. *Source:* IEC 60285.

4.5 TERMINALS

Terminals are another aspect of the shape characteristics for cells and batteries. It is obvious that without standardization of terminals, and the other shape variables, a battery may not be available to match the receptacle facilities provided in the appliance. Some of the variety of terminal arrangements for batteries are listed in Table 4.5.

When applicable, the terminal arrangement is specified in the standard within the same nomenclature designators used for shape and size. The designators thus determine all interchangeable physical aspects of the cells and batteries in addition to the voltage.

Terminals that have the cylindrical side of the battery insulated from the terminal ends Terminals in which the cylindrical side forms part of the positive end terminal Terminals that have a threaded rod and accent either an insulated or a metal nut
Flat metal surfaces used for electrical contact
Terminals that are flat metal strips or spirally wound wire
Terminals consisting of a stud (nonresilient) and a socket (resilient)
Single or multistranded wire leads
Metal clips that will accept a wire lead
Metal flat tabs attached to battery terminals

TABLE 4.5	Terminal	Arrangements	for	Batteries
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4.6 ELECTRICAL PERFORMANCE

In terms of the requirement to provide fit and function in the end product the actual appliance does not require specific values of electrical performance. The correct battery voltage, needed to protect the appliance from overvoltage, is assured by the battery designation. Batteries of the same voltage but having differences in capacity can be used interchangeably, but will operate for different service times. The minimum electrical performance of the battery is therefore cited and specified in the standards either by application or by capacity testing.

1. *Application tests:* This is the preferred method of testing the performance specified for primary batteries. Application tests are intended to simulate the actual use of a battery in a specific application. Table 4.6*a* illustrates typical application tests.

Nomenclature				R20C	R20P	R20S	LR20
Electrochemical system				Zinc-carbon (high capacity)	Zinc-carbon (high power)	Zinc-carbon (standard)	Zinc/manganese dioxide
Nominal voltage				1.5	1.5	1.5	1.5
Application	Load, Ω	Daily period	End point		Minimum ave	rage duration†	
Portable lighting (1)	2.2	*	0.9	300 min	320 min	100 min	810 min
Tape recorders	3.9	1 h	0.9	9 h	13 h	4 h	25 h
Radios	10	4 h	0.9	30 h	35 h	18 h	81 h
Toys	2.2	1 h	0.8	4.0 h	6 h	2 h	15 h
Portable lighting (2)	1.5	**	0.9	130 min	137 min	32 min	450 min

TABLE 4.6a Example of Application Tests for R20 Type Batteries

*4 min beginning at hourly intervals for 8 h/day; **4 min/15 min, 8 h/day. †Proposed IEC values. **2.** *Capacity (service output) tests:* A capacity test is generally used to determine the quantity of electric charge which a battery can deliver under specified discharge conditions. This method is the one that has been generally used for rechargeable batteries. It is also used for primary batteries when an application test would be too complex to simulate realistically or too lengthy to be practical for routine testing. Table 4.6b lists some examples of capacity tests.

Test conditions in the standard must consider and therefore specify the following:

Cell (battery) temperature

Discharge rate (or load resistance)

Discharge termination criteria (typically loaded voltage)

Discharge duty cycle

If rechargeable, charge rate, termination criteria (either time or feedback of cell response) and other conditions of charge

Humidity and other conditions of storage may also be required.

Nomenclature Electrochemical system Nominal voltage	(Ret (Ret	fer to Table 4 fer to Table 4 fer to Table 4	SR54 S 1.55	
Application*	Load, kΩ	Daily period	End point	Minimum average duration†
Capacity (rating) test	15	24 h	1.2	580 h

TABLE 4.6b Example of Capacity Tests

* Application for this battery is watches. As an application test could take up to 2 years to test, a capacity test is specified.

[†] Value under IEC consideration.

4.7 MARKINGS

Markings on both primary and secondary (rechargeable) batteries may consist of some or all of the printed information given in Table 4.7 in addition to the form and dimension nomenclature discussed.

TABLE 4.7 Marking Information for Batteries

Marking information	Primary batteries	Primary small batteries	Rechargeable round batteries
Nomenclature	×*	×	×
Date of manufacture or code	×	$\times \times \dagger$	×
Polarity	×	×	×
Nominal voltage	×	$\times \times$	×
Name of manufacturer/supplier	×	××	×
Sealed, rechargeable— nickel-cadmium			×
Charge rate/time			×
Rated capacity			×

*×—on battery.

 $^{+\times\times}$ —on battery or package.

Linden, D., & Reddy, T. (2001). Handbook of batteries. Retrieved from http://ebookcentral.proquest.com Created from uc on 2019-05-28 16:53:43.

4.8 CROSS-REFERENCES OF ANSI IEC BATTERY STANDARDS

Table 4.8 lists some of the more popular ANSI battery standards and cross-references to the international standard publications for primary and secondary batteries.

ANSI	IEC	ANSI	IEC
13A	LR20	1137SO	SR48
13AC	LR20	1138SO	SR54
!3C	R20S	1139SO	SR42
13CD	R20C	1158SO	SR58
13D	R20C	1160SO	SR55
13F	R20S	1162SO	SR57
14A	LR14	1163SO	SR59
14AC	LR14	1164SO	SR59
14C	R14S	1165SO	SR57
14CD	R14C	1166A	LR44
14D	R14C	1170SO	SR55
14F	R14S	1175SO	SR60
15A	LR6	1179SO	SR41
15AC	LR6	1181SO	SR48
15C	R6S	1184SO	SR44
15CD	R6C	1406SOP	4SR44
15D	R6C	1412AP	4LR61
15F	R6S	1414A	4LR44
24A	LR03	1604	6F22
24AC	LR03	1604A	6LR61
24D	R03	1604AC	6LR61
905	R40	1604C	6F22
908	4R25X	1604CD	6F22
910A	LR1	1604D	6F22
918	4R25-2	5018LC	CR17345
918D	4R25-2	5024LC	CR-P2
1107SOP	SR44	5032LC	2CR5
1131SO	SR44	7000ZD	PR48
1132SO	SR43	7001ZD	PR43
1133SO	SR43	7002ZD	PR41
1134SO	SR41	7003ZD	PR44
1135SO	SR41	7005ZD	PR70
1136SO	SR48		

TABLE 4.8a	ANSI/IEC Cross-Reference for Primary
Batteries	

TABLE 4.8bANSI/IEC Select Cross-References for Rechargeable Batteries

ANSI	IEC
1.2K1	KR03
1.2K2	KR6
1.2K3	KR14
1.2K4	KR20

4.9 LISTING OF IEC STANDARD ROUND PRIMARY BATTERIES

The tenth edition of IEC 60086-2 for primary batteries lists over one hundred types with dimensional, polarity, voltage, and electrochemical requirements. The third edition of IEC 60285 for rechargeable nickel-cadmium cells (batteries) lists 18 sizes with diameter and height specified in chart form. Several rechargeable nickel-cadmium and nickel-metal hydride batteries are also packaged to be interchangeable with the popular sizes in the primary replacement market. These have physical shapes and sizes that are identical to primary batteries and have equivalent voltage outputs under load. These batteries carry, in addition to the rechargeable nomenclature, the equivalent primary cell or battery size designations and therefore must comply with the dimensional requirements set forth for primary batteries. Table 4.9*a* lists the dimensions of round primary batteries and Table 4.9*b* lists some nickel-cadmium rechargeable batteries that are interchangeable with the primary batteries.

In addition to the many designations in national and international standards, of which there may typically be both old and new versions, there are trade association designations. Cross-reference to many of these may be found in sales literature and point-of-purchase information.

IEC	inimum 43.3 29.1 49.2 48.6 59.5 3.3 3 3
R03 10.5 9.5 44.5 R1 12.0 10.9 30.2	43.3 29.1 49.2 48.6 59.5 3.3 3 3
R1 12.0 10.9 30.2	29.1 49.2 48.6 59.5 3.3 3 3
	49.2 48.6 59.5 3.3 3 3
R6 14.5 13.5 50.5	48.6 59.5 3.3 3 3
R14 26.2 24.9 50.0	59.5 3.3 3.3
R20 34.2 32.2 61.5	3.3
R41 7.9 7.55 3.6	33
R42 11.6 11.25 3.6	5.5
R43 11.6 11.25 4.2	3.8
R44 11.6 11.25 5.4	5.0
R48 7.9 7.55 5.4	5.0
R54 11.6 11.25 3.05	2.75
R55 11.6 11.25 2.1	1.85
R56 11.6 11.25 2.6	2.3
R57 9.5 9.15 2.7	2.4
R58 7.9 7.55 2.1	1.85
R59 7.9 7.55 2.6	2.3
R60 6.8 6.5 2.15	1.9
R62 5.8 5.55 1.65	1.45
R63 5.8 5.55 2.15	1.9
R64 5.8 5.55 2.7	2.4
R65 6.8 6.6 1.65	1.45
R66 6.8 6.6 2.6	2.4
R67 7.9 7.65 1.65	1.45
R68 9.5 9.25 1.65	1.45
R69 9.5 9.25 2.1	1.85
R1220 12.5 12.2 2.0	1.8
R1620 16 15.7 2.0	1.8
R2016 20 19.7 1.6	1.4
R2025 20 19.7 2.5	2.2
R2032 20 19.7 3.2	2.9
R2320 23 22.6 2.0	1.8
K2430 24.5 24.2 3.0	2.7
R11108 11.6 11.4 10.8 R12600 12.0 10.7 60.4	10.4 58

TABLE 4.9a Dimensions of Round Primary Batteries

			Diamet	ter, mm	Height, mm	
IEC designation†	Consumer designation	ANSI designation	Maximum	Minimum	Maximum	Minimum
KR03	AAA	1.2K1	10.5	9.5	44.5	43.3
KR6	AA	1.2K2	14.5	13.5	50.5	49.2
KR14	С	1.2K3	26.2	24.9	50.0	48.5
KR20	D	1.2K4	34.3	32.2	61.5	59.5

TABLE 4.9*b* Dimensions of Some Popular Nickel-Cadmium Rechargeable Batteries That Are Interchangeable with Primary Batteries*

*IEC plans to add the following to IEC Standard 61436 on Nickel-Metal Hydride batteries: HR03(AAA), HR6 (AA), HR14(C), HR20(D). These will be interchangeable with the respective primary batteries.

See IEC and ANSI standards referenced in Tables 4.1a and 4.1b for a more complete listing of rechargeable batteries. † From IEC Standard 60285.

4.10 STANDARD SLI AND OTHER LEAD-ACID BATTERIES

SLI battery sizes have been standardized by both the automotive industry through the Society of Automotive Engineers (SAE), Warrendale, PA and the battery industry through the Battery Council International (BCI), Chicago, IL.^{1,2} The BCI nomenclature follows the standards adopted by its predecessor, the American Association of Battery Manufacturers (AABM). The latest standards are published annually by the Battery Council International. Table 4.10 is a listing of the Standard SLI and other lead-acid batteries abstracted from the BCI publication.³

TABLE 4.10	Standard SL	I and Other	Lead-Acid	Batteries
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								Performanc	e ranges
		1	Maximun	n overall di	mensions		Cold cranking	Reserve	
BIC	Ν	Aillimete	rs	_	Inches		Assembly	amps.	min @
group number	L	W	Н	L	W	Н	figure no.	@ 0°F (-18°C)	80°F (27°C)
			Passer	nger car and	d light com	mercial batteri	es 12-volt (6 cells))	
21	208	173	222	83/16	613/16	83/4	10	310-400	50-70
21R	208	173	222	83/16	613/16	8 ³ /4	11	310-500	50-70
22F	241	175	211	9½	67/8	85/16	11F	220-425	45-90
22HF	241	175	229	9 ¹ / ₂	67/8	9	11F	400	69
22NF	240	140	227	97/16	51/2	815/16	11F	210-325	50-60
22R	229	175	211	9	67/8	85/16	11	290-350	45-90
24	260	173	225	101/4	613/16	87/8	10	165-625	50-95
24F	273	173	229	103/4	613/16	9	11F	250-585	50-95
24H	260	173	238	101/4	613/16	9 ³ /8	10	305-365	70-95
24R	260	173	229	101/4	613/16	9	11	440-475	70-95
24T	260	173	248	101/4	613/16	9 ³ /4	10	370-385	110
25	230	175	225	$9^{1/16}$	67/8	87/8	10	310-490	50-90
26	208	173	197	6 ³ /16	6 ¹³ /16	73/4	10	310-440	50-80
26R	208	173	197	6 ³ /16	6 ¹³ /16	73/4	11	405-525	60-80
27	306	173	225	$12^{1/16}$	6 ¹³ /16	87/8	10	270-700	102 - 140
27F	318	173	223	$12^{1/2}$	6 ¹³ /16	8 ¹⁵ /16	11F	360-660	95-140
27H	298	173	235	$11^{3}/_{4}$	6 ¹³ /16	9 ¹ /4	10	440	125
29NF	330	140	200	13	5 ¹ /2	816/16	10 11F	330-350	95
27R	306	173	225	$12^{1/16}$	6 ¹³ /16	87%	11	270-700	102 - 140
33	338	173	223	135/16	6 ¹³ /16	0 ³ / ₀	11 11F	1050	165
33	260	173	200	101/4	6 ¹³ /16	77%	10	375 650	100 110
24D	260	173	200	10/4	613/16	776	10	675	110
25 25	200	175	200	01/4	676	074	11	210 500	×0 110
33 26D	250	1/3	223	9/16	078	0 /8	11	510-500	120
30K 40D	203	185	200	10%	674	878 677	19	600 650	110 120
40K	278	175	175	10-9/16	078	078	15	000-030	110-120
41	293	175	175	11/16	0'/8	0 / 8	15	255-650	65-95
42	242	1/5	1/5	91/2	6 ¹³ /16	6 ¹ /16	15	260-495	65-95
43	334	1/5	205	131/8	6%	8 ¹ /16	15	3/5	115
45	240	140	227	9%16	51/2	815/16	10F	250-470	60-80
46	273	173	229	10¾	6 ¹³ /16	9	10F	350-450	75-95
47	242	175	190	91/2	61/8	/1/2	24(A.F)♦	370-550	75-85
48	278	175	190	121/16	61/8	7%16	24	450-895	85-95
49	353	175	190	131/8	61/8	7%16	24	600-810	140–150
50	343	127	254	131/2	5	10	10	400-600	85-100
51	238	129	223	93/8	51/16	813/16	10	405-435	70
51R	238	129	223	93/8	51/16	813/16	11	405-435	70
52	186	147	210	75/16	513/16	81/4	10	405	70
53	330	119	210	13	411/16	8 ¹ /4	14	280	40
54	186	154	212	75/16	6 ¹ /16	8 ³ /8	19	305-330	60
55	216	154	212	85/8	6 ¹ /16	8 ³ /8	19	370-450	75
56	254	154	212	10	6 ¹ /16	8 ³ /8	19	450-505	90

DCI group numbers, unnensional specifications and faungs	BCI group nu	umbers, dimens	ional specification	ons and ratings
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TABLE 4.10	Standard SLI	and Other	Lead-Acid	Batteries (Continued)
						,

			BCI g	roup numb	ers, dimensi	onal specificat	ions and ratings		
								Performanc	e ranges
			Maximur	n overall d		Cold cranking	Reserve		
BIC	Ν	Millimet	ers		Inches		Assembly	amps.	min @
group number	L	W	Н	L	W	Н	figure no.	@ 0°F (-18°C)	80°F (27°C)
		Pass	enger car	and light o	commercial	batteries 12-vo	olt (6 cells) (Conti	inued)	
57	205	183	177	81/16	73/16	615/16	22	310	60
58	255	183	177	10¼16	7 ³ /16	6 ¹⁵ /16	26	380-540	75
58R	255	183	177	10 ¹ /16	7 ³ /16	615/16	19	540-580	75
59	255	193	196	10¼16	75/8	73/4	21	540	100
60	332	160	225	13 ¹ /16	65/16	81/8	12	305-385	65–115
61	192	162	225	7%16	63/8	81/8	20	310	60
62	225	162	225	87/8	63/8	81/8	20	380	75
63	258	162	225	103/16	63/8	81/8	20	450	90
64	296	162	225	1111/16	63/8	81/8	20	475-535	105-120
65	306	192	192	121/16	$7\frac{1}{2}$	7%16	21	650-850	130–165
66	306	192	194	121/16	71/16	75/8	13	650-750	130–140
70	208	179	196④	8 ³ /16	71/16	$7^{11}/_{16}$	17	260-525	60-80
71	208	179	216	83/16	71/16	81/2	17	275-430	75–90
72	230	179	210	9 ¹ /16	71/16	81/4	17	275-350	60–90
73	230	179	216	9 ¹ / ₁₆	71/16	81/2	17	430–475	80-115
74	260	184	222	10¼	$7\frac{1}{4}$	83/4	17	350-550	75–140
75	230	179	196④	9 ¹ /16	71/16	$7^{11}/_{16}$	17	430-690	90
76	334	179	216④	131/8	71/16	81/24	17	750–1075	150-175
78	260	179	196@	10¼	71/16	$7^{11}/_{16}$	17	515-770	105-115
79	307	179	188	121/16	7 ¹ /16	$7^{3}/_{8}$	35	880	140
85	230	173	203	9 ¹ /16	6 ¹³ /16	8	11	550-630	90
86	230	173	203	91/16	6 ¹³ /16	8	10	430–525	90
90	242	175	175	9 ¹ / ₂	61/8	61/8	24	520	80
91	278	175	175	11	61/8	61/8	24	600	100
92	315	175	175	121/2	61/8	61/8	24	650	130
93	353	175	175	131/8	61/8	61/8	24	800	150
94R	315	175	190	123/8	61/8	71/2	24	640	135
95R	394	175	190	15%16	61/8	/1/2	24	900	190
96K	242	173	175	9%16	6 ¹ /16	6'/8	15	590	95
9/K	252	175	190	9 ¹⁵ /16	6′/8	71/2	15	550	90
98K	283	1/5	190	11%16	0'/8	1 1/2	15	620	120
99	207	175	1/5	8%16	6'/8	6'/8	34	360	50
100	260	1/9	188	104	/	/ 2/16	55 17	//0	115
101	260	1/9	170	101/4	/	011/16	17	690	115

TABLE 4.10 Standard SLI and Other Lead-Acid Batteries (Continued)

								Performanc	e ranges
		1:11: oto	Maximu	m overall di		Cold cranking performance	Reserve		
BIC	N	mmete	rs		Inches		Assembly	amps.	min @
number	L	W	Н	L	W	Н	no.	(-18°C)	80 F (27°C)
			Pass	enger car ar	nd light comn	nercial batteri	es 6-volt (3 cells)		
1	232	181	238	9 ¹ /8	71/8	9 ³ / ₈	2	475-650	135-230
2	264	181	238	103/8	71/8	9 ³ /8	2	475-650	136-230
2E	492	105	232	197/16	41/8	9 ¹ /8	5	485	140
2N	254	141	227	10	5%16	815/16	1	450	135
17HF- *①	187	175	229	73/8	67/8	9	2B	—	—
				Heavy-duty	commercial	batteries 12-v	volt (6 cells)		
4D	527	222	250	203/4	83/4	97/8	8	490–950	225-325
6D	527	254	260	203/4	10	101/4	8	750	310
8D	527	283	250	203/4	11 ¹ /8	91/8	8	850-1250	235-465
28	261	173	240	105/16	613/16	97/16	18	400-535	80-135
29H	334	171	232	131/8	63/4	9 ¹ /8	10	525-840	145
30H	343	173	235	13 ¹ /2	613/16	9¼	10	380-685	120-150
31	330	173	240	13	613/16	97/16	18(A,T)♦	455–950	100-200
				Heavy-dut	y commercial	batteries 6-v	olt (3 cells)		
3	298	181	238	113⁄4	71/8	9 ³ / ₈	2	525-660	210-230
4	334	181	238	131/8	71/8	93/8	2	550-975	240-420
5D	349	181	238	133/4	$7\frac{1}{8}$	9 ³ /8	2	720-820	310-380
7D	413	181	238	16¼	71/8	93/8	2	680–875	370–426
				Speci	al tractor batt	eries 6-volt (3	3 cells)		
3EH	491	111	249	195/16	43/8	913/16	5	740-850	220-340
4EH	491	127	249	195/16	5	913/16	5	850	340-420
				Specia	l tractor batte	eries 12-volt (6 cells)		
3EE	491	111	225	195/16	43/8	87/8	9	260-360	80-105
3ET	491	111	249	195/16	4 ³ /8	9 ³ /16	9	355-425	130-135
4DLT	508	208	202	20	83/16	715/16	16L	650-820	200-290
12T	177	177	202	7 ¹ /16	615/16	715/16	10	460	160
16TF	421	181	283	16%16	71/8	111/8	10F	600	240
17TF	433	177	202	171/16	615/16	715/16	11L	510	145

BCI group numbers, dimensional specifications and ratings

TABLE 4.10 Standard SLI and Other Lead-Acid Batteries (Continued)

								Performance ranges	
			Maximu	m overall d		Cold cranking performance	Reserve		
BIC	Ν	Aillimete	rs		Inches		Assembly	amps.	capacity min
group number	L	W	Н	L	W	Н	figure no.	@ 0°F (-18°C)	@ 80°F (27°C)
				General	l-utility batter	ries 12-volt (6 cells)		
U1	197	132	186	73⁄4	53/16	75/16	10(X) ♦	120–295	23–40
U1R	197	132	186	73/4	53/16	75/16	11(X)♦	220-235	25-37
U2	160	132	181	65/16	53/16	71/8	10(X)♦	120	17
				Electric gol	If car/utility	batteries 6-ve	olt (3 cells)		
GC2 GC2H୭	264 264	183 183	290 295	10 ³ /8	7 ³ /16 7 ³ /16	117/16 115%	2	3	3
	201	105	275	Electric gol	If car/utility	batteries 8-ve	olt (4 cells)		
GC8	264	183	290	103/8	73/16	117/16	31	_	_
				Electric	vehicle batte	eries 8-volt (4 cells)		
202	388	116	175	151/4	4%16	67/8	30	_	_
				Electric	vehicle batte	ries 12-volt	(6 cells)		
201	388	116	175	151/4	4%16	67/8	29		—
				Electric	vehicle batter	ries 12-volt (10 cells)		
203 203R	388 388	116 116	175 175	15 ¹ /4 15 ¹ /4	4%/16 4%/16	6 ⁷ /8	32 33	_	_
		110	175	Ordn	ance batteries	s 12-volt (6 (cells)		
2H	260	135	230	10 ¹ /4	5%16	%16	28		75
6T	286	267	230	111/4	101/2	9⁄16	27	600	200

BCI group numbers, dimensional specifications and ratings

◆ Letter in parentheses indicates terminal type.

*Rod end types-Extend top ledge with holes for holddown bolts.

*Ratings for batteries recommended for motor coach and bus service are for double insulation. When double insulation is used in other types, deduct 15% from the rating values for cold cranking performance.

^①Not in application section but still manufactured.

⁽²⁾ Special-use battery not shown in application section.

[®]Capacity test in minutes at 75 amperes to 5.25 volts at 80°F (27°C); cold cranking performance test not normally required for this battery.

[®]Maximum height dimension shown includes batteries with raised-quarter cover design. Flat-top design model height (minus quarter covers) reduced by approximately ³/₈ inch (10 mm).





BCI ASSEMBLY NUMBERS, CELL LAYOUTS, HOLDDOWNS AND POLARITY

with L Terminal

BCI ASSEMBLY NUMBERS, CELL LAYOUTS, HOLDDOWNS AND POLARITY



12-VOLT ASSEMBLIES - TERMINAL POSITIONS & CELL LAYOUTS





BCI ASSEMBLY NUMBERS, CELL LAYOUTS, HOLDDOWNS AND TERMINALS

4.11 REGULATORY AND SAFETY STANDARDS

With the increasing complexity and energy of batteries and the concern about safety, greater attention is being given to developing regulations and standards with the goal to promote the safe operation in use and transport. Stand-alone safety documents on primary and re-chargeable batteries have been published by IEC and ANSI. In addition, the Underwriters Laboratories (UL) has published several battery safety standards aimed at the safe operation of UL-approved equipment.⁴

Table 4.11a is a list of organizations working on safety standards and the safety standards they prepared that cover various primary and secondary battery systems.

While the various groups involved in developing safety standards are dedicated to the principle of harmonization, there are still differences in the procedures, tests, and criteria between the various standards. It is recommended that users of these standards follow them on a judicious basis, and place their battery or application in the proper context.

Table 4.11b is a list of organizations that have focused on the safe transport of various goods and the regulations they have published. These regulations include procedures for the transport of batteries, including lithium batteries.

Publication	Title
American Standards Institute	
ANSI C18.1M, Part 2	American National Standard for Portable Primary Cells and Batteries with Aqueous Electrolyte—Safety Standard
ANSI C18.2M, Part 2	American National Standard for Portable Rechargeable Cells and Batteries—Safety Standard
ANSI C18.3M, Part 2	American National Standard for Portable Lithium Primary Cells and Batteries—Safety Standard
International Electrotechnical Commission	
IEC 60086-4	Primary Batteries—Part 4: Safety for Lithium Batteries
IEC 60086-5	Primary Batteries—Part 5: Safety of Batteries with Aqueous Electrolyte
IEC 61809	Safety for Portable Sealed Alkaline Secondary Cells and Batteries
Underwriters Laboratories	
UL1642	Standard for Lithium Batteries
UL2054	Standard for Household and Commercial Batteries

TABLE 4.11 <i>a</i>	Safety	Standards
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TABLE 4.11 <i>b</i>	Transportation	Recommendations	and Regulations
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Organization	Title
Department of Transportation (DOT)	Code of Federal Regulations—Title 49 Transportation
Federal Aviation Administration (FAA)	TSO C042, Lithium Batteries (referencing RTCA Document DO-227 "Minimum Operational Performance Standards for Lithium Batteries")
International Air Transport Association (IATA)	Dangerous Goods Regulations
International Civil Aviation Association (ICAO)	Technical Instructions for the Safe Transport of Dangerous Goods
United Nations (UN)	Recommendations on the Transportation of Dangerous Goods Manual of Tests and Criteria

In the United States, this responsibility for regulating the transport of goods rests with the Department of Transportation (DOT) through its Research and Special Programs Administration (RSPA).⁵ These regulations are published in the Code of Federal Regulations (CFR49), which include the requirements for the shipment and transport of batteries under all modes of transportation. Under the DOT, the Federal Aviation Administration (FAA) is responsible for the safe operation of aircraft and has also issued regulations covering the use of batteries in aircraft.^{6,7} Similar organizations are part of the governments of most countries throughout the world.

Internationally, transport is regulated by such organizations as the International Civil Aviation Association (ICAO),⁸ the International Air Transport Association (IATA)⁹ and the International Maritime Organization. Their regulations are guided by the United Nations (UN) through their Committee of Experts on the Transport of Dangerous Goods, which has developed recommendations for the transportation of dangerous goods. These recommendations, which also include tests and criteria,^{10,11} are addressed to governments and international organizations concerned with regulating the transport of various products. Currently, the UN Committee of Experts is developing new guidelines covering the transport of lithium primary and secondary batteries. The quantity of lithium or lithium equivalent content in each cell and battery will determine which specific rules and regulations are applied concerning the packaging, mode of shipment, marking, and other special provisions.

As these standards, regulations, and guidelines can be changed on an annual or periodic basis, the current edition of each document should be used.

NOTE

It is imperative that only the latest version of each standard be used. Due to the periodic revision of these standards, only the latest version can be relied upon to provide reliable enforceable specifications of battery dimensions, terminals, marking, general design features, conditions of electrical testing for performance verification, mechanical tests, test sequences, safety, shipment, storage, use, and disposal.

REFERENCES

- 1. Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096. www.sae.org
- 2. Battery Council International, 401 North Michigan Ave., Chicago, IL 60611. www.batterycouncil.org
- 3. Battery Council International, Battery Replacement Data Book, 2000.
- 4. Underwriters Laboratories, Inc., 333 Pfingsten Road, Northbrook, IL 60062.
- Department of Transportation, Office of Hazardous Materials Safety, Research and Special Programs Administration, 400 Seventh St., SW, Washington, DC 20590.
- Department of Transportation, Federal Aviation Administration, 800 Independence Ave., SW, Washington, DC 20591.
- 7. RTCA, 1140 Connecticut Ave., NE, Washington, DC 20036.
- 8. International Civil Aviation Organization, 1000 Sherbrooke St., W., Montreal, Quebec, Canada.
- 9. International Air Transport Association, 2000 Peel St., Monteal, Quebec, Canada.
- United Nations, Recommendation on the Transport of Dangerous Goods, New York, NY and Geneva, Switzerland.
- 11. United Nations, Manual of Tests and Criteria, New York, NY and Geneva, Switzerland.

CHAPTER 5 BATTERY DESIGN

John Fehling

5.1 GENERAL

Proper design of the battery or the battery compartment is important to assure optimum, reliable, and safe operation. Many problems attributed to the battery may have been prevented had proper precautions been taken with both the design of the battery itself and how it is designed into the battery-operated equipment.

It is important to note that the performance of a cell in a battery can be significantly different from that of an individual cell depending on the particular environment of that cell in the battery. Specifications and data sheets provided by the manufacturers should only be used as a guide as it is not always possible to extrapolate the data to determine the performance of multicell batteries. Such factors as the cell uniformity, number of cells, series or parallel connections, battery case material and design, conditions of discharge and charge, temperature, to name a few, influence the performance of the battery. The problem is usually exacerbated under the more stringent conditions of use, such as high-rate charging and discharging, operation, and extreme temperatures and other conditions which tend to increase the variability of the cells within the battery.

Further, specific energy and energy density data based on cell or single-cell battery performance have to be derated when the weight and volume of the battery case, battery assembly materials, and any ancillary equipment in the battery have to be considered in the calculation.

Another factor that must be considered, particularly with newly developing battery technologies, is the difficulty of scaling up laboratory data based on smaller individual batteries to multicell batteries using larger cells manufactured on a production line.

This chapter will address the issues that the product designer should consider. Cell and battery manufacturers should also be consulted to obtain specific details on their recommendations for the batteries they market.

5.2 DESIGNING TO ELIMINATE POTENTIAL SAFETY PROBLEMS

Batteries are sources of energy and when used properly will deliver their energy in a safe manner. There are instances, however, when a battery may vent, rupture, or even explode if it is abused. The design of the battery should include protective devices and other features which can prevent, or at least minimize, the problem.

Some of the most common causes for battery failure are:

- 1. Short-circuiting of battery terminals
- **2.** Excessive high rate discharge or charge
- 3. Voltage reversal, that is, discharging the cells of the battery below 0 V
- 4. Charging of primary batteries
- 5. Improper charge control when charging secondary batteries

These conditions may cause an internal pressure increase within the cells, resulting in an activation of the vent device or a rupture or explosion of the battery. There are a number of means to minimize the possibilities of these occurrences.

5.2.1 Charging Primary Batteries

All major manufacturers of primary batteries warn that the batteries may leak or explode if they are charged. As discussed in Sec. 7.4, some primary batteries can be recharged if done under controlled conditions. Nevertheless, charging primary batteries is not usually recommended because of the potential hazards.

Protection from External Charge. The simplest means of preventing a battery from being charged from an external power source is to incorporate a blocking diode in the battery pack, as shown in Fig. 5.1. The diode chosen must have a current rating in excess of the operating current of the device. It should be rated, at a minimum, at twice the operating current. The forward voltage drop of the diode should be as low as possible. Schottky diodes are commonly used because of their typical 0.5-V drop in the forward direction. Another consideration in selecting the diode is the reverse voltage rating. The peak inverse voltage (PIV) rating should be at least twice the voltage of the battery.



FIGURE 5.1 Battery circuit incorporating a blocking diode to prevent charge.

FIGURE 5.2 Series/parallel battery. (*a*) Without diode protection. (*b*) With diode protection.

Protection from Charging within Battery. When multiple series stacks are paralleled within a battery pack, charging may occur when a detective or a low-capacity cell is present in one of the stacks (Fig. 5.2*a*). The remaining stacks of cells will charge the stack with the defective cell. At best this situation will discharge the good stack, but it could result in rupture of the cells in the weak stack. To avoid this, diodes should be placed in each series string to block charging currents from stack to stack (Fig. 5.2*b*).

When diode protection is used in each series stack, the diode will prevent the stack containing the defective cell from being charged. The diode should have the following characteristics:

- 1. Forward voltage drop should be as low as possible, Schottky type preferable.
- 2. Peak inverse voltage should be rated at twice the voltage of the individual series stack.
- **3.** Forward current rating of the diodes should be a minimum of

$$I_{\min} = \frac{I_{\text{op}}}{N} \times 2$$

where I_{op} = device operating current N = number of parallel stacks

5.2.2 Preventing Battery Short-Circuit Conditions

When a battery is short-circuited through the external terminals, the chemical energy is converted into heat within the battery. In order to prevent short-circuiting, the positive and negative terminals of the battery should be physically isolated. Effective battery design will incorporate the following:

- 1. The battery terminals should be recessed within the external case (Fig. 5.3*a*).
- **2.** If connectors are used, the battery should incorporate the female connection. The connector should also be polarized to only permit for correct insertion (Fig. 5.3*b*).



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Additional Short-Circuit Protection. In addition it may be also necessary to include some means of circuit interruption. There are a number of devices which can perform this function, including:

- 1. Fuses or circuit breakers
- 2. Thermostats designed to open the battery circuit when the temperature or current reaches a predetermined upper limit
- **3.** Positive-temperature-coefficient (PTC) devices that, at normal currents and temperatures, have a very low value of resistance. When excessive currents pass through these devices or the battery temperature increases, the resistance increases orders of magnitude, limiting the current. These devices are incorporated internally in some cells by the cell manufacturer. When using cells with internal protection, it is advisable to use an external PTC selected to accommodate both the current and the voltage levels of the battery application (see Sec. 5.5.1).

5.2.3 Voltage Reversal

Due to variability in manufacturing, capacities will vary from battery to battery. When discharged in a series configuration, the capacity of the weakest cell in the series string of a multicell battery will be depleted before the others. If the discharge is continued, the voltage of the low-capacity cell will reach 0 V and then reverse. The heat generated may eventually cause pressure buildup in the cell and subsequent venting or rupture. This process is sometimes referred to as "forced discharge."

A common test to determine the ability of cells to withstand voltage reversal is the forceddischarge test. The cells are deliberately discharged, at specified currents, to below 0 V by other cells in a series string or by an external power supply to determine whether a venting, rupture, or other undesired safety problem arises.

Some cells are designed to withstand a forced discharge to specified discharge currents. The cells may also be designed with internal protection, such as fuses or thermal cutoff devices, to interrupt the discharge if an unsafe condition develops.

This condition of cell unbalance could be exacerbated with rechargeable cells as the individual cell capacities could change during cycling. To minimize this effect, rechargeable batteries should at least be constructed with "matched" cells, that is, cells having nearly identical capacities. Cells are sorted, within grades, by at least one cycle of charge and discharge. Typically cells are considered matched when the capacity range is within 3%. Recent advances in manufacturing control have reduced the number of cell grades. Some manufacturers have reached the optimal goal of one grade, which negates the need of matching. This information is readily available from the battery companies.

Battery Design to Prevent Voltage Reversal. Even though matched cells are used, other battery designs or applications can cause an imbalance in cell capacity. One example is the use of voltage taps on cells of a multicell battery in a series string. In this design, the cells are not discharged equally. Figure 5.4 illustrates a battery incorporating voltage taps that could result in voltage reversal.

For illustration assume $I_2 = 3$ A, $I_1 = 2$ A, and the cell capacity is 15 Ah. Cells 3 and 4 are being discharged at the 5-h rate, while cells 1 and 2 are being discharged at the combination of $I_1 + I_2$, or 5 A, a 3-h rate. After 3 h, cells 1 and 2 will be almost depleted of capacity and will go into voltage reversal if the discharge is continued. Many early battery designs using Leclanché-type cells incorporated the use of voltage taps. Batteries with as many as 30 cells in series (45 V) were common with taps typically at 3, 9, 13.5 V, and so on. When the cells with the lower voltage taps were discharged, they could leak. This leakage could cause corrosion, but usually these cells would not be prone to rupture. With the advent



FIGURE 5.4 Battery circuit using voltage taps.

of the high-energy, tightly sealed cells, this is no longer the case. Cells driven into voltage reversal may rupture or explode. In order to avoid problems, the battery should be designed with electrically independent sections for each voltage output. If possible, the device should be designed to be powered by a single input voltage source. DC to DC converters can be used to safely provide for multiple voltage outputs. Converters are now available with efficiencies greater than 90%.

Parallel Diodes to Prevent Voltage Reversal. Some battery designers, particularly for multicell lithium primary batteries, add diodes in parallel to each cell to limit voltage reversal. As the cell voltage drops below zero volts and into reversal, the diode becomes conducting and diverts most of the current from flowing through the cell. This limits the extent of the voltage reversal to that of the characteristic of the diode. This use of diodes is shown in Fig. 5.6.

5.2.4 Protection of Cells and Batteries from External Charge

Many battery-powered devices are also operated from rectified alternating-current (AC) sources. These could include devices which offer both AC and battery operation or devices which use the battery for backup when the AC power supply fails or is not available.

In the case where the battery is a backup for the main power supply as, for example, in memory backup, the primary battery must be protected from being charged by the main power supply. Typical circuits are shown in Fig. 5.5. In Fig. 5.5a two blocking diodes are used redundantly to provide protection in case of the failure of one. A resistor is used in Fig. 5.5b to limit the charge current if the diode fails in a closed position. This blocking diode should have the features of a low voltage drop in the forward direction to minimize the loss of battery backup voltage, and a low leakage current in the reverse direction to minimize the charging current.



FIGURE 5.5 Protective circuitry for memory backup batteries. (*a*) Using two diodes. (*b*) Using diode and resistor, V_{cc} = power supply voltage.

5.2.5 Special Considerations When Designing Lithium Primary Batteries

Lithium primary batteries contain an anode of elemental lithium (see Chap. 14) and, because of the activity of this metal, special precautions may be required in the design and use of the batteries, particularly when multiple cells are used in the battery pack. Some of the special precautions that should be taken in the design of these batteries, include the following:

- 1. When multiple cells are required, due to voltage and/or the capacity requirement of the application, they should be welded into battery packs, thus preventing the user mixing cells of different chemistries or capacities if replaceable cells were used.
- **2.** A thermal disconnect device should be included to prevent the build-up of excessive heat. Many of the batteries now manufactured include a PTC or a mechanical disconnect, or both, within the cell. Additional protective thermal devices should be included, external to the cells, in the design of a multicell battery pack.
- 3. The following protective devices should be included:
 - a. Series diode protection to prevent charging must be included
 - **b.** Cell bypass diode protection to prevent excessive voltage reversal of individual cells in a multicell series and/or series parallel configuration
 - c. Short circuit protection by means of a PTC, permanent fuse or electronic means, or a combination of all three
- **4.** In order to make the used battery safe for disposal, for some lithium batteries the remaining lithium within the battery must be depleted. This is accomplished by placing a resistive load across the cell pack to completely discharge the battery after use. The resistive load should be chosen to ensure a low current discharge, typically at a five (5) day rate of the original capacity of the battery. This feature has been used mainly in military primary lithium batteries.

Figure 5.6 illustrates a typical schematic showing the use of the safety features discussed.


FIGURE 5.6 Lithium primary battery schematic with series and bypass protection.

5.3 BATTERY SAFEGUARDS WHEN USING DISCRETE BATTERIES

5.3.1 Design to Prevent Improper Insertion of Batteries

When designing products using individual single-cell batteries, special care must be taken in the layout of the battery compartment. If provisions are not made to ensure the proper placement of the batteries, a situation may result in which some of the batteries that are improperly inserted could be exposed to being charged. This could lead to leakage, venting, rupture, or even explosion. Figure 5.7 illustrates simple battery-holder concepts for cylindrical and button batteries, which will prevent the batteries from being inserted incorrectly. Figure 5.8 shows several other design options for preventing improper installation.

Two commonly used battery circuits that are potentially dangerous without proper battery orientation are:

- 1. Series/parallel with one battery reversed (Fig. 5.9). In this circuit, battery 3 has been reversed. As a result, batteries 1–3 are now in series and are charging battery 4. This condition can be avoided, if possible, by using a single series string of larger batteries. Further, as discussed in Sec. 5.2.1, the use of diodes in each series section will at least prevent one parallel stack from charging the other.
- 2. Multicell series stack with one battery reversed in position (Fig. 5.10). The fourth battery is reversed and will be charged when the circuit is closed to operate the device. Depending on the magnitude of the current, the battery may vent or rupture. The magnitude of the current is dependent on the device load, the battery voltage, the condition of the reversed battery, and other conditions of the discharge.

To minimize the possibility of physically reversing a battery, the proper battery orientation should be clearly marked on the device, with simple and clear instructions. Blind battery compartments, where the individual batteries are not visible, should be avoided. The best practice is to use oriented or polarized battery holders, as discussed previously.



FIGURE 5.7 Battery holders. (Left) Cylindrical. (Right) Button or flat.



FIGURE 5.8 Battery contact designs that prevent reverse installation of cells.



Current direction _____

FIGURE 5.9 Series/parallel circuit; cell 4 being charged.

FIGURE 5.10 One cell reversed in a series stack; cell 4 being charged.

5.3.2 Battery Dimensions

At times equipment manufacturers may design the battery cavity of their device around the battery of a single manufacturer. Unfortunately the batteries made by the various manufacturers are not exactly the same size. While the differences may not be great, this could result in a cavity design that will not accept batteries of all manufacturers.

Along with variations in size, the battery cavity design must also be able to accommodate unusual battery configurations that fall within IEC standards. For example, several battery manufacturers offer batteries with negative recessed terminals that are designed to prevent contact when they are installed backward. Unfortunately negative recessed terminals will mate only with contacts whose width is less than the diameter of the battery's terminal. Figure 5.11*a* illustrates the dimensional differences between cells with standard and recessed terminals.

The battery cavity should not be designed around the battery of a single manufacturer whose battery may be a unique size or configuration. Instead, cavity designs should be based on International Electrotechnical Commission (IEC) standards and built to accommodate maximum and minimum sizes. IEC and ANSI standards (see Chap. 4) provide key battery dimensions, including overall height, overall diameter, pip diameter, pip height, and diameter of negative cap. Maximum and minimum values are usually specified, as shown in Fig. 5.11*b*. As these standards are revised periodically, the latest edition should be used.



FIGURE 5.11 (*a*) Types of battery terminals falling within IEC standards. (*b*) Illustration of typical standard IEC dimensions.

5.4 BATTERY CONSTRUCTION

The following constructional features also should be considered in the design and fabrication of batteries:

- 1. Intercell connections
- 2. Encapsulation of cells
- 3. Case configuration and materials
- 4. Terminals and contact materials

5.4.1 Intercell Connections

Soldering is the method of connection for batteries using Leclanché-type cells. Wires are soldered between the negative zinc can and the adjoining positive cap. This effective method of construction for these cells is still widely used.

Welding of conductive tabs between cells is the preferred method of intercell connection for most of the other battery systems. The tab materials for most applications are either pure nickel or nickel-plated steel. The corrosion resistance of the nickel and its ease of welding result in reliable permanent connections. The resistance of the tab material must be matched to the application to minimize voltage loss. The resistance can be calculated from the resistivity of the material, which is normally expressed in ohm-centimeters,

Resistance = $\frac{\text{resistivity} \times \text{length (cm)}}{\text{cross-sectional area (cm}^2)}$

The resistivity values of nickel and nickel-plated steel are

Nickel	$6.84 \times 10^{-6} \Omega \cdot \mathrm{cm}$
Nickel-plated steel	$10 \times 10^{-6} \Omega \cdot \mathrm{cm}$

For example, the resistance of a tab with dimensions of 0.635-cm width, 0.0127-cm thickness, and 2.54-cm length is

for nickel,

$$\frac{6.84 \times 10^{-6} \times 2.54}{0.635 \times 0.0127} = 2.15 \times 10^{-3} \ \Omega$$

for nickel-plated steel,

$$\frac{10 \times 10^{-6} \times 2.54}{0.635 \times 0.0127} = 3.15 \times 10^{-3} \ \Omega$$

As is evident, the resistance of the nickel-plated steel material is 50% higher than that of nickel for an equivalent-size tab. Normally this difference is of no significance in the circuit, and nickel-plated steel is chosen due to its lower cost.

Resistance spot welding is the welding method of choice. Care must be taken to ensure a proper weld without burning through the cell container. Excessive welding temperatures could also result in damage to the internal cell components and venting may occur. Typically AC or capacitance discharge welders are used.

Both types of welders incorporate two electrodes, typically made of a copper alloy. A current path is established between the electrodes, melting and fusion of the materials will occur at the interface of the tab and the cell due to resistance heating. Figure 5.12 illustrates the commonly used welding techniques. The method shown in Fig. 5.12a is used in more than 90% of the joints where a tab is welded to a cell surface. Two weld nuggets are formed for each weld action. When welding circular leads to a cell or tab surface, the procedure shown in Fig. 5.12b will result in one weld spot per weld action. The procedure in Fig. 5.12c is commonly used when a tab-to-tab weld or similar joints are needed. This latter method is not recommended for welding to a cell.



FIGURE 5.12 Various welding configurations used in battery construction.

In all instances the weld should have a clean appearance, with discoloration of the base materials kept to a minimum. At least two weld spots should be made at each connection joint. When the weld is tested by pulling the two pieces apart, the weld must hold while the base metal tears. For tabs the weld diameter, as a rule of thumb, should be three to four times the tab thickness. For example, a 0.125-mm-thick tab should have a tear diameter of 0.375–0.5 mm. Statistical techniques of weld pull strength for process control are helpful, but a visual inspection of the weld diameter must accompany the inspection process.

The least preferred method of battery connection is the use of pressure contacts. Although this technique is used with some inexpensive consumer batteries, it can be the cause of battery failure where high reliability is desired. This type of connection is prone to corrosion at the contact points. In addition, under shock and vibration intermittent loss of contact may result.

5.4.2 Cell Encapsulation

Most applications require that the cells within the battery be rigidly fixed in position. In many instances this involves the encapsulation of the cells with epoxy, foams, tar, or other suitable potting materials.

Care must be taken to prevent the potting material from blocking the vent mechanisms of the cells. A common technique is to orient the cell vents in the same direction and encapsulate the battery to a level below the vent, as shown in Fig. 5.13. If possible the preferred method to keep the cells immobile, within the battery, is through careful case design without the use of potting materials. Although this method may increase initial tooling costs, future labor savings could be realized.



(a) Vertical cell orientation



(b) Horizontal cell orientation

FIGURE 5.13 Battery encapsulation techniques. (*a*) Vertical cell orientation. (*b*) Horizontal cell orientation.

5.4.3 Case Design

Careful design of the case should include the following:

- 1. Materials must be compatible with the cell chemistry chosen. For example, aluminum reacts with alkaline electrolytes and must be protected where cell venting may occur.
- **2.** Flame-retardant materials may be required to comply with end-use requirements. Underwriters Laboratories, the Canadian Standards Association, and other agencies may require testing to ensure safety compliance.
- **3.** Adequate battery venting must allow for the release of vented cell gases. In sealed batteries this requires the use of a pressure relief valve or breather mechanisms.
- **4.** The design must provide for effective dissipation of heat to limit the temperature rise during use and especially during charge. High temperatures should be avoided as they reduce charge efficiency, increase self-discharge, could cause cell venting, and generally are detrimental to battery life. The temperature increase is greater for a battery pack than

for an individual or separated cells as the pack tends to limit the dissipation of heat. The problem is exacerbated when the pack is enclosed in a plastic case. This is illustrated in Fig. 5.14, which compares the temperature rise of groups of cells with and without a battery case.



FIGURE 5.14 Temperature increase characteristics during charge of battery pack.

5.4.4 Terminal and Contact Materials

Terminal material selection must be compatible with the environments of the battery contents as well as the surroundings. Noncorrosive materials should be selected. Nickel-cadmium and Nickel-metal hydride batteries typically use solid nickel contacts to minimize corrosion at the terminal contacts.

A number of factors must be considered when specifying contact materials. Several principles apply to the substrate. The normal force provided by the contact must be great enough to hold the battery in place (even when the device is dropped) and to prevent electrical degradation and any resulting instability. Contacts must be able to resist permanent set. This refers to the ability of the contact to resist permanent deformation with a set number of battery insertions. Temperature rise at high current drains due to the resistance of the contact material must be limited. Excessive temperature increase could lead to stress relaxation and loss in contact pressure as well as to the growth of oxide films which raise contact resistance.

A common way to minimize contact resistance is to provide a wiping action of the device contact to the battery contact when the battery is inserted in place. Most camcorder batteries incorporate this feature.

Coatings should be selected to satisfy requirements not met by the substrate material, such as conductivity, wear, and corrosion resistance. Gold is an optimal coating due to its ability to meet most of the requirements. However, other materials may be used. Table 5.1 lists the characteristics of various materials used as contacts.

Gold plating	Provides the most reliable metal-to-metal contact under all environmental conditions
Nickel (solid)	Provides excellent resistance to environmental corrosion and is second only to gold plating as a contact material; material can be drawn or formed.
Nickel-clad stainless steel	Performs almost as well as solid nickel, with excellent resistance to environmental corrosion
Nickel-plated stainless steel	Very good material; unplated stainless steel is not recommended due to the adverse impact of passive films which develop on stainless steel resulting in poor electrical contact
Inconel alloy	Provides good electrical conductivity and good corrosion resistance; if manufacturers prefer to solder the contact piece in the circuit, soldering may be difficult unless an active flux is used
Nickel-plated cold-rolled steel	The most economical contact material; continuous, nonporous nickel plating of 200 $\mu \rm m$ is preferred

TABLE 5.1 Contact Materials

5.5 DESIGN OF RECHARGEABLE BATTERIES

All of the criteria addressed for the design of primary batteries should be considered for the design of rechargeable batteries.

In addition, multicell rechargeable batteries should be built using cells having matched capacities. In a series-connected multicell battery, the cell with the lowest capacity will determine the duration of the discharge, while the one with the highest capacity will control the capacity returned during the charge. If the cells are not balanced, the battery will not be charged to its designed capacity. To minimize the mismatch, the cells within a multicell battery should be selected from one production lot, and the cells selected for a given battery should have as close to identical capacities as possible. This is especially important with lithium-ion batteries, because due to the need for limiting current during charge, it is not possible to balance the capacity of the individual cells with a top-off or trickle charge.

Furthermore, safeguards must be included to control charging to prevent damage to the battery due to abusive charging. Proper control of the charge process is critical to the ultimate life and safety of the battery. The two (2) major considerations to be addressed include:

- 1. Voltage and current control to prevent overcharge
- **2.** Temperature sensing and response to maintain the battery temperature within the range specified by the battery manufacturers.

5.5.1 Charge Control

The controls for voltage and current during charge for most batteries are contained in the charger. Nickel–cadmium and nickel–metal hydride batteries may be charged over a fairly broad range of input current, ranging from less than a 0.05C rate to greater than 1.0C. As the charge rate increases, the degree of charger control increases. While a simple, constant current control circuit may be adequate for a battery being charged at a 0.05C rate, it would not suffice at a rate of 0.5C or greater. Protective devices are installed within the battery to stop the charge in the event of an unacceptable temperature rise. The thermal devices that can be used include the following:

- 1. Thermistor: This device is a calibrated resistor whose value varies inversely with temperature. The nominal resistance is its value at 25°C. The nominal value is in the Kohm range with 10K being the most common. By proper placement within the battery pack, a measurement of the temperature of the battery is available and T_{max} , T_{min} and $\Delta T/\Delta t$ or other such parameters can be established for charge control. In addition, the battery temperature can be sensed during discharge to control the discharge, e.g., turn off loads to lower the battery temperature, in the event that excessively high temperatures are reached during the discharge.
- **2.** *Thermostat (Temperature Cutoff, TCO)*: This device operates at a fixed temperature and is used to cut off the charge (or discharge) when a preestablished internal battery temperature is reached. TCOs are usually resettable. They are connected in series within the cell stack.
- **3.** *Thermal Fuse:* This device is wired in series with the cell stack and will open the circuit when a predetermined temperature is reached. Thermal fuses are included as a protection against thermal runaway and are normally set to open at approximately 30–50°C above the maximum battery operating temperature. They do not reset.
- **4.** *Positive Temperature Coefficient (PTC) Device:* This is a resettable device, connected in series with the cells, whose resistance increases rapidly when a preestablished temperature is reached, thereby reducing the current in the battery to a low and acceptable current level. The characteristics of the PTC device are shown in Fig. 5.15. It will respond to high circuit current beyond design limits (such as a short circuit) and acts like a resettable fuse. It will also respond to high temperatures surrounding the PTC device, in which case it operates like a temperature cutoff (TCO) device.

Figure 5.16 shows a schematic of a battery circuit, indicating the electrical location of these protective devices. The location of the thermal devices in the battery assembly is critical to ensure that they will respond properly as the temperature may not be uniform throughout the battery pack. Examples of recommended locations in a battery pack are shown in Fig. 5.17. Other arrangements are possible, depending on the particular battery design and application.

Details of the specific procedures for charging and charge control are covered in the various chapters on rechargeable batteries.



FIGURE 5.15 Characteristics of a typical positive temperature coefficient (PTC) device.







FIGURE 5.17 Location of protective devices in battery. Linden, D., & Reddy, T. (2001). Handbook of batteries. Retrieved from http://ebookcentral.proquest.com Created from uc on 2019-05-28 16:53:43.

5.5.2 Example of Discharge / Charge Control

Electronic circuitry can be used to maximize battery service life by cutting off the discharge as close to the specified end or cut-off voltage as possible.¹ Ending the discharge at too high a voltage will result in a loss of a significant amount of battery capacity; ending it at too low an end voltage and, thus, discharging the battery beyond its safe cut-off could cause permanent damage to the battery.² Similarly, on charge, accurate control, as discussed above, will enable a maximum charge under safe conditions without damage to the battery.

This is especially important for the lithium-ion battery for which the preferred charge protocol for a high rate charge is to start the charge at a relatively high, usually constant current to a given voltage and then taper charging at a constant voltage to a given current cutoff. Exceeding the maximum voltage is a potential safety hazard and could cause irreversible damage to the battery. Charging to a lower voltage will reduce the capacity of the battery.³

Another interesting example is the control of charge for hybrid electric vehicles (HEV). In this application, it is advantageous to obtain close to 100% charge efficiency or charge acceptance rather than maximum battery capacity. The charge acceptance for a battery at the low state-of-charge (SOC) is close to 100%. As the battery is charged, charge acceptance becomes progressively poorer, particularly above 80% SOC.⁴ (At full charge, the charge acceptance is zero). In the HEV application using nickel-metal hydride batteries, the charge control keeps the stage-of-charge, under normal driving and regenerative braking conditions, as close to 50% SOC as possible, and preferably within 30 to 70%. At these states-of-charge, the coulombic charge efficiency is very high.⁵

Other useful information also can be included in the chip, such as manufacturing information, chemistry, design data serial number, and cycle count.

5.5.3 Lithium-Ion Batteries

Special controls should be used with Lithium-ion batteries for management of charge and discharge. Typically, the control circuit will address the following items that affect battery life and safety.

Cell Voltage: The voltage of each individual cell in the battery pack is monitored on a continuous basis. Depending on the specific lithium-ion battery chemistry that is used, the upper voltage limit on charge, as specified by the manufacturer, is usually limited between 4.1 to 4.3 volts. On discharge, the cell voltage should not fall below 2.5 to 2.7 volts.

Temperature Control: As with any battery system, high temperature will cause irreversible damage. Internal battery temperature, for most applications, should be kept below 75°C. Temperature cutoff, with a trip of 70°C and reset temperature in the range of 45°C, is routinely used. Temperatures in excess of 100°C could result in permanent cell damage. For this, permanent type fuses are used; typically set for 104°C with a tolerance of +/-5°C.

Short Circuit Protection: Normally, current limits are incorporated into the protection circuits. As a backup, a PTC device or fuse is placed in series with the battery pack. It is advisable to place the PTC between the pack assembly and the output of the battery. By placing it at this point, the PTC will not interfere with the operation of the upper or lower voltage detection of the electronic control circuit.

5.6 ELECTRONIC ENERGY MANAGEMENT AND DISPLAY— "SMART" BATTERIES

During the past decade, an important development in rechargeable battery technology has been the introduction of the use of electronic microprocessors to optimize the performance of the battery, control charge and discharge, enhance safety and provide the user with information on the condition of the battery. The microprocessor can be incorporated into the battery (the so-called *smart battery*), into the battery charger, or into the host battery-using equipment.

Some of the features include:

- 1. Charge control. The microprocessor can monitor the battery during charge controlling charge rate and charge termination, such as t, V_{max} , $-\Delta V$, ΔT , and $\Delta T/\Delta t$, to cut off the charge or to switch to a lower charge rate or another charge method. Constant current to constant voltage charge can be controlled and options can be incorporated into the chip for pulse charging, "reflex" charging (a brief periodic discharge pulse during charge), or other appropriate control features.
- **2.** *Discharge control.* Discharge control is also provided to control such conditions as discharge rate, end-of-life cutoff voltage (to prevent overdischarge), cell equalization and temperature management. Individual cells, as well as the entire battery pack, can be monitored to maintain cell balance during cycling.
- **3.** *State-of-charge indicator.* These devices, commonly known as "gas gauges," estimate the remaining battery capacity by factoring in such variables as the discharge rate and time, temperature, self-discharge, charge rate and duration. The remaining capacity is normally displayed by a sequence of illuminated LEDs or as a direct output to the device being powered.
- **4.** *Other information.* Data is collected during the life of the battery to update the database and, as needed, make changes to maintain optimum performance. Other information can also be included or collected, such as battery chemistry and characteristics, manufacturing information (battery manufacturer can electronically "stamp" batteries at time of manufacture) and battery history, cycle count and other such data for a complete accounting of the battery's usage.

There are several main elements to consider in the design of smart batteries:⁶

1. *Measurement.* There are several parameters that can be measured directly to provide the basic information for the microprocessor. These include voltage, current, temperature and time. It is important that these measurements be made as accurately as possible to provide the best data for control.

For example, voltage measurements are critical as the charge control (charge termination) depends on the battery voltage which, in some instances, should be accurate to at least 0.05 volts. An inaccurate measurement could result in under or overcharge which could result in short service life or damage to the battery, respectively. Or, in the case of the lithium-ion battery, overcharge could be a safety hazard. Similarly, on discharge, cutting off the discharge prematurely results in an unnecessarily shortened service life while overdischarge could, again, result in damage to the battery.

Errors in the measurement of current affect not only the calculation of capacity and the state-of-charge "gas gauge," but influence the termination of charge and discharge as the termination voltages may vary depending on the current. Complicating this measurement is that the current is not a constant value, particularly during the discharge, with multiple power modes and high current pulses as short as milliseconds.

Likewise, temperature is an important parameter as the performance of batteries is highly temperature dependent and exposure to high temperatures can cause irreversible damage to the cells. **2.** *Calculation.* The calculation step covers the procedures for using the measured data as well as the algorithms to estimate battery performance (e.g. capacity at various discharge loads and temperature), charge acceptance, self-discharge, etc. Early "smart battery" electronics used simple linear models for these parameters which severely limited the accuracy in predicting the battery's performance. As noted in the descriptions of battery performance in the various chapters in this Handbook, battery performance, e.g. with respect to current drain and temperature is not linear. Self-discharge, similarly, is a complex relationship influenced at least by temperature, time, state of charge and the discharge load at which it is measured. Further, the performance of even those batteries using the same chemistry, varies with design, size, manufacturer, age, etc. A good algorithm will account for these relationships for control, predicting remaining service life and assuring safe operation.

As an example, Fig. 29.23 is an illustration showing the non-linear relationship of the rate of self discharge with temperature and time.

- **3.** *Communication.* Clear, accurate and secure communication is important between the battery and host charger and the battery-using equipment for each component to obtain data or provide needed data to one of the other components. For example, the battery charger must be informed of the characteristics of the battery it is charging, the battery's state of charge, charge voltage and current requirements, charge-off, etc. The smart battery must also communicate to the user who may require information, such as remaining battery life, power levels, charge time and other characteristics to facilitate the use of the equipment.
- **4.** *Errors.* As discussed under *Measurement*, it is important that parameters be measured accurately as inaccurate ones would not only result in incorrect decisions on the battery's capability but could result in damage to the battery or safety problems. In addition, the Smart Battery provides information on the margin-of-error in the state-of-charge calculation. This function is called "MaxError" and has a range of 0 to 100%. If the "MaxError" displays 20% and the "State-of-Charge" displays 30%, the actual state-of-charge is between 30 and 50%. If this loss of capacity is due to self-discharge while the battery is on stand and the rate of self-discharge does not follow the installed algorithm, the "MaxError" will increase. The user can correct this by, for example, fully charging the battery after a full discharge. This will restore the battery to full capacity and the battery will sense the "Reset" condition and return the MaxError to zero. It is possible to output an alarm when the MaxError has reached a programmed limit, alterting the user that a reset cycle is warranted.

5.6.1 The Smart Battery System

In order to ensure effective communication between the battery and host device, standard methods of communication are required. One method developed by battery manufacturers and microprocessor companies is the Smart Battery System (SBS) based on the System Management Bus. In 1995, the "Smart Battery Data Specification" was released by the SBS Forum. These specifications detail the communications method, protocols and the data interfaces between various devices. These specifications are periodically updated and available on the forum website, *www.sbs-forum.org*.

The goal of the Smart Battery interface is to provide adequate information for power management and charge control regardless of the particular battery's chemistry. Even though the major consumer of the battery information is the user, the system can also take advantage by using power consumption information to better manage its own power use. A charging system will be able to tell the user how long it will take to fully charge the battery.

One possible Smart Battery model is a system consisting of a battery, battery charger and a host (notebook computer, video camera, cellular phone, or other portable electronic equipment) as illustrated in Figure 5.18.



FIGURE 5.18 Outline of a Smart Battery System (from Reference 7).

The Smart Battery consists of a collection of cells or single-cell batteries and is equipped with specialized hardware that provides present state, calculated and predicted information to its SMBus Host. These may monitor particular environmental parameters in order to calculate the required data values. The electronics need not be inside the Smart Battery if the battery is not removable from the device.

The Smart Battery communicates with the other devices (such as the SM (System Management) Bus Host and the Smart Battery Charger) via two separate communication interfaces:

The first uses the SMBus CLOCK and DATA lines and is the primary communication channel between the Smart Battery and other SMBus devices. The Smart Battery will provide data when requested, send charging information to the Stuart Battery Charger, and broadcast critical alarm information when parameters (measured or calculated) exceed predetermined limits within the particular Smart Battery.

The other required communication interface is the secondary signaling mechanism or 'Safety Signal' on a Smart Battery pack connector. This is a variable resistance output from the Smart Battery which indicates when charging is permitted. It is meant as an alternate signaling method should the SMBus become inoperable. It is primarily used by the Smart Battery Charger to confirm correct charging.

The Smart Battery Charger is a charging circuit that provides the Smart Battery with charging current and charging voltage to match the Smart Battery's requested requirements. The battery charger periodically communicates with the Smart Battery and alters its charging characteristics in response to information provided by the Smart Battery. This allows the battery to control its own charge cycle. Optionally, the Smart Battery Charger may not allow the Smart Battery to supply power to the rest of the system when the Smart Battery is fully charged and the system is connected to AC power, thus prolonging the life of the battery.

The Smart Battery Charger will also receive critical events from the Smart Battery when it detects a problem. These include alarms for charging conditions or temperature conditions which exceed the limits set within the particular Stuart Battery.

The SM Bus is a specific implementation of a PC-bus that describes data protocols, device addresses and additional electrical requirements that is designed to physically transport commands and information between the components of the Smart Battery system.

The SMBus Host represents a piece of electronic equipment that is powered by a Smart Battery and that can communicate with the Smart Battery. The SMBus Host requests information from the battery and then uses it in the systems power management scheme and/or uses it to provide the user information about the battery's state and capabilities. The SMBus Host will also receive critical events from the Smart Battery when it detects a problem. In addition to the alarms sent to the Smart Battery Charger, it receives alarms for end of discharge, remaining capacity below the user set threshold value and remaining run time below the user set threshold value.

Figure 5.19 is a schematic block diagram of a Smart Battery system, in this case for a three cell Lithium-Ion battery.



FIGURE 5.19 Schematic block diagram of a Lithium Ion three cell battery with SMBus output or gas gauge display.

The battery incorporates five terminals, battery plus and minus, clock, data and a safety signal, typically temperature. If the battery is hard wired into the host, the electronics need not be inside the battery. When the mechanical construction is complete, it must be programmed with the information such as chemistry, charge current, maximum voltage, etc. The information that is available to the host and charger includes:

- 1. Charge instructions for voltage, current and temperature
- 2. Battery design capacity
- 3. Remaining time to full charge
- 4. Remaining run time
- 5. Operating voltage, current, power, and temperature
- 6. Battery cycle count
- 7. Manufacturer's name, model, serial number and date of manufacture
- 8. Other information

5.7 GUIDELINES

In addition to the material covered in the preceding sections, the following should be considered in the design and fabrication of batteries:

- **1.** Allow for the thermal expansion of battery components as well as the change in cell volume which accompanies discharge.
- **2.** Consider the implications of cell leakage on equipment components, intercell weld or solder connections, and other battery components such as potting compounds, wire insulation, and adhesives. Locate the battery compartment in the device, such as to minimize the effects of possible leakage.
- **3.** Wire leads and intercell connectors should be properly isolated and insulated to preclude the development of short circuits during the assembly process as well as during the life of the battery.
- **4.** Intercell and battery connections need to be carefully made to withstand the severity of the equipment environment. Intercell connections shall be welded rather than soldered to avoid heat conduction to the interior of the cell.
- 5. Handle cells carefully to avoid inadvertent short circuits and discharge.
- 6. Avoid the use of high-exotherm potting compounds during battery fabrication.
- **7.** Always vent the battery compartment in the device, allowing for release of any buildup of gas pressure. Avoid any confined pockets in the device where these gases may accumulate.

REFERENCES

- 1. V. Drori, and C. Martinez, "Smart Battery Chips Maximize Usable Battery Capacity and Battery Life," *Battery Power Products and Technology*, April 1999.
- 2. Section 28.4.2 of this handbook.
- 3. Section 35.5 of this handbook.
- 4. Sections 28.5 and 33.5 of this handbook.
- 5. Section 30.8.7 of this handbook.
- 6. D. Friel, "How Smart Should a Battery Be," Battery Power Products and Technology, March 1999.
- 7. Smart Battery Data Specification, Rev. 1.1, www.sbs_forum.org.

CHAPTER 6 SELECTION AND APPLICATION OF BATTERIES

David Linden

6.1 GENERAL CHARACTERISTICS

The many and varied requirements for battery power and the different environmental and electrical conditions under which they must operate necessitate the use of a number of different types of batteries and designs, each having the most advantageous performance under specific operational conditions.

Although many advances have been made in battery technology in recent years, as illustrated in Fig. 1.6 and discussed in more detail in Secs. 7.1 and 22.1, both through continued improvement of a specific electrochemical system and the development and introduction of new battery chemistries, there is still no one "ideal" battery that performs optimally under all operating conditions. As a result, over time, many different electrochemical systems and battery types have been and are still being investigated and promoted. However, a relatively small number have achieved wide popularity and significant production and sales volumes. The less conventional systems are typically used in military and industrial applications requiring the specific capabilities offered by these special batteries.

The "ideal" electrochemical cell or battery is obviously one that is inexpensive, has infinite energy, can handle all power levels can operate over the full range of temperature and environmental conditions, has unlimited shelf life, and is completely safe and consumerproof. In practice, energy limitations do exist as materials are consumed during the discharge of the battery, temperature and discharge rate affect performance and shelf life is limited due to chemical reactions and physical changes that occur, albeit slowly in some cases, during storage. The use of energetic component materials and special designs to achieve high energy and power densities may require precautions during use to avoid electrical and physical abuse and problems related to safety. Further, the influence of the conditions of discharge, charge and the use of the battery, as discussed in Chap. 3, must the considered.

It should be recognized that while the demands of battery-using equipments continually seek smaller and more energetic and powerful batteries, these requirements may not necessarily be met because of the theoretical and practical limits of battery technology.

The selection of the most effective battery and the proper use of this battery are critical in order to achieve optimum performance in an application.

6.2 MAJOR CONSIDERATIONS IN SELECTING A BATTERY

A number of factors must be considered in selecting the best battery for a particular application. The characteristics of each available battery must be weighed against the equipment requirements and one selected that best fulfills these needs.

It is important that the selection of the battery be considered at the beginning of equipment development rather than at the end, when the hardware is fixed. In this way, the most effective compromises can be made between battery capabilities and equipment requirements.

The considerations that are important and influence the selection of the battery include:

- 1. Type of Battery: Primary, secondary, or reserve system
- 2. *Electrochemical System:* Matching of the advantages and disadvantages and of the battery characteristics with major equipment requirements
- **3.** *Voltage:* Nominal or operating voltage, maximum and minimum permissible voltages, voltage regulation, profile of discharge curve, start-up time, voltage delay
- **4.** Load Current and Profile: Constant current, constant resistance, or constant power; or others; value of load current or profile, single-valued or variable load, pulsed load
- 5. Duty Cycle: Continuous or intermittent, cycling schedule if intermittent
- 6. Temperature Requirements: Temperature range over which operation is required
- 7. Service Life: Length of time operation is required
- 8. Physical Requirements: Size, shape, weight; terminals
- **9.** *Shelf Life:* Active/reserve battery system; state of charge during storage; storage time a function of temperature, humidity and other conditions
- **10.** Charge-Discharge Cycle (if Rechargeable): Float or cycling service; life or cycle requirement; availability and characteristics of charging source; charging efficiency
- 11. Environmental Conditions: Vibration, shock, spin, acceleration, etc.; atmospheric conditions (pressure, humidity, etc.)
- **12.** *Safety and Reliability:* Permissible variability, failure rates; freedom from outgassing or leakage; use of potentially hazardous or toxic components; type of effluent or signature gases or liquids, high temperature, etc.; operation under severe or potentially hazardous conditions; environmentally friendly
- **13.** Unusual or Stringent Operating Conditions: Very long-term or extreme-temperature storage, standby, or operation; high reliability for special applications; rapid activation for reserve batteries, no voltage delay; special packaging for batteries (pressure vessels, etc.); unusual mechanical requirements, e.g., high shock or acceleration, nonmagnetic
- **14.** *Maintenance and Resupply:* Ease of battery acquisition, accessible distribution; ease of battery replacement; available charging facilities; special transportation, recovery, or disposal procedures required
- 15. Cost: Initial cost; operating or life-cycle cost; use of critical or exotic (costly) materials

Electrochemical batteries are an important power source and are used in a wide variety of consumer, industrial, and military applications. Annual worldwide sales exceed \$50 billion.

The use of batteries is increasing at a rapid rate, much of which can be attributed to advancing electronics technology, lower power requirements, and the development of portable devices which can best be powered by batteries. Other contributing factors are the increased demand for battery-operated equipment, the opening of many new areas for battery applications ranging from small portable electronic devices to electric vehicles and utility power load leveling.

Batteries have many advantages over other power sources, as outlined in Table 6.1 They are efficient, convenient, and reliable, need little maintenance, and can be easily configured to user requirements. As a result, batteries are used in an extremely wide range and variety of sizes and applications—from as small as 3 mAh for watches and memory backup to as large as 20,000 Ah for submarine and standby power supplies.

TABLE 6.1	Application	of	Batteries
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Advantages	Limitations
Self-contained power source Adaptable to user configuration: Small size and weight—portability Variety of voltages, sizes, and configurations Compatible with user requirements	High cost (compared with utility power) Use of critical materials Low energy density Limited shelf life
Ready availability Reliable, low maintenance, safe, minimum, if any, moving parts Efficient conversion over a wide range of power demands Good power density (with some types) Efficient energy-storage device	

6.3.1 Summary of Battery Applications

A generalized summary of battery applications, listing the various battery types and identifying the power level and operational time in which each finds its predominant use, is shown in Fig. 6.1 As with any generalization, there are many instances in which the application of a particular battery will fall outside the limits shown.

Primary batteries are used typically from low to moderately high power drain applications, to a large extent with the familiar flat, button, or cylindrical configurations. They are a convenient, usually relatively inexpensive, lightweight source of packaged power and, as a result, are used in a variety of portable electric and electronic equipment. The so-called "dry-cell" is widely used in lighting devices, toys, radios, cameras, PDA's, and many other such consumer products. Flat or button batteries are popular in watches, calculators, photographic equipment, and as a battery backup for memory preservation. Similarly, primary batteries are used extensively in industrial and military applications to power portable communication, radar, night vision, surveillance, and other such equipment. Larger-sized primary batteries are also produced, mainly for special applications such as navigation aids, standby power, and remote-area uses, where their high capacity and energy density, long shelf life, and freedom from recharging and maintenance are important requisites. Secondary (rechargeable) batteries are used as energy-storage devices, generally connected to and charged by a prime energy source and delivering their energy to the load on demand. Examples of this type of service are the lead-acid automotive starting, lighting, and ignition (SLI) battery, which is by far the major secondary battery application, hybrid electric vehicles standby electric systems including uninterruptible power systems (UPS) and load leveling. Secondary batteries are also used in applications where they are discharged and recharged subsequently from a separate power source. Examples of this type of service are electric vehicles and many applications, particularly portable devices, such as computers, cellular phones and camcorders, where the secondary battery is preferred in place of primary batteries, either for cost saving as they can be recharged or to handle power levels beyond the capability of conventional primary batteries.

The *special and reserve primary batteries* are used in selected applications usually requiring batteries which are capable of high-rate discharges for short periods of time after long-term storage in an inactivated or "reserve" condition. Many of these are used by the military for munitions and missiles.

The *solid electrolyte batteries* are low-rate batteries, operating in the microampere range, but with extremely long operational and shelf life. They are used in computer memory backup, cardiac pacemakers, and other applications requiring high reliability and extremely long active life.

The *fuel cell* is used in those applications requiring long-term continuous operation. Its major application to date has been as the power source in space flights. Larger sizes are now in development as alternatives to moderate-power engine generators, utility load leveling and electric vehicle propulsion. Most recently, portable-sized air-breathing fuel cells, using fuels, such as hydrogen and methanol stored in containers, are being investigated in the subkilowatt power level alternatives to batteries. (See Part IV.)



FIGURE 6.1 Predominant application field for various types of batteries.

6.3.2 Portable, Industrial and Electric Vehicle Applications

A listing of a number of the major applications of batteries is given in Table 6.2a. These are listed in the following three major categories.

Portable Applications. This is a rapidly expanding area as many new portable devices are being introduced which are designed to operate only with batteries or, in some instances such as laptop computers, to operate with either batteries or AC line power. Both primary and secondary batteries are used in these portable equipments depending on service life and power requirements, convenience, cost and other factors discussed in Sec. 6.4.

Industrial Applications. Larger-sized batteries, usually rechargeable, are used in these applications. In many of these applications, the batteries are used as back-up power in the event of an AC power failure. In some instances, such as with munitions, navigation aids and satellites, primary or reserve type batteries are used where an electrical source is not available for recharging. This is another area that is expanding rapidly to meet the demands for uninterrupted power sources (UPS) for computer and other sophisticated systems which require 24/7 operation with extremely high reliability.

Vehicular and Traction Applications. Batteries have been an important power source for these applications, including starting, lighting and ignition (SLI) application and for the main power source for fork-lift trucks, golf carts and other such vehicles. This also is a growing area for battery application with the goal to replace the internal combustion engine with an environmental-friendly power source or provide a hybrid system which will improve the efficiency of fossil fuel engines and reduce the amount of objectionable and hazardous effluents.

The specific types of batteries in each classification and the major applications and characteristics of the batteries are covered in the appropriate chapters of this Handbook. Table 6.2a also lists the Chapters and Sections in this Handbook where some of the applications are discussed in more detail.

The current drains of some of the portable equipments are listed in Table 6.2b to illustrate the wide range of the requirements, from microamperes to over an ampere. Although the values are specified in amperes, some of the equipments, such as flashlights, have a resistive load. Many of the newer equipments present a constant current or a constant power load, and in some cases, a constant energy load as the photoflash cameras. In fact, with the more sophisticated equipments, the load is not constant, but will vary, not only in current or power drain, but in the type of load, depending on the particular function of the device that is operating at a particular time.

Note. As discussed in Chap. 3, when evaluating batteries for a specific application, it is important to use the equipment loads and discharge conditions as inaccurate results will be obtained in these conditions are not correctly simulated. Further, the results could also be significantly different from the rated capacity or generalized performance data and characteristics of a particular battery.

Portable	Industrial and government	Vehicular
Applicances and household equipment Audio and communication equipment Cameras and photographic equipment Computers and calculators, PDAs Emergency transmitters Hearing aids Implants Lighting Medical appliances Memory back-up Meteorological equipment Meters, test equipment, and instrumentation Signals and alarms Telephones Tools Toys Watches, clocks	Auxillary and emergency (standby power) Electrical energy storage Load leveling Munitions and missiles Navigations aids Oceanographic equipment Railway signaling Satellites and spacecraft Surveillance and detection Uninterruptible power systems	Aircraft batteries Electric vehicles, including golf carts, bicycles Engine starting Industrial and commercial equipment Submarine and underwater propulsion Vehicle (SLI batteries)
References	References	References
Section 6.4.2 Section 7	Section 16.2 Section 23.1, 23.6	Section 23.1, 23.4, 23.5 Section 24.9.4
Section 13	Section 24.9.5	Section 25.4, 25.5, 25.6
Section 17.6	Section 32.6	Section 26.6.4

Section 30.5, 30.8

Section 31.7

Section 38.5

Section 39.1.1

Section 41.5.2

Section 40.3.2, 40.4.2

Chapter 37

Section 33.8

Section 39.7.2

Section 41.5.1

Chapter 43

Section 38.3.3, 38.4

Section 40.3.2, 40.4.2

Chapter 37

TABLE 6.2a Typical Battery Applications

Section 21

Section 38.3.2, 38.3.3

Section 42.3, 42.4

Device	Current drain, mA
Cassette recorders	70–130 (low) 90–150 (medium) 100–200 (high)
Disk players Calculators: (LCD)	100–350 <1
Cameras: Photo flash Autowind Digital cameras	800–1600 200–300 500–1600
Cellular phones Camcorders	300–800 700–1000
Computers Palm held Note book Laptop	400-800 500-1500 800-1000
Fluorescent lamps Flashlights Memory Remote controls	500–1000 100–700 microamperes 10–60
Radios: With 9-V battery With cylindrical cells	8–12 (low volume) 10–15 (medium) 15–45 (high) 10–20 (low volume) 20–30 (medium)
Walkman	30–100 (high) 200–300
Smoke detector: Background Alarm	10–15 microamperes 10–35
Toys: Motorized (radio controlled) Electronic games Video games	600–1500 20–250 20–200
Travel shaver	400-700 300-500
Watches: LCD LED	10-25 (backlight) 10-40

TABLE 6.2b	Current Drain in Battery-Operated
Portable Devi	ces

6.4 PORTABLE APPLICATIONS

6.4.1 General Characteristics

The characteristics of the conventional and advanced primary and secondary batteries on a theoretical basis are summarized in Table 1.2. This table also lists the characteristics of each of these batteries, based on the actual performance of a practical battery, under conditions close to optimum for that battery. As discussed in Chaps. 1 and 3:

- The actual capacity available from a battery is significantly less (about 20 to 30%) than the theoretical capacity of the active materials.
- The actual capacity is also less than the theoretical capacity of a practical battery, which includes the weight of the non-energy-producing materials of construction as well as the active materials.
- The capacity of a battery under specific conditions of use could vary significantly from the values listed in Table 1.2. These values are based on designs and discharge conditions optimized for energy density, and while they can be helpful to characterize the energy output of each battery system, the performance of the battery under specific conditions of use should be obtained before any final comparisons or judgments are made.

In general, the capacity of the conventional aqueous secondary batteries is lower than that of the conventional aqueous primary batteries (Table 1.2), but they are capable of performance on discharges at higher current drains and lower temperatures and have flatter discharge profiles (see Figs. 6.2 to 6.6). The conventional primary batteries have and advantage in shelf life or charge retention compared to the secondary batteries (see Fig. 6.7). Most primary batteries can be stored for several years and still retain a substantial portion of their capacity, while most of the conventional secondary batteries lose their charge more rapidly and must be kept charged during storage or charged just before use.

These differences are due to both the electrochemical systems and the cell designs that were selected for the conventional batteries. Typically the more energetic and not readily rechargeable materials, such as zinc, were selected for the primary cells. Also, the bobbin construction was usually used for the primary batteries to obtain higher energy densities while designs providing more surface area lower internal resistance and higher rate capability were used for the rechargeable batteries.

Some of these differences are not longer that distinct as similar chemistries and designers are used for some of the primary and secondary batteries. For example, a primary battery, using the spirally wound electrode design, will have a similar rate capability as the secondary battery using the same design and chemistry. Likewise, the charge retention of that secondary battery will be similar to the charge retention of that primary battery. However, the capacity of the primary battery should always be higher because of the features that have to be added to the secondary battery to achieve effective recharging.

The advantages and general characteristics of primary and secondary batteries for portable applications also are compared in the next section. More detailed characteristics of the different battery types are presented in the appropriate chapter of this handbook. These data, rather than the more generalized data presented in this section, should be used to evaluate the specific performance of each battery.

6.4.2 Characteristics of Batteries for Portable Equipment

Portable, battery-operated electric and electronic equipments once were typically powered by primary batteries. However, the development of small, maintenance-free rechargeable batteries made it possible for secondary batteries to be used in applications which had been almost exclusively the domain of the primary battery. The trade-off, thus, is between a possible lower life-cycle cost of the secondary battery because it can be recharged and reused and the convenience of using a replaceable primary battery.

The development of new portable applications, such as power tools, computer camcorders, PDAs, and cellular phones, with high power requirements accelerated the use of these rechargeable batteries because of their power advantage over conventional types of primary batteries. The newer primary batteries, particularly those using the lithium anode, which have a high specific energy and energy density and good power density, can be used in some of these higher-power applications. Further, advances in electronics technology are gradually reducing the power requirements of a number of these equipments to levels where the primary battery can give acceptable performance. In some applications, therefore, the equipment is being designed to be powered by either a rechargeable or a primary battery, leaving the choice to the user. The user can opt for the convenience, freedom from charging, and longer shelf life of the primary or the potential cost saving with the rechargeable batteries.

Tables 1.2 and 6.3 and the figures in this section compare the performance of the major primary and rechargeable batteries used for portable applications. These comparisons show the following.

1. The primary batteries, particularly the lithium types, depending on the discharge conditions can deliver up to eight times the watthour capacity of the conventional aqueous secondary batteries. Similarly, the new rechargeable batteries using lithium and other highenergy materials will have higher capacities than the conventional secondary batteries. These capacities, however, will most likely be lower than those of the primary batteries using similar chemistries.

2. The aqueous secondary batteries generally have better high-rate performance than the primary batteries. The lithium primary batteries, using spirally wound or other high-rate electrode structures, provide higher output compared to the conventional secondary batteries, even at fairly high rates, because of their better normal temperature performance and generally good performance at high discharge rates. This is illustrated in Fig. 6.2, which compares the performance of the different battery types at different discharge rates. In this figure the service that each of the battery types will deliver at various levels of power density (watts per liter) is plotted. A slope parallel to the idealized line indicates that the capacity of the battery, in watthours, is invariant, regardless of the discharge load. A flatter slope, or one that levels off as the load is increased, indicates a loss of capacity as the discharge rate is increased. This figure shows that the conventional rechargeable or secondary batteries maintain their capacity even at the higher current drains while capacity of the conventional primary batteries begins to drop off at a 20 to 50-h rate. The lithium primary batteries, however, can maintain their advantage over the conventional secondary batteries to fairly high discharge rates because of their significantly higher capacities at the lower discharge rates. The lithium-ion rechargeable battery, which was introduced commercially during the 1990s, has a significantly higher specific energy and energy density compared to the conventional rechargeable batteries, although still below that of the lithium primary batteries. Its high rate and low temperature performance is superior to the nickel-cadmium and nickel-metal hydride batteries because of its higher specific energy, except at the very high discharge rates (see Figs. 6.2 and 6.3). The lithium-ion battery is rapidly becoming the battery of choice in highend portable equipment and performance advances and cost reduction continue to be achieved as a result of extensive R&D programs (see Chap. 35).

Figure 6.2 is a comparison on a volumetric basis, while Fig. 6.3 is a Ragone plot presenting similar information on a gravimetric basis. This shows a greater advantage for the lithium batteries because of their lower density.

TABLE 6.3 Characteristics of Batteries for Portable Equipment

				Secondary batteries			
	Prim Zn/alkaline/MnO ₂	hary batteries	Li/SO ₂	Nickel-cadmium	Lead-acid	Nickel-metal hydride	Lithium-ion
Nominal cell voltage, V	1.5	3.0	3.0	1.2	2.0	1.2	4.1
Specific energy (Wh/kg) Energy density (Wh/L)	145 400	230 535	260 415	35 100	35 70	75 240	150 400
Charge retention at 20°C (shelf life)	3–5 years	5-10 years	5-10 years	3–6 months	6–9 months	3–6 months	9–12 months
Calendar life, years Cycle life, cycles	_	_		4–6 400–500	3–8 200–250	4–6 400–500	5+ yrs 1000
Operating temperature, °C Relative cost per watthour (initial unit cost to consumer)	-20 to 45 1	-20 to 70 6	-40 to 70 5	-20 to 45 15	-40 to 60 10	-20 to 45 25	-20 to 60 45



FIGURE 6.2 Performance characteristics of primary (P) and secondary (S) batteries on a volumetric basis, 20°C.



FIGURE 6.3 Performance capabilities of various cylindrical primary (P) and secondary (S) batteries—energy vs. specific power. A: Li/MnO₂ (P); B: Zn/alkaline/MnO₂ (P); C: Ni-Cd (S); D: Ni-MH (S); E: Zn/alkaline/MnO₂ (S); F: Li-ion (S).



3. The conventional aqueous secondary batteries generally have a flatter discharge profile than the primary or lithium batteries. Figure 6.4 compares the discharge curves of several primary and secondary batteries and illustrates this characteristic.

4. The conventional aqueous secondary batteries general have better low-temperature performance than the conventional aqueous primary batteries. The comparative performances on a gravimetric basis (watthours per kilogram) and on a volumetric basis of the various types of batteries at a moderate 20-h rate are shown in Figs. 6.5 and 6.6 respectively. While the specific energy and energy density of the primary batteries is higher at room temperature, their performance drops off more significantly as the temperature is reduced compared to conventional secondary batteries. Again, the lithium batteries have better low-temperature characteristics than the conventional primary batteries, but percentage wise they are poorer compared to the conventional secondary batteries.



FIGURE 6.4 Discharge profiles of primary (P) and secondary (S) batteries.



FIGURE 6.5 Effect of temperature on specific energy of primary (P) and secondary (S) batteries.



FIGURE 6.6 Effect of temperature of primary (P) and secondary (S) batteries.

5. The charge retention or shelf life of the primary batteries is much superior to that of the conventional aqueous secondary cells. Hence these secondary batteries have to be maintained in a charged condition or recharged periodically to maintain them in a state of readiness. Figure 6.7 compares the charge retention of various types of batteries when stored at different temperatures. The superior charge retention of most of the lithium batteries, both primary and secondary, is illustrated.

6. The secondary batteries are capable of being recharged to their original condition after discharge and reused rather than being discarded. For those applications where recharging facilities are available, convenient, and inexpensive, a lower life-cycle cost can be realized with secondary batteries, even with their higher initial cost, if their full cycle life is utilized.



FIGURE 6.7 Shelf life (charge retention) characteristics of various batteries—primary (P), secondary (S).

6.4.3 Cost Effectiveness

Specific cost effectiveness versus life cycle analyses can be used to evaluate the best choice primary or secondary battery—for a particular application or deployment. Figure 6.8 summarizes such an analysis comparing lithium/sulfur dioxide primary and nickel-cadmium secondary batteries.¹ Figure 6.8*a* depicts a military training situation in which charging facilities are readily available and inexpensive, recharging is convenient, and the batteries are used regularly (thus employing the full cycle life of the secondary battery). In this situation, the initial higher cost of the secondary battery is easily recovered, and the payback or breakeven point occurs early. Figure 6.8*b* presents a field situation in which batteries are not used regularly, special charging facilities are required, and recharging is not convenient. In this case, the payback time occurs much later, and the use of secondary batteries may not be cost-effective since the break-even time is close to or beyond the calendar life of the battery.



FIGURE 6.8 Life-cycle cost analysis—Li/SO₂ primary vs. Ni-Cd secondary cells. (*a*) Military training situation. (*b*) Field situation.

Similar analyses can be made for specific commercial and industrial applications. For example, the cost of the use of zinc/alkaline/manganese dioxide primary batteries versus nickel-cadmium rechargeable batteries in a typical portable electronic device applications are compared in Table 6.4. If the usage rate is low and the drain rate moderate, the primary battery is more cost-effective besides offering the convenience of not having to be periodically recharged.

TABLE 6.4	Cost-Effectiveness of Primary
(Zn/alkaline	$/MnO_2$) vs. Secondary
(Nickel-Cadr	nium) Batteries

Assumptions Nominal voltage: 3 V 2 "AA" Zn/MnO₂ batteries: \$1.60 2 "AA" Ni-Cd batteries: \$8.00 Ni-Cd charger: \$5.00

a. Comparison at 150 mA

Usage (hrs/day)	Change Ni-Cd (days)	Change Zn/MnO ₂ (days)	Ni-Cd battery payback (days)
0.5	8	26	210
1.0	4	13	105
2.0	2	6.5	52
4.0	1.0	3.3	36
6.0	0.67	2.2	17
8.0	0.5	1.7	13

b. Comparison in a Walkman Radio

Usage (hrs/week)	Change Ni-Cd (days)	Change alkaline (days)	Ni-Cd battery payback (months)
1	21	49	25
3	7	16	9
5	4	10	5.4
7	3	7	3.7
14	1.5	3.5	1.9
21	1	2.3	1.2
35	.6	1.4	.8

6.4.4 Other Comparisons of Performance

Figure 6.9 provides another illustration comparing the performance of several types of primary and secondary batteries in a typical miliary portable radio transceiver application at several temperatures, based on 1994 data. The primary batteries give the longest service at 20°C, but only the secondary batteries and the Li/SO₂ primary battery are capable of performance at the very low temperatures. This equipment is being phased out of use.

A more current example is the performance characteristics of the 24-V military battery type "590" which has been designed in several versions using several different battery chemistries, but all within the same physical envelope. The characteristics of these batteries are listed in Table 6.5. This battery is used in a number of portable military communication and surveillance equipments and the particular type of battery that is used depends on the equipment requirements and deployment. For example, for training and policing, a rechargeable battery would most likely be chosen. In forward, areas and under combat, where lightweight is critical and recharging facilities are not available nor recharging feasible, a primary battery will usually be used. Figure 6.10 compares the performance of the different batteries under an 18-watt discharge load at 25°C. Under heavier discharge current) and at low temperatures, the zinc/air battery would not perform satisfactorily. The performance of the rechargeable batteries would be comparatively better because of their relatively superior performance under these more stringent operating conditions.





Battery type	Capacity (Ah)	Weight (kg)	Specific energy (Wh/kg)	Power density (Wh/L)
Primary				
BA-5590 (Li/SO ₂)	6.8	1.02	160	185
BA-5390 (Li/MnO ₂)	8.5	1.25	170	240
BA-XX90 (Zn/Air)	10.0	1.00	250	285
Secondary				
BB-690 (Lead-acid)	1.8	1.68	27	50
BB-590 (Ni-Cd)	2.2	1.75	31	62
BB-390 (NiMH)	4.6	1.82	65	135
BB-XX90 (Li-ion, cvlindrical cells)	4.5	1.25	105	150
BB-X590 (Li-ion, prismatic cells)	6.0	1.68	100	190

TABLE 6.5 Characteristics of Batteries in "590" Envelope





FIGURE 6.10 Comparison of "590" battery chemistries, discharge at 18 watts, 25°C.

Figures 6.11 and 6.12 are two other examples comparing the performance of several "AAsize" primary and rechargeable batteries. In Fig. 6.11, the performance of these batteries is plotted over a range of discharge current. Depending on the battery system, the primary batteries have the advantage at low current drains but lose their advantage as the discharge rate is increased. As shown, low drain applications, such as PDAs and Palm devices, generally use primary batteries, mainly the zinc/alkaline/manganese dioxide battery. Some more sophisticated PDAs, with higher power requirements will use rechargeable batteries. Laptop computers typically use rechargeable batteries.



FIGURE 6.11 Performance of AA- (or equivalent) size battery at various current drains at 20°C. A: Ni-Cd battery; B: Ni-MH battery; C: Li-Ion; D: zinc-alkaline battery; E: Li/MnO₂ battery (2/3A size); F: Zn/air battery (button configuration). A-C are secondary batteries. D-F are primary batteries.



Number of Pulses

FIGURE 6.12 Photo simulation test; 900 mA, 3 seconds on 27 seconds, OFF, 20°C (Li/MnO₂ (2/3 A size), others (AA), 2 cells each).

Figure 6.12 compares the performance of these "AA-size" batteries on a photo simulation test of the flash in an automatic camera. The lithium primary batteries deliver the larger number of cycles. Although the zinc/alkaline/manganese dioxide battery delivers a significant number of pulses, as it operates at a lower voltage, the recycle time is longer than the batteries operating at a higher voltage. (See Figs. 10.1*b* and 14.85.) As the power requirements are increasing with the newer camera models, the battery systems capable of high rate discharge will be favored.

Another comparison of the characteristics of each type of battery is shown in Fig. 6.13 which examines one performance parameter—the total weight of a power sources required to deliver a given power output (in this example, 5 watts) for different lengths of operation. For very short missions, the conventional secondary batteries are lightest because of their high rate capability. At moderate and light loads, the primary and lithium batteries become the lighter ones because of their higher specific energy and energy density under these load conditions.

Figure 6.13 also shows the advantage of a hybrid system: combining a battery with a high specific energy with a rechargeable battery having a high rate capability. The example illustrates a hybrid design using a zinc/air battery (which has a high specific energy at moderate-to-low discharge rates but poor high-rate performance) with a nickel-cadmium battery (which has a low specific energy, but comparatively good performance at high discharge rates). The nickel-cadmium battery is sized to handle the load for the specified time (in this example for 6 minutes) and is then recharged by the zinc/air battery. Curve F shows that at the longer operating times (a low discharge rate for the size of the battery) the zinc/air battery, alone, can handle the load and is the lightest power source. It loses its advantage at the shorter operating times which correspond to a higher discharge rate. For these shorter missions, a rechargeable battery, such as the nickel cadmium battery is sized to handle the load for a specified time, the total weight and size of the hybrid battery is dependent on the time established for the pulse load.

Figure 6.14 shows the distribution of current in another example of a zinc/air, nickelcadmium hybrid battery, this one designed to handle a transmit load for 2 minutes at 900 mA and a receive load of 50 mA for 18 minutes, similar to the application illustrated in Fig. 6.9. During the "receive" period, the load is carried by the zinc/air battery which, at the same time, charges the nickel-cadmium battery. During the "transmit" period, the load is carried by both batteries.

This hybrid technology is applicable to other batteries, as well as to fuel cells and other power sources, as an efficient and effective way of handling pulse requirements and attaining an optimum system specific energy. It is being considered for use in a wide range of applications, for small portable devices to large systems, such as the hybrid electric vehicle (HEV).




- A Nickel-cadmium (S) 35 Wh/Kg
- B Nickel-metal hydride (S) 75 Wh/Kg C Zinc/MnO₂ (P) 145 Wh/Kg
- D Lithium-ion (S) 150 Wh/Kg
- F Zinc/air (P) 370 Wh/Kg
- G Zinc air, Nickel-cadmium hybrid (6 minute pulse) (P) Primary Battery (S) Secondary Battery



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6.4.5 Criteria for Battery Selection—Portable Equipment

A number of different battery systems are available to the equipment designer and user, each offering particular advantages for powering portable electronic equipment. The selection of a battery system, even the first decision of using a primary or secondary battery, may not be clear-cut and is influenced by many factors, such as deployment of the equipment, operating environment, size, weight, required service time, duty cycle, frequency of use, capital investment and cost, and other factors listed in Sec. 6.2. An important consideration, as well, is the end-user's biases and preferences. The selection is further complicated by the overlapping performance characteristics of many of the batteries since the characteristics of a particular battery system or chemistry can be altered by the design features and design changes as the technology develops and matures.

Table 6.6 is a summary, albeit simplified, of criteria that should be considered in making a preliminary determination of the type of battery—primary or secondary—to be used. It is most applicable to comparing the conventional systems and lithium primary batteries. As pointed out in Sec. 6.4, the characteristics of the rechargeable lithium batteries may difference from these generalizations.

- 1. A primary battery will usually be the battery of choice if the power requirement is low or in applications where the battery will be used infrequently over a long period of time.
- **2.** For applications where the battery will be used frequently (assuming that both primary and secondary batteries are capable of meeting the power requirements of the equipment), the choice should depend on user preference. Will the user opt for the convenience of the primary battery and freedom from the charger, or will the user tolerate the "inconvenience" of the rechargeable battery and opt for its possible lower operating cost?
- **3.** For high discharge rates, high-rate secondary batteries will be the choice as the performance of the primary battery falls off, particularly at lower operating temperatures.

Conditions of use	Secondary batteries	Primary batteries
 Assuming acceptable load capability 		
Frequent use, repeated cycling	Lower life-cycle cost (\$/kWh) if charging is convenient and inexpensive (work force and equipment)	Lighter or smaller—or longer service per "charge" or replacement
		No maintenance or recharging
		Ready availability (for replacement)
Frequent use, low drain capacity or	Aqueous secondary batteries have poor charge retention; have to be charged periodically	Long service per "charge"; cost advantage of secondary disappears
Infrequent use	Li-ion batteries have better charge retention, but still require charging	Infrequent replacement, cost advantage of secondary disappears
		Good charge retention; no need for charging or maintenance
2) Assuming high discharge rates	Best comparative performance at heavy loads	Hybrid battery system may provide longer service, freedom from line power

TABLE 6.6 Advantages of Primary and Secondary Batteries

Table 6.7 illustrates the selection of primary and secondary batteries. As the power requirements of the application increase (going from the bottom of the list to the top) and the size of the battery becomes larger, the trend for the battery-of-choice shifts from the primary to the secondary battery. The primary battery dominates in the lower power applications and where a long service life is required, such as smoke detectors, implants and memory backup.

Application	Primary or secondary battery
Utility systems (load-leveling)	SECONDARY
Electric vehicle hybrid (HEV)	~
Central telephone system	
Fork lifts	
Electric vehicles (EV)	
Golf carts	
Electric bikes	
Automotive SLI	
Spacecraft power	
Emergency lighting	
Portable tools	
Laptop computers	
Transceivers	
Cordless telephone	
Camcorders	
Portable equipment	
(e.g. Dustbuster, shaver)	
Cellular phone	
PDAs, Palm devices	
Radio	
Pagers	
Flashlight	
Toys	
Cameras	
Instruments	
Hearing aids	
Implants	
Smoke detectors	
Remote controllers	$\overline{}$
Memory back-up	PRIMARY

TABLE 6.7 Application of Batteries—Primary vs. Secondary

REFERENCE

 "Cost Effectiveness Comparison of Rechargeable and Throw-away Batteries for the Small Unit Transceiver," U.S. Army Electronics Command, Ft. Monmouth, N.J. Jan. 1977. This page intentionally left blank