J. Webster (ed.), *Wiley Encyclopedia of Electrical and Electronics Engineering*

PRIMARY CELLS

Batteries are reactors that convert chemical energy into electric energy on demand. Battery reactions are oxidation–reduction reactions similar to those that occur in ordinary chemical reactors. However, in an electrochemical cell, the basic component of a battery, the charge-transfer aspect of the oxidation–reduction reaction occurs on a surface rather than in the bulk. The electron transfer is isolated and is available as a direct current. The reduction and oxidation intermediates are transported through electrolytically conductive media. The electrode referred to as an anode is the site of the oxidation reaction. The reduction reaction of the electrochemical couple occurs at the electrode referred to as the cathode. Oxidation is a chemical process in which an electron is given up by the reactant. Reduction is a chemical process in which an electron is accepted by the reactant. The oxidation–reduction reaction proceeds when the exchange electron from the reaction is conducted from one electrode to the other through an external wire (or electrically conducting circuit) and intermediate ions formed in the process are internally transported through the electrolyte to complete the reaction. The current of an electrochemical cell results from this chemical reaction in which electrons are released at one electrode and taken up at the other. Equations (1) and (2) show the oxidation half-cell reaction and the reduction half-cell reaction. Equation (3) shows the overall cell reaction:

$$M \rightarrow M^{+} + e^{-} \tag{1}$$

$$R + e^{-} \rightarrow R^{-} \tag{2}$$

$$M + R \rightarrow M^{+} + R^{-} \tag{3}$$

where M is the species that will be oxidized, R is the species that will be reduced, e^{-} represents an electron, and $-$ and $+$ denote the charge of the species.

Traditionally, the simplest electrochemical cells have a pair of electrodes (an anode and a cathode), or more, submerged in a common electrolyte separated by a porous mechanical separator. The electrolyte is required to be an ionically conducting (usually a solution of a solvent and a solute), electrically nonconductive and chemically stable. The separator must be an electrical insulator and mechanically and chemically stable as well as porous to the electrolyte. The porosity of the separator allows for the continuum of the electrolyte and a transport path for the ions of the reaction. An electrically conductive wire provides the path for the exchanged electrons. It is also possible to have solid electrolytes.

In ordinary bulk chemical reactions, an oxidizer and fuel react directly with nonisolated electron transfer to form the reaction products and release and absorb energy as heat. In electrochemical reactions the reaction

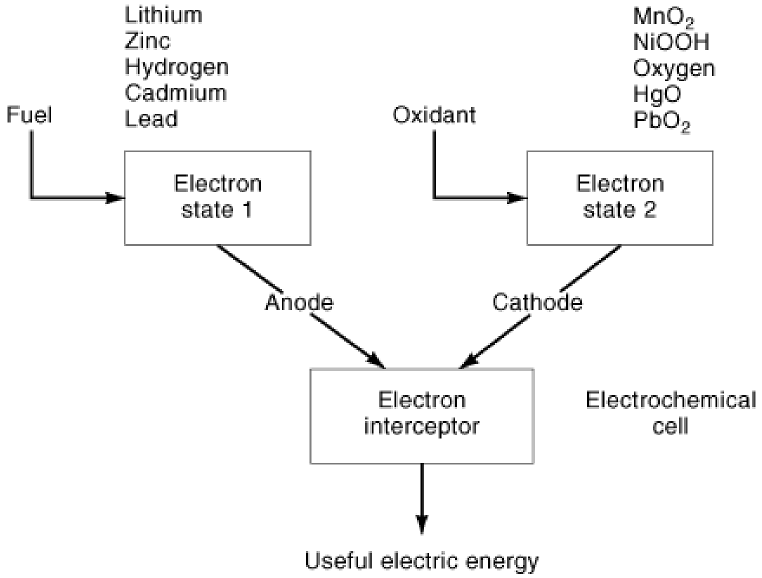


Fig. 1. Schematic diagram of an electrochemical cell. In electrochemical reactions, in which the oxidizer and fuel are isolated, energy is manifested as a voltage and current flow through a wire (conducting lead). Bulk chemical reactions, with nonisolated electron transfer that forms the reaction products, release and absorb energy as heat.

is manifested as a voltage and current flow through a wire (conducting lead). Figure 1 depicted schematically the energy transfer in electrochemical reactions. In generating electric current, the electrons involved in the electrochemical reaction are transferred from the active materials undergoing oxidation to the oxidizing agent by means of an external circuit. The passage of electrons through the external circuit provide a direct means for utilizing energy without heat as an intermediate step. Figure 2 gives a graphical depiction of a cell or battery (1).

Electrochemical Thermodynamics

An electrochemical cell keeps the oxidation and reduction reactions separate with the exchanged electron traveling through a wire and ionic species transported through an ionically conducting electrolyte. The separation of the reaction allows for work to be performed by the electrons as they travel through the wire. The electromotive force (*emf*) is a measure of energy available to perform such work. This energy is a function of the equilibrium constant for the chemical reaction of the cell and the activities of the reactants and products. The electromotive force itself is measured by the difference in electric potential between the electrode active materials and can be related to fundamental thermodynamic properties (relating to the energy of formation and solvation of the materials involved).

The electric potential of an electrochemical cell reaction is a function of an isothermal formation process that does not involve pressure–volume work. Therefore the work performed in a oxidation–reduction reaction (the quantity of electric charge transported through a potential difference) can be expressed as a change in Gibbs energy.

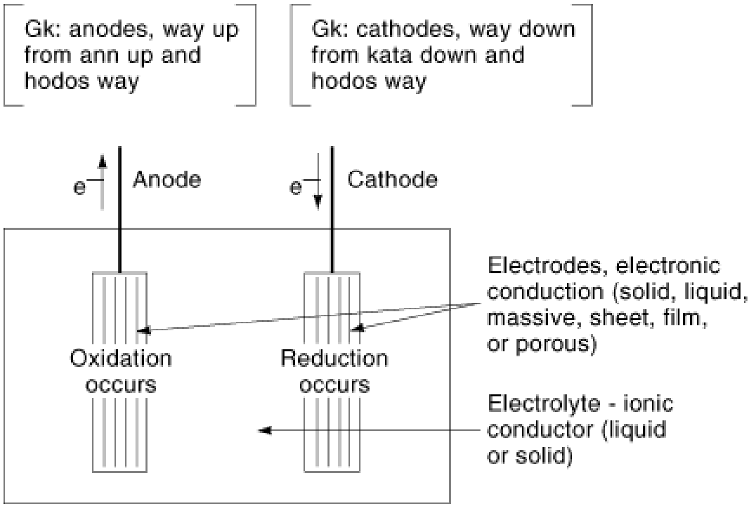


Fig. 2. Graphical representation of an electrochemical cell. In generating electric current, the electrons involved in the electrochemical reaction are transferred from the active materials undergoing oxidation to the oxidizing agent by means of an external circuit. The passage of electrons through the external circuit provides a direct means for utilizing energy without heat as an intermediate step.

Equation (4) shows the relation between the change in Gibbs energy and the electromotive force.

$$\Delta G = -n\mathscr{F}\mathscr{E} \qquad (4)$$

where ΔG is the change in Gibbs energy (J/mol), n is the stoichiometry of the electron exchange, $\mathscr{F}$ is the Faraday constant (96,487 C/equivale mol), and $\mathscr{E}$ is the electrochemical potential (V).

The electrochemical potential for each group of chemicals comprising a battery system is unique. However, it is extremely important in the design and use of batteries to realize that the reaction thermodynamics depends on the surface chemistry and not the bulk chemistry of the reacting species.

In considering the free-energy relationship for bulk chemical reactions an alternative representation of the change in the Gibbs energy is shown as

$$\Delta G = \Delta G^0 + RT\ \ln(a_{\mathrm{C}}^{\mathrm{c}}\,a_{\mathrm{D}}^{\mathrm{d}}/a_{\mathrm{A}}^{\mathrm{a}}\,a_{\mathrm{B}}^{\mathrm{b}}) \qquad (5)$$

where $\Delta\ G^0$ is the standard molar Gibbs energy, R is the gas constant (8.31433 J/mol·K), a is the activities of the reactants (A, B) and products (C, D), a and b are the stoichiometry of the reactants A and B, and c and d are the stoichiometry of the products C and D.

Equation (6) is the expression of the relation between the standard molar Gibbs energy and the standard electrode potential:

$$\Delta G^0 = -n\mathscr{F}\mathscr{E}^0 \qquad (6)$$

where $\mathscr{E}^0$ is the standard electrochemical potential of the reaction. Substituting Eqs. (4) and (6) results in Eq. (7), relating the electrochemical potential to the standard electrochemical potential and the reactant and products activities. The relation shown in Eq. (7) is called the Nernst equation:

$$\mathscr{E} = \mathscr{E}^0 - (RT/n\mathscr{F})\ln(a_{\mathrm{C}}^{\mathrm{c}}\, a_{\mathrm{D}}^{\mathrm{d}}/a_{\mathrm{A}}^{\mathrm{a}}\, a_{\mathrm{B}}^{\mathrm{b}}) \tag{7}$$

The value of $\mathscr{E}^0$, the reversible potential, is determined by the atomic structure of the reactants, especially the energy levels related to the work function and the valence electrons. The value of $\mathscr{E}^0$ can be predicted by summing the enthalpies of atomization, ionization, and solvation in a Born–Haber cycle as discussed by Sanderson 2. It is important to realize that only the surface composition of the electrode in contact with the electrolyte should be considered in calculating $\mathscr{E}^0$. Material buried deep in an electrode completely covered with active material, and without direct electronic contact to the current collector, has no effect on $\mathscr{E}^0$ and measured values of cell voltage. When the reactants and product of an electrode reaction share a single phase or crystal habitat or form an intercalate, the voltage of that electrode depends on the ratio of concentration of the species. This results in a sloping discharge curve that is typical of cells with MnO_2, TiS_2, MoS_2, etc., electrodes. When the reactants and product of an electrode reaction form separate phases, the voltage of the electrode is constant during discharge in the multiphase region. Typical examples are cells with Hg/HgO, $Cd/Cd(OH)_2$, and $PbO_2/PbSO_4$ electrodes. These are often used as reference electrodes in experimental studies because of their invariant voltages.

Equations (8) and (9) are fundamental thermodynamic equations relating entropy with the Gibbs energy and enthalpy with entropy and Gibbs energy:

$$(\delta G/\delta T)_P = -\Delta S \tag{8}$$

$$\Delta H = \Delta G + T\Delta S \tag{9}$$

where T is the temperature (K), P denotes constant pressure, ΔS is the change in entropy (J/mol·K), and ΔH is the change in enthalpy (J/mol).

From Eqs. (4), (8), and (9) the change in entropy and the change in enthalpy can be expressed in terms of the electrochemical potential. Equations (10) and (11) show the introduction of Eq. (4) into Eq. (8) and then into Eq. (9). They define fundamental thermodynamic properties of the Gibbs energy, entropy, and enthalpy in terms of the electrochemical potential:

$$\Delta S = n\mathscr{F}(\delta\mathscr{E}/\delta T)_P \tag{10}$$

$$\Delta H = -n\mathscr{F}\mathscr{E} + n\mathscr{F}T(\delta\mathscr{E}/\delta T)_P \tag{11}$$

By measuring the voltage of a cell as a function of temperature, one can derive the entropy and enthalpy of the electrochemical couple by using Eqs. (10) and (11), respectively. Table 1 is a listing for the standard electrochemical reduction potentials for some common electrochemical half-cell reactions. The standard electrode potentials are determined with respect to the standard electrode potential of hydrogen, $H^+ + e^- \rightarrow \frac{1}{2}H_2$ at 1 atm, which has been assigned by international convention a zero value. (The basis for the standard hydrogen electrode potential is a weak acid.) An electrode that is more negative than the hydrogen electrode

Table 1. Standard Reduction Potentials for Electrode Reactions at 25°C

Half-Cell Reaction Reduction	$\mathscr{E}^0$ (V)	Half-Cell Reaction Reduction	$\mathscr{E}^0$ (V)
$Li^+ + e^- \rightleftharpoons Li$	−3.01	$H^+ + e^- \rightleftharpoons \frac{1}{2} H_2$ (1 atm)	0.000
$K^+ + e^- \rightleftharpoons K$	−2.92	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	0.34
$Na^+ + e^- \rightleftharpoons Na$	−2.71	$\frac{1}{2} O_2 + H_2O + 2e^- \rightleftharpoons 2OH^-$	0.40
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.38	$Cu^+ + e^- \rightleftharpoons Cu$	0.52
$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.66	$Ag^+ + e^- \rightleftharpoons Ag$	0.80
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76	$Br_2 + 2e^- \rightleftharpoons 2Br^-$	1.07
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.44	$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	1.23
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0.23	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	1.36
$H^+ + e^- \rightleftharpoons \frac{1}{2} H_2$ (1 atm)	0.000	$F_2 + 2e^- \rightleftharpoons 2F^-$	2.87

will have a negative standard potential, and an electrode that is more positive than the hydrogen electrode will have a positive standard potential. An electrochemical cell comprising two half-cell reactions will result in one electrode being reduced and the other oxidized. The electrode that has a more negative standard potential will be oxidized and the electrode with the more positive standard potential will be reduced. This type of analysis allows for the determination of the cell reaction.

The combination of standard electrode potentials for two half-cell reactions can be used to determine the cell voltage. Equation (12) shows the relation between the standard potential for oxidation and the standard potential for reduction, and Eq. (13) shows how the cell voltage can be determined from the standard electrode potential data.

$$\mathscr{E}^0_{\mathrm{ox}} = -\mathscr{E}^0_{\mathrm{red}} \tag{12}$$

$$\mathscr{E}^0_{\mathrm{cell}} = \mathscr{E}^0_{\mathrm{red}} + \mathscr{E}^0_{\mathrm{ox}} \tag{13}$$

Standard electrode potentials can be determined from the standard Gibbs energy. Equation (14) shows this relationship, which is a form of Eq. (10):

$$\mathscr{E}^0 = -\Delta G^0/n\mathscr{F} \tag{14}$$

Equation (15) shows the thermodynamic equilibrium constant defined as a function of the activities of the reactants and products:

$$K = a_{\mathrm{C}}^{\mathrm{c}}\, a_{\mathrm{D}}^{\mathrm{d}} / a_{\mathrm{A}}^{\mathrm{a}}\, a_{\mathrm{B}}^{\mathrm{b}} \tag{15}$$

where K is the thermodynamic equilibrium constant. Equation (16) shows the relation between chemical potential and the thermodynamic equilibrium constant. For reactants and products in their standard state, the standard molar Gibbs energy is equal to the chemical potential. Equation (17) shows the relation between the Gibbs energy and the chemical potential.

$$\Delta\mu^0 = -RT\ln(K) \tag{16}$$

$$\Delta G^0 = \Delta \mu^0 \tag{17}$$

where μ is the chemical potential. Combining Eqs. (16) and (17) gives Eq. (18):

$$\Delta G^0 = -RT \ln(K) \tag{18}$$

Combining Eqs. (10) and (18) as shown in Eq. (10) gives the relation between the standard electrochemical potential and the thermodynamic equilibrium constant. The thermodynamic equilibrium constant K is defined in Eq. (20) by rearranging this equation:

$$\mathscr{E}^0 = RT/n\mathscr{F} \ln(K) \tag{19}$$

$$K = \exp(\mathscr{E}^0 n\mathscr{F}/RT) \tag{20}$$

This thermodynamic analysis of the electrochemical cell shows how the cell potential and standard electrochemical potential are related to fundamental thermodynamic properties. This analysis also shows how electrochemical measurements can be used to determine fundamental thermodynamic properties.

Electrochemical Kinetics

The reaction rates of electrochemical reactions follow the usual kinetic laws. The rate of reaction is expressed as a current flow in coulombs per second (amperes) rather than a change in concentration per unit time. Operational battery systems exhibit a kinetic hindrance when producing current, which manifests itself as a loss in voltage. Thus the voltage during use (discharge) is lower than the voltage measured under open-circuit (reversible) conditions. This lowering of voltage is called polarization and is usually represented by η. There are three types of polarization: (1) activation or reaction rate polarization, (2) concentration polarization, and (3) resistance or ohmic polarization. Activation polarization is related to the charge-transfer mechanism process, concentration polarization is related to the availability of reacting species at the electrode–solution interface (often a diffusion- or mass-transfer-controlled process usually in the electrolyte but occasionally in the solid crystalline lattice of the active material), and resistance polarization is related to the ohmic hindrance to electron or ion flow. The same kinetic factors take place during the recharging of secondary cells, and the energy loss is reflected as higher voltage necessary to recharge.

In almost all cases, the positive electrode in a battery system is a metal oxide, sulfide, or halide. In general, these are relatively poor electric conductors and would give extremely high ohmic polarization (impedance) if not blended or reinforced with supporting conductors. An exception is pyrite (FeS_2), which is a semiconductor. Conductors added to positive electrodes include graphite, lead, silver, copper, nickel, and other materials in rod, mesh, wire, grid, and other shaped configurations. In almost all cases the negative electrode is a metallic element of sufficient conductivity to require only minimal supporting conditions. An exception is the hydrogen electrode, which requires a substantial conductive surface support, which also serves for electron transfer.

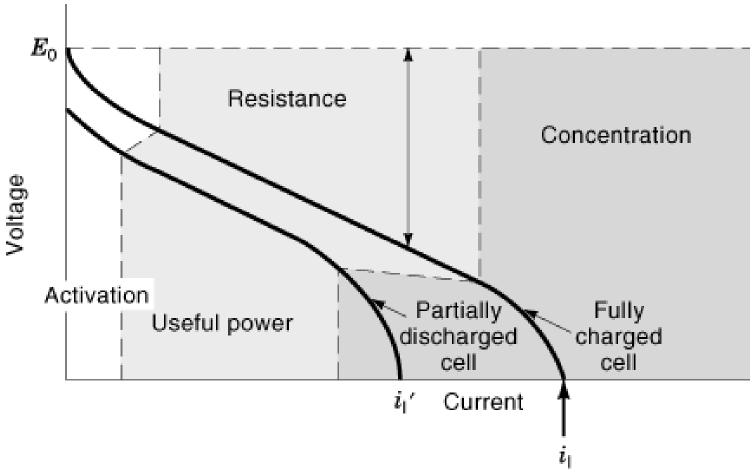


Fig. 3. Current–voltage curve of an electrochemical cell, showing polarization regions. This plot shows cell voltage versus discharge current and is known as a power curve. This curve shows the regions controlled by activation, concentration, and resistance polarization and the change as the battery is discharged.

The thermodynamics of electrochemical reactions does not provide information regarding the cell when work is being performed. The complex mechanisms of electrochemical cell reactions require thorough analysis. The voltage of the electrochemical cell, when current is flowing, can be represented by an empirical equation.

At low reaction rates the polarization in battery reactions is almost always controlled by activation energy (charge transfer). This is illustrated in Fig. 3. Using reaction-rate theory it can be shown that the activation-energy barrier can bdisplaced by application of a potential for a net current flow. Equation (21) shows the relation among the current density, the exchange current density, and the charge-transfer coefficient. The exchange current density is the reversible current density when the electrochemical reaction is in equilibrium.

$$i_p = i_0\{\exp(\alpha\eta\mathscr{F}/RT) - \exp[-(1-\alpha)\eta\mathscr{F}/RT]\} \qquad (21)$$

where i_p is the current density (mA/cm^2), i_0 is the exchange current density (mA/cm^2), α is the charge-transfer coefficient, and η is the overpotential (V). At equilibrium the net current $i_p = 0$ and the overpotential $\eta = 0$ and the rate of the forward and reverse reactions are equal. The forward and reverse action rates can be expressed as a current flow i_0 across the activation energy barrier at equilibrium (reversible potential) and is termed *exchange current*. The exchange current is directly related to the reaction-rate constant, and the usual kinetic expressions apply directly to battery reactions. A low rate constant is associated with a high degree of irreversibility, so that the smaller the i_0 the more irreversible the reaction and hence the greater the activation polarization for a given net current flow. This implies that high exchange currents are favored for battery reactions. However, high exchange currents often lead to changes in electrode morphology with a consequent and sometimes deleterious change in surface structure.

When the electrode reaction occurs with polarization larger than about 0.05 V, then Eq. (21) can be simplified. Equation (21) reduces to Eq. (22) at large positive overpotentials and reduces to Eq. (23) at large negative overpotentials.

$$i_p = i_0\exp(\alpha\eta\mathscr{F}/RT) \qquad (22)$$

$$I_p = i_0 \exp[-(1-\alpha)\eta \mathscr{F}/RT] \qquad (23)$$

Equations (24) and (25) are the result of taking the logarithm of Eqs. (22) and (23), respectively:

$$\eta = (-RT/\alpha\mathscr{F})\ \ln(i_0) + (RT/\alpha\mathscr{F})\ \ln(i_p) \qquad (24)$$

$$\eta = [RT/(1-\alpha)\mathscr{F}]\ \ln(i_0) - [RT/(1-\alpha)\mathscr{F}]\ \ln(i_\mathrm{p}) \qquad (25)$$

Equation (26) relates the voltage deviation of a cell from the rest potential caused by a pulse of current (this also depends on surface area of the electrode and the pulse should be defined in terms of A/cm^2). This relation is referred to as the Tafel relation.

$$\eta = a \pm b\ \ln(i_p) \qquad (26)$$

where a is an empirical constant and b is a constant referred to as the Tafel slope.

From a comparison of Eqs. (26) and (24), the constants of the Tafel relation, a and b, can be determined for large positive overpotentials: $a = -RT/\alpha\ \mathscr{F} \ln\ (i_0)$ and $b = RT/\alpha\mathscr{F}$. From comparison of Eqs. (26) and (25), the constants of the Tafel relation can be determined for large negative overpotentials: $a = [RT/(1-\alpha)\ \mathscr{F}] \ln(i_0)$ and$b = -RT/(1-\alpha)\ \mathscr{F}$. Equation (27) shows the Tafel relation, which defines the discharge current density of a cell as a function of overpotential and exchange current density:

$$\ln(i_p) = \ln(i_0) - \eta/[RT/(1-\alpha)\mathscr{F}] \qquad (27)$$

The Tafel relation holds true for most of the electrochemical reactions over a wide range of overpotentials. At low overpotentials the relationship fails to fit the data. By plotting the data of overpotential against the logarithm of current, a linear relation is clear at large overpotentials. The slope of the line is the Tafel slope and the x-axis intercept, after extrapolating the curve, is the exchange current density. Figure 4 shows a Tafel plot demonstrating the relationship (3).

Whenever the local concentration of a reacting component in a battery is low or nears exhaustion, the rate of reaction becomes controlled by the transport of that component to the reaction surface site on the surface or within the electrode. At this point diffusion equations, for example, Fick's laws, apply. Equation (28) shows this relation:

$$i_\mathrm{l} = Dn\mathscr{F}[A]_\mathrm{B}/\delta(1-t_\pm) \qquad (28)$$

where i_l is the limiting current density, D is the diffusion coefficient, $[A]_\mathrm{B}$ is the concentration of the diffusing species in the bulk solution, δ is the thickness of the diffusion layer, $t_\pm$ is the transference number of the reacting species. The relationship between concentration polarization and limiting current density is

$$\eta = (RT/n\mathscr{F})\ \ln(1 - i/i_\mathrm{l}) \qquad (29)$$

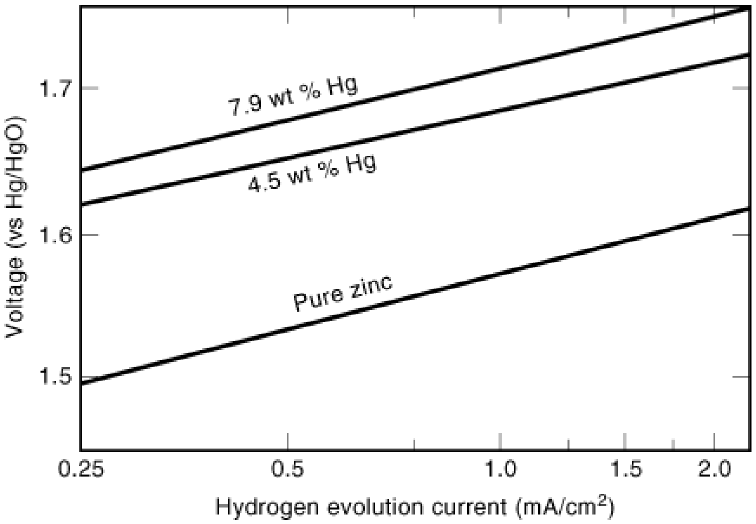


Fig. 4. Tafel plots for zinc and zinc–mercury alloys in 33% KOH.

Figure 3 shows the performance of a typical cell. This plot, showing cell voltage versus discharge current, is known as a power curve. This curve shows the regions controlled by activation, concentration, and resistance polarization and the change as the battery is discharged (1).

Equation (30) shows the relation between discharge capacity and the mass of the electroactive species. Equation (30) is a form of Faraday's law, and Eqs. (31) and (32) define Q and G_{ew}.

$$Q = \mathscr{F}W/G_{\mathrm{ew}} \tag{30}$$

where Q is the discharge capacity (C), W is the mass of the electroactive species, and G_{ew} is the gram equivalent mass of the electroactive species.

$$G_{\mathrm{ew}} = \mathrm{MW}/n \tag{31}$$

where MW is the molecular weight of the electroactive species and n is the stoichiometry of the electrons involved in the reaction.

$$Q = it \tag{32}$$

where i is the discharge current (A) and t is time(s).

Rearranging Eq. (30), we arrive at Eq. (33). Equation (33) shows the reaction rate in mass per unit time as a function of discharge current and the gram equivalent mass of the reacting species:

$$W/t = iG_{\mathrm{ew}}/\mathscr{F} \tag{33}$$

The activation energy and reduced diffusion are the major contributions to the reduced voltage during discharge at lower temperatures. Thus, the energy must be initially introduced to a system in order for the reaction to proceed. This energy is called the activation energy. Equation (34) shows a chemical reaction and its activated state:

$$A \rightleftharpoons X^* \rightarrow B \qquad (34)$$

where A are the reactants, B are the products, and $X*$ is the activated species.

The activated species is a molecule in which a bond is in the process of being formed or broken. Equation (35) shows the rate constant defined as a function of both the activation energy and temperature:

$$k = C \exp(E_a/RT) \qquad (35)$$

where K is the rate constant, C is a constant, and E_a is the activation energy (J/mol). In an electrochemical reaction, E_a appears as a voltage drop due to cell reactions. Catalysts are often employed to alter the speed of a reaction. Catalysts provide an alternative path for the reaction but remain unchanged after the completion of the reaction. This alternative path typically has a lower activation energy and thus proceeds at a faster rate. The other source of voltage drop during discharge is diffusion. Diffusion is a function of viscosity and temperature, as shown in Eq. (36). It defines the diffusion coefficient of a noncharged sphere as a function of temperature and viscosity. Viscosity is an activated process describing the tendency of a liquid to flow defined by Eq. (37).

$$D = RT/(N_0 6\pi r \eta) \qquad (36)$$

where D is the diffusion coefficient(cm^2/s), N_0 is Avogadro's number(6.02252×10^{23} molecules/mol), r is the radius of the sphere (cm), and n is the diffusing media viscosity (P).

$$\eta = A \exp(E_v/RT) \qquad (37)$$

where A is constant and E_v is the activation energy for viscosity.

During discharge, diffusion introduces a resistive component to the reaction, lowering the voltage of the cell due to IR losses. Another property of an electrochemical cell that adds a resistive component is conductivity. Conductivity for electric systems is the measure of the resistance that a material exerts on the flow of current. Ohm's law gives us the relation shown in Eq. (38). Equation (39) is the identity defining conductance as a function of resistance. Equation (40) shows the relation among resistance, conductance, and the dimensional properties of the material. The resistivity of a material is the proportionality constant for Eq. (40), and the conductivity of a material is the reciprocal of the proportionality constant.

$$E = iR \qquad (38)$$

where E is the electromotive force (V), i is the current (A), and R is the resistance(Ω).

$$L = 1/R \qquad (39)$$

where L is the conductance.

$$R \propto (\text{length})/(\text{cross section}) \qquad (40)$$

Techniques that are used for studying electrochemical reactions in non-steady-state conditions include (1) sweep voltammetry, (2) chronopotentiometry, (3) chronoamperometry, (4) pulse voltammetry, and (5) impedance spectroscopy. These techniques provide data regarding the processes governing and limiting electrochemical cells.

Sweep voltammetry is a technique in which a linear voltage sweep is imposed across a cell and the resultant current is observed. Cyclic voltammetry is a form of sweep voltammetry in which the voltage scan is reversed after the initial sweep. Qualitative and limited quantitative electrode data can be obtained from sweep voltammetry. Reversibility of an electrode, voltage stability of an interface, charge transfer versus diffusion limitations, rate constants, and reaction mechanisms are examples of physical properties that can be determined by sweep voltammetry. The data for evaluating the Tafel relation for a cell can also be obtained through sweep voltammetry.

Chronopotentiometry is a technique that studies voltage transients at an electrode during constant current discharge. Chronoamperometry is a technique that studies current transients at an electrode when a potential change is imposed across the electrode. Chronoamperometry can aid in determining diffusion coefficients and for investigating kinetic mechanisms. Pulse voltammetry is similar to chronoamperometry, but the voltage input to the electrode being studied is in the form of a square wave. This allows for many variations depending on the setup of the wave amplitude and sign. This includes reverse current through positive and negative amplitudes.

Impedance spectroscopy is a technique in which a cell is perturbed from steady state by a frequency sweep of alternating current of low magnitude. The potential of the cell due to the signal gives insight to the electrochemical processes at the interface. Impedance spectroscopy will be discussed in more detail in the next section.

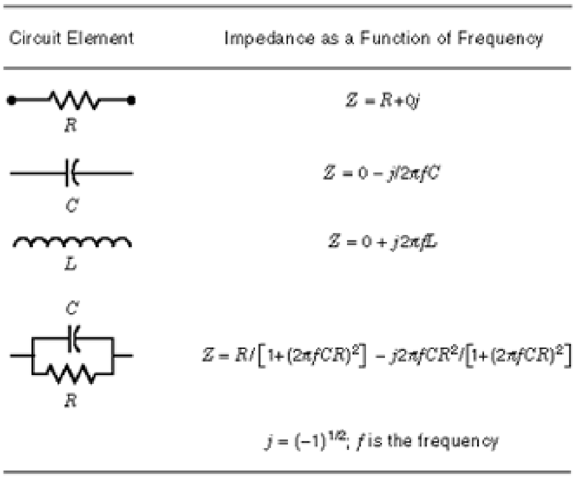
Impedance Spectroscopy and Electrochemical Modeling

Impedance spectroscopy is a technique for studying electrode processes directly at the interface. The interface between electrode and electrolyte when subjected to an ac signal sweep provides an output signal that can be modeled as an electronic equivalent circuit. Impedance spectroscopy measures the change in the electrical impedance and phase of a system by analyzing the response to a sweep alternating signal (*ac*) input. This response to the frequency sweep for electrochemical systems relates to the electrode–electrolyte interface. In order to understand the significance of this response, it is necessary to establish an equivalent circuit with passive and reactive elements that represent the dynamic characteristics of the interface. The elements considered for this equivalent circuit is resistive, capacitive, and inductive. Table 2 shows the ac impedance of these elements.

When evaluating impedance spectroscopy data, it is important to note the sign of the imaginary portion of the elements. This allows for proper selection of elements to represent the electrochemical system. Nearly all electrochemical reactions exhibit negative imaginary impedance. Since inductance has a positive imaginary part, typically this element will not be considered. Inductance in its pure form can appear in data, but this, in most cases, can be traced to the wire leads and cell geometry in the setup. Equipment setup can introduce stray capacitance. This is typically due to pressure contacts. The last circuit element in Table 2, a capacitor and resistor in parallel, has both real and imaginary resistance as a function of frequency. This circuit constitutes the building blocks for equivalent-circuit analysis. Figure 5 is a simple representation of an electrochemical interface. This representation is simplified by not taking into account diffusion or absorption phenomena.

The expression defining the various electrochemical parameters are relatively straightforward to derive but can be complex in format. This is especially true when absorption and capacity effects are considered. Typically, a network of resistive and capacitive elements can represent the impedance behavior of electrochemical processes. The building block of this equivalent circuit is represented by Fig. 5. This network describes a simple interface between two different phases. This equivalent circuit typically describes the electrode and electrolyte interface. The components represent the combined resistance of the electrolyte and the electrode

Table 2. Impedance Equations for Basic Equivalent-Circuit Elements



Circuit Element	Impedance as a Function of Frequency
R	$Z = R + 0j$
C	$Z = 0 - j/2\pi fC$
L	$Z = 0 + j2\pi fL$
C R	$Z = R/\left[1+(2\pi fCR)^2\right] - j2\pi fCR^2/\left[1+(2\pi fCR)^2\right]$
	$j = (-1)^{1/2}$; f is the frequency

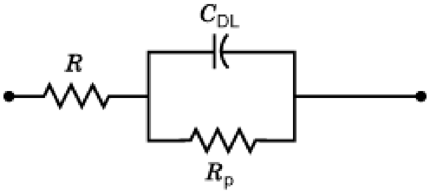


Fig. 5. Equivalent circuit for a simple electrochemical interface. This network describes a simple interface between two different phases. This equivalent circuit typically describes the electrode and electrolyte interface.

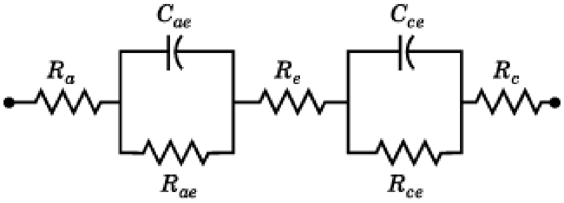


Fig. 6. Equivalent circuit for a two-electrode electrochemical cell. This network describes a simple electrochemical cell including the anode, cathode, and electrolyte ionic conductivity.

substrates, R, and double-layer capacitance of the interface, C_{DL}, with its associated polarization resistance R_p. The resistance associated with double-layer capacitance represents charge transfer. By linking a series of these equivalent circuits, a complex multi-interface electrochemical system can be described. Figure 6 shows the basic equivalent circuit for a two-electrode electrochemical cell.

The elements for the equivalent circuit described in Fig. 6 are (1) R_a, the resistance of the anode substrate, (2) C_{ae}, the double-layer capacitance of the anode–electrolyte interface, (3) R_{ae}, the polarization resistance of the anode, (4) R_e, the electrolyte resistance (ionic conductivity), (5) C_{ce}, the double-layer capacitance of the

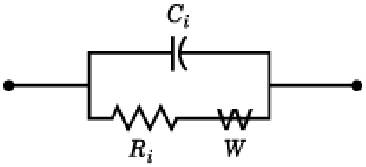


Fig. 7. Equivalent circuit for an electrode interface with Warburg impedance. This network describes the equivalent circuit representing an electrode with additional diffusion-controlled processes at the interface.

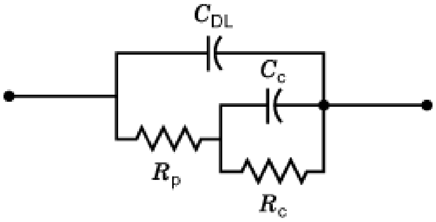


Fig. 8. Equivalent circuit for an electrode interface with an adsorption intermediate. This network describes the equivalent circuit representing the addition of absorption process at an electrode.

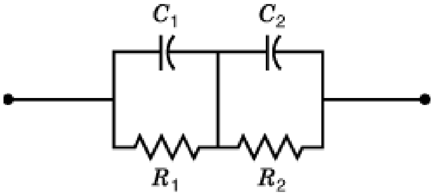


Fig. 9. Equivalent circuit for a multilayer electrode with two interfaces. This network describes the equivalent circuit for a multilayer electrode.

cathode–electrolyte interface, and (6) R_{ce}, the polarization resistance of the anode, and (7) R_c, the resistance of the cathode substrate.

Elements also need to be added to the basic building block to represent additional phenomena within the electrochemical interfaces. Diffusion, represented by Warburg impedance, and absorption are good examples of phenomena that require additional elements to be added to the basic network. Figure 7 shows the equivalent circuits representing an electrode with additional diffusion-controlled processes at the interface. Here C_i is the double-layer capacitance of the interface, R_i is the polarization resistance of the interface, and W is the Warburg impedance. The mass-transfer Warburg impedance follows the mathematical relationship.

$$|Z_W| = (2/\pi f)^{-1/2}\sigma \tag{41}$$

where σ is the Warburg diffusion coefficient.

Figure 8 shows the equivalent circuits representing the addition of absorption process at an electrode. Here C_c is the capacitance of the absorption layer and R_c is the resistance of the absorption layer. Figure 9 shows the equivalent circuit for a multilayer electrode. In this equivalent circuit, each resistor–capacitor network represents an interface between phases. For Figs. 7 to 9, the electrolyte resistance as well as the electrode substrate resistance has been eliminated, thus providing an equivalent circuit for the interface only.

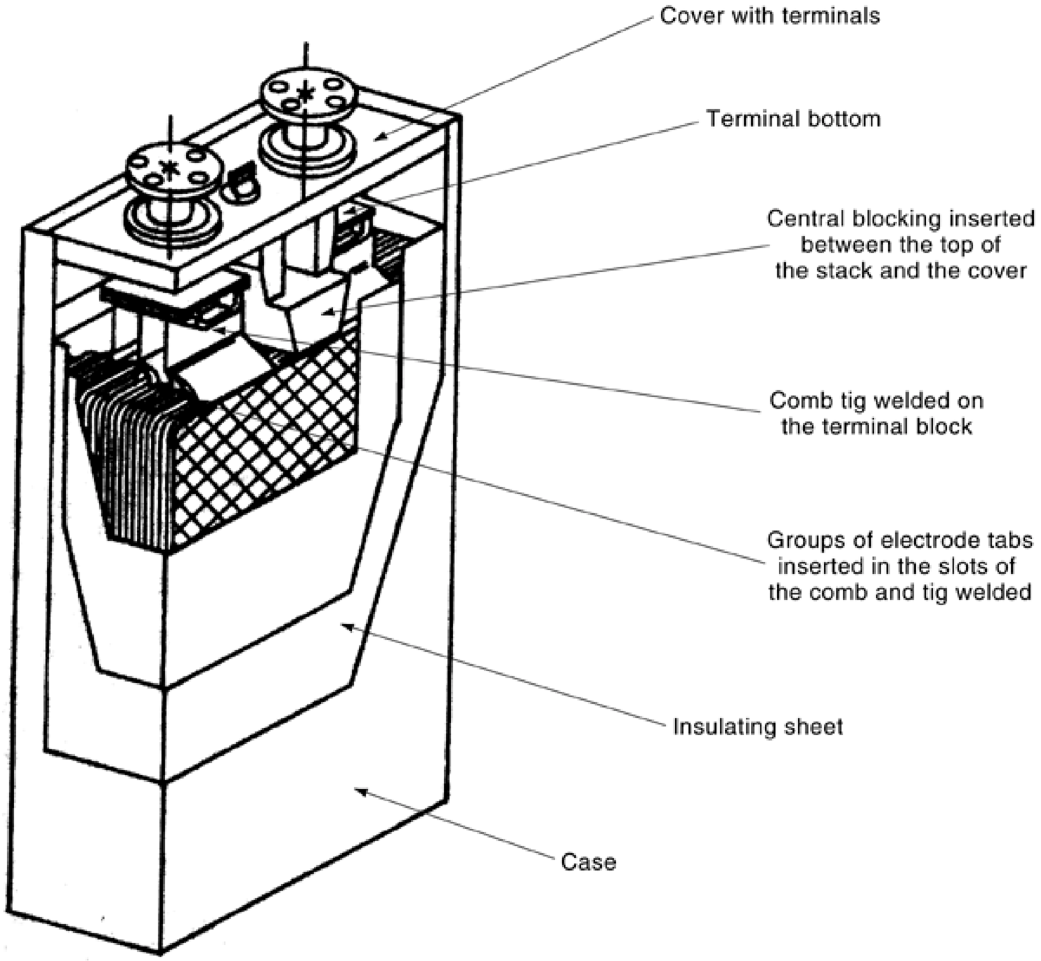


Fig. 10. Prismatic cell. This cell design typically has a high power density and low-to-moderate energy densities.

The value of the proposed equivalent circuit is in its ability to simulate and represent the physical properties of the electrochemical process being examined. Typically, the data suggest an equivalent circuit that can then be refined once the data are fitted to the model.

Cell Design Characteristics

A knowledge of current distribution and factors that affect current densities are essential in battery design considerations. The distribution of current on electrodes may not be uniform, even when the electrodes are vertically opposed and uniformly spaced. If the current distribution across the surface and/or through the electrode is nonuniform, undesirable effects in cell operation occur, including nonuniform chemistry, excessive heat evolution, and low utilization of active materials (4).

Most battery electrodes are porous structures, often with a mixture of solid nonconducting active mass and solid electronically conductive inert materials, filled with an electrolyte permeating the structure. The porous

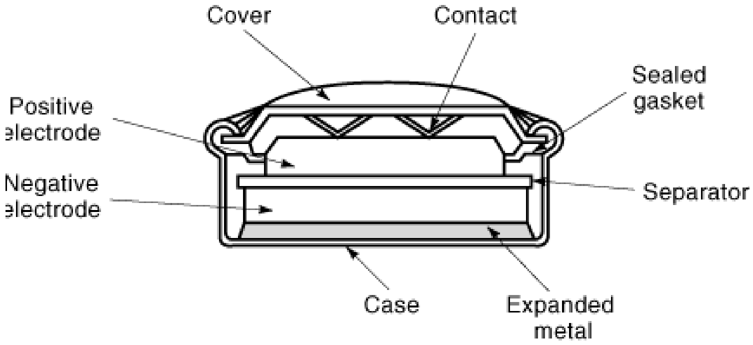


Fig. 11. Button cell. These are characterized as high energy density but low power density, and they are simple to manufacture.

electrode may be viewed as a macroscopically homogeneous volume of electrolyte, inert electronic conductor, and electroactive material. This electrode structure does t have a well-defined planar surface but has a complex surface extended throughout the porous electrode volume. Porous electrodes offer an enhanced surface area for the electrode reaction and increased mass-transfer rates because of shorter diffusion paths. Current-producing reactions can occur at the surface, as well as at a considerable distance inside the surface of the electrode. The effectiveness of a porous electrode over a plane surface electrode is given by the product of the active surface area A_s (cm^2/cm^3) and the penetration depth L_p of the reaction process into the porous electrode. The penetration depth is directly related to the diffusion coefficient and concentration of the reactant and product, to the exchange-current density, and to electrode thickness. When the L_pA_s product is large, the performance of the porous electrode is enhanced over that expected for a planar surface of the same geometric surface area.

The reaction distribution in a porous electrode can be predicted, based on Ohm's law and the equation for reaction kinetics and transport phenomena. Porosity, pore size, and tortuosity all play a role. The equations show that the ratio of the volume conductivity of the electrolyte and electrode materials, the exchange-current density, the diffusional characteristics of reactants and products, and the total current, all determine the current distribution. The nonuniform current distribution lowers efficiency and increases heat evolution due to lower operating voltages and to incomplete usage of the active materials inside the porous electrode.

Cell geometry, such as terminal positioning and battery configuration, can also influence current distribution. Figures 10, 11, 12, 13 show the basic cell designs (5). The basic prismatic cell designs are shown in Figs. 10, 11 Figure 10 shows the prismatic plate cell. This cell design typically has a high power density and low-to-moderate energy densities. Figure 11 shows a variation of the prismatic design, the button cell. Button cells are characterized as high energy density but low power density, and they are simple to manufacture. The basic cylindrical cell designs, spiral wound and bobbin, are shown in Figs. 12 and 13, respectively. Spirally wound cells characteristically provide moderate-to-high power and energy. Bobbin cells, like button cells, are simple to manufacture and provide high energy with low-to-moderate power capability.

The current distribution across the face of an electrode in a battery system is seldom uniform. In general, the current tends to be higher on the edges of the electrode and lower in the middle surface. This primary current distribution is governed by geometric factors such as height (or length) and the distance between the electrodes, by the resistance of the anode and cathode structures, by the resistance of the electrolyte and by the polarization resistance or hindrance of the electrode reaction processes. More uniform distribution is favored by shorter, highly conductive electrode structures, by high solution resistance and wide spacing between electrodes, and by a high polarization resistance. These are the same considerations used for predicting uniformity of electroplating. The slope of the Tafel plot, b, is an indicator of the degree of modification to primary current

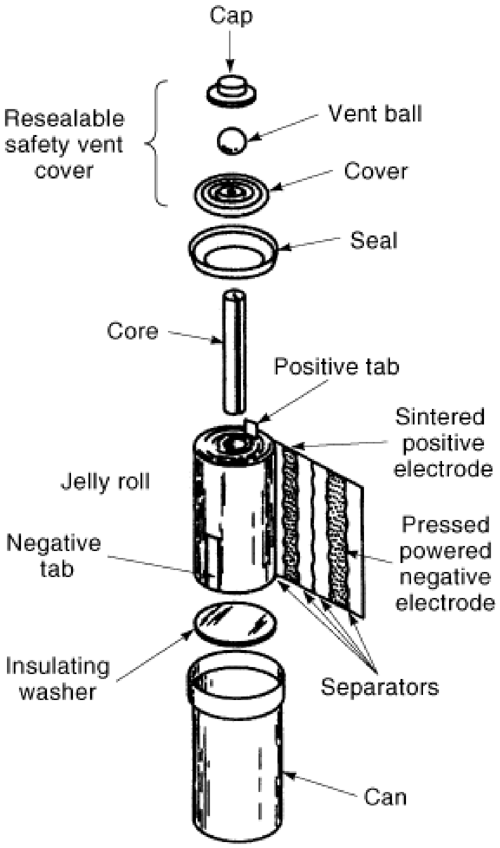


Fig. 12. Spirally wound cell. These cells characteristically provide moderate to high power and energy.

distribution by electrode polarization to produce a more uniform distribution. The addition of polymers and gelling agents to electrolytes is one common method of controlling current distribution, as these increase the slope of the Tafel plot. Most battery designers attempt to minimize high current areas by masking surfaces such as edges on the electrode.

Performance Characteristics of Battery Systems

The value of production of primary batteries was approximately $14 billion in 1998. The most common portable battery systems use MnO_2 as the positive electrode and zinc as the negative in three different electrolytes,$ZnCl_2$–NH_4Cl, $ZnCl_2$, and KOH. These electrolytes represent LeClanché, heavy duty (zinc chloride), and alkaline batteries, respectively, and are used largely in flashlights, portable electronic devices such as radio, cassette players, and toys. They are available in a wide variety of sizes and shapes. They have a sloping discharge voltage, which is a function of the thermodynamics of the manganese dioxide (MnO_2) crystal habitat.

The silver and mercury cells are used to power smaller electronic devices that do not have moving parts, such as hearing aids, cameras, and calculators. They are usually manufactured in small, round, thin

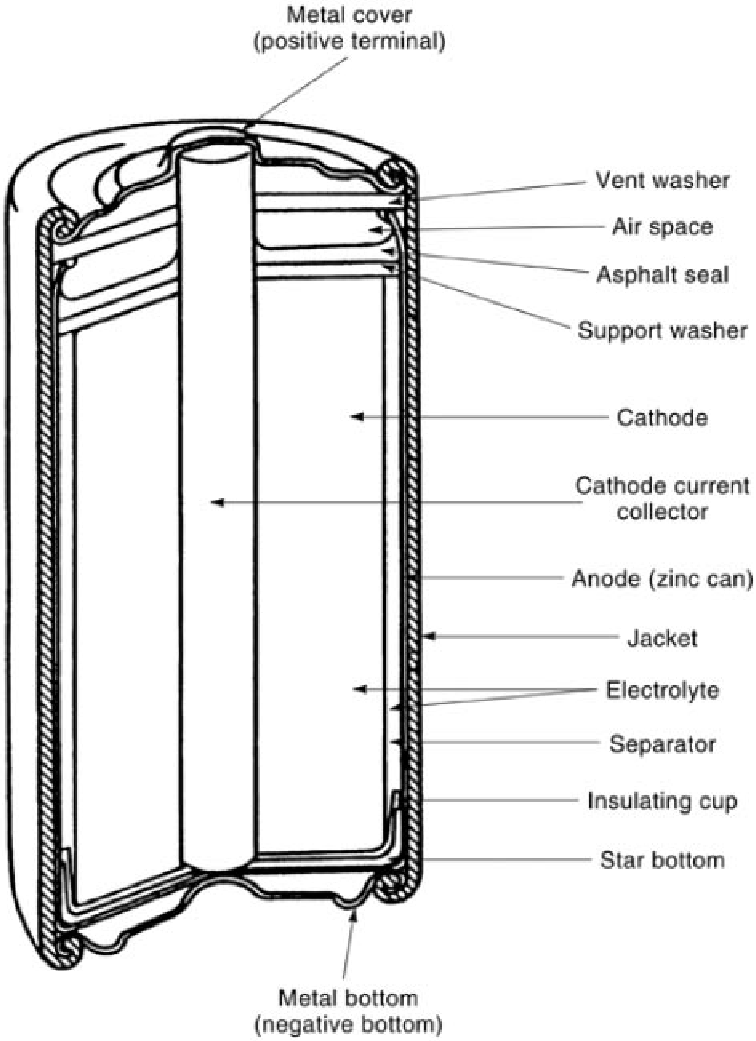


Fig. 13. Bobbin Cell. Bobbin cells, like button cells, are simple to manufacture, provide high energy with low-to-moderate power capability.

configurations, often called button or miniature cells. They have a flat or constant discharge voltage. The zinc air cell is used for hearing aids. It has a short (one month) life after being activated but can deliver twice the energy of the same size silver and mercury cells. It also has a flat discharge curve. Mercury cells have largely been phased out, since 1990, for environmental reasons.

Lithium–copper oxide Li/CuO and lithium–iron sulfide Li/FeS systems are 1.5 V replacements for the mercury and silver button cells. The Li/CuO system also has potential as a long-life, higher-energy replacement for the Zn/MnO_2 systems. They find application for which high-current pulse demands are not required. They have excellent shelf or storage life and operate over a very wide temperature range. A higher-voltage cell ($\sim$3 V) can be made using FeS_2^{2-} with lithium.

Two lithium systems,Li/MnO_2 and Li/CF_x, have 3.0 V cell voltages and take advantage of the high electronegativity of lithium on the EMF scale. These systems find application in a large number of small electronic devices such as cameras and calculators. They have exceptional shelf or storage life and operate over a wide temperature range. They do not have the good pulse power capability of the zinc-based mercury, silver, and alkaline systems.

The Li/l_2 system is used primarily to power low-rate (current) cardiac pacemakers, but some high-rate pacemakers use other cathode materials, for example, CuS and Ag_2CrO_4. Over 95% of the heart pacemakers use a lithium battery to power the pacing systems. It has a 7 to 10 year life in these applications. For higher-current pulse devices, such as defibrillators, lithium vanadium oxide and lithium silver vanadium oxide systems are used.

Li/SO_2 and Li/$SOCl_2$ systems are used, almost exclusively, for military applications. They have reasonably good high-current capability, have a flat discharge profile, have outstanding long shelf or storage life, and operate over a wide temperature range (-40°C to $+70^\circ$C).

There are many other battery systems, not listed here, that have been developed for specialty uses. Thermally activated ("thermal") batteries are one example. These cells employ an electrolyte (typically, an alkali halide mixture) that is solid at room temperature but that becomes very conductive at operating temperatures of 400°C to 600°C. An internal pyrotechnic is used to bring the cell to its operating temperature (6). The conductivities of the molten salt electrolytes can be orders of magnitude greater than aqueous or organic electrolytes, which allows for large power and current densities to be attained.

Many battery chemistries are capable of a single discharge but are incapable of having the original chemistry restored by electric means internal to a cell. This lack of reversibility choccurs from charges in morphology, crystal habitat, conductivity, and inability to be chemically formed in the battery electrolyte. 7 characterized the material irreversibility as arising from (1) irreversibility in phase changes and chemical interconversion, (2) isolation, electrolytically or electronically, of active materials, and (3) local poor conductivity of materials in the discharged state.

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