BATTERIES, INTRODUCTION

1. Introduction

Batteries are storehouses for electrical energy “on demand”. They range in size from large house-sized batteries for utility storage, cubic foot-sized batteries for automotive starting, lighting, and ignition, down to tablet-sized batteries for hearing aids and paper-thin batteries for memory protection in electronic devices. The historical development of batteries starting with Galvani and Volta has been summarized (1–5) and useful texts are available for a more detailed discussion of the topics covered herein (5–12).

In bulk chemical reactions, an oxidizer (electron acceptor) and fuel (electron donor) react to form products resulting in direct electron transfer and the release or absorption of energy as heat. By special arrangements of reactants in devices called batteries, it is possible to control the rate of reaction and to accomplish the direct release of chemical energy in the form of electricity on demand without intermediate processes.

Figure 1 schematically depicts an electrochemical reactor in which the chemical energy stored in the electrodes is manifested directly as a voltage and current flow. The electrons involved in the chemical reactions are transferred from the active materials undergoing oxidation to the oxidizing agent by means of an external circuit. The passage of electrons through this external circuit generates

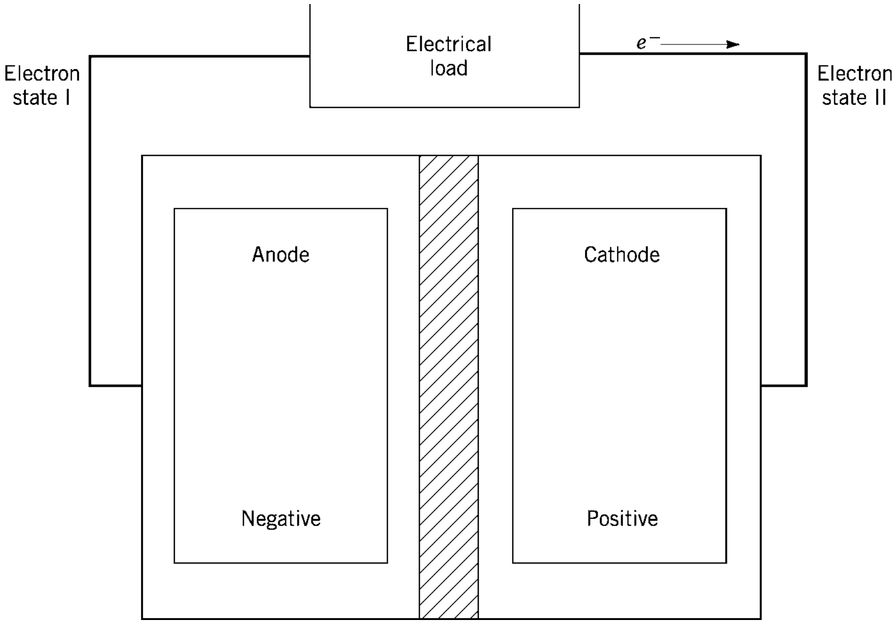


Fig. 1. Schematic representation of a battery system also known as an electrochemical transducer where the anode, also known as electron state I, may be comprised of lithium, magnesium, zinc, cadmium, lead, or hydrogen, and the cathode, or electron state II, depending on the composition of the anode, may be lead dioxide, manganese dioxide, nickel oxide, iron disulfide, oxygen, silver oxide, or iodine.

an electric current, thus providing a direct means for energy utilization without going through heat as an intermediate step. As a result, electrochemical reactors can be significantly more efficient than Carnot cycle heat engines.

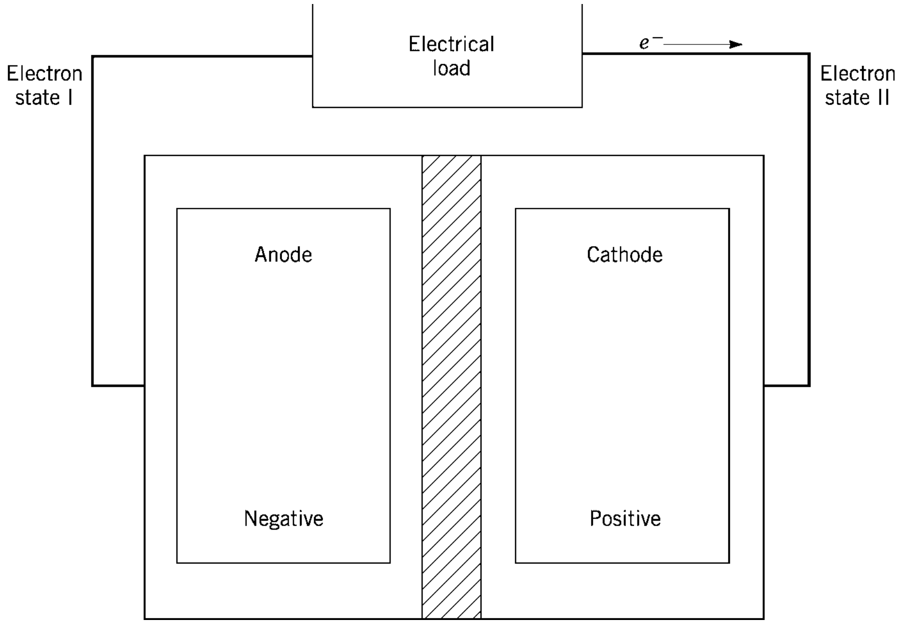
The relationship between current flow and chemical reactions was established by Faraday who demonstrated that the amount of chemical change was directly proportional to the quantity of charge passed (*It*) and to the equivalent weight of the reacting material.

$$g = \frac{MIt}{nF} \tag{1}$$

where g is the mass of material (g) that reacts during electrolysis, M is the molecular weight (g/mol), n is the number of charges transferred in the electrode reaction (equiv/mol), t is the time of electrolysis, F is Faraday's constant (26.8 A·h/g – equiv), and I is the current (amperes) passed. Equation 1 can be expressed in current per unit area *i,*

$$i = I/A = \frac{nFg}{MtA} \tag{2}$$

The names for the electrodes in a battery are taken from the Greek *hodes* (pathway) for the path of electron flow. The anode, from the Greek *anodos* (up



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The names for the electrodes in a battery are taken from the Greek *hodes* (pathway) for the path of electron flow. The anode, from the Greek *anodos* (up and out), or negative electrode of the cell is defined as the electrode from which an electron leaves the cell and oxidation occurs. The cathode, from the Greek *kathodos* (down and in or descent), or positive electrode of the cell is the electrode from which electrons enter the cell and reduction occurs. These terms, anode and cathode, work well for primary batteries but are not adequate for secondary or rechargeable ones. Since electron flow changes direction on charge and discharge, whereas, the electrodes retain their polarity, the terms negative and positive electrode are best used to describe the terminals of rechargeable systems.

The three main types of batteries are primary, secondary, and reserve. A primary battery is used or discharged once and discarded. Secondary or rechargeable batteries can be discharged, recharged, and used again. Reserve batteries are normally special constructions of primary battery systems that store the electrolyte apart from the electrodes, until put into use. They are designed for long-term storage before use. Fuel cells (qv) are not discussed herein.

Useful definitions include

Battery is one or more electrically connected electrochemical cell having terminals/contacts to produce electrical energy.

Primary battery is an electrolytic cell or group of cells for the generation of electric energy intended to be used until exhausted and then discarded.

Secondary battery is an electrolytic cell or group of cells for the generation of electric energy in which the cell, after being discharged, may be restored to its original charged condition by an electric current flowing in the direction opposite to the flow of current when the cell was discharged.

Reserve battery is a primary battery that is stored dry to improve the shelf life of the cell or battery and activated just before use by the addition of an electrolyte, or a battery in which the electorlyte is solid or “frozen” at room temperature and becomes conductive on heating. The electrolyte is usually stored in the battery.

Anode is the negative electrode of a primary cell associated with chemical reactions that release electrons into the external circuit.

Cathode is the positive electrode of a primary cell associated with chemical reactions that gain electrons from the external circuit

Electrolyte is a material that provides ionic conductivity between the positive and negative electrodes of a cell.

Separator is a physical barrier between the positive and negative electrodes incorporated into most cell designs to prevent electrical shorting. The separator can be a gelled electrolyte or a microporous plastic film or other porous inert material filled with electrolyte. Separators must be permeable to ions and inert in the battery environment.

Active mass is the material that generates electrical current by means of a chemical reaction within the battery.

Open circuit voltage is the voltage across the terminals of a cell or battery when no external current flows. It is usually close to the thermodynamic voltage for the system.

Closed circuit voltage is the voltage of a cell or battery when the battery is producing current into the external circuit.

Discharge is an operation in which a battery delivers electric energy to an external load.

Charge is an operation in which the battery is restored to its original charged condition by reversal of the current flow.

Internal impedance is the impedance that a battery or cell offers to alternating current flow at a given frequency.

Internal resistance is the resistance that a battery or cell offers to current flow.

Faraday constant (F) is the amount of charge (C) that transfers when an equivalent weight of active mass reacts, 96,485.3 C/g-equiv = 26.8015 Ah /g-equiv).

2. Economic Aspects

The U.S. primary battery market is divided according to the chemical system used in the batteries, whereas the secondary battery market is usually divided according to usage. The 2000 estimate of the total battery market is given in Table 1. The lead–acid battery accounts for >64% of the secondary battery market.

3. Thermodynamics

Batteries can be thought of as miniature chemical reactors that convert chemical energy into electrical energy on demand. The thermodynamics of battery systems follow directly from that for bulk chemical reactions (13). For the general reaction

$$aA + bB \rightleftharpoons cC + dD \tag{3}$$

Table 1. **Estimated 2002 World Battery Market, $ × 10^6**

primary	
alkaline manganese	7,400
carbon–zinc	5,800
lithium, alkaline button, medical and military	3,300
total primary	16,500
rechargeable	
lead acid	16,300
Ni–Cd (sealed)	1,200
Ni–MH (Sealed)	1,400
lithium-ion	3,200
other (vented nickel, etc.)	3,200
total rechargeable	*25,300*
total market	*41,800*

the basic thermodynamic equations for a reversible electrochemical transformation are given as

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5}$$

where ΔG is the Gibbs free energy, or the energy of a reaction available for useful work, ΔH is the enthalpy, or the energy released by the reaction, ΔS is the entropy, or the heat associated with the organization of material, and T is the absolute temperature. The superscript $^\circ$ is used to indicate that the value of the function is for the material in the standard state at 25°C and unit activity. Although the Helmholtz free energy ΔA is used to describe constant volume situations found in battery systems, the use of the Gibbs free energy ΔG is adequate to describe practical battery systems.

The terms ΔG, ΔH, and ΔS are state functions and depend only on the identity of the materials and the initial and final states of the reaction. Tables of thermodynamic quantities are available for most known materials (see also THERMODYNAMIC PROPERTIES) (14).

Because ΔG is the net useful energy available from a given reaction, in electrical terms, the net available electrical energy from a reaction is given by

$$-\Delta G = nFE \tag{6}$$

and

$$-\Delta G^\circ = nFE^\circ \tag{7}$$

where n is the number of electrons transferred in the reaction, F is Faraday's constant, E is the voltage or electromotive force (emf) of the cell, and E° is the voltage at 25°C and at unit activity. The voltage is unique for each group of reactants comprising the battery system. The amount of electricity produced is determined by the total amount of materials involved in the reaction. The voltage may be thought of as an intensity factor, and the term nF may be considered a capacity factor.

The more negative the value of ΔG, the more energy or useful work can be obtained from the reaction. Reversible processes yield the maximum output. In irreversible processes, a portion of the useful work or energy is used to help carry out the reaction. The cell voltage or emf also has a sign and direction. Spontaneous processes have a negative free energy and a positive emf; the reaction, written in a reversible fashion, goes in the forward direction.

From equations 4 and 6, it can be shown that

$$\Delta G = \Delta H - nFT(\partial E/\partial T)_P \tag{8}$$

$$\Delta S = nF(\partial E/\partial T)_P \tag{9}$$

$$-\Delta H = nF\left[E - T(\partial E/\partial T)_P\right] \tag{10}$$

where $(\partial E/\partial T)_P$ is the temperature coefficient of the emf of a reversible cell at constant pressure. Equations 8–10 permit the calculation of heats of reaction from simple measurements of the voltage of an electrochemical cell as a function of temperature.

Once the values of thermodynamic functions, ΔH_{T1}, ΔS_{T1}, are known at a given temperature T_1 the value for the function can be calculated at any other temperature T_2 by

$$\Delta H_{T2} = \Delta H_{T1} \int_{T_1}^{T_2} \Delta C_P \, dT \quad \text{and} \quad \Delta S_{T2} = \Delta S_{T1} \int_{T_1}^{T_2} \Delta C_P \, dT \tag{11}$$

where ΔC_P is the heat capacity at constant pressure.

The relationship between the chemical equilibrium constant K and the Gibbs free energy is

$$-RT \ln K = \Delta G^\circ \tag{12}$$

The Van't Hoff isotherm identifies the free energy relationship for bulk chemical reactions.

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\Pi A^s(\text{products})]}{[\Pi A^s(\text{reactants})]} \tag{13}$$

By combining equation 6 and 7 with the Van't Hoff isotherm, the Nernst equation for electrochemical reactions is obtained

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\Pi A^s(\text{products})]}{[\Pi A^s(\text{reactants})]} \tag{14}$$

where ΠA^s (products) is the product of the activities of the products, each raised to its stoichiometric power, and ΠA^s (reactants) is the corresponding term for the reactants, R is the gas constant, T is the absolute temperature, and E° is the reversible cell voltage under standard conditions. It is important to realize that only the surface composition of the electrode in contact with the electrolyte should be considered in calculating E°. Material buried deep within an electrode, completely covered with active material, and without direct electronic contact to the current collector, does not affect E° and the measured values of cell voltage.

The activity or effective concentration of the reactants and products often differs from the actual concentration of the material. The activity is related to the chemical potential μ_i of the species i by

$$\mu_i = (\partial G/\delta n_i)_{T,P,nj \neq 1} \tag{15}$$

where n_i is the mole fraction of species i. Then for species A

$$\mu_\mathrm{A} = \mu_\mathrm{A}^\circ + RT \ln \mathrm{A}_\mathrm{A} \tag{16}$$

where $A_A = f_A x_A$, the activity of species A; f_A is the activity coefficient; and x_A is the concentration. In dilute solutions, $f_A \longrightarrow 1$ as $x_A \longrightarrow 0$. In concentrated solutions the activity coefficient often decreases through a minimum as the concentration increases.

The modern definition of electricity involves the flow of current from a higher potential to a lower one. This places materials having a high electron energy level as the negative material (anodes) in an electrochemical cell and those having a lower electron energy level as the positive material (cathodes). Whereas the potentials of electrodes can be calculated using a Born–Haber cycle, the absolute electrode potentials of single electrodes cannot be measured experimentally. Only differences in the potential between two electrodes can be measured. For convenience, the potential of the hydrogen electrode at 25°C, 101.3 kPa (1 atm) H_2 pressure, and unit activity of hydrogen ions is chosen as the reference point for potential measurements. The standard hydrogen electrode (SHE) is defined as the zero point on the potential scale.

$$H_2 - 2e^- = 2\mathrm{H}^+ \qquad E^\circ = 0.000\ \mathrm{V} \tag{17}$$

Table 2 illustrates the potential scale for selected battery reactions. The sign for the electrode potential indicates whether the electrode is negative or positive to the potential of the hydrogen electrode. Reactions, in both acid and basic media, are included to indicate the influence of pH on the electrode potential. In a battery, the electrode with the more negative potential becomes

Table 2. **Selected Standard Potentials for Battery in Acid and Basic Media**[a,b]

Electrode reaction	E°
Standard potentials in acid media	
$Li^+ + e^- = Li$	−3.045
$Na^+ + e^- = Na$	−2.714
$Mg^{2+} + 2\,e^- = Mg$	−2.356
$Al^{+3} + 3e^- = Al$	−1.676
$Zn^{+2} + 2\,e^- = Zn$	−0.7626
$S + 2\,e^- = S^{-2}$	−0.447
$Cd^{+2} + 2\,e^- = Cd$	−0.4025
$PbSO_4 + 2\,e^- = Pb + SO_4{}^{2-}$	−0.3505
$2\,H^+ + 2\,e^- = H_2$	0.0000
$AgCl + e^- = Ag + Cl^-$	0.2223
$O_2 + 2\,H^+ + 2\,e^- = H_2O_2$	0.695
$\gamma\text{-}MnO_2 + H^+ + e^- = MnOOH$	1.0
$Br_2 + 2\,e^- = 2\,Br^-$	1.06
$O_2 + 4\,H^+ + 4\,e^- = 2\,H_2O$	1.229
$PbO_2 + 4\,H^+ + 4\,e^- = Pb + 2\,H_2O$	1.698
Standard potentials in basic media	
$Zn(OH)_4{}^{2-} + 2\,e^- = Zn + 4OH^-$	−1.285
$CdO + H_2O + 2\,e^- = Cd + 2\,OH^-$	−0.783
$\gamma\text{-}MnO_2 + H_2O + e^- = MnOOH + OH^-$	0.36
$Ag_2O + H_2O + e^- = 2Ag + 2\,OH^-$	0.342
$O_2 + 2\,H_2O + 4\,e^- = 4\,OH^-$	0.401
$NiOOH + H_2O + e^- = Ni(OH)_2 + OH^-$	0.41

[a] Ref. 15.

[b] Potentials are given in volts (V).

the battery's negative electrode. The voltage of a battery is the algebraic difference between the individual electrode potentials on the scale. For example, the voltage of a zinc [7440-66-6]−silver(I) oxide [20667-12-3] cell in alkaline media is $1.627\ \text{V} = 0.342\ \text{V} - (-1.255)\ \text{V}$. Several excellent compilations of electrode potentials are available (15,16). Similar scales of electrode potentials can be constructed for each nonaqueous electrolyte.

When the reactants and products 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 product to reacting species. This results in a sloping discharge curve that is typical of cells having manganese dioxide [1313-13-9], MnO_2, titanium disulfide [12039-13-3], TiS_2, molybdenum disulfide [1317-33-5], MoS_2, etc, electrodes. When the reactants and products of an electrode reaction form separate phases, the voltage of the electrode is constant during discharge. This is illustrated in electrodes of mercury [7439-97-6]−mercuric oxide [21908-53-2], ie, Hg/HgO, cadmium [7440-43-9]−cadmium hydroxide [21041-95-2], ie, $Cd/Cd(OH)_2$, and lead dioxide [1309-60-0]−lead sulfate [7446-14-2], $PbO_2/PbSO_4$. These electrodes are often used as reference electrodes in experimental studies because of their invariant voltages.

Because batteries directly convert chemical energy to electrical energy in an isothermal process, they are not limited by the Carnot efficiency. The thermodynamic efficiency ε for electrochemical processes is given by:

$$\epsilon = \frac{\Delta G^\circ}{\Delta H^\circ} = 1 - \frac{T\Delta S^\circ}{\Delta H^\circ} \tag{18}$$

In electrochemical units, equation 18 becomes

$$\epsilon = 1 - \frac{nFT(\partial E/\partial T)_P}{\Delta H^\circ} \tag{19}$$

Whenever energy is transformed from one form to another, an inefficiency of conversion occurs. Electrochemical reactions having efficiencies of 90% or greater are common. In contrast, Carnot heat engine conversions operate at $\sim$ 40% efficiency. The operation of practical cells always results in less than theoretical thermodynamic prediction for release of useful energy because of irreversible (polarization) losses of the electrode reactions. The overall electrochemical efficiency is, therefore, defined by

$$\text{Eff}_{\text{electrochem}} = \int \frac{(E'I\,dt)}{\Delta G} \tag{20}$$

where E' is the closed circuit terminal voltage when the net current I is flowing at time t.

The performance of a battery is often designed to be limited by one electrode in order to achieve special performance characteristics, such as overcharge protection and safety. The Coulombic efficiency of the active mass is of particular interest in battery design and performance.

$$\text{Eff}_{\text{Coulombic}} = It/Q \tag{21}$$

where Q is the quantity of coulombs expected from a given amount of active mass based on the equivalent weight and the amount of material. Utilization of the active mass may vary during the course of battery operation and depends on the cutoff voltage, rate of discharge–charge, and the nature of the electrode structure.

In addition to reversible heat absorbed, or released, as a result of the entropy of reaction, heat is released in batteries during operation because of the irreversibility of the reaction processes involved in converting chemical into electrical energy. The amount of heat q generated during battery operation is given by

$$q = \frac{T\Delta S}{nF} + I(E - E')\,dt \tag{22}$$

The total heat released is the sum of the entropy contribution plus the irreversible contribution. This heat is released inside the battery at the reaction site. Heat release is not a problem for low rate applications; however, high rate batteries must make provisions for heat dissipation. Failure to accommodate heat can lead to thermal runaway and other catastrophic situations.

4. Electrolytes

Electrolytes are a key component of electrochemical cells and batteries. Electrolytes are formed by dissolving an ionogen into a solvent. When salts are dissolved in a solvent such as water, the salt dissociates into ions through the action of the dielectric solvent. Strong electrolytes, ie, salts of strong acids and bases, are completely dissociated in solution into positive and negative ions. The ions are solvated but positive ions tend to interact more strongly with the solvent than do the anions. The ions of the electrolyte provide the path for the conduction of electricity by movement of charged particles through the solution. The electrolyte also provides the physical separation of the positive and negative electrodes needed for electrochemical cell operation.

Electrical conduction in electrolytic solutions follows Ohm's law:

$$I = \kappa V \tag{23}$$

where I is the current in amperes, V is the voltage drop in volts across the electrolytic resistor of conductivity κ in $(\Omega \cdot \mathrm{cm})^{-1}$. The conductivity κ is the reciprocal of the resistivity ρ in $\Omega{\cdot}\mathrm{cm}$. The resistance of the electrolyte depends on the length l and cross-sectional area A of the conductor.

$$R = \rho l/A \tag{24}$$

The Debye-Hückel theory of electrolytes, based on the electric field surrounding each ion, forms the basis for modern concepts of electrolyte behavior (17,18). The two components of the theory are the relaxation and the electrophoretic effect. Each ion has an ion atmosphere of equal opposite charge surrounding it. During movement, the ion may not be exactly in the center of its ion atmosphere, thereby, producing a retarding electrical force on the ion. A finite time is required to reestablish the ion atmosphere at any new location. Thus the ion atmosphere produces a drag on the ions in motion and restricts their freedom of movement, which is termed a relaxation effect. When a negative ion moves under the influence of an electric field, it travels against the flow of positive ions and solvent moving in the opposite direction, which is termed an electrophoretic effect. The Debye–Hückel theory combines both effects to calculate the behavior of electrolytes. The theory predicts the behavior of dilute (≤ 0.05 m) solutions but does not portray accurately the behavior of concentrated solutions found in practical batteries.

Ions of an electrolyte are free to move about in solution by Brownian motion and, depending on the charge, have specific direction of motion under the influence of an external electric field. The movement of the ions under the influence of an electric field is responsible for the current flow through the electrolyte. The velocity of migration of an ion v_{i} is given by

$$v_i = -z_i u_i F d\phi/dx \tag{25}$$

where z_i is the charge number of the ion, $d\phi/dx$ is the electric field gradient, and u_i is the mobility of the ion. Solutions are electrically neutral so

$$\Sigma z_i c_i = 0 \tag{26}$$

When current I is passed through an electrolyte, the total current is given by

$$I = \Sigma z_i c_i \tag{27}$$

Each ion has its own characteristic mobility. The total conductivity of the electrolyte is the sum of the conductivities of the positive and negative ions, which is known as Kohlrausch's law of independent migration of ions.

Because both positive and negative ions move under the influence of an electric field, albeit in opposite directions, the fraction of the current carried by an ion is given by the ratio of the mobility of the ion and the total mobility of all the ions in solution. This ratio is called the transference number t of the ion. Thus

$$t_+ = u_+/(u_+ + u_-)t_- = u'_-/(u_+ + u_-) \tag{28}$$

where

$$t_+ + t_- = 1 \tag{29}$$

The term equivalent conductance Λ is often used to describe the conductivity of electrolytes. It is defined as the conductivity of a cube of solution having a cross-section of 1/cm^2 and containing 1 equiv of dissolved electrolyte.

$$\Lambda = k/C^* \quad \text{or} \quad \Lambda = 1000\ k/C \tag{30}$$

where C^* and C are the concentration in equiv/mL and equiv/L, respectively. It can be easily shown that

$$\Lambda = F(u_+ + u_-) \tag{31}$$

Transport properties of the electrolyte, as well as electrode reactions, have a significant impact on battery operation. The electrode reactions and ionic transference that occur during discharge result in considerable modifications to the solution composition at each electrode compartment. The negative and positive electrode compartments can lose or gain electrolyte and solvent depending on the transference numbers of the ions and the electrode reactions. The composition of the electrolyte in the separator between the two compartments generally remains unchanged.

Battery electrolytes are concentrated solutions of strong electrolytes and the Debye–Hückel theory of dilute solutions is only an approximation. Typical values for the resistivity of battery electrolytes range from about 1 ohm·cm for sulfuric acid [7664-93-9], H_2SO_4, in lead–acid batteries, and for potassium hydroxide [1310-58-3], KOH, in alkaline cells to ~100 ohm·cm for organic electrolytes in lithium [7439-93-2], Li, batteries.

The physical picture in concentrated electrolytes is more aptly described by the theory of ionic association (19,20). As the solutions become more concentrated, the opportunity to form ion pairs held by electrostatic attraction increases. This tendency increases for ions with smaller ionic radii and in the lower dielectric constant solvents used for lithium batteries. A significant amount of ion-pairing and triple-ion formation exists in the high concentration electrolytes used in batteries. The ions are solvated, causing solvent molecules to be highly oriented and polarized. In concentrated solutions the ions are close together and the attraction between them increases ion-pairing of the electrolyte. Solvation can tie up a considerable amount of solvent and increase the viscosity of concentrated solutions.

Lithium batteries must use nonaqueous electrolytes, usually combinations of solvents, for stability because lithium reacts readily with water. Many of these electrolytes dissolve a high concentration of solute but are relatively poor conductors. The cause appears to be related to the increase of ion-pair and triple-ion formation in the lower dielectric constant, relative to water, solvents and to the increased viscosity of concentrated solutions. For example, a 1 *M,* lithium perchlorate [7791-03-9], $LiClO_4$, solution in propylene carbonate (PC) [108-32-7], $C_4H_6O_3$, has only ~ 20% of the conductivity expected because ~80% of the ions are involved in ion-pairing and triple-ion formation. Tables of electrolyte properties are available for most aqueous electrolytes(21,22) and selected nonaqueous electrolytes (23,24).

Each electrolyte is stable only within certain voltage ranges. Exceeding these limits results in decomposition. The stable range depends on the solvent, electrolyte composition, and purity level. In aqueous systems, hydrogen and oxygen form when the voltage limit is exceeded. In the nonaqueous organic solvent-based systems used for lithium batteries, exceeding the voltage limit can result in polymerization or decomposition of the solvent system. It is especially important to remove traces of water from the nonaqueous electrolytes as water can catalyze the electrolytic decomposition of the organic solvent.

In addition to the liquid conductors described above, two types of solid-state ionic conductors have been developed; one involves inorganic compounds and the other is based on polymeric materials. Several inorganic solids have been found to have excellent conductivity resulting wholly from ionic motion in the crystal lattice. Conductivity is related to specific crystal structures in which one ion, usually the cation, can move freely through the lattice. In the case of the solid materials, silver rubidium iodide, $AgRb_4I_5$, the silver ion moves freely through the lattice and $t_{Ag^+} = 1$. The voltage of batteries constructed with these materials is limited only by the decomposition voltage of the electrolyte. One solid electrolyte, lithium iodide [10377-51-2], LiI, has found application in heart-pacer batteries even though it has a fairly low conductivity.

A second type of solid ionic conductor, which is based around polyether compounds such as poly(ethylene oxide) [25322-68-3] (PEO), has been discovered and characterized (25,26). These materials follow equations 23–31 as opposed to the electronically conducting polyacetylene [26571-64-2] and polyaniline type materials. The polyethers can complex and stabilize lithium ions in organic media. They also dissolve salts such as $LiClO_4$ to produce conducting solid solutions. The use of these materials in rechargeable lithium batteries is under development for stationary energy storage and electric vehicle applications at Avistor Corp.(27,28).

A third type of "solid" ionic conductor is based on the ability of some polymers to absorb organic electrolytes, while maintaining a solid physical dimension. These are called "plasticized" or "gel" polymer electrolytes. These electrolytes have good conductivity at room temperature in contrast to the pure polymer electrolytes that have good conductivity only $>60°C$.

5. Electrical Double Layer

When two conducting phases come into contact with each other, a redistribution of charge occurs as a result of any electron energy level difference between the phases. If the two phases are metals, electrons flow from one metal to the other until the electron levels equilibrate. When an electrode, ie, electronic conductor, is immersed in an electrolyte, ie, ionic conductor, an electrical double layer forms at the electrode–solution interface resulting from the unequal tendency for distribution of electrical charges in the two phases. Because overall electrical neutrality must be maintained, this separation of charge between the electrode and solution gives rise to a potential difference between the two phases, equal to that needed to ensure equilibrium.

On the electrode side of the double layer, the excess charges are concentrated in the plane of the surface of the electronic conductor. On the electrolyte side of the double layer, the charge distribution is quite complex. The potential drop occurs over several atomic dimensions and depends on the specific reactivity and atomic structure of the electrode surface and the electrolyte composition. The electrical double layer strongly influences the rate and pathway of electrode reactions. The reader is referred to several excellent discussions of the electrical double layer at the electrode–solution interface (29–31).

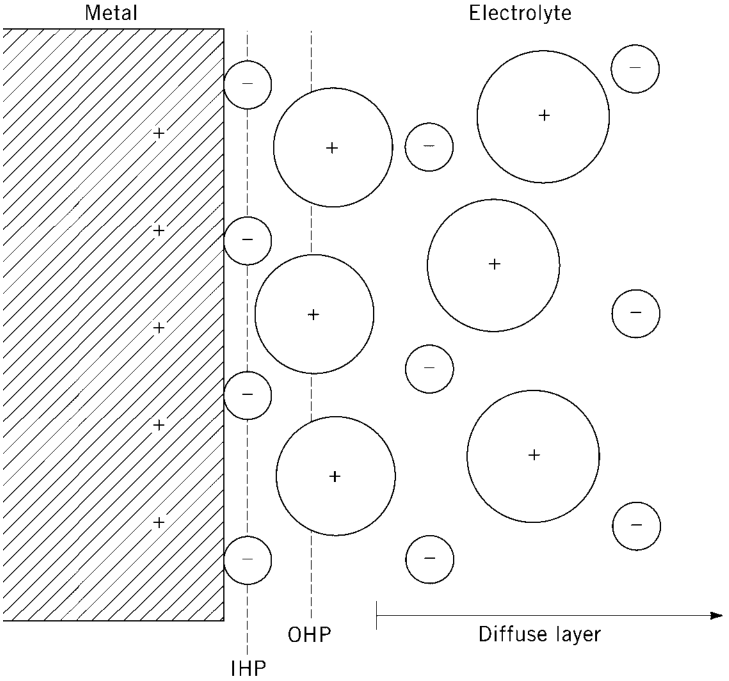

Fig. 2. Representation of the electrical double layer at a metal electrode–solution interface for the case where anions occupy the IHP and cations occupy the OHP.

Figure 2 schematically depicts the structure of the electrode–solution interface. The inner-Helmholtz plane (IHP) refers to the distance of closest approach of specifically adsorbed ions, generally anions to the electrode surface. In aqueous systems, water molecules adsorb onto the electrode surface. The outer-Helmholtz plane (OHP) refers to the distance of closest approach of nonspecifically adsorbed ions, generally cations. The interactions of the ions of the OHP with the surface are not specific and have the character of longer range Coulombic interactions. Cations that populate the OHP are usually solvated and are generally larger in size than the anions.

To a first approximation, the ions in both Helmholtz layers can be considered point charges. They induce an equal and opposite image charge inside the conductive electrode. When the electrode is negative to the point of zero charge, cations populate the IHL.

When the electrode is positive to the point of zero charge, anions occupy the IHP. Anions are smaller in size and are solvated to a lesser degree than are the cations. Anions are more likely to adsorb specifically or bond to the electrode surface. If this is the case, the electrode can reach a considerable negative potential before strongly bonded anions are repelled from the inner layer. When an ion bonds to the surface it partially transfers charge to the surface. This charge transfer reduces the effective charge of the ion and causes the potential difference produced by the ion at the surface to be less than would be expected by a point charge an atomic distance from the surface.

The region of the gradual potential drop from the Helmholtz layer into the bulk of the solution is called the Gouy or diffuse layer (32,33). The Gouy layer has similar characteristics to the ion atmosphere from electrolyte theory. This layer has an almost exponential decay of potential with increasing distance. The thickness of the diffuse layer may be approximated by the Debye length of the electrolyte.

Electrical double layers are not confined to the interface between conducting phases. Solid particles of active mass, or of conductive additives of colloidal size, can acquire an electric charge by specific adsorption of cations or anions from the electrolyte or by reaction of surface moieties with components of the solution. The resulting excess charge on the particle is neutralized by a diffuse or Gouy layer in the solution. The electrokinetic properties of the interface and zeta potential concepts are based on the characteristics of the Gouy layer. Migration of the colloidal-sized solid particles can occur under the influence of an applied electric field during battery operations.

Electrically, the electrical double layer may be viewed as a capacitor with the charges separated by a distance of the order of molecular dimensions. The measured capacitance ranges from about two to several hundred microfarads per square centimeter depending on the structure of the double layer, the potential, and the composition of the electrode materials. Figure 3 illustrates the behavior of the capacitance and potential for a mercury electrode where the double layer capacitance is $\sim$ 16 μF/cm^2 when cations occupy the OHP and $\sim$ 38 μF/cm^2 when anions occupy the IHP. The behavior of other electrode materials is judged to be similar.

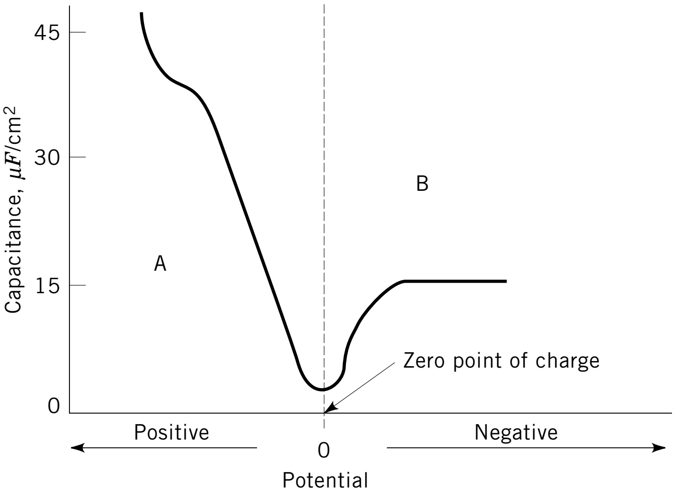

Fig. 3. Capacitance–potential relationship at a mercury electrode for a nonspecific absorbing electrolyte where regions A and B represent inner-layer anions and cations, respectively.

6. Kinetics and Transport

6.1. Activation Processes. Reactions must occur at a reasonable rate to be useful in battery applications. The rate or ability of battery electrodes to produce current is determined by the kinetic processes of electrode operations, not by thermodynamics. Thermodynamics describes the characteristics of reactions at equilibrium when the forward and reverse reaction rates are equal. Electrochemical reaction kinetics (34–37) follow the same general considerations as those of bulk chemical reactions. Two differences are a potential drop that exists between the electrode and the solution because of the electrical double layer at the electrode interface, and the reaction that occurs at interfaces that are two-dimensional (2D) rather than in the three-dimensional (3D) bulk.

Electrode kinetics lend themselves to treatment using the absolute reaction rate theory or the transition state theory (38–40). In these treatments, the path followed by the reaction proceeds by a route involving an activated complex where the element determining the reaction rate, ie, the rate–limiting step, is the dissociation of the activated complex. The general electrode reaction may be described as

$$A = C^{n+} + ne^{-} \tag{32}$$

where n is the number of electrons in the reaction. By using reaction rate theory, it can be shown that the current flow results from a change in the activation energy barrier introduced by a departure from the equilibrium potential drop across the electrode–solution interface. The free energies of activation for the forward ΔG_f and reverse ΔG_r reactions are given by

$$\Delta G_f = \Delta G^{*} - \alpha n FE' \tag{33}$$

$$\Delta G_r = \Delta G^{**} + (1-\alpha)n FE' \tag{34}$$

where E' is the potential of the electrode in its operating environment, α is the transfer coefficient or the fraction of the potential drop through the electrical double layer that operates on the activated complex, and $\Delta G^{**} = \Delta G^{*} + \Delta G^{\circ}$. The rate of electrochemical reactions are expressed as a current flow I in coulombs per second (amperes), rather than as a change in concentration per unit time. The direction of the potential change from the equilibrium potential E determines the direction of current flow. In terms of net current flow where $i = I/\mathrm{cm}^2$, it can be shown that

$$i = i_f - i_r = nFk_1A_{\mathrm{A}}e^{(-\Delta G^{*}-\alpha nFE^{*}/RT)} - nF_{k-1}A_{\mathrm{C}}e^{(-\Delta G^{**}+(1-\alpha)nFE^{*}RT)} \tag{35}$$

where A_{A} and A_{C} are the activities of reactants and products, k_1 and k_{-1} are the specific rate constants, and ΔG^{*} and ΔG^{**} are the free energy of activation for the forward and reverse reactions, respectively. The free energy of activation is strongly influenced by the fraction of the potential drop across the electrode–solution interface that acts on the activated complex. Thus the structure of the electrical double layer plays a key role in the kinetics and rate of electrode reactions.

At equilibrium, there is no net current flow, the rate of the forward and reverse reactions are equal and $E' = E$. The rate of the forward and reverse reactions at equilibrium

$$i_f = i_r = i_0 \tag{36}$$

expressed as a current flow i_o are given the special term exchange current. Because electrode reactions are in dynamic equilibrium, the term i_o is the rate of the reaction at the equilibrium potential E.

The exchange current is directly related to the reaction rate constant, to the activities of reactants and products, and to the potential drop across the double layer. The larger i_0, the more reversible the reaction and, hence, the lower the polarization for a given net current flow. Electrode reactions having high exchange currents are favored for use in battery applications.

By taking the polarization η as the departure from equilibrium potential ($\eta = E' - E$), it follows from equations 35 and 36 that

$$i = i_0\{e^{-(\alpha nF\eta/RT)} - e^{((1-\alpha)nF\eta/RT)}\} \tag{37}$$

The expected behavior of a current–potential diagram is given in Figure 4. These plots constitute the classic method for investigating electrode kinetics and for characterizing battery reactions. The value of α, and the relationship of i_o with concentration, provide valuable insight into the kinetics of the electrode reactions. At low current drains, the polarization in battery reactions is almost always activation energy (charge-transfer) controlled. When the electrode

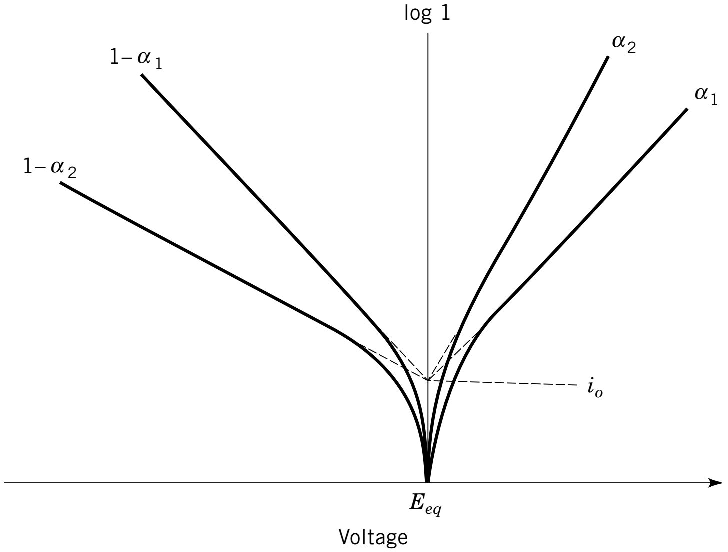

Fig. 4. Currrent–potential behavior of an electrode reaction based on equation 37. Tafel behavior is noted at high currents for two different values of α.

reaction occurs and the polarization is larger than ~ 0.05 V, the term for the reverse reaction in equation 37 may be neglected and equation 37 can be simplified.

$$i = i_0\{e^{-(\alpha nF\eta/RT)}\} \tag{38}$$

or

$$\eta = \alpha - b\log i \tag{39}$$

where $a = (2.303\ RT/\alpha nF)\log i_0$ and $b = 2.303\ RT/\alpha nF$. Equation 39 is the well-known Tafel equation that describes the voltage–current behavior for processes under activation control, and is illustrated in Figure 4 by the linear portion of the plot. The kinetic parameters for many electrode reactions have been summarized (41).

6.2. Transport Processes. The velocity of electrode reactions is controlled by the charge-transfer rate of the electrode process or by the velocity of the approach of the reactants to the reaction site. The movement or transport of reactants to and from the reaction site at the electrode interface is a common feature of all electrode reactions. Transport of reactants and products occurs by diffusion, by migration under a potential field, and by convection. The complete description of transport requires a solution to the transport equations. A full account is given in texts and discussions on hydrodynamic flow (42,43) (see FLUID MECHANICS). Molecular diffusion in electrolytes is relatively slow. Although the process can be accelerated by stirring, enhanced mass transfer (qv) by stirring or convection is not possible in most battery designs. Natural convection from density changes does occur but does not greatly enhance transport in battery operation. Lead acid batteries, used for motive power and stationary applications, are given a gassing overcharge on a regular basis. The gas evolution stirs up the electrolyte and equalizes the sulfuric acid concentration in the electrolyte.

Whenever the local concentration of a reacting component in a battery departs significantly from its equilibrium value, the rate of reaction becomes controlled by the transport of that component to the reaction site. The polarization resulting from these concentration changes η_c is given by

$$\eta_c = \frac{RT}{nF}\ln(C_e/C) \tag{40}$$

where C_e is the concentration at the electrode surface and C is the concentration in the bulk of the electrolyte.

The limiting current density i_l for the transport of species i to the reacting site is given from Fick's law by

$$i_l = \frac{DnFC_B}{\delta} \tag{41}$$

where δ is the thickness of the stationary diffusion layer, D is the diffusion coefficient, C_B is the concentration on the bulk of the solution, and n and F are as previously defined. Allowing for electromigration, equation 41 becomes

$$i_l = \frac{DnFC_B}{\delta(1 - t_i)} \tag{42}$$

where t_{i} is the transference number of the reacting species. The limiting current calculation corresponds to the case where the concentration at the electrode surface is zero and the thickness of the diffusion layer is very thin. For many aqueous electrolytes the limiting current can be estimated by

$$i_l = 0.025\ C \tag{43}$$

where C is in g-equiv/L. The relationship between concentration polarization and limiting current density is given by

$$\eta_c = \frac{RT}{nF} \ln{(1 - i/i_e)} \tag{44}$$

Whereas, the above discussion on concentration polarization was developed for electrolyte-side supply of reactants, concentration polarization can also arise from surface diffusion, diffusion into the solid structure (intercalation) of the active mass, and diffusion of products away from the reaction site. The deposition and dissolution reactions can involve movement of surface atoms to and from the deposition site to the equilibrium position in the lattice.

The detailed mechanism of battery electrode reactions often involves a series of chemical and electrochemical or charge-transfer steps. Electrode reaction sequences can also include diffusion steps on the electrode surface. Because of the high activation energy required to transfer two electrons at one time, the charge-transfer reactions are believed to occur by a series of one electron-transfer steps illustrated by the reactions of the zinc electrode in strongly alkaline medium (44).

$$\mathrm{Zn} + \mathrm{OH}^- = \mathrm{Zn(OH)} + e^- \tag{45}$$

$$\mathrm{Zn(OH)} + \mathrm{OH}^- = \mathrm{Zn(OH)}_2^- \tag{46}$$

$$\mathrm{Zn(OH)}_2^- + \mathrm{OH}^- = \mathrm{(Zn)OH}_3^- + e^- \tag{47}$$

$$\mathrm{Zn(OH)}_3^- + \mathrm{OH}^- = \mathrm{Zn(OH)}_4^{2-} \tag{48}$$

In this reaction sequence, equation 47, the formation of the complex ion, $\mathrm{Zn(OH)}_3^-$, is the rate determining step. Once the solubility of zincate, $\mathrm{Zn(OH)}_4^{2-}$, is exceeded, zinc hydroxide [20427-58-1], $\mathrm{Zn(OH)_2}$, precipitates. The crystal form that falls out of solution depends on the concentration of the alkali.

7. Experimental Techniques

In the thermodynamic treatment of electrode potentials, the assumption was made that the reactions were reversible, which implies that the reactions occur infinitely slowly. This is never the case in practice. When a battery delivers current, the electrode reactions depart from reversible behavior and the battery voltage decreases from its open circuit or equilibrium voltage E. Thus the voltage during battery use or discharge E' is lower than the voltage measured under open circuit or reversible conditions E by a quantity called the polarization η.

$$\eta = E' - E \tag{49}$$

Likewise, the battery voltage is increased from its open circuit voltage on charge.

Three sources for the departure of battery operation from equilibrium voltage are activation, concentration, and ohmic polarizations. The regions controlled by each of these change as the battery is discharged. *Activation polarization* arises from a kinetic hinderance in one or more of the detailed reaction processes. Slow or rate-limiting steps of the reaction mechanism may occur in the charge-transfer process or in the chemical steps preceding or following the charge-transfer process. An activation barrier and an activation energy characterize these processes. On initiation or cessation of current flow, activation polarization generally builds up or decays in an exponential manner. *Concentration polarization* is associated with the decrease in availability of reacting species at the reaction site in the electrode–solution interface. Changes in concentration occur when the transport rate of reactants and/or products is slower than the rate of reaction. On initiation or cessation of current flow, the concentration polarization builds up or decays in a complex manner and is slower to recover than either activation and ohmic polarization. *Ohmic polarization* arises from the electrical resistances of the electrolyte, current collectors, the active mass, the conductive additives, and the contact of the collector to the active mass. It may also be associated with a resistive film formation on the electrode surface. Ohmic polarization follows Ohm's law. On cessation of current flow, the ohmic polarization disappears instantaneously.

A variety of experimental techniques are used to study electrochemical and battery reactions (37,45–47). The direct measurement of the instantaneous current–voltage characteristics or power curve, and the discharge curve at various discharge rates, are the two most common techniques. Indeed, the discharge performance of a typical battery is characterized by these curves as depicted in Figure 5. The characteristics of the power curve varies, depending on the state of charge of the battery.

The impedance behavior of a battery can reveal a significant amount of information about battery operation characteristics (38,48). The impedance of an electrode or battery is given by

$$Z = R + jX \tag{50}$$

where $X = \omega L - 1/(\omega C)$, $j = \sqrt{-1}$, ω is the angular frequency ($2\pi f$), L the inductance, and C is the capacitance. Each of the characteristic polarizations has a distinctive impedance behavior. A schematic of a battery circuit, and the corresponding Argand diagram, illustrating the behavior of the simple processes, are shown in Figure 6. In ideal behavior, activation processes exhibit a semicircular behavior with frequency that is characteristic of relaxation processes;

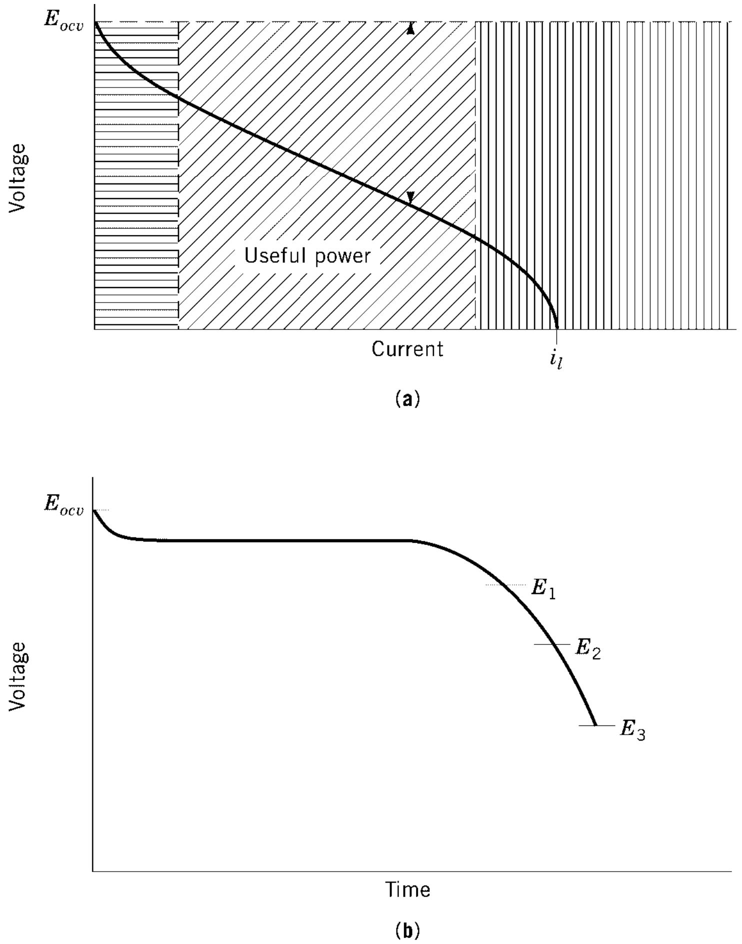

Fig. 5. Discharge behavior of a battery where E_{ocv} is the open circuit voltage; (**a**) current–potential or power curve showing activation, ohmic, and concentration polarization regions where the double headed arrow represents polarization loss and (**b**) voltage–time profile depicting different end point voltages for the discharge.

concentration processes exhibit a 45° behavior characteristic of diffusion processes; and ohmic polarizations are independent of frequency. Battery electrodes have large surface areas and, therefore, exhibit large capacitances. It is common for larger cells to have a capacitance of farads and a resistance of milliohms in measurements of battery impedances.

8. Practical Battery Systems

Most battery electrodes are porous structures in which an interconnected matrix of solid particles, consisting of both nonconductive and electronically conductive materials, is filled with electrolyte. When the active mass is nonconducting,

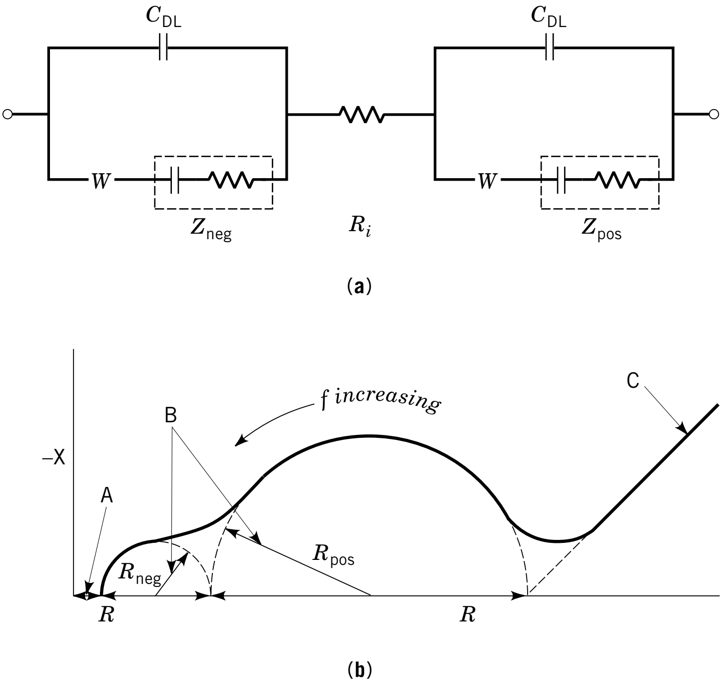

Fig. 6. (**a**) Simple battery circuit diagram where C_{DL} represents the capacitance of the electrical double layer at the electrode–solution interface, Z_{meg} and Z_{pos} are the inpedance associated with the electrode reaction processes at the anode and cathode respectively, *W* depicts the Warburg impedance for diffusion processes, and R_i is internal resistance. (**b**) The corresponding Argand diagram of the behavior of impedance with frequency, *f*, for an idealized battery system, where the characteristic behavior of A, ohmic; B, activation; and C, diffusion or concentration (Warburg behavior) processes are shown. The parameter *X* is as defined in equation 50.

conductive materials, usually carbon or metallic powders, are added to provide electronic contact to the active mass. The solids occupy 60–80% of the volume of a typical porous battery electrode. Most battery electrode structures do not have a well-defined planar surface but have a complex surface extending throughout the volume of the porous electrode. Macroscopically, the porous electrode behaves as a homogeneous unit

When a battery produces current, the sites of current production are not uniformly distributed on the electrodes (48). The nonuniform current distribution lowers the expected performance from a battery system and causes excessive heat evolution and low utilization of active materials. Two types of current distribution, primary and secondary, can be distinguished. The primary distribution is related to the current production based on the geometric surface area of the battery construction. Secondary current distribution is related to current production sites inside the porous electrode itself. Most practical battery constructions have nonuniform current distribution across the surface of the electrodes. This primary current distribution is governed by geometric factors such as height (or length) of the electrodes, the distance between the electrodes, the resistance of the anode and cathode structures, by the resistance of the electrolyte, and by the polarization resistance or hinderance of the electrode reaction processes.

Cell geometry, such as tab/terminal positioning and battery configuration, strongly influence primary current distribution. The monopolar construction is most common. Several electrodes of the same polarity may be connected in parallel to increase capacity. The current production concentrates near the tab connections unless special care is exercised in designing the current collector. Bipolar construction, wherein the terminal or collector of one cell serves as the anode and cathode of the next cell in pile formation, leads to greatly improved uniformity of current distribution. Several representations are available to calculate the current distribution across the geometric electrode surface (49–51).

Whereas, current producing reactions occur at the electrode surface, they also occur at considerable depth below the surface in porous electrodes. Porous electrodes offer enhanced performance through increased surface area for the electrode reaction and through increased mass-transfer rates from shorter diffusion path lengths. The key parameters in determining the reaction distribution include the ratio of the volume conductivity of the electrolyte to the volume conductivity of the electrode matrix, the exchange current, the diffusion characteristics of reactants and products, and the total current flow. The porosity, pore size, and tortuosity of the electrode all play a role. Figure 7 illustrates the reaction distribution in porous electrodes. The location of the reaction sites is seen to be strongly dependent on the characteristics of the electrode structure and reactions.

The effectiveness of a porous electrode over a plane surface electrode is given by the product of the active surface area S in cm^2/mL and the penetration depth L_P of the reaction process into the porous electrode.

$$\text{Effectiveness} = SL_P \tag{51}$$

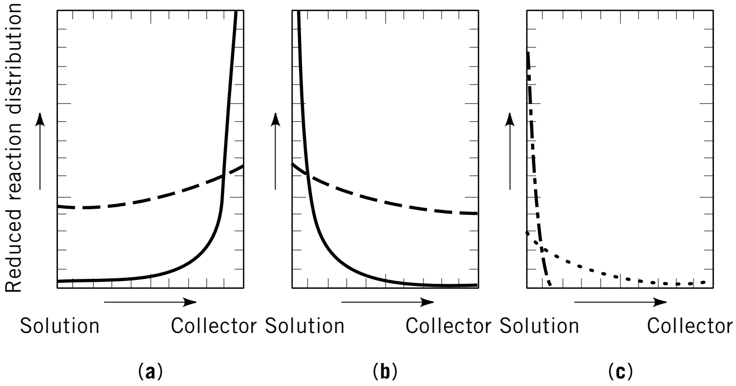

Fig. 7. Representation of the current distribution in porous electrodes showing the effect of conductivities of the electrolyte and electrodes where for (**a**) $K_{\text{electrolyte}} \ll K_{\text{matrix}}$ and (**b**) $K_{\text{matrix}} \gg K_{\text{electrolyte}}$ (52) (———) represents low current and (–) high current; and for (**c**) the effect of exchange current (53) where (•••) represents low i_0 and (— – —) high i_0.

An effectiveness value >1 indicates that the porous electrode is more effective than an electrode of the same geometric surface area, and that the reaction extends into the porous electrode structure.

Mathematical formulations, based on models of primary and secondary battery systems, permit rapid optimization in the design of new battery configurations. Models to describe and predict porous electrode performance in the lead–acid battery system have been developed (54–56) and used in industry to speed the development of new battery configurations giving superior performance. The high rate performance of the present starting, lighting, and ignition (SLI) automotive batteries have evolved directly from coupling collector designs with the porous electrode compositions identified from modeling studies. Modeling has proven useful in primary as well as rechargeable as well as in the development of new battery systems as well (57,58).

In practice, the Peukert equation, equation 52, finds wide use in reporting and comparing battery performance (59).

$$It^n = \text{constant} \tag{52}$$

where I is the current, t the time to a given discharge voltage, and n is a constant. If the system is reversible, $n = 1$. However, because battery systems have limitations in reaction rate, diffusion, and internal resistance, $n > 1$ for most practical systems. Figure 8 shows the Peukert curve constructed from the performance of a given battery to different cutoff voltages. Other equations for describing and predicting battery performance have also been developed (60,61).

The positive electrode in a battery system is most often a metal oxide, but it may also be a metal sulfide or halide. Generally, these materials are relatively poor electrical conductors and exhibit extremely high ohmic polarizations (impedances) if not combined with supporting electronic conductors such as graphite

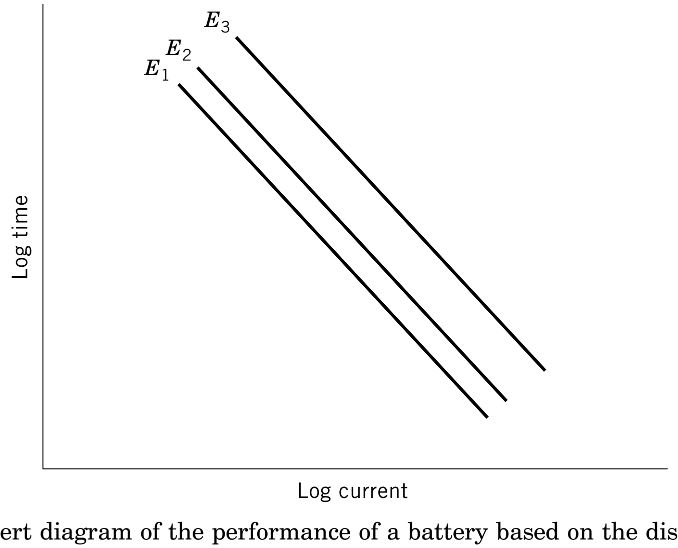

Fig. 8. Peukert diagram of the performance of a battery based on the discharge curves from Figure 5**b**, where $E_1 > E_2 > E_3$.

[7782-42-5], lead [7439-92-1], silver [7440-22-4], copper [7440-50-8], or nickel [7440-02-0] in the form of powder, rod, mesh, wire, grid, or other configurations. In almost all cases, the negative electrode is a metallic element of sufficient conductivity to require only minimal supporting conductive structures. Exceptions are the oxygen (air, positive) and hydrogen gas (negative) electrodes that require a substantial conductive, catalytically active, surface support that also serves as current collector.

Although there are a multitude of chemical reactions that can store and release energy, only a few have the characteristics requisite for use in commercial batteries. A set of criteria can be established to characterize reactions suitable for battery development(62,63). The principal features necessary for battery reactions include (*1*) Mechanical and chemical stability, ie, the reactants or active masses and cell components must be stable over time (5 years or more) in the operating environment and must reform in their original condition on recharge; (*2*) energy content, ie, the reactants must have sufficient energy content to provide a useful voltage and current level; (*3*) power density, ie, the reactants must be capable of reacting at rates sufficient to deliver useful rates of electricity; (*4*) temperature range, ie, the reactants must be able to maintain energy, power, and stability over a normal operating environment; (*5*) safety, ie, the battery must be safe in the normal operating environment as well as

Table 3. **Specialty Batteries: Military, Medical**

			Nominal		
Common name	Cell reaction	Nominal voltage	Wh/l	Wh/l	Comments
thionyl chloride	$Li + 2\ SOCl_2 = 4\ LiCl + 2\ S + SO_2$	3.6	1000	550	oil well logging
lithium sulfur dioxide	$2\ Li + 2\ SO_2 = Li_2S_2O_4$	2.8	425	330	military radios
lithium iron sulfide	$2\ Li + FeS = Li_2S + Fe$	1.8	40	120	military fuse battery excellent high rate 450°C operation
lithium iodine	$2\ Li + I_2 = 2\ LiI$	2.8	1000	300	heart pacers high energy storage
lithium SVO	$3.5\ Li + AgV_2O_{5.5} = Li_{3.5}\ AgV_2O_{5.5}$	3.2	780	270	heart defibrilators excellent pulse capability
seawater	$Mg + 2\ AgCl = MgCl_2 + 2\ Ag$	1.5	360	150	sonobouys weather balloons
nickel hydrogen	$H_2 + 2\ NiOOH = 2\ Ni(OH)_2$	1.2	90	60	long cycle life spacecraft power
silver zinc	$Zn + AgO = ZnO + Ag$	1.8	180	90	rechargeable good high rate performance limited cycle life

under mild abusive conditions; and (*6*) cost, ie, the reactants and the materials of construction should be inexpensive and in good supply as well as manufacturing employing high speed automated production processes. Figures 9 and 10 contain characteristics of large-scale commercial primary and secondary battery systems. The alkaline $Zn-MnO_2$ battery sets the standard for primary battery systems. This battery was first introduced commercially in 1958 and replaced the carbon–zinc battery as the principal primary battery system in ~1985. Lithium batteries were first developed in the early 1970s for military applications and the commercial market began to develop in the late 1970s, largely in Japan. They now power most watches and cameras. The lead–acid battery dominates the rechargeable battery market for automotive and stationary energy storage applications: sales of lead–acid batteries account for over 64% of the rechargeable battery market. The lithium-ion and nickel hetal hydride systems have shown high growth rates based on portable electronic devices such as cellular telephone and notebook applications. Table 3 contains performance parameters for specialty batteries and Table 4 describes promising rechargeable battery systems in various stages of research and commercial development. Table 5 gives the theoretical energy content of selected high energy systems that are under consideration for use in electric vehicle propulsion and other applications where these high energy battery systems are required. Several of the systems are more energetic than gasoline. They also are significantly greater than for any commercial rechargeable battery system.

Table 4. **Battery Systems in Various Stages of Research and Development and Early Stages of Commercialization**

			Nominal		
Common name	Cell reaction	Nominal voltage	Wh/l	Wh/l	Comments
zinc-bromine	$Zn + Br_2 = ZnBr_2$	1.6	95	60	low cost, high rate capability limited cycle life
zinc air	$2\,Zn + O_2 = 2\,ZnO$	1.4	150	180	electrically or mechaniclly rechargeable system
sodium-sulfur	$2\,Na + 3\,S = Na_2S_3$	2.1	120	160	solid-Al_2O_3 electrolyte operates at high temperatures
aluminum-air	$4\,Al + 3\,O_2 + 2\,H_2O = 2\,Al_2O_3(H_2O)$	1.6	360	250	mechanically rechargeable
“super iron”	$2\,BaFeO_4 + 3\,Zn = Fe_2O_3 + ZnO + 2\,BaZnO_2$	1.7	NA	319	primary or rechargeable possible lithium system
lithium polymer	$8\,Li + V_6O_{13} = Li_8V_6O_{13}$	2.4	333	420	solid polymer electrolyte
ultracapacitor	electrical double layer charge and discharge	2.5	12	12	nonaqueous electrolyte excellent pulse capability

Table 5. **Theoretical High Energy Systems**

System/reaction	Cell voltage, V	Wh/kg
$2\,Li + H_2O_2 = 2\,LiOH$	3.98	4400
$4\,Li + O_2 + 2\,H_2O = 4\,LiOH$	4.47	3240
$2\,Mg + O_2 + 2\,H_2O = 2\,Mg(OH)_2$	3.09	2850
$4\,Al + 3\,O_2 + 2\,H_2O = 2\,Al_2O_3{\cdot}2\,H_2O$	2.7	2791
$2\,Li + Cl_2 = 2\,LiCl$	3.95	2510
gasoline (octane) + $12.5\,O_2 = 8\,CO_2 + 9\,H_2O$		2300
$2\,H_2 + O_2 = 2\,H_2O$	1.23	1940

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