What Are Batteries, Fuel Cells, and Supercapacitors?

Contents

1. Introduction

1.1. Batteries versus Fuel Cells versus Electrochemical Capacitors

Energy consumption/production that rely on the combustion of fossil fuels is forecast to have a severe future impact on world economics and ecology. Electrochemical energy production is under serious consideration as an alternative energy/power source, as long as this energy consumption is designed to be more sustainable and more environmentally friendly. Systems for electrochemical energy storage and conversion include batteries, fuel cells, and electrochemical capacitors (ECs). Although the energy storage and conversion mechanisms are different, there are "electrochemical similarities" of these three systems. Common features are that the energy-providing processes take place at the phase boundary of the electrode/electrolyte interface and that electron and ion transport are separated. Figures 1 and 2 show the basic operation mechanisms of the three systems. Note that batteries, fuel cells, and supercapacitors all consist of two electrodes in contact with an electrolyte solution. The requirements on electron and ion conduction in electrodes and the electrolyte are given in Figure 1 and are valid for all three systems.

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In batteries and fuel cells, electrical energy is generated by conversion of chemical energy via redox reactions at the anode and cathode. As reactions at the anode usually take place at lower electrode potentials than at the cathode, the terms negative and positive electrode (indicated as minus and plus poles) are used. The more negative electrode is designated the anode, whereas the cathode is the more positive one. The difference between batteries and fuel cells is related to the locations of energy storage and conversion. Batteries are closed systems, with the anode and cathode being the charge-transfer medium and taking an active role in the redox
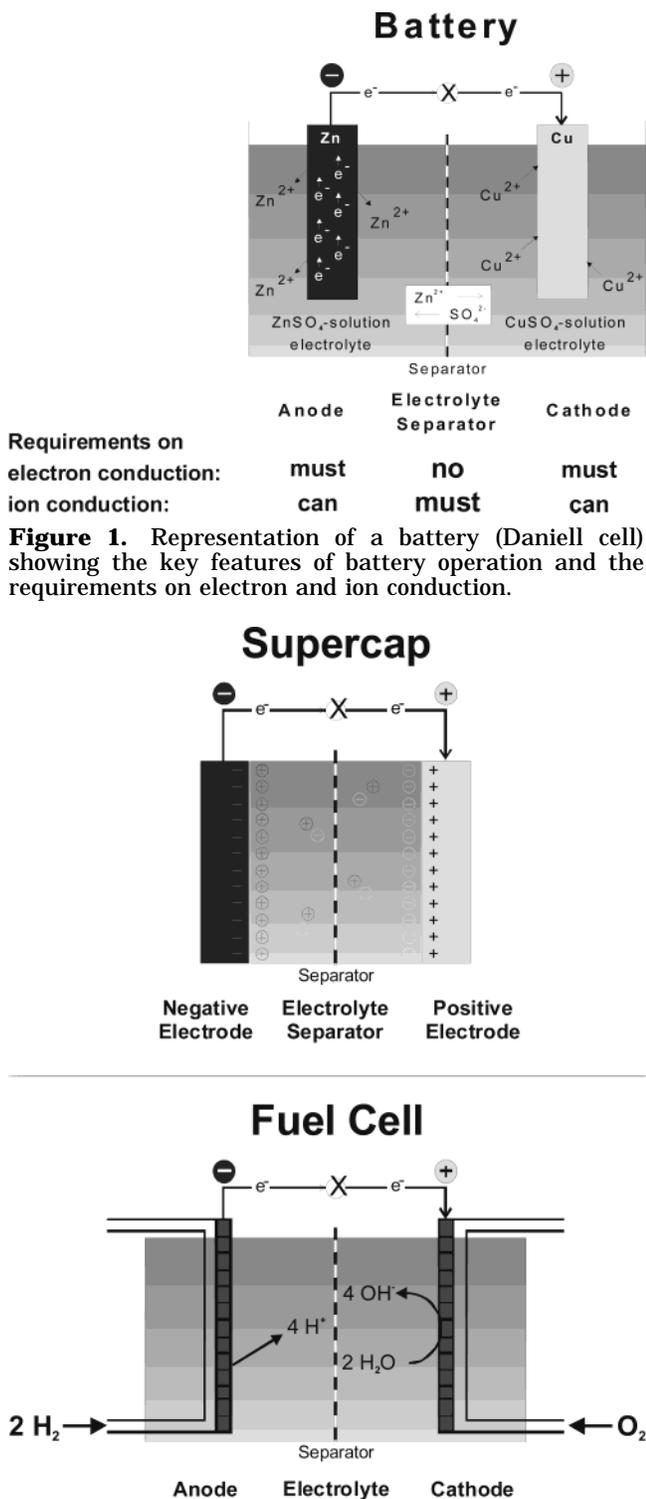
Battery

Figure 1. Representation of a battery (Daniell cell) showing the key features of battery operation and the requirements on electron and ion conduction.

Supercap

Fuel Cell

Figure 2. Representation of (A, top) an electrochemical capacitor (supercapacitor), illustrating the energy storage in the electric double layers at the electrode−electrolyte interfaces, and (B, bottom) a fuel cell showing the continuous supply of reactants (hydrogen at the anode and oxygen at the cathode) and redox reactions in the cell.

reaction as "active masses". In other words, energy storage and conversion occur in the same compartment. Fuel cells are open systems where the anode and cathode are just charge-transfer media and the active masses undergoing the redox reaction are delivered from outside the cell, either from the environment, for example, oxygen from air, or from

a tank, for example, fuels such as hydrogen and hydrocarbons. Energy storage (in the tank) and energy conversion (in the fuel cell) are thus locally separated.[1]

In electrochemical capacitors (or supercapacitors), energy may not be delivered via redox reactions and, thus the use of the terms anode and cathode may not be appropriate but are in common usage. By orientation of electrolyte ions at the electrolyte/electrolyte interface, so-called electrical double layers (EDLs) are formed and released, which results in a parallel movement of electrons in the external wire, that is, in the energy-delivering process.

In comparison to supercapacitors and fuel cells, batteries have found by far the most application markets and have an established market position. Whereas supercapacitors have found niche markets as memory protection in several electronic devices, fuel cells are basically still in the development stage and are searching to find a "killer application" that allows their penetration into the market. Fuel cells established their usefulness in space applications with the advent of the Gemini and Apollo space programs. The most promising future markets for fuel cells and supercapacitors are in the same application sector as batteries. In other words, supercapacitor and fuel cell development aim to compete with, or even to replace, batteries in several application areas. Thus, fuel cells, which originally were intended to replace combustion engines and combustion power sources due to possible higher energy conversion efficiencies and lower environmental impacts, are now under development to replace batteries to power cellular telephones and notebook computers and for stationary energy storage. The motivation for fuel cells to enter the battery market is simple. Fuel cells cannot compete today with combustion engines and gas/steam turbines because of much higher costs, inferior power and energy performance, and insufficient durability and lifetime. With operation times of typically <3000 h and, at least to an order of magnitude, similar costs, batteries are less strong competitors for fuel cells.

The terms "specific energy" [expressed in watt-hours per kilogram (Wh/kg)] and "energy density" [in watt-hours per liter (Wh/L)] are used to compare the energy contents of a system, whereas the rate capability is expressed as "specific power" (in W/kg) and "power density" (in W/L). Alternatively, the attributes "gravimetric" (per kilogram) and "volumetric" (per liter) are used. To compare the power and energy capabilities, a representation known as the Ragone plot or diagram has been developed. A simplified Ragone plot (Figure 3) discloses that fuel cells can be considered to be high-energy systems, whereas supercapacitors are considered to be high-power systems. Batteries have intermediate power and energy characteristics. There is some overlap in energy and power of supercapacitors, or fuel cells, with batteries. Indeed, batteries with thin film

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[1] Strictly speaking, a single electrochemical power system is denoted a cell or element, whereas a series or parallel connection of cells is named a battery. The literature is confusing, as the terms fuel CELL and BATTERY are used independent of the number of cells described.
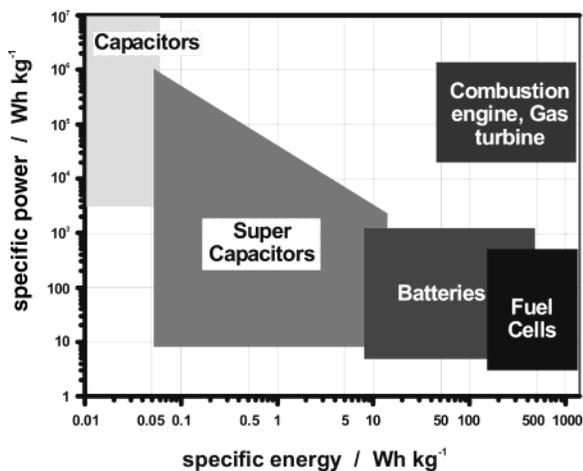
Figure 3. Simplified Ragone plot of the energy storage domains for the various electrochemical energy conversion systems compared to an internal combustion engine and turbines and conventional capacitors.
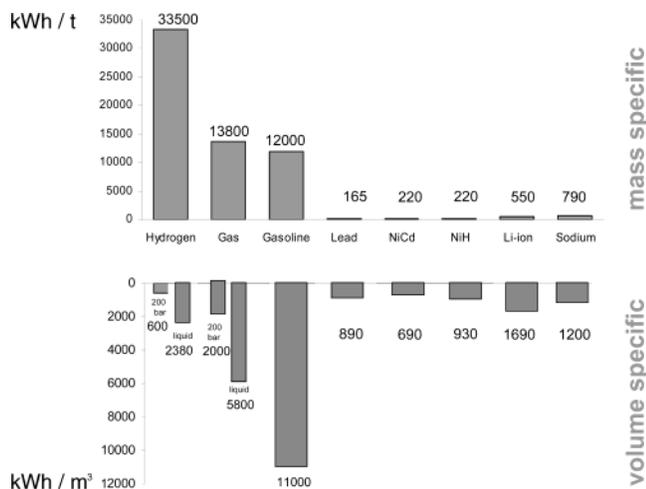

Figure 4. Theoretical specific energies [(kW h)/tonne] and energy densities [(kW h)/m³] of various rechargeable battery systems compared to fuels, such as gasoline, natural gas, and hydrogen.

electrodes exhibit power characteristics similar to those of supercapacitors. Moreover, there are also hybrids such as metal/air batteries (or, in other words, metal/air fuel cells), which contain a battery electrode (metal anode) and a fuel cell electrode (air cathode). Finally, Figure 3 also shows that no single electrochemical power source can match the characteristics of the internal combustion engine. High power *and* high energy (and thus a competitive behavior in comparison to combustion engines and turbines) can best be achieved when the available electrochemical power systems are combined. In such hybrid electrochemical power schemes, batteries and/ or supercapacitors would provide high power and the fuel cells would deliver high energy.

Figure 4 shows the theoretical specific energies [(kW h)/t] and energy densities [(kW h)/m³)] of various rechargeable battery systems in comparison to fuels, such as gasoline, natural gas, and hydrogen. The inferiority of batteries is evident. Figure 5, showing driving ranges of battery-powered cars in comparison to a cars powered by a modern combustion engine, gives an impressive example of why fuel
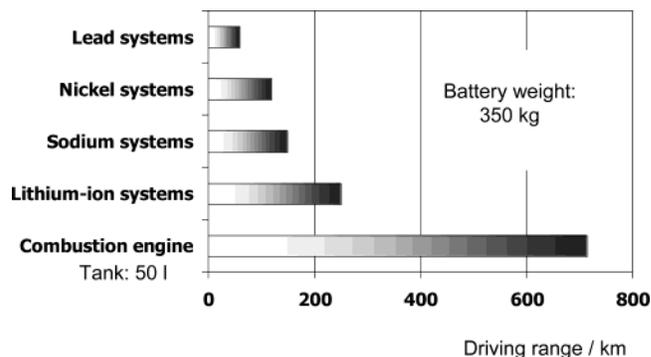

Figure 5. Comparison of the driving ranges for a vehicle powered by various battery systems or a gasoline-powered combustion engine.

cells, and not batteries, are considered for replacement of combustion engines. The theoretical values in Figure 4 are an indication for the maximum energy content of certain chemistries. However, the practical values differ and are significantly lower than the theoretical values. As a rule of thumb, the practical energy content of a rechargeable battery is 25% of its theoretical value, whereas a primary battery system can yield >50% of its theoretical value in delivered energy. In the future, fuel cells might be able to convert the used fuels into electrical energy with efficiencies of >70%. The difference between the theoretical and practical energy storage capabilities is related to several factors, including (1) inert parts of the system such as conductive diluents, current collectors, containers, etc., that are necessary for its operation, (2) internal resistances within the electrodes and electrolyte and between other cell/battery components, resulting in internal losses, and (3) limited utilization of the active masses, as, for example, parts of the fuel in a fuel cell leave the cell without reaction or as, for example, passivation of electrodes makes them (partially) electrochemically inactive. However, as batteries and fuel cells are not subject to the Carnot cycle limitations, they may operate with much higher efficiencies than combustion engines and related devices.

1.2. Definitions

The following definitions are used during the course of discussions on batteries, fuel cells, and electrochemical capacitors.

A *battery* is one or more electrically connected electrochemical cells having terminals/contacts to supply electrical energy.

A *primary battery* is a cell, or group of cells, for the generation of electrical energy intended to be used until exhausted and then discarded. Primary batteries are assembled in the charged state; discharge is the primary process during operation.

A *secondary battery* is a cell or group of cells for the generation of electrical 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. Other terms for this type of battery are rechargeable battery or accumulator. As secondary batteries are ususally assembled in the

discharged state, they have to be charged first before they can undergo discharge in a secondary process.

A *specialty battery* is a primary battery that is in limited production for a specific end-use. In this paper specialty batteries will not be particularly addressed.

The *anode* is the negative electrode of a cell associated with oxidative chemical reactions that release electrons into the external circuit.

The *cathode* is the positive electrode of a cell associated with reductive chemical reactions that gain electrons from the external circuit.

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

An *electrolyte* is a material that provides pure ionic conductivity between the positive and negative electrodes of a cell.

A *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 the ions and inert in the battery environment.

A *fuel cell* is an electrochemical conversion device that has a continuous supply of fuel such as hydrogen, natural gas, or methanol and an oxidant such as oxygen, air, or hydrogen peroxide. It can have auxiliary parts to feed the device with reactants as well as a battery to supply energy for start-up.

An *electrochemical capacitor* is a device that stores electrical energy in the electrical double layer that forms at the interface between an electrolytic solution and an electronic conductor. The term applies to charged carbon−carbon systems as well as carbon−battery electrode and conducting polymer electrode combinations sometimes called ultracapacitors, super-capacitors, or hybrid capacitors.

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 electrical 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 resistance or *impedance* is the resistance or impedance that a battery or cell offers to current flow.

The *Faraday constant*, *F*, is the amount of charge that transfers when one equivalent weight of active mass reacts, 96 485.3 C/g-equiv, 26.8015 Ah/g-equiv.

Thermal runaway is an event that occurs when the battery electrode's reaction with the electrolyte becomes self-sustaining and the reactions enter an autocatalytic mode. This situation is responsible for many safety incidents and fires associated with battery operations.

1.3. Thermodynamics

The energy storage and power characteristics of electrochemical energy conversion systems follow directly from the thermodynamic and kinetic formulations for chemical reactions as adapted to electrochemical reactions. First, the basic thermodynamic considerations are treated. The basic thermodynamic equations for a reversible electrochemical transformation are given as

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

and

$$\Delta G° = \Delta H° - T\Delta S° \qquad (2)$$

where ΔG is the Gibbs free energy, or the energy of a reaction available (= free) for useful work, ΔH is the enthalpy, or the energy released by the reaction, ΔS is the entropt, and T is the absolute temperature, with $T\Delta S$ being the heat associated with the organization/disorganization of materials. 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. The degree symbol is used to indicate that the value of the function is for the material in the standard state at 25 °C and unit activity.

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

$$\Delta G = -nFE \qquad (3)$$

and

$$\Delta G° = -nFE° \qquad (4)$$

where n is the number of electrons transferred per mole of reactants, F is the Faraday constant, being equal to the charge of 1 equiv of electrons, and E is the voltage of the cell with the specific chemical reaction; in other words, E is the electromotive force (emf) of the cell reaction. The voltage of the cell is unique for each reaction couple. The amount of electricity produced, nF, is determined by the total amount of materials available for reaction and can be thought of as a capacity factor; the cell voltage can be considered to be an intensity factor. The usual thermodynamic calculations on the effect of temperature, pressure, etc., apply directly to electrochemical reactions. Spontaneous processes have a negative free energy and a positive emf with the reaction written in a reversible fashion, which goes in the forward direction. The van't Hoff isotherm identifies the free energy relationship for bulk chemical reactions as

$$\Delta G = \Delta G° + RT\ln(A_P/A_R) \qquad (5)$$

where R is the gas constant, T the absolute temperature, A_P the activity product of the products and A_R the activity product of the reactants. Combining eqs 4 and 5 with the van't Hoff isotherm, we have the

Nernst equation for electrochemical reactions:

$$E = E^\circ + (RT/nF) \ln(A_P/A_R) \qquad (6)$$

Faraday's laws, as summarized in eq 7, give the direct relationship between the amount of reaction and the current flow. There are no known exceptions to Faraday's laws.

$$g = \frac{It(MW)}{nF} \qquad (7)$$

g is the grams of material transformed, I is the current flow (amps), t is the time of current flow (seconds, hours), MW is the molecular or atomic weight of the material being transformed, and n is the number of electrons in the reaction.

Assuming thermodynamic reversibility[2] of the cell reaction and with the help of eqs 1 and 3, we can obtain the reversible heat effect.

$$\Delta G = -nFE = \Delta H - T\Delta S \qquad (8)$$
$$= \Delta H - nFT(dE/dT) \qquad (9)$$

By measuring the cell voltage as a function of temperature, the various thermodynamic quantities for the materials in an electrode reaction can be determined experimentally. If dE/dT is positive, the cells will heat on charge and cool on discharge. Lead acid is an example of a negative dE/dT, where the cells cool on charge and heat on discharge. Ni–Cd is an example of a positive dE/dT, where the cells heat on charge and cool on discharge. Heating and cooling of the cell can proceed with heat exchange with the environment. In general, the entropic heat is negligibly small compared to the irreversible heat released, q, when a cell is in operation. Equation 10 describes total heat release, including the reversible thermodynamic heat release along with the irreversible joule heat from operation of the cell in an irreversible manner, during charge or discharge at finite current/rate. Irreversible behavior manifests itself as a departure from the equilibrium or thermodynamic voltage. In this situation, the heat, q, given off by the system is expressed by an equation in which E_T is the practical cell terminal voltage and E_{OCV} is the voltage of the cell on open circuit.

$$q = T\Delta S + I(E_{OCV} - E_T) \qquad (10)$$

$$q = \text{heat given off by the system} \qquad (11)$$

The total heat released during cell discharge is the sum of the thermodynamic entropy contribution plus the irreversible contribution. This heat is released inside the battery at the reaction site on the surface of the electrode structures. Heat release is not a

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[2] A process is thermodynamically reversible when an infinitesimal reversal in a driving force causes the process to reverse its direction. Since all actual processes occur at finite rates, they cannot proceed with strict thermodynamic reversibility and thus additional nonreversible effects have to be regarded. In this case, under practical operation conditions, voltage losses at internal resistances in the cell (these kinetic effects are discussed below) lead to the irreversible heat production (so-called Joule heat) in addition to the thermodynamic reversible heat effect.

problem for low-rate applications; however, high-rate batteries must make provisions for heat dissipation. Failure to accommodate/dissipate heat properly can lead to thermal runaway and other catastrophic situations.

1.4. Kinetics

Thermodynamics describe reactions at equilibrium and the maximum energy release for a given reaction. Compared to the equilibrium voltage (= open ciruit voltage, E_{OCV}), the voltage drops off (= "electrode polarization" or "overvoltage") when current is drawn from the battery because of kinetic limitations of reactions and of other processes must occur to produce current flow during operation. Electrochemical reaction kinetics follow the same general considerations as those for bulk chemical reactions. However, electrode kinetics differs from chemical kinetics in two important aspects: (1) the influence of the potential drop in the electrical double layer at an electrode interface as it directly affects the activated comples and (2) the fact that reactions at electrode interfaces proceed in a two-dimensional, not three-dimensional, manner. The detailed mechanism of battery electrode reactions often involves a series of physical, chemical, and electrochemical steps, including charge-transfer and charge transport reactions. The rates of these individual steps determine the kinetics of the electrode and, thus, of the cell/battery. Basically, three different kinetics effects for polarization have to be considered: (1) *activation* polarization is related to the kinetics of the electrochemical redox (or charge-transfer) reactions taking place at the electrode/electrolyte interfaces of anode and cathode; (2) *ohmic* polarization is interconnected to the resistance of individual cell components and to the resistance due to contact problems between the cell components; (3) *concentration* polarization is due to mass transport limitations during cell operation. The polarization, η, is given by

$$\eta = E_{OCV} - E_T \qquad (12)$$

where E_{OCV} is the voltage of the cell at open circuit and E_T is the terminal cell voltage with current, I, flowing.

Activation polarization arises from kinetics hindrances of the charge-transfer reaction taking place at the electrode/electrolyte interface. This type of kinetics is best understood using the absolute reaction rate theory or the transition state theory. In these treatments, the path followed by the reaction proceeds by a route involving an activated complex, where the rate-limiting step is the dissociation of the activated complex. The rate, current flow, i ($I = I/A$ and $I_0 = I_0/A$, where A is the electrode surface area), of a charge-transfer-controlled battery reaction can be given by the Butler–Volmer equation as

$$i = i_0 \exp(\alpha F\eta/RT) - \exp((1 - \alpha)F\eta)/RT \qquad (13)$$

where the exchange current density, $i_0 = k_0FA$ is the exchange current density (k_0 is the reaction rate

constant for the electrode reaction, and A is the activity product of the reactants), η is the polarization or departure (overpotential) from equilibrium ($\eta = E_{OCV} - E_T$), and α is the transfer coefficient, which is best considered as the fraction of the change of overpotential that leads to a change in the rate constant for charge-transfer reaction. The exchange current density is directly related to the reaction rate constant, to the activities of reactants and products, and to the potential drop across the double layer. Reactions with larger i_0 are more reversible and have lower polarization for a given current flow. Electrode reactions having high exchange currents (i_0 in the range of 10^{-2} A/cm^2) at room temperature are favored for use in battery applications. The buildup and decay of the activation polarization are fast and can be identified by the voltage change on current interruption in a time frame of 10^{-2}–10^{-4} s.

The activation polarization follows the Tafel equation derived from eq 13

$$\eta = a - b \log(I/I_0) \tag{14}$$

where a and b are constants.

Ohmic polarization arises from the resistance of the electrolyte, the conductive diluent, and materials of construction of the electrodes, current collectors, terminals, and contact between particles of the active mass and conductive diluent or from a resistive film on the surface of the electrode. Ohmic polarization appears and disappears instantaneously ($\leq 10^{-6}$ s) when current flows and ceases. Under the effect of ohmic resistance, R, there is a linear Ohm's Law relationship between I and η.

$$\eta = IR \tag{15}$$

As the redox reactions proceed, the availability of the active species at the electrode/electrolyte interface changes. Concentration polarization arises from limited mass transport capabilities, for example, limited diffusion of active species to and from the electrode surface to replace the reacted material to sustain the reaction. Diffusion limitations are relatively slow, and the buildup and decay take $\geq 10^{-2}$ s to appear. For limited diffusion the electrolyte solution, the concentration polarization, can be expressed as

$$\eta = (RT/n) \ln(C/C_0) \tag{16}$$

where C is the concentration at the electrode surface and C_0 is the concentration in the bulk of the solution. The movement or transport of reactants from the bulk solution to the reaction site at the electrode interface and vice versa is a common feature of all electrode reactions. Most battery electrodes are porous structures in which an interconnected matrix of small solid particles, consisting of both nonconductive and electronically conductive materials, is filled with electrolyte. Porous electrode structures are used to extend the available surface area and lower the current density for more efficient operation.

1.5. Experimental Techniques

In practical batteries and fuel cells, the influence of the current rate on the cell voltage is controlled
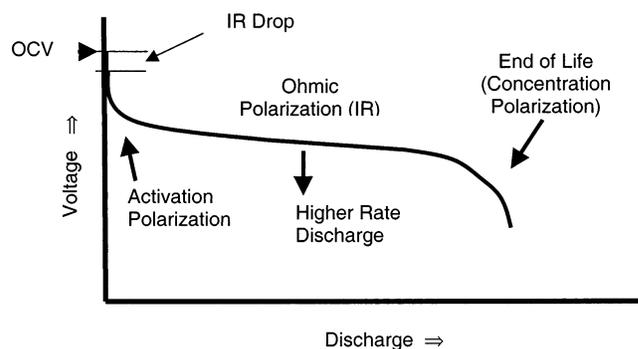

Figure 6. Typical discharge curve of a battery, showing the influence of the various types of polarization.

by all three types of polarization. A variety of experimental techniques are used to study electrochemical and battery reactions. The most common are the direct measurement of the instantaneous current–voltage characteristics on discharge curve shown in Figure 6. This curve can be used to determine the cell capacity, the effect of the dischage–charge rate, and temperature and information on the state of health of the battery.

The impedance behavior of a battery is another common technique that can reveal a significant amount of information about battery operation characteristics. The impedance of an electrode or battery is given by

$$Z = R + j\omega X \tag{17}$$

where $X = \omega L - 1/(\omega C)$, $j = \sqrt{-1}$, and ω is the angular frequency ($2\pi f$); L is the inductance, and C is the capacitance. A schematic of a battery circuit and the corresponding Argand diagram, illustrating the behavior of the simple electrode processes, are shown in Figure 7a. Activation processes exhibit a semicircular behavior with frequency that is characteristic of relaxation processes; concentration processes exhibit a 45° behavior characteristic of diffusion processes often referred to as Warburg behavior; ohmic components are independent of frequency.

Each electrode reaction has a distinctive, characteristic impedance signature. A schematic of a battery circuit and the corresponding Argand diagram, illustrating the behavior of the simple processes, are shown in Figure 7b. In ideal behavior, activation processes exhibit a semicircular behavior with frequency that is characteristic of relaxation processes; concentration processes exhibit a 45° behavior characteristic of diffusion processes, and ohmic polarizations have no capacitive character and are independent of frequency. The frequency of the maximum, f_m, of the semicircle gives the relaxation time, where $\tau = 1/f_m = RC$. Here R is related to the exchange current for the reaction and C is called the polarization capacitance, C_P. Typically, the C_P is of the order of 200 μF/cm, ~10 times larger than the capacitance of the EDL. Some electrochemical capacitors take advantage of this capacitance to improve their performance of the supercapacitors. Battery electrodes have large surface areas and, therefore, exhibit large
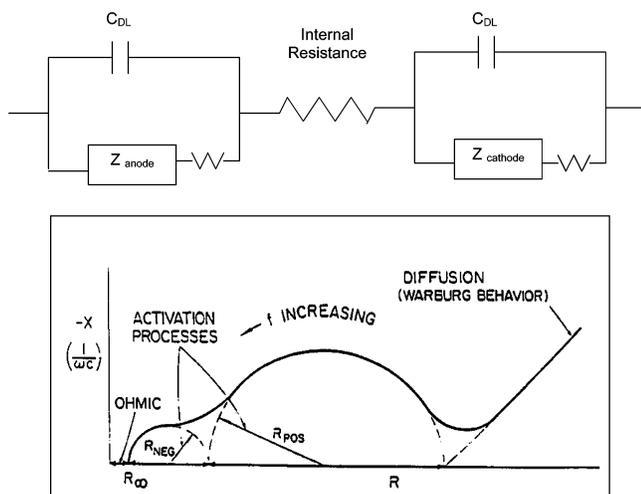
Figure 7. (A, top) Simple battery circuit diagram, where C_{DL} represents the capacitance of the electrical double layer at the electrode−solution interface (cf. discussion of supercapacitors below), W depicts the Warburg impedance for diffusion processes, R_i is the internal resistance, and Z_{anode} and $Z_{cathode}$ are the impedances of the electrode reactions. These are sometimes represented as a series resistance capacitance network with values derived from the Argand diagram. This reaction capacitance can be 10 times the size of the double-layer capacitance. The reaction resistance component of Z is related to the exchange current for the kinetics of the reaction. (B, bottom) Corresponding Argand diagram of the behavior of impedance with frequency, f, for an idealized battery system, where the characteristic behaviors of ohmic, activation, and diffusion or concentration polarizations are depicted.

Figure 8. Primary current distribution on the front surface of the electrodes based on Kirkhof's law calculation for three different cell constructions: (A) Both connections to the cell are at the top. The higher resistance path at the bottom sections of the electrode reduces the current flow and results in a nonuniform current distribution. (B) All paths have equal resistance, and a uniform current distribution results. (C) The bipolar construction has equal resistance from one end to the other.

capacitances. It is common for cells to have a capacitance of farads and a resistance of milliohms.

The experimental techniques described above of charge−discharge and impedance are nondestructive. "Tear-down" analysis or disassembly of spent cells and an examination of the various components using experimental techniques such as Raman microscopy, atomic force microscopy, NMR spectroscopy, transmission electron microscopy, XAS, and the like can be carried out on materials-spent battery electrodes to better understand the phenomena that lead to degradation during use. These techniques provide diagnostic techniques that identify materials properties and materials interactions that limit lifetime, performance, and thermal stabiity. The accelerated rate calorimeter finds use in identifying safety-related situations that lead to thermal runaway and destruction of the battery.

1.6. Current Distribution and Porous Electrodes

Most practical electrodes are a complex composite of powders composed of particles of the active material, a conductive diluent (usually carbon or metal powder), and a polymer binder to hold the mix together and bond the mix to a conductive current collector. Typically, a composite battery electrode has ~30% porosity with a complex surface extending throughout the volume of the porous electrode. This yields a much greater surface area for reaction than the geometric area and lowers polarization. The pores of the electrode structures are filled with electrolyte.
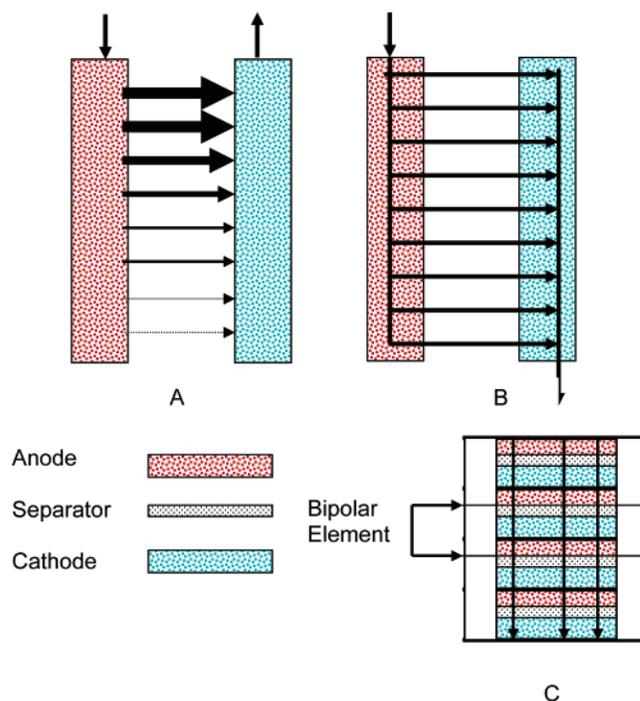
Although the matrix may have a well-defined planar surface, there is a complex reaction surface extending throughout the volume of the porous electrode, and the effective active surface may be many times the geometric surface area. Ideally, when a battery produces current, the sites of current production extend uniformly throughout the electrode structure. A nonuniform current distribution introduces an inefficiency and lowers the expected performance from a battery system. In some cases the negative electrode is a metallic element, such as zinc or lithium metal, of sufficient conductivity to require only minimal supporting conductive structures.

Two types of current distribution, primary and secondary, can be distinguished. The primary distribution is controlled by cell geometry. The placing of the current collectors strongly influences primary current distribution on the geometric surface area of the electrodes. The monopolar construction is most common. The differences in current distribution for top connections and opposite end current collection are shown in Figure 8A,B. With opposite end connections the current distribution is more uniform and results in a more efficient use of the active material. The bipolar construction depicted in Figure 8C gives uniform current distribution wherein the anode terminal or collector of one cell serves as the current collector and cathode of the next cell in pile configuration.

Secondary current distribution is related to current production sites inside the porous electrode itself. The
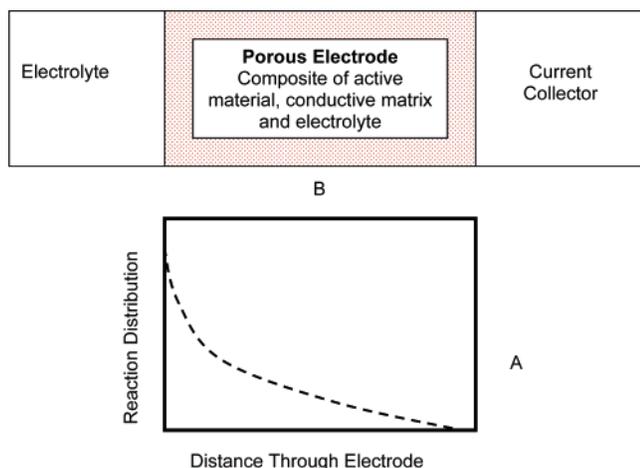
Figure 9. Schematic porous electrode structure: (A) Electrons from the external circuit flow in the current collector which has contact to the conductive matrix in the electrode structure. The redox reaction at the electrode produces electrons that enter the external circuit and flow through the load to the cathode, where the reduction reaction at the cathode accepts the electron from the external circuit and the reduction reaction. The ions in the electrolyte carry the current through the device. (B) The reaction distribution in the porous electrode is shown for the case where the conductivity of the electrode matrix is higher than the conductivity of the electrolyte.

incorporation of porous electrode structures increases the surface area and shortens diffusion path lengths to the reaction site. Current-producing reactions can penetrate into a porous electrode structure to considerable depth below the surface of the electrodes as noted in Figure 9. The location of the reaction site inside a porous electrode is strongly dependent on the characteristics of the electrode structure and reactions themselves. The key parameters include the conductivity of the electrode matrix, electrolyte conductivity, the exchange current, the diffusion characteristics of reactants and products, and the total current flow. In addition, the porosity, pore size, and tortuosity of the electrode play a role. The effectiveness of a porous electrode can be estimated from the active surface area, S, in cm^2/cm^3, and the penetration depth L_P of the reaction process into the porous electrode. Factors that influence the secondary current distribution are the conductivity of the electrolyte and electrode matrix, the exchange current of the reactions, and the thickness of the porous layer. Sophisticated mathematical models to describe and predict porous electrode performance of practical systems have been developed. These formulations based on models of primary and secondary battery systems permit rapid optimization in the design of new battery configurations. The high-rate performance of the present SLI automotive batteries has evolved directly from coupling current collector designs with the porous electrode compositions identified from modeling studies.

Modeling has become an important tool in developing new battery technology as well as for improving the performance of existing commercial systems. Models based on engineering principles of current distribution and fundamental electrochemical reaction parameters can predict the behavior of porous

electrode structures from the older lead acid automotive technology to the newest lithium ion (Li ion) technology.

2. Batteries

2.1. Introduction and Market Aspects

Batteries are self-contained units that store chemical energy and, on demand, convert it directly into electrical energy to power a variety of applications. Batteries are divided into three general classes: primary batteries that are discharged once and discarded; secondary, rechargeable batteries that can be discharged and then restored to their original condition by reversing the current flow through the cell; and specialty batteries that are designed to fulfill a specific purpose. The latter are mainly military and medical batteries that do not find wide commercial use for various reasons of cost, environmental issues, and limited market application. They generally do not require time to start-up. At low drains, up to 95% of the energy is available to do useful work.

advantages	disadvantages
operate over a wide temperature range	low energy content compared to gasoline and other fuels
choice of chemical system and voltage	expensive compared to coal and gasoline
operate in any orientation	no single general purpose system
do not require pumps, filters, etc.	
variable in size	
commonality of cell sizes, worldwide	
can deliver high current pulses	
can choose best battery for a specific purpose (portable, mobile, and stationary applications)	

Success in the battery market depends largely on four factors, noted in Figure 10. The market for batteries in Table 1 is directly related to the applications they serve, such as automobiles, cellular phones, notebook computers, and other portable electronic devices. The growth in any particular segment follows closely the introduction of new devices powered by batteries. The introduction of new materials with higher performance parameters gives the various designers freedom to incorporate new functionality in present products or to create new products to
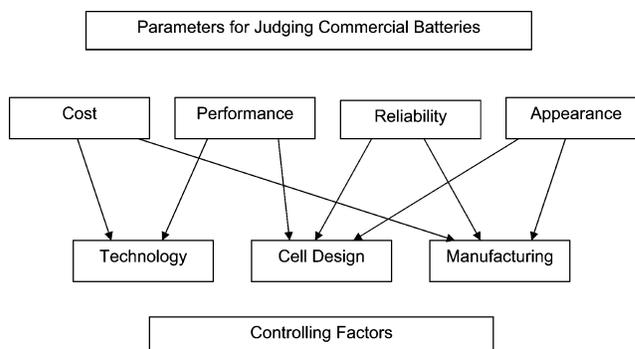

Figure 10. How batteries are judged by users and the factors that control these criteria.

Table 1. Estimated Battery Market in 2003 ($ Millions of Dollars)

system	market size
primary	
carbon−zinc	6500
alkaline	10000
lithium, military, medical, etc.	3400
subtotal	**19900**
secondary	
lead acid	18400
small sealed rechargeable cells	
lithium ion	3500
nickel metal hydride	1800
nickel cadmium	1500
other[a]	3100
subtotal	**28300**
total battery market	**48200**

[a] Large vented and sealed Ni−Cd, Ni−Fe, Ag−Zn, etc.

expand the market scope. Batteries for notebook computers have experienced double-digit growth, whereas the automobile SLI market segment has grown with the gross national product. Batteries can range in size from aspirin tablet (and even smaller) with a few tens of mAh, for in-the-ear hearing aids, to a building with 40 MWh for energy storage and emergency power.

2.2. Battery Operations

Figure 11 depicts the basic elements of a battery. Figure 12 illustrates the operation of a battery, showing the energy levels at the anode (negative) and cathode (positive) poles and the electrolyte expressed in electronvolts. The negative electrode is a good reducing agent (electron donor) such as lithium, zinc, or lead. The positive electrode is an electron acceptor such as lithium cobalt oxide, manganese dioxide, or lead oxide. The electrolyte is a pure ionic conductor that physically separates the anode from the cathode.
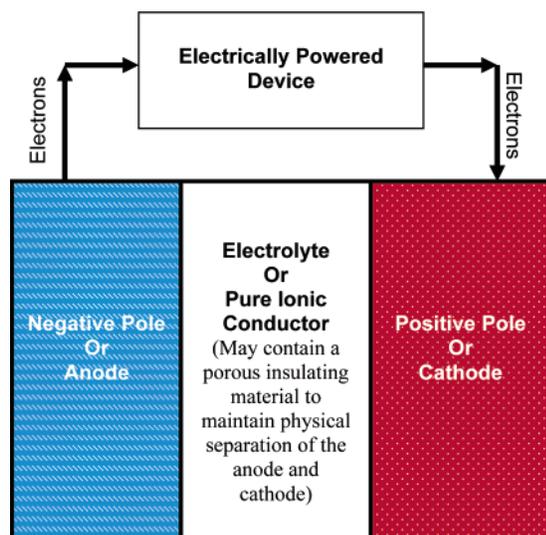
Figure 11. Block diagram of a cell or battery powering a device. If a battery is recharged, the load is replaced with an energy source that imposes a reverse voltage that is larger than the battery voltage and the flow of electrons is reversed.
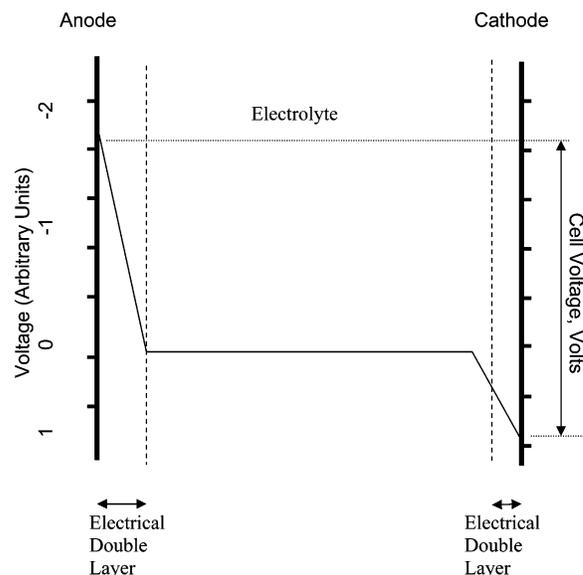
Figure 12. Voltage levels in the various sections of the unit cell of a battery, fuel cell, or electrochemical capacitor. The structure and composition of the electrical double layer differ at the anode and cathode.

In practice, a porous electrically insulating material containing the electrolyte is often placed between the anode and cathode to prevent the anode from directly contacting the cathode. Should the anode and cathode physically touch, the battery will be shorted and its full energy released as heat inside the battery. Electrical conduction in electrolytic solutions follows Ohm's law: $E = IR$.

Battery electrolytes are usually liquid solvent-based and can be subdivided into aqueous, nonaqueous, and solid electrolytes. Aqueous electrolytes are generally salts of strong acids and bases and are completely dissociated in solution into positive and negative ions. The electrolyte provides an ionic conduction path as well as a physical separation of the positive and negative electrodes needed for electrochemical cell operation. Each electrolyte is stable only within certain voltage ranges. Exceeding the electrochemical stability window results in its decomposition. The voltage stability range depends on the electrolyte composition and its purity level. In aqueous systems, conductivities of the order of 1 S/cm are common. The high conductivity of aqueous solvent-based electrolytes is due to their dielectric constants, which favor stable ionic species, and the high solvating power, which favors formation of hydrogen bridge bonds and allows the unique Grotthus conductivity mechanism for protons. Thermodynamically, aqueous electrolytes show an electrochemical stability window of 1.23 V. Kinetic effects may expand the stability limit to ∼2 V.

In the nonaqueous organic solvent-based systems used for lithium batteries, the conductivities are of the order of $10^{-2}-10^{-3}$ S/cm^{-1}. Compared to water, most organic solvents have a lower solvating power and a lower dielectric constant. This favors ion pair formation, even at low salt concentration. Ion pair formation lowers the conductivity as the ions are no longer free and bound to each other. Organic electrolytes show lower conductivities and much higher

Table 2. Common Commercial Battery Systems

common name	nominal voltage	anode	cathode	electrolyte
primary				
Leclanché (carbon−zinc)	1.5	zinc foil	MnO_2 (natural)	aq $ZnCl_2$−NH_4Cl
zinc chloride (carbon−zinc)	1.5	zinc foil	electrolytic MnO_2	aq $ZnCl_2$
alkaline	1.5	zinc powder	electrolytic MnO_2	aq KOH
zinc−air	1.2	zinc powder	carbon (air)	aq KOH
silver−zinc	1.6	zinc powder	Ag_2O	aq KOH
lithium−manganese dioxide	3.0	lithium foil	treated MnO_2	$LiCF_3SO_3$ or $LiClO_4$[a]
lithium−carbon monofluoride	3.0	lithium foil	CFx	$LiCF_3SO_3$ or $LiClO_4$[a]
lithium−iron sulfide	1.6	lithium foil	FeS_2	$LiCF_3SO_3$ and/or $LiClO_4$[a]
rechargeable				
lead acid	2.0	lead	PbO_2	aq H_2SO_4
nickel−cadmium	1.2	cadmium	NiOOH	aq KOH
nickel−metal hydride	1.2	MH	NiOOH	aq KOH
lithium ion	4.0	Li(C)	$LiCoO_2$	$LiPF_6$ in nonaqueous solvents[a]
specialty				
nickel−hydrogen	1.2	H_2 (Pt)	NiOOH	aq KOH
lithium−iodine	2.7	Li	I_2	LiI
lithium−silver−vanadium oxide	3.2	Li	$Ag_2V_4O_{11}$	$LiAsF$[a]
lithium−sulfur dioxide	2.8	Li	SO_2 (C)	SO_2−LiBr
lithium−thionyl chloride	3.6	Li	$SOCl_2$ (C)	$SOCl_2$−$LiAlCl_4$
lithium−iron sulfide (thermal)	1.6	Li	FeS_2	LiCl−LiBr−LiF
magnesium−silver chloride	1.6	Mg	AgCl	seawater

[a] In nonaqueous solvents. Exact composition depends on the manufacturer, usually propylene carbonate−dimethyl ether for primary lithium batteries and ethylene carbonate with linear organic carbonates such as dimethyl carbonate, diethyl carbonate, and ethylmethyl carbonate for lithium ion cells.
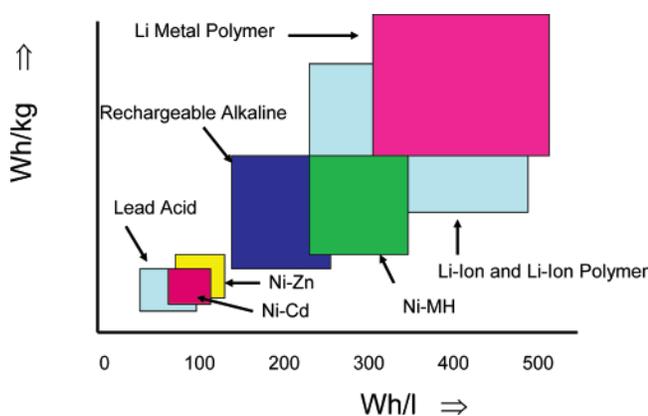

Figure 13. Energy storage capability of common commercial primary battery systems.
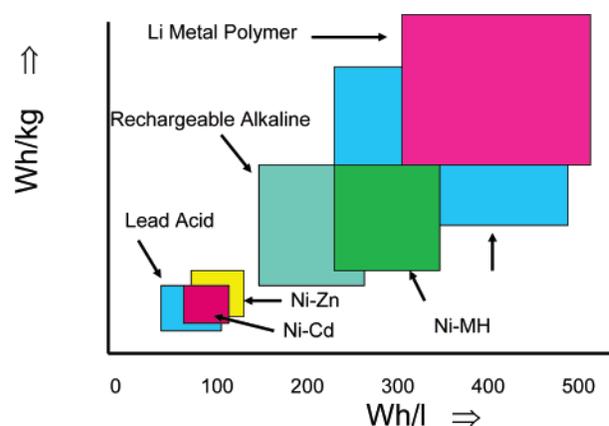

Figure 14. Energy storage capability of common rechargeable battery systems.

viscosities than aqueous electrolytes. Organic solvent-based electrolytes (again with the help of kinetics) are limited to ~4.6 V. Exceeding the voltage limit in the organic electrolytes results in polymerization or decomposition of the solvent system. Solid electrolyte batteries have found limited use as the power source for heart pacemakers and for use in military applications. The basic principles described above apply to fuel cells and electrochemical capacitors as well as to batteries.

2.3. Characteristics of Common Battery Systems

A list of common commercial systems is found in Table 2. A graphical representation of the energy storage capability of common types of primary and secondary batteries is shown in Figures 13 and 14. It is beyond the scope of this paper to discuss all systems in detail. Instead, we want to review the most common electrode mechanisms for discharge and charge depicted in Figure 15.

2.4. Primary Batteries

Figure 15A shows the discharge reaction of a CuS electrode in a Li−CuS cell. During the cell reaction, Cu is displaced by Li and segregates into a distinct solid phase in the cathode. The products of this displacement type of reaction, Li_2S and Cu, are stable, and the reaction cannot be easily reversed. Hence, the electrode reactions cannot be recharged and the cell is considered to be a primary cell, as the discharge reaction is not reversible. The Li electrode in Figure 15B is discharged by oxidation. The formed Li^+ cation is going into solution. The reaction is reversible by redeposition of the lithium. However, like many other metals in batteries, the redeposition of the Li is not smooth, but rough, mossy, and dendritic, which may result in serious safety problems. This is in contrast to the situation with a lead electrode in Figure 15C, which shows a similar solution electrode. Here, the formed Pb^{2+} cation is only slightly soluble in sulfuric acid solution, and $PbSO_4$ precipitates at the reaction site on the elec-
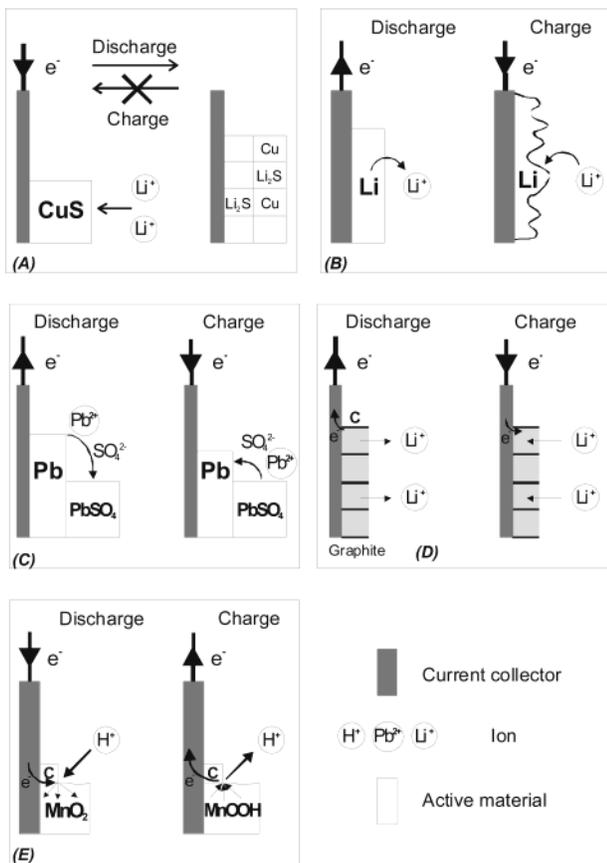
Figure 15. Schematics showing various discharge and charge mechanisms of battery electrodes, which serve as examples of the battery electrode charge/discharge mechanisms discussed in the text.

Figure 16. Two-step discharge curve of a MnO_2 electrode in aqueous solution showing the influence of one- and two-phase discharge reaction mechanisms on the shape of the discharge curve. The different shapes of the discharge curves can be explained with the help of the Gibbs phase rule.

trode surface. This solution−precipitation mechanism is also working during the charge reaction, when $PbSO_4$ dissolves and is retransformed into metallic Pb. Figure 15D shows a typical electrochemical insertion reaction. The term "electrochemical insertion" refers to a solid-state redox reaction involving electrochemical charge transfer, coupled with insertion of mobile guest ions (in this case Li^+ cations) from an electrolyte into the structure of a solid host, which is a mixed, that is, electronic and ionic, conductor (in this case graphite). Unlike displacement type electrodes (Figure 15A) and solution type electrodes (Figure 15B), the insertion electrodes (Figure 15D) have the capability for high reversibility, due to a beneficial combination of structure and shape stability. Many secondary batteries rely on insertion electrodes for the anode and cathode. A prerequisite for a good insertion electrode is electronic and ionic conductivity. However, in those materials with poor electronic conductivity, such as MnO_2, good battery operation is possible. In this case, highly conductive additives such as carbon are incorporated in the electrode matrix, as in Figure 15E. The utilization of the MnO_2 starts at the surface, which is in contact with the conductive additive and continues from this site throughout the bulk of the MnO_2 particle. Most electrodes in batteries follow one of the basic mechanisms discussed in Figure 15.
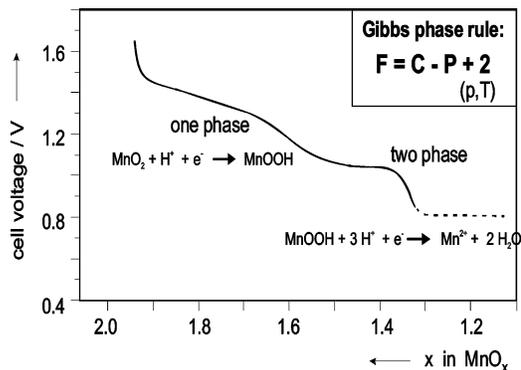
Zinc manganese batteries consist of MnO_2, a proton insertion cathode (cf. Figure 15E), and a Zn anode of the solution type. Depending on the pH of the electrolyte solution, the Zn^{2+} cations dissolve in the electrolyte (similar to the mechanism shown in Figure 15B) or precipitate as $Zn(OH)_2$ (cf. mechanism in Figure 15C).

The discharge reaction of the MnO_2 electrode proceeds in two one-electron reduction steps as shown in the discharge curve (Figure 16). Starting at cell voltages of 1.5 V, a coupled one-electron transfer and proton insertion reaction takes place. The transformation of MnO_2 into MnOOH is a one-phase reaction. Further reduction leads to a phase change as the solid MnOOH turns into Mn^{2+} soluble in the solution, that is, a two-phase reaction. This is consistent with the Gibbs phase rule that predicts the shape of the discharge curve for one- and two-phase reactions (Figure 16). When the number of phases, P, is equal to the number of components, C, taking part in the reaction as in the case of a two-phase reaction, the number of degrees of freedom $\mathscr{F}$ (= number of thermodynamic parameters that have to be specified to define the system) is 2. If the values of two parameters, usually pressure, p, and temperature, T, are specified, there is no degree of freedom left and other parameters of the system such as voltage have to be constant. Hence, the cell voltage stays constant for a two-phase discharge reaction. If there is a degree of freedom left, as in the case of a one-phase reaction, the cell voltage can be a variable and changes (slopes-off) during discharge.

Zinc−manganese batteries dominate the primary battery market segment. Leclanché invented the original carbon−zinc cell in 1860. He used a natural manganese dioxide−carbon black core cathode with aqueous zinc chloride−ammonium chloride electrolyte, contained in a zinc can. An alternative version employs a zinc chloride electrolyte and a synthetic electrolytic manganese dioxide and has better performance than the original Leclanché cell. The carbon−zinc with zinc chloride electrolyte gives about the same performance, on lower radio-type drains, as the alkaline cell and is strong in the Japanese and European markets. The carbon−zinc cell still finds
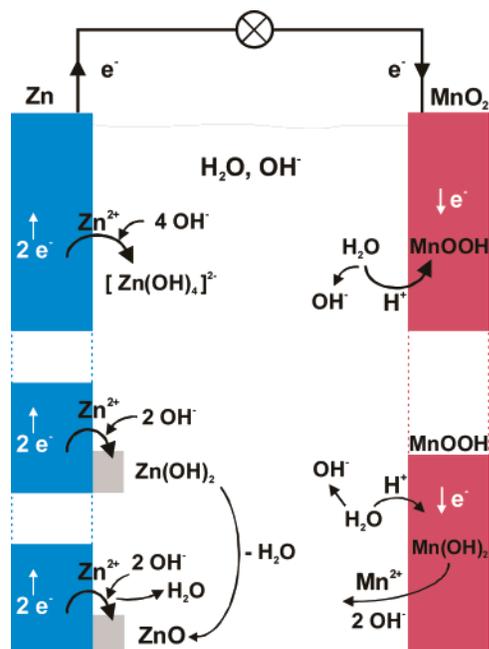
Figure 17. Discharge mechanism of a $Zn-MnO_2$ cell. From top to bottom, various stages of the discharge reaction are depicted. On the Zn side, the local change of the pH alters the composition of the discharge product.

wide use, and in 2003, worldwide it outsold the alkaline cell about 30 billion to 12 billion cells.

In the Unites States, the alkaline electrolyte (KOH) version accounts for ∼80% of sales. The detailed discharge reaction mechanism is shown in Figure 17. The influence of the pH and the change of the pH of the electrolyte solution during discharge on the formation/solubility of various zincate compounds [e.g., $Zn(OH)_4^{2+}$, etc.] to a change from a one phase to a two phase reaction at the point where $Zn(OH)_2$ begins to precipitate. It should be noted that local pH changes occur also during discharge of the MnO_2 electrode (Figure 15E).

Compared to the carbon−zinc cell, the alkaline cell is more reliable, has better performance, and is best for higher rate applications required for advanced portable electronic devices. The current version of the alkaline cell is mercury free. Instead, it uses a combination of alloying agents and corrosion inhibitors to lower the hydrogen gas generation from corrosion of the zinc anode and to compensate for the corrosion protection originally provided by the mercury. A synthetic gel holds the zinc powder anode together. The cathode is composed of an electrolytic manganese dioxide−graphite mixture with critical impurities controlled to a ≤1 ppm level.

The zinc−air battery system has the highest energy density of all aqueous batteries and equals that of the lithium thionyl chloride battery (which is the highest energy density lithium battery). The high energy density results from the cell design, as only the zinc powder anode is contained in the cell. The other reactant, oxygen, is available from the surrounding air. The air electrode is a polymer-bonded carbon, sometimes catalyzed with manganese dioxide. The electrode has a construction similar to that of fuel cell electrodes (see section 3). The zinc−air

system has captured the hearing aid market. Cells are available in sizes smaller than an aspirin tablet that fit into the ear to power the hearing aid.

The main applications of $Zn-Ag_2O$ cells are button cells for watches, pocket calculators, and similar devices. The cell operates with an alkaline electrolyte. The Zn electrode operates as discussed, whereas the Ag_2O electrode follows a displacement reaction path (cf. Figure 15A).

Primary lithium cells use a lithium metal anode, the discharge reaction of which is depicted in Figure 15B. Due to the strong negative potential of metallic lithium, cell voltages of 3.7 V or higher are possible. As the lithium metal is very reactive, the key to battery chemistry is the identification of a solvent system that spontaneously forms a very thin protective layer on the surface of metallic lithium, called the solid electrolyte interphase (SEI) layer. This electronically insulating film selectively allows lithium ion transport. Lithium batteries show higher energy density than the alkaline cells but have a lower rate capability because of the lower conductivity of the nonaqueous electrolyte and the low lithium cation transport rate through the SEI.

Commercial lithium primary batteries use solid and liquid cathodes. Solid cathodes include carbon monofluoride, CF_x, manganese dioxide (MnO_2), FeS_2, and CuS. Chemical (CMD) or electrolytic manganese dioxide (EMD) is used as the cathode with high-temperature treatment to form a water-free active material. The CF_x is made from the elements, and its cost is somewhat higher than that of the manganese dioxide cathode material. These cells are designed for relatively low-rate applications. Both chemistries are very stable, and cells can deliver ≥80% of their rated capacity after 10 years of storage. The lithium iron sulfide (FeS_2) system has been developed for high-rate applications and gives superior high-rate performance compared to the alkaline zinc−manganese cells. Typically, the electrolyte is propylene carbonate−dimethyl ether (PC-DME) with lithium triflate ($LiSO_3CF_3$) or lithium perchlorate ($LiClO_4$) salt.

The lithium thionyl chloride system employs a soluble cathode construction. The thionyl chloride acts as the solvent for the electrolyte and the cathode active material. It has the highest energy density of any lithium cell and is equal to that of the zinc−air aqueous cell. The reaction mechanism of the cell is explained in Figure 18. In the inorganic electrolyte ($LiAlCl_4$ dissolved in $SOCl_2$) the lithium metal and the electrolyte react chemically and form a SEI mainly consisting of LiCl and S. LiCl and S are also the products of the electrochemical discharge reaction at the carbon positive electrode, where the liquid cathode $SOCl_2$ is reduced. The cell discharge stops when the electronically insulating discharge products block the carbon electrode.

Lithium−sulfur dioxide cells also use a liquid cathode construction. The SO_2 is dissolved in an organic solvent such as PC or acetonitrile. Alternatively, SO_2 is pressurized at several bars to use it in the liquid state. The cell reaction is similar to that depicted in Figure 18, with electronically insulating
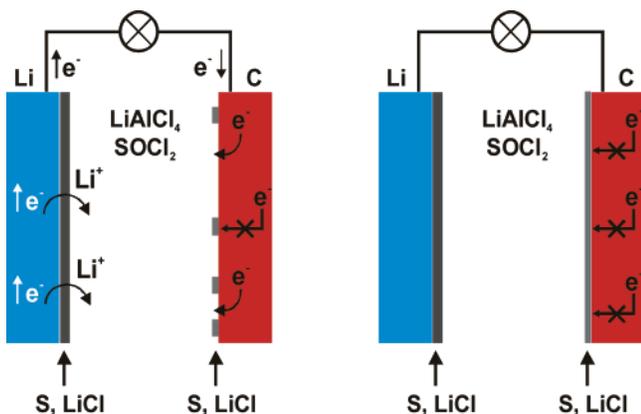
Figure 18. Discharge mechanism of a Li−SOCl₂ cell. The cell can operate until the surface of the carbon cathode is fully covered by electronically insulating LiCl and S discharge products. The Li−SO₂ cell is also a soluble cathode system with a cell construction similar to that of the Li−SOCl₂ cell. It follows a similar discharge reaction where the reaction product is LiS_2O_4.

$Li_2S_2O_4$ being the SEI component at the Li anode and the solid discharge product at the carbon cathode. The Li−SOCl₂ and Li−SO₂ systems have excellent operational characteristics in a temperature range from −40 to 60 °C (SOCl₂) or 80 °C (SO₂). Typical applications are military, security, transponder, and car electronics. Primary lithium cells have also various medical uses. The lithium−silver−vanadium oxide system finds application in heart defibrillators. The lithium−iodine system with a lithium iodide solid electrolyte is the preferred pacemaker cell.

2.5. Rechargeable Batteries

Rechargeable cells generally have lower energy storage capability than primary cells. The additional requirements for rechargeability and long operation limit the choice of chemical systems and constructions to those that are more robust than for primary batteries. The lead acid battery dominates the rechargeable market. Both the Pb and PbO₂ electrode reaction mechanisms follow the solution−precipitation mechanism as depicted in Figure 15C and the cell reaction shown in Figure 19. In addition to the lead and lead oxide electrodes, sufficient amounts of
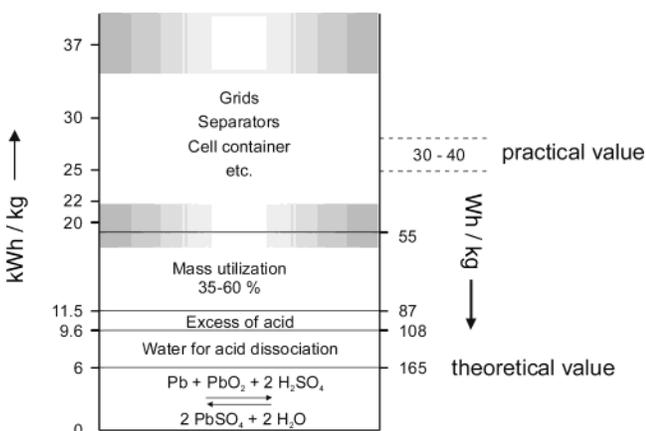

Figure 19. Depiction of the components of a lead acid battery showing the differences between theoretical and practical energy density of a lead acid battery and source of the differences.

sulfuric acid and water have to be provided for the cell reaction and formation of the battery electrolyte. For ionic conductivity in the charged and discharged states, an excess of acid is necessary. Considering the limited mass utilization and the necessity of inactive components such as grids, separators, cell containers, etc., the practical value of specific energy (Wh/kg) is only ∼25% of the theoretical one (Figure 19) for rechargeable batteries. Due to the heavy electrode and electrolyte components used, the specific energy is low.[3] Nevertheless, the lead acid system serves a variety of applications from automotive SLI and motive power for forklift trucks and the like to stationary energy storage for uninterruptible power supplies. Its low cost and established recycling processes make it one of the "greenest" battery systems. According to Battery Council International, Inc., ∼98% of the lead acid batteries in the United States are recycled.

Nickel−cadmium (Ni−Cd) was the first small sealed rechargeable cell. In alkaline (KOH) electrolyte, the Cd negative electrode functions reversibly, according to a solution−precipitation mechanism (cf. Figure 15C) with Cd(OH)₂ being the discharge product. The Ni positive electrode is actually a Ni(OH)₂ electrode, which is able to reversibly de-insert/insert protons during discharge/charge. It has excellent low-temperature and high-rate capabilities. For a long time, it was the only battery available for power tools. It powered the early cellular phones and portable computers. The availability of stable hydrogen storage alloys provided the impetus for the creation of the nickel−metal hydride (Ni−MH) cell. The hydrogen storage alloy is a proton-inserting negative electrode material that replaced the environmentally threatened cadmium negative electrode in the Ni−Cd. The positive electrode and the electrolyte stayed the same. Ni-MH quickly replaced the Ni−Cd for electronic applications because of its significantly higher energy storage capability and somewhat lighter weight. The Ni−MH has poor low-temperature capability and limited high-rate capability, but its higher energy density served to spur the development of the portable electronic device market. Today, it is the battery of choice for hybrid gasoline−electric vehicles and is beginning to challenge the Ni−Cd for power tool applications.

The Li ion battery, with significantly higher energy density and lighter weight, replaced the Ni−MH as soon as production capability was available. It is now the battery of choice for portable electronic devices and is challenging the Ni−MH for the hybrid vehicle application. The Li ion cell has a carbon/graphite anode, a lithium−cobalt oxide cathode, and an organic electrolyte of lithium hexafluorophosphate (LiPF₆) salt with ethylene carbonate−organic solvent mixture. As in the Ni−MH battery, both the anode and cathode in the Li ion cell follow an insertion mechanism; however, instead of protons, lithium cations are inserted and de-inserted (cf. Figure 15D).[4]

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[3] A specific energy of 30 Wh/kg literally means that 1 kg of a lead acid battery is able to power a 60 W lamp for only 0.5 h.

[4] For layered host materials as used in the lithium ion cell, the term "intercalation" is used for the insertion of guests into the host structure.
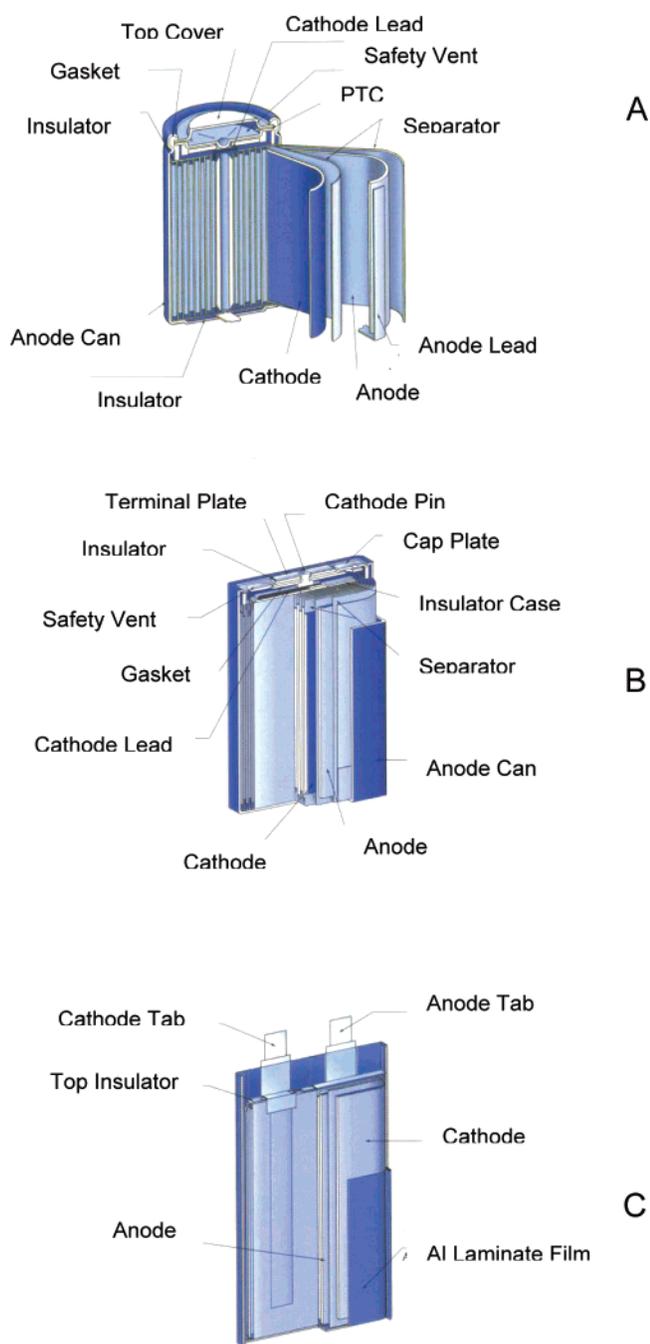
Figure 20. Construction of (A) cylindrical, (B) prismatic, and (C) polymer Li ion cells. (Reprinted with permission from a brochure by Sony Corporation).

Sony introduced the Li ion in 1991. Since its introduction, it has more than doubled in capacity in response to the demand for higher performance portable electronic devices, such as cellular phones and notebook computers. The construction of the Li ion cells is shown in Figure 20. Cells are available in both liquid electrolyte and plasticized polymer electrolyte configurations. New anode and cathode materials hold promise to double the present performance over the next 10 years. The Li ion market is poised to segment into the higher performance, higher cost segment, which continues the increase in energy density, and a segment with lower cost

materials but with high-rate performance for hybrid electric vehicle and power tool applications. The new materials that make possible this improvement in performance are discussed elsewhere and are beyond the scope of this overview.

Lithium metal rechargeable cells would have the highest energy of all battery systems. Unfortunately, on recharge, the lithium has a strong tendency to form mossy deposits and dendrites in the usual liquid organic solvents (cf. Figure 15B). This limits the cycle life to $\sim 100-150$ cycles (considerably lower that the 300 cycles required for a commercial cell), as well as increasing the risk of a safety incident. Rechargeable lithium metal−vanadium oxide cells (Li−VO$_x$) with poly(ethylene oxide) polymer electrolytes have been developed for stationary energy storage applications.

Only a few of the thousands of proposed battery systems have been commercialized. A set of criteria can be established to characterize reactions suitable for use in selecting chemical systems for commercial battery development. Very few combinations can meet all of the criteria for a general purpose power supply. The fact that two of the major battery systems introduced more than 100 years ago, lead acid (rechargeable) and zinc−manganese dioxide (primary), are still the major systems in their category is indicative of the selection process for chemical reactions that can serve the battery marketplace.

2.6. Selection Criteria for Commercial Battery Systems

A set of criteria that illustrate the characteristics of the materials and reactions for a commercial battery system follow.

1. Mechanical and Chemical Stability. The materials must maintain their mechanical properties and their chemical structure, composition, and surface over the course of time and temperature as much as possible. This characteristic relates to the essential reliability characteristic of energy on demand. Initially, commercial systems were derived from materials as they are found in nature. Today, synthetic materials can be produced with long life and excellent stability. When placed in a battery, the reactants or active masses and cell components must be stable over time in the operating environment. In this respect it should be noted that, typically, batteries reach the consumer ~ 9 months after their original assembly. Mechanical and chemical stability limitations arise from reaction with the electrolyte, irreversible phase changes and corrosion, isolation of active materials, and local, poor conductivity of materials in the discharged state, etc.

2. Energy Storage Capability. The reactants must have sufficient energy content to provide a useful voltage and current level, measured in Wh/L or Wh/kg. In addition, the reactants must be capable of delivering useful rates of electricity, measured in terms of W/L or W/kg. This implies that the kinetics of the cell reaction are fast and without significant kinetics hindrances. The carbon−zinc and Ni−Cd systems set the lower limit of storage and release capability for primary and rechargeable batteries, respectively.

3. Temperature Range of Operation. For military applications, the operational temperature range is from −50 to 85 °C. Essentially the same temperature range applies to automotive applications. For a general purpose consumer battery, the operating temperature range is ∼0−40 °C, and the storage temperatures range from −20 to 85 °C. These temperatures are encountered when using automobiles and hand-held devices in the winter in northern areas and in the hot summer sun in southern areas.

4. Self-Discharge. Self-discharge is the loss of performance when a battery is not in use. An acceptable rate of loss of energy in a battery depends somewhat on the application and the chemistry of the system. People expect a battery to perform its intended task on demand. Li−MnO₂ primary cells will deliver 90% of their energy even after 8 years on the shelf; that is, their self-discharge is low. Some military batteries have a 20-year storage life and still deliver their rated capacity. On the other hand, rechargeable batteries can be electrically restored to their operating condition and generally have more rapid loss of capacity on storage. The rechargeable Ni−MH cell, for instance, will lose up to 30% of its capacity in a month. Usually, self-discharge increases with temperature.

5. Shape of the Discharge Curve. The issue of a sloping versus a flat discharge depends on the intended use. For operation of an electronic device, a flat, unchanging, discharge voltage is preferred. A sloping discharge is preferred for applications when determining the state-of-charge is important. This may be modified somewhat by the impact of cost. Although a constant brightness is preferred in a flashlight, the user may select carbon−zinc with a sloping discharge for its lower cost. The influence of one- or two-phase reactions on the shape of the discharge curve was discussed previously (cf. Figure 16).

6. Cost. The cost of the battery is determined by the materials used in its fabrication and the manufacturing process. The manufacturer must be able to make a profit on the sale to the customer. The selling price must be in keeping with its perceived value (tradeoff of the ability of the user to pay the price and the performance of the battery). Alkaline primary Zn−MnO₂ is perceived to be the best value in the United States. However, in Europe and Japan the zinc chloride battery still has a significant market share. In developing countries, the lower cost Leclanché carbon−zinc is preferred. Likewise, lead acid batteries are preferred for automobile SLI over Ni−Cd with superior low-temperature performance but with a 10 times higher cost.

7. Safety. All consumer and commercial batteries must be safe in the normal operating environment and not present any hazard under mild abuse conditions. The cell or battery should not leak, vent hazardous materials, or explode.

Added criteria for rechargeable batteries are as follows:

8. Ability To Recharge and Deliver Power. The rechargeable battery systems place a severe added requirement. The active materials must be capable of being restored exactly to their original condition (crystal structure, chemical composition, etc.) on reversal of the current flow (charging). After being recharged by current reversal, the electrode materials must be able to deliver the same rate of discharge while maintaining their voltage level. Very few chemical systems exhibit this characteristic.

9. Cycle Life. It is not enough for a chemical system to be recharged and deliver power to qualify as a commercial rechargeable system. A commercial cell must be capable of completely discharging its energy and then fully recharging a minimum of 300 times and not lose >20% of its capacity. This requires a very robust system and reversible electrode reactions. There can be no side reactions that result in the loss of the active materials during the charge−discharge cycle.

10. Charge Time. The time it takes to recharge a battery completely relates to the use. For convenience, recharging in 15 min is accepted for many consumer applications. However, fast charging places a stress on the robustness of the electrode reactions and may result in shortened cycle life. Most batteries require 3−8 h to recharge completely and maintain their required cycle life. This slower charge rate allows time for the atoms and molecules to find their correct positions in the charged material.

11. Overcharge/Overdischarge Protection. When a battery is forced outside its thermodynamic voltage levels, the reaction path becomes unstable; irreversible new reactions can occur, and new compounds can form. These events harm the active material and either reduce the capacity or render the system inoperable. In addition, unsafe battery conditions may occur under overcharge/overdischarge conditions. The Ni−Cd, Ni−MH, and lead acid have a built-in overcharge and overdischarge characteristic based on an oxygen recombination mechanism. Cell designs often use the ratio of the capacities of each electrode (cell balance) to accomplish protection of the battery system. It is also possible to use electronic controls to control the charge and discharge voltage limits within safe limits. The lithium−cobalt oxide cathode in the Li ion system is protected from overvoltage and overdischarge by electronic means. Voltage excursions outside its operating range can cause irreversible changes in its crystal structure and damage cell operations.

3. Fuel Cells

3.1. Introduction and Market Aspects

The chemical energy stored in hydrogen and several hydrocarbon fuels is significantly higher than that found in common battery materials. This fact provides the impetus to develop fuel cells for a variety of applications. Fuel cells are an ideal primary energy conversion device for remote site locations and find application where an assured electrical supply is required for power generation, distributed power, remote, and uninterruptible power. Figure 21 depicts the operation of typical fuel cells. The various components of a functioning fuel cell are shown in Figures 22 and 23. Operating fuel cells are complex
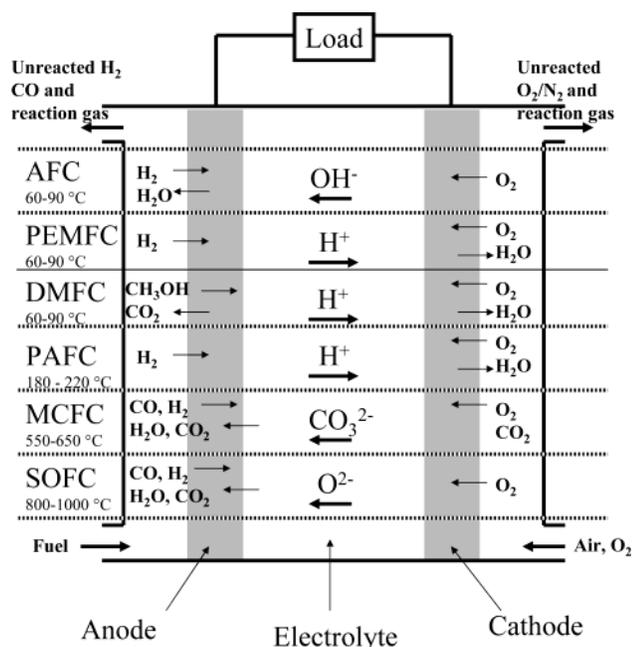
Figure 21. Summary of the reactions and processes that occur in the various fuel cell systems.

Figure 22. Block diagram of the component parts of a functioning fuel cell.

Figure 23. Depiction of the components of a complete fuel cell system including the re-former and power conditioning unit.

chemical plants that require sophisticated manufacturing techniques and control circuitry.

Some companies, hospitals, and buildings are choosing to install fuel cell power in order to be free from the outages experienced in utility supply lines. Previously, emphasis had been placed on the development of large fuel cells in the 200−300 kW range for these applications. Several demonstration projects of 1 MW and larger fuel cells have been undertaken, usually composed of units of 250 kW output. Smaller fuel cells in the range of 50−75 kW are now under intense development for use in automobile and bus propulsion, where their low emission characteristic finds favor. The direct conversion methanol fuel cells in the range of 5−25 W are proposed for portable electronics as a replacement for Li ion and Ni−MH batteries. The more promising commercial applications of fuel cells appear to be as a stationary power source for central and dispersed power stations (megawatts) and as mobile power for portable electronic devices and automobiles.

advantages	disadvantages
efficient energy conversion	complex to operate
modular construction	best as primary energy source
nonpolluting	impurities in gas stream shorten life
low maintenance	pulse demands shorten cell life
silent	expensive
safe	limited availability
high energy density	low durability
	low power density per volume

Although several fuel cell technologies are reaching technical maturity, the economics of a fuel cell are not clear. The commercial potential of fuel cells will depend on the ability to reduce catalyst and other expensive materials costs and to manufacture the units at a competitive cost. Many uses of fuel cells place a premium on specific performance characteristics. The relatively simple alkaline fuel cells (AFC)
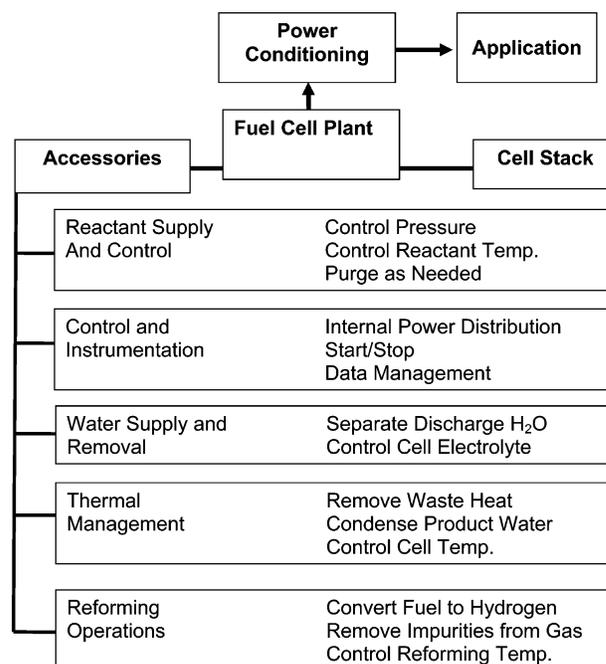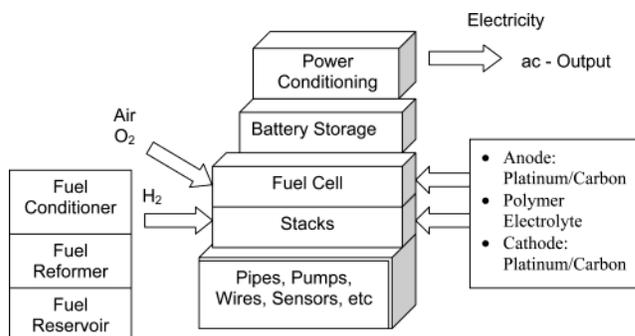
will continue to be used in space applications, where high energy densities and cryogenic storage of hydrogen and oxygen represent a cost savings by lowering the weight of the launch vehicle. They are also used for longer space missions, when the high reliability and the production of drinking water are important considerations. The high cost of qualifying a new technology is a strong impediment for replacing the AFC in space applications.

Fuel cells offer the cleanest power generation possible. They are quiet in operation and can be located close to the application. They produce much less greenhouse emissions and can be more efficient in conversion of the energy in a fuel into power than gasoline engines or utility thermal power plants. Fuel cells are best utilized as a steady energy source and not as a power source to supply dynamic demands. For applications that require varying power demands, such as automotive propulsion, the use of the fuel cell in a hybrid configuration with a battery or EC will be required. The fuel cell provides steady power demand while the battery or EC handles the surge for regenerative breaking and acceleration as well as initial start-up.

Table 3. Types of Fuel Cells

advantages	disadvantages	comments
	Alkaline (AFC)[a]	
mechanically rechargeable	limited activated life	original development >30 years ago
low-cost KOH electrolyte	intolerant of impurities in gas streams CO_2 and CO	Apollo fuel cell
	pure H_2 only suitable fuel	operates at room temp to 80 °C
		demo in vehicles in the 1970s
	Polymer Electrolyte Membrane Fuel Cell (PEMFC)	
nonvolatile electrolyte	expensive catalysts required	operates best at 60–90 °C
few materials problems	CO a strong poison	originally developed for space by GE
CO_2 rejecting electrolyte	H_2O management essential	hydrogen fuel (re-formed hydrocarbons, pure H_2, MH storage)
pressure differential between anode and cathode	high-cost electrolyte	main development efforts for automotive and stationary applications
polymer electrolyte	pure H_2 only suitable fuel	
	oxygen kinetics are slow	
	intolerant of impurities	
	limited life	
	water management essential	
	Direct Methanol Fuel Cell (DMFC)	
direct fuel conversion	stable reaction intermediates	operates best at 60 to 90 °C)
slow electrode kinetics	high catalyst loadings	same construction as PEMFC
improved wt and vol	water management essential	methanol fuel eliminates reformer
polymer electrolyte	low overall efficiency	lower current capability
	methanol hazardous	methanol crossover reduces efficiency
		needs new membrane, higher efficiency
		high catalyst loadings
		main effort for portable electronic devices
	Phosphoric Acid Fuel Cell (PAFC)	
CO_2 rejecting electrolyte	H_2 only suitable fuel	operates best at ~200 °C
high fuel efficiency	anode CO catalyst poison	stationary energy storage (nominal units, 250 kW)
	O_2 kinetics hindered	available commercially
	low conductivity electrolyte	
	high-cost catalysts	
	limited life	
	Molten Carbonate Fuel Cell (MCFC)	
fast electrode kinetics	materials problems and life	operates best at 550 °C
high efficiency	low sulfur tolerance	nickel catalysts, ceramic separator membrane
CO/CH_4 usable fuel	high ohmic electrolyte	hydrocarbon fuels re-formed in situ
direct reforming feasible	low tolerance to sulfur	several large demonstration units
high-grade heat available	need to recycle CO_2	significant government support
	limited life	
	Solid Oxide Fuel Cell (SOFC)	
high grade heat available	high fabrication costs	operates at 900 °C
fast electrode kinetics	severe materials constraints	conducting ceramic oxide electrodes
in situ reforming feasible	high electrolyte conductivity	hydrocarbon fuels re-formed in situ
no electrolyte management		least sensitive to sulfur, etc.
high system efficiency		
tolerant of impurities		

[a] Metal air batteries with replaceable anodes are often considered to be a fuel cell but are not considered here.

Fuel cells have been identified as a nearly ideal solution to power the requirements for motor vehicle manufacturers, utility and nonutility generators, and portable electronic devices. Each segment has significant incentives to develop alternate power sources. For automakers, the incentive is environmentally related, coupled with strong support from government programs designed to move away from fossil hydrocarbon fuels. For the utilities, increasing environmental pressure and power demand, coupled with limited generation capability, have created a need for distributed power generation and storage. In a similar vein, those who need an uninterruptible power supply, or freedom from the utility grid, find fuel cells to be an attractive option. Direct methanol fuel cells for portable electronic devices such as notebook computers seem close to commercial reality and will compete with batteries for this market. The key challenge for each will be to meet the cost-perfor-mance barrier in a small size as well as governmental regulations.

It is estimated that the fuel cell market for distributed power and demonstration projects and contracts amounted to about $100 million for 2003. Research and development contracts to develop fuel cells for automotive propulsion and stationary energy storage are an order of magnitude larger.

3.2. Fuel Cell Operation

Fuel cells, like batteries, convert the chemical energy residing in a fuel into electrical energy on demand. As in batteries and other electrochemical cells, fuel cells consist of an anode, where oxidation occurs, a cathode, where reduction occurs, and an electrolyte, where ions carry the current between the electrodes. Fuel cells differ from batteries in that the fuel and oxidant are not contained within the fuel
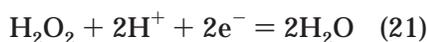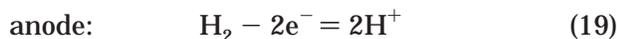
cell compartment but supplied continuously from an external source. In a real sense, fuel cells are like internal combustion engines, as they operate only so long as the fuel is supplied. Fuel cells are not electrically recharged, but after use, the tank is refilled with fuel. From an operational point of view, the fuel of choice is hydrogen gas, with the exhaust gas being water. Other fuels and hydrocarbons must be converted to hydrogen for use in a fuel cell. The direct conversion of fuels such as CH_3OH and CH_4 is possible under certain conditions. Each type of fuel cell has a unique set of processes and reactions to describe its operation. A summary of the characteristics for the various fuel cell systems is given in Tables 3 and 4.

The basic reaction of a H_2-O_2 fuel cell is

$$H_2 + {}^1/_2O_2 = H_2O \qquad E° = 1.229 \text{ V} \qquad (18)$$

For this reaction $\Delta G° = -235.76$ kJ/mol and $\Delta H° = -285.15$ kJ/mol. Fuel cells follow the thermodynamics, kinetics, and operational characteristics for electrochemical systems outlined in sections 1 and 2. The chemical energy present in the combination of hydrogen and oxygen is converted into electrical energy by controlled electrochemical reactions at each of the electrodes in the cell.

Fuel cells can be roughly divided into low-temperature (ca. <200 °C) and high-temperature (ca. >450 °C) fuel cells. Low-temperature fuel cells typically use alkaline or acidic electrolytes. In acidic electrolytes the electrode reactions are

anode: $\qquad H_2 - 2e^- = 2H^+ \qquad (19)$

cathode: $\qquad O_2 + 2H^+ + 2e^- = H_2O_2 \qquad (20)$

$\qquad\qquad H_2O_2 + 2H^+ + 2e^- = 2H_2O \quad (21)$

overall: $\qquad O_2 + 4H^+ + 4e^- = 2H_2O \qquad (22)$

Oxygen undergoes a two-step indirect reduction reaction. The stable H_2O_2 intermediate is undesirable, as it lowers the cell voltage and H_2O_2 attacks and corrodes the carbonaceous electrode material commonly used. Better catalysts are needed to speed the decomposition of H_2O_2 to reduce its impact on the overall reaction. Similarly, a catalyst can enhance the H_2 dissociation rate at the anode. Platinum or platinum alloys are usually employed as catalysts to speed the reactions on both electrodes in low-temperature fuel cells. The hydrogen reaction kinetics are fairly fast and do not require as high platinum loading to deliver high currents. To suppress the two-step oxygen reduction, significantly more catalyst is required. Due to the very high price of nanostructured Pt, the Pt may be distributed on a porous high surface area carbon. Typical catalyst loadings are $\sim$0.1 mg/cm^2 of platinum or platinum alloy catalyst on the anode and $\sim$0.5 mg/cm^2 catalyst on the cathode. However, the catalyst loading varies, depending on the type of fuel cell and its application. A major thrust in research on low-temperature fuel cells is to reduce the catalyst loading, to improve CO tolerance, and to identify lower cost catalysts. As the

Table 4. Typical Characteristics of Various Fuel Cell Systems

type	anode feed	anode composition	cathode feed	cathode composition	electrolyte	operating temp, °C
alkaline (AFC)	pure hydrogen	carbon/platinum catalyst	oxygen (or air)	carbon/platinum catalyst and alternatives	aq KOH	ambient–90
PEM (PEMFC)	pure hydrogen	carbon/platinum catalyst	oxygen or air	carbon/platinum catalyst	acidic polymer	ambient–90
direct methanol (DMFC)	methanol or methanol–water	carbon/platinum catalyst	oxygen or air	carbon/platinum catalyst	acidic polymer	60–90
phosphoric acid (PAFC)	pure hydrogen	carbon/platinum catalyst	oxygen or air	carbon/platinum catalyst	phosphoric acid in SiC matrix	200
molten carbonate (MCFC)	hydrogen or natural gas	porous Ni	oxygen or air	porous NiO	molten Li_2CO_3 in $LiAlO_2^-$	550
solid oxide (SOFC)	gasoline or natural gas	porous cermet of Ni or Co and yttria–zirconia	oxygen or air	strontia-doped lanthanum–manganite Perovskite	yttria-stabilized or yttria/calcia-stabilized zirconia support	900^a

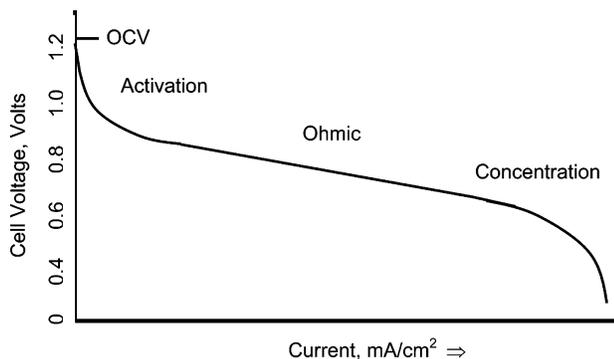^{a} Mg- or Sr-doped lanthanum chromate as cell interconnects.

Figure 24. Typical power curve for a fuel cell. The voltage drops quickly from the OCV due to the formation of the peroxide intermediate. Operation of the fuel cell at the knee of the curve where concentration is limiting performance can damage the electrodes and lead to rapid deterioration of cell operation.

O_2 and H_2 dissociation kinetics are better at higher temperatures (>400 °C), low-cost electrode structures of high surface area Ni and oxides such as spinels or perovskites to replace the very effective, but costly, Pt catalysts have been sought.

Fuel cell electrodes are more complex structures than battery electrodes. They serve three functions: (1) to ensure a stable interface between the reactant gas and the electrolyte, (2) to catalyze the electrode reactions, and (3) to conduct the electrons from or to the reaction sites. A significant problem is the control of the interface at the juncture of the reactant (gas) phase, the electrolyte medium, and the catalyzed conducting electrode, the so-called "three-phase boundary", where the electrolyte, electrode, and gas all come together. A stable three-phase boundary is critical to good performance and long operation. Therefore, the porosity and the wetting behavior with electrolyte and the electrode surface must be precisely adjusted.

Fuel cells can operate with very high electrical efficiencies approaching 60−70%. If the waste heat of the fuel cell is also used, fuel efficiencies of 90% are possible. The performance of the fuel cell is judged by the voltage−current curve depicted in Figure 24. The operating voltage is significantly less than the theoretical 1.23 V as the actual cell reaction involves H_2, O_2, and H_2O and also the peroxide intermediate (cf. above), the latter influencing the Nernst voltage and the OCV. The activation, ohmic, and diffusion polarization characteristics determine the shape of the fuel cell discharge curve as they do for batteries (cf. Figure 7).

As for the other electrochemical storage/conversion devices, the fuel cell electrolyte must be a pure ionic conductor to prevent an internal short circuit of the cell. It may have an inert matrix that serves to physically separate the two electrodes. Fuel cells may contain all kinds of electrolytes including liquid, polymer, molten salt, or ceramic.

Hydrogen gas is the preferred fuel for low-temperature fuel cells. The main obstacle in the use of hydrogen as energy carrier is that hydrogen is not a readily available fuel. In high-temperature fuel cells, a hydrocarbon fuel, for example, methane or gasoline, can be fed directly into the cell. To use hydrocarbons
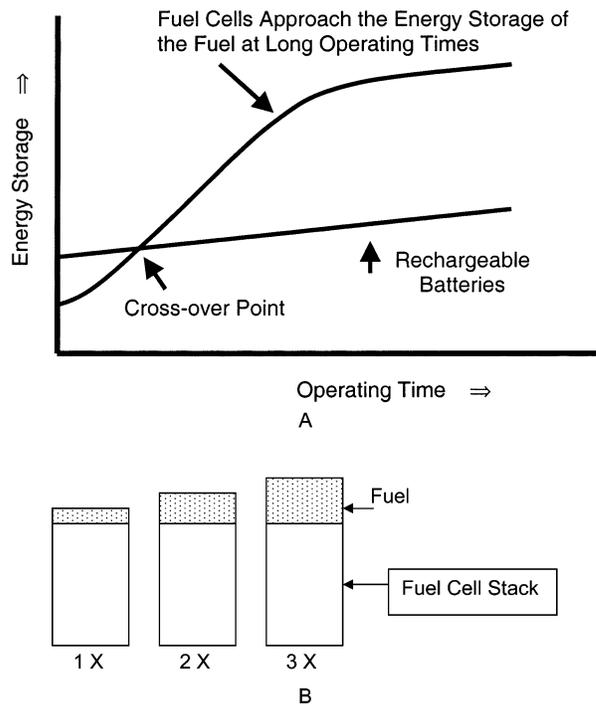

Figure 25. (A) Comparison of the energy storage capability of fuel cells and batteries. Only after several refueling operations are fuel cells more efficient energy storage devices on a Wh/L and Wh/kg basis. (B) Fuel cells have a set volume and weight for the fuel cell stack and peripherals to supply the reactants to the stack. The small incremental fuel volume to continue operation supplying energy makes them more efficient for longer operations.

in low-temperature fuel cells, the hydrocarbon fuels must be converted into hydrogen through a separate re-forming step placed between the tank and the fuel cell. Any trace amounts of CO, CO_2, and H_2S found in the hydrogen-rich re-formate gas must be removed before using the gas, as they irreversibly block the Pt catalyst and thus "poison" the electrode. To reduce dependence on hydrocarbon fuels, the use of off-peak electricity from a series of new nuclear plants has been proposed, to produce the hydrogen for use in automotive applications.
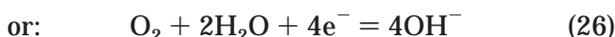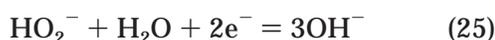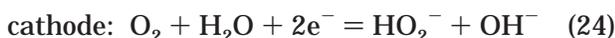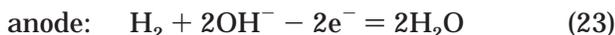
Apart from hydrocarbons and gasoline, other possible fuels include hydrazine, ammonia, and methanol, to mention just a few. Fuel cells powered by direct conversion of liquid methanol have promise as a possible alternative to batteries for portable electronic devices (cf. below). These considerations already indicate that fuel cells are not stand-alone devices, but need many supporting accessories, which consume current produced by the cell and thus lower the overall electrical efficiencies. The schematic of the major components of a so-called "fuel cell system" is shown in Figure 22. Fuel cell systems require sophisticated control systems to provide accurate metering of the fuel and air and to exhaust the reaction products. Important operational factors include stoichiometry of the reactants, pressure balance across the separator membrane, and freedom from impurities that shorten life (i.e., poison the catalysts). Depending on the application, a power-conditioning unit may be added to convert the direct current from the fuel cell into alternating current.

Fuel cell systems are not very volume efficient. The ancillary equipment to operate the device can be two to three times larger than the fuel cells themselves, where energy conversion actually occurs. Everything considered, the fuel cell stack[5] is much less than 50% of the total volume of the unit. In addition, fuel cell stacks themselves have a low energy density in Wh/L and Wh/kg compared to batteries as the gas distribution system requires significant extra volume and weight. Only by taking into account the continuous supply of fuel to the system during long-term operation is the energy density of the fuel cell greater than that of advanced battery systems, as shown in Figure 25. However, due to the slow kinetics, especially at the oxygen cathode side, the power capability of fuel cells is lower than that of most batteries and inferior to combustion engines and gas turbines (cf. Figure 3). The detrimental impact of the weight and volume of the fuel cell may be hidden by giving the "power capability" in A/cm^2 and not in W/L or W/kg.

3.3. Characteristics of Various Types of Fuel Cells

Fuel cells are typically classified by the type of electrolyte. Apart from certain specialty types, the five major types of fuel cells are alkaline fuel cell (AFC), polymer electrolyte fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC).

The AFC is one of the oldest fuel cell types. The cell reactions are as follows (the existence of the peroxide intermediate HO_2^- has been already discussed):

$$\text{anode:} \quad H_2 + 2OH^- - 2e^- = 2H_2O \qquad (23)$$

$$\text{cathode:} \quad O_2 + H_2O + 2e^- = HO_2^- + OH^- \qquad (24)$$

$$HO_2^- + H_2O + 2e^- = 3OH^- \qquad (25)$$

$$\text{or:} \quad O_2 + 2H_2O + 4e^- = 4OH^- \qquad (26)$$

The AFC was first developed for the Apollo missions. An updated version has been developed and is still in use to provide electrical power for shuttle missions. These power plants reach efficiencies of 60% in space applications. The electrolyte is potassium hydroxide based. Noble metal catalysts are very active in the AFC for both the hydrogen and oxygen electrodes. The hydrogen and oxygen kinetics are more facile in alkaline than acid electrolytes, thus resulting in higher cell voltages.[6] This permits the use of non-noble metal catalysts, such as Raney nickel, for the fuel electrode. Silver and spinel-type oxides along with iron phthalocyanines and other porphyrins are good catalysts for the oxygen (air) electrodes. These catalysts cannot be used in acidic
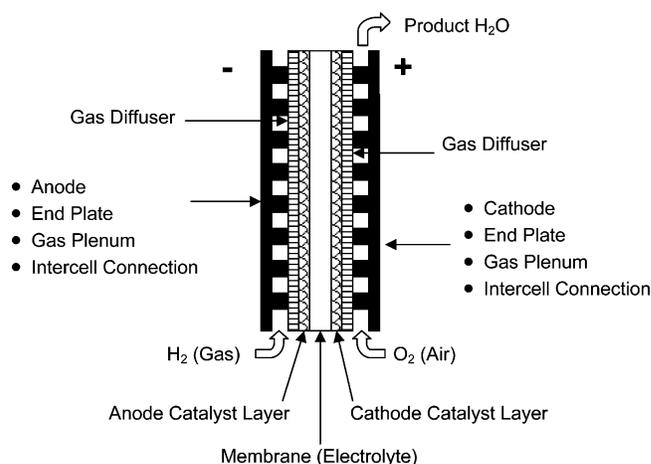

Figure 26. Schematic of a polymer electrolyte membrane (PEM) fuel cell. The fuel cell stacks operate at 30−180 °C with 30−60% efficiency. Fuel options include pure hydrogen, methanol, natural gas, and gasoline.

electrolytes, as they are soluble in acidic media. The AFC is susceptible to CO_2 contamination of the electrolyte (clogs the pores) when air is used as well as to poisoning of the Pt and Ni catalyst by sulfide and CO impurities in the feedstock. In other words, the AFC requires pure hydrogen and oxygen as reactants. Because of the requirement of pure fuels and elimination of CO_2 for long life, terrestrial applications are limited. Both electrodes are fabricated with an active layer of platinum catalyst on carbon support and binder that is backed by a wet-proofed Teflon [PTFE, poly(tetrafluoroethylene)] bonded carbon layer to control the wetting of the electrodes by the electrolyte and thus the location of the three-phase boundary. The carbons are generally treated to remove active entities on the surface before being catalyzed. Graphite bipolar endplates contain the gas flow channels and serve to provide waste heat removal. On shutdown, it is common to have the electrolyte empty into a sump on earthbound applications, as the cathode needs to be protected from both absorption of CO_2 by the electrolyte and corrosion by wet O_2. The AFC operates at up to 1 A/cm^2 at 0.7 V.

The PEMFC was first developed for the Gemini space vehicle. The electrodes are formed on a thin layer on each side of a proton-conducting polymer membrane, used as electrolyte. In a sense, the electrolyte is composed similarly to plasticized electrolyte in a Li ion cell, where a liquid electrolyte component is immobilized in a polymer matrix. It consists of a solid polymer PTFE backbone with a perfluorinated side chain that is terminated with a sulfonic acid group. Hydration of the membrane yields dissociation and solvation of the proton of the acid group. The solvated protons are mobile within the polymer and provide electrolyte conductivity. The membrane has low permeability to oxygen and hydrogen (crossover) for high coulombic efficiency. A typical PEMFC is depicted in Figure 26.
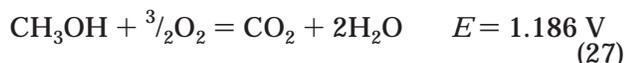
A graphite (or metal) plate serves as the plenum for the gas supply and for heat removal. A catalyzed carbon layer is applied to the membrane surface. A thicker gas diffusion layer or porous carbon paper

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[5] A fuel stack is a series connection of fuel cells. Strictly speaking, it is fuel cell battery (cf. footnote 1). The composition and design of the fuel cell stack differ for the implementation of each type of cell.

[6] The higher voltage is not only due to better kinetics but also due to the fact that oxygen reaction via the intermediate peroxide (HO_2^- in alkaline electrolytes) is more facile.

provides gas transport to the reaction zone. The composition and amount of catalyst differ for each electrode. The anode has a lower catalyst loading than the cathode. The platinum-based catalysts are sensitive to H_2S and CO impurities among others so they must be eliminated from the feedstock for long operation. The catalyst content of the anode is $\sim$0.1 mg/cm^2, and that of the cathode is $\sim$0.5 mg/cm^2.

Water management in the membrane is critical to long-term performance. The proton transport carries water along (water drag) while carrying the current. The water concentration gradient results in back-diffusion. However, for operation at high current, the anode side of the membrane must be humidified or it will dehydrate. By the same token, product water is removed from the cathode side in the air stream to prevent flooding of the active layer. For reliable operation, a water content of 30−60% in the membrane is preferred for reliable operation.

For higher temperature operation, a polybenzimidazole-based polymer electrolyte may be preferred. The PEMFC structures have good mechanical integrity under compression and expansion from differential temperature and pressure gradients that occur during operation. This system has minimal materials problems, except for the cost and operation characteristics of the membrane. The PEMFC operates at $\sim$1 A/cm^2 at 0.7 V. The electrode reactions in acidic media have been discussed above.
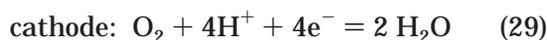
The DMFC uses the same basic cell construction as for the PEMFC. It has the advantage of a liquid fuel in that is easy to store and transport. There is no need for the re-former to convert the hydrocarbon fuel into hydrogen gas. The anode feedstock is a methanol and water mixture or neat methanol, depending on cell configuration. The DMFC is under development as a power source for portable electronic devices such as notebook computers and cellular phones. The pure methanol or a methanol−water mixture would be stored in a cartridge similar to that used for fountain pens. Refueling would involve the quick replacement of the cartridge. The platinum−ruthenium catalyst loadings for the anode are higher than for the PEMFC and are in the range of 1−3 mg/cm^2. Without the ruthenium, that is, with neat Pt, the anode reaction produces a stable formic acid intermediate. The reaction for the direct conversion of methanol has a similar voltage as for hydrogen. The overall cell reaction is

$$CH_3OH + {}^3/_2O_2 = CO_2 + 2H_2O \qquad E = 1.186 \text{ V} \tag{27}$$

The reaction at the anode is

$$\text{anode: } CH_3OH + H_2O - 6e^- = 6H^+ + CO_2 \tag{28}$$

and

$$\text{cathode: } O_2 + 4H^+ + 4e^- = 2\,H_2O \tag{29}$$

Due to the chemical similarity of water and methanol, the methanol has considerable solubility in the polymer membrane, leading to significant crossover from the anode side to the cathode side of the cell. On reaching the cathode, the methanol is oxidized. This significantly lowers the cathode voltage and the overall efficiency of cell operation. The typical DMFC yields $\sim$0.5 V at 400 mA/cm^2 at 60 °C.
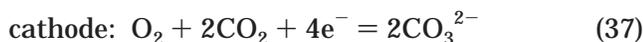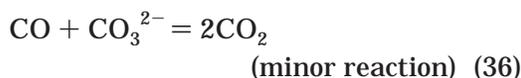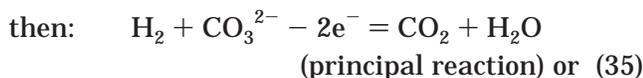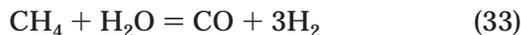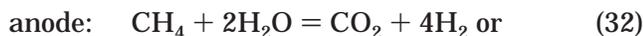
The PAFC is another fuel cell operating in acidic media. It has been frequently used in energy storage applications. The cell operates at $\sim$200 °C. Below 150 °C, its conductivity is reduced, and above 220 °C, the phosphoric acid is too volatile and tends to decompose. A SiC matrix separator holds the acid. The acid rejects the water reaction product. Above 150 °C, some CO can be tolerated in the anode feedstock. The kinetic hindrance at the oxygen cathode is the major source of losses. The active layer of platinum catalyst on carbon black support and polymer binder is backed by a carbon paper with 90% porosity, reduced somewhat by PTFE binder. The active layer consists of pores in the range of 3−50 μm with micropores in the range of 0.0035 μm. The anode operates at nearly reversible voltage with $\sim$0.1 mg/cm^2 catalyst loading. The cathode requires a higher catalyst loading of $\sim$1 mg/cm^2 of catalyst. Graphite bipolar endplates contain the gas flow channels and serve to provide heat removal by liquid flow. On shutdown, the cathode needs to be protected from corrosion by wet O_2. The electrode reactions are
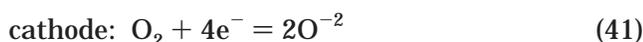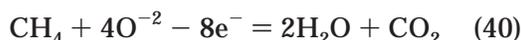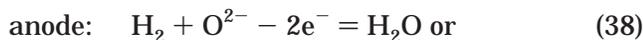
$$\text{anode: } H_2 - 2e^- = 2H^+ \tag{30}$$

$$\text{cathode: } O_2 + 4H^+ + 4e^- = 2H_2O \tag{31}$$
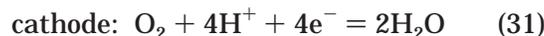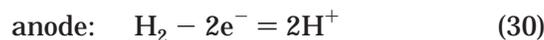
The hot H_3PO_4 electrolyte rejects water, the reaction product. The high temperature favors H_2O_2 decomposition, and peroxide buildup is less pronounced than for the aqueous electrolyte systems.

The MCFC finds application in energy storage applications. It operates best at $\sim$560 °C, and the waste heat can be used in cogeneration. The system does not use any noble metal catalysts and has a higher efficiency than the PEMFC and the PAFC. The separator is a LiAlO$_2$ ceramic tile separator filled with molten carbonates to prevent crossover of the reactants and aid in CO_3^{-2} transport. Lithium-rich carbonate electrolytes have higher conductivity but lower gas solubility and higher corrosion rates. At the operating temperature, problem areas include NiO dissolution and structural stability of the anodes and cathodes, changes in pore size distribution, and distortion of the electrode structures. Alternate LiFeO$_2$ cathode materials have low conductivity, and Ni−Cr anode materials have creep and stability issues. Control of the pore diameter is critical in the separator tiles. Increased pressure raises voltage but increases gas solubility and cathode dissolution and lowers operating life. The performance is limited by the electrolyte resistivity and the removal of the heat generated by the losses in electrode polarization. The cells are sensitive to sulfur contamination because of its effect on the nickel electrode materials and catalyst. Other problem areas include seal stability during thermal cycling and electrolyte creep. Typical operating parameters are 150 mA/cm^2 at 0.8 V at 600 °C. The anode reactions using the fuel methane (or

CO and H_2 stemming from CH_4 conversion) are

anode: $\quad CH_4 + 2H_2O = CO_2 + 4H_2$ or $\qquad$ (32)

$\qquad CH_4 + H_2O = CO + 3H_2$ $\qquad$ (33)

then: $\quad CO + H_2O = CO_2 + H_2$ $\qquad$ (34)

then: $\quad H_2 + CO_3^{2-} - 2e^- = CO_2 + H_2O$

$\qquad$ (principal reaction) or (35)

$\qquad CO + CO_3^{2-} = 2CO_2$

$\qquad$ (minor reaction) (36)

cathode: $O_2 + 2CO_2 + 4e^- = 2CO_3^{2-}$ $\qquad$ (37)

The SOFC operates at $\sim 800-1000$ °C with O^{2-} conduction in the solid phase. Limitations and problems arise from the high operating temperatures and place severe restrictions on the choice of materials. The materials must have very similar coefficients of expansion and be chemically stable in oxidizing and reducing conditions. At the operating temperatures, the hydrocarbon fuels (plus water, if needed) are quickly and completely re-formed in situ. The system operates at close to 96% thermodynamic efficiency and is tolerant to most impurities. It can deliver high-quality heat for cogeneration applications. The SOFC can operate on most any hydrocarbon or hydrogen fuel and is tolerant of short circuiting and to overloads. No noble metal catalysts are required. The anode consists of a porous cermet of Ni or Co catalyst on yttria-stabilized zirconia. The zirconia acts to inhibit grain growth of the catalyst particles of nickel or cobalt and protects against thermal expansion. The electrolyte itself consists of yttria-stabilized zirconia, which can be additionally deposited onto a calcia-stabilized zirconia. Yttria and calcia doping provide oxygen defects for better conductivity. The cathode is generally a strontia-doped lanthanum−manganite perovskite. The Sr dopant provides for oxygen transfer to the cathode−electrolyte interface. A Mg- or Sr-doped lanthanum chromate is used for the current collector and the intercell connection. It is impervious to the fuel and oxygen gases and is chemically and structurally stable in thin, dense, layered configurations. The cells operate at ~ 1 A/cm^2 at 0.7 V. Cells are constructed in cylindrical form or in the flat plate format shown in Figure 27. The cell reactions are

anode: $\quad H_2 + O^{2-} - 2e^- = H_2O$ or $\qquad$ (38)

$\qquad CO + O^{-2} - 2e^- = CO_2$ or $\qquad$ (39)

$\qquad CH_4 + 4O^{-2} - 8e^- = 2H_2O + CO_2$ (40)

cathode: $O_2 + 4e^- = 2O^{-2}$ $\qquad$ (41)

4. Electrochemical Capacitors (ECs)

4.1. Introduction and Market Aspects

ECs are sometimes called supercapacitors, ultracapacitors, or hybrid capacitors. The term ultracapacitor or supercapacitor is usually used to describe
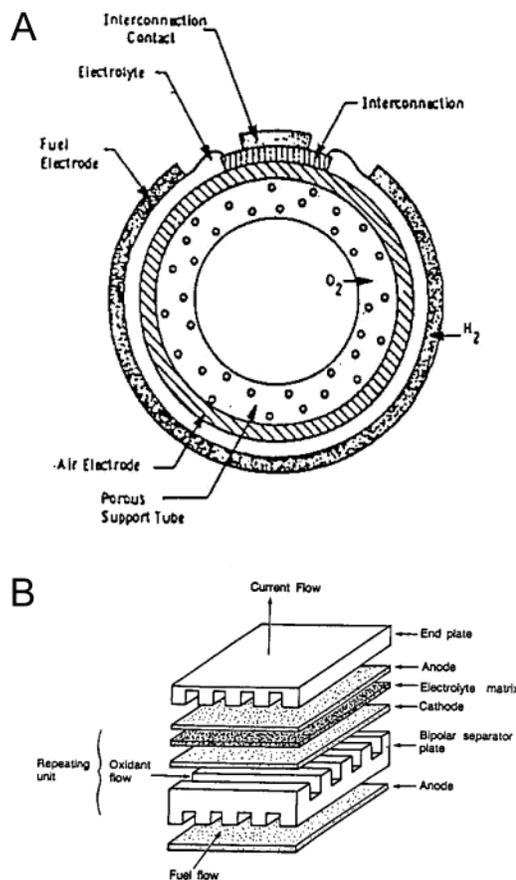

Figure 27. Schematic view of SOFC cylindrical and flat plate cell constructions.

an energy storage device based on the charge storage in the electrical double layer (EDL) of a high-surface-area carbon in aqueous electrolytes. The market for these devices used for memory protection in electronic circuitry is about $150−$200 million annually. New potential applications for ECs include the portable electronic device market, the power quality market, due particularly to distributed generation, and low-emission hybrid cars, buses, and trucks.

There is no commonly accepted nomenclature for ECs except that the definitions of anode, cathode, etc., carry over from battery and fuel cell usage, such as the anode as the negative terminal and cathode as the positive terminal. In general, ultracapacitors have referred to capacitors with two high-surface-area carbon electrodes for the anode and cathode. This arrangement where both electrodes have the same configuration will be referred to as a symmetric capacitor. The term supercapacitor has also been used to refer to the symmetric combination of two carbon electrodes that are catalyzed with ruthenium dioxide (RuO_2). The RuO_2 introduces a redox couple between two valence states of ruthenium, to result in higher capacitance for the carbon electrodes, but with a penalty in slower time constant for reacting to a pulse demand. A second type of EC combines a battery or redox electrode with a carbon electrode, such as nickel hydroxide cathode with a carbon anode. These supercapacitor or hybrid capacitors will be referred to as an asymmetric EC.
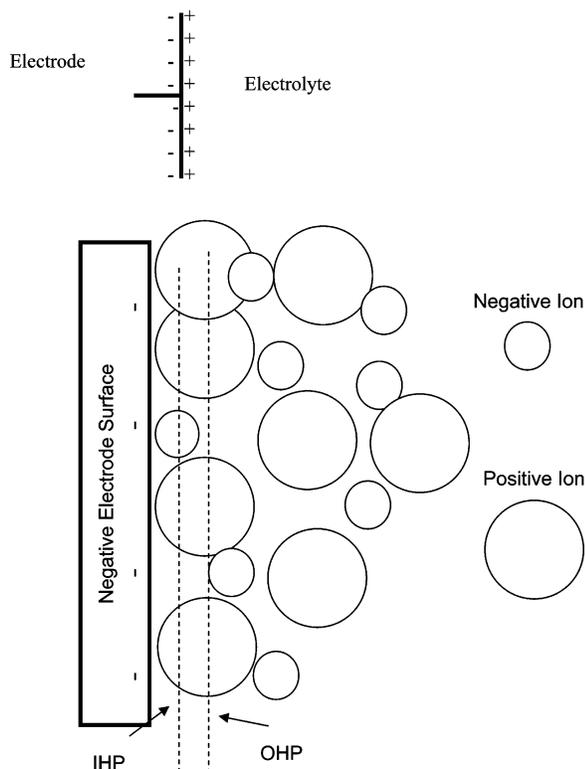
Figure 28. (A, top) Simple Helmholtz model of the electrical double layer. It is essentially a picture of a conventional capacitor. (B, bottom) Depiction of the electrical double layer at the surface of the negative electrode showing the outer Helmholtz plane (OHP) and the inner Helmholtz plane (IHP). The inner Helmholtz plane (IHP) refers to the distance of closest approach of specifically adsorbed ions and solvent molecules to the electrode surface. The outer Helmholtz plane (OHP) refers to the distance of ions, which are oriented at the interface by coulomb forces.

4.2. Characteristics of the Electrical Double Layer

When an electrode, that is, an electronic conductor, is immersed into an electrolyte solution, that is, an ionic conductor, there is a spontaneous organization of charges at the surface of the electrode and in the electrolyte facing the electrode. This EDL forms at the electrode−electrolyte interface with one layer at the surface inside the conductor and the other layer in the electrolyte as depicted in Figure 28. The two charged layers are considered to behave as a physical capacitor, with the charges in the solution and in the conductor separated by a distance of the order of molecular dimensions. The characteristics of the EDL depend on the electrode surface structure, the composition of the electrolyte, and the potential field between the charges at the interface. Depending on the surface charge of the electrode materials, positive or negative ions from the electrolyte form the solution part of the EDL at the interface between the electrode and the electrolyte. A simplified structure is shown in Figure 28A for the case of a negatively charged electrode surface. According to this simple Helmholtz model, the charges are concentrated on each side of the electrode surface. A more complex model of the EDL structure in Figure 28B takes into account the different sizes of the ions and their

reactivity with the surface. The outer Helmholtz plane (OHP) refers to the distance of closest approach of nonspecifically adsorbed ions (generally cations) in solution. Cations that populate the OHP are usually solvated and thus are generally larger than the less solvated anions. The interactions of the ions of the OHP with the surface charge have the character of coulombic interactions. The inner Helmholtz plane (IHP) refers to the distance of closest approach of specifically adsorbed ions (generally anions) and/or adsorbed solvent molecules to the electrode surface. These adsorption processes are determined by chemical affinities of the ions to the electrode surface and the field strength in the EDL. In practice, the structure of the EDL is much more complex than the models discussed above.

The double layer at the electrode surface forms and relaxes almost instantaneously. It has a time constant, or time of formation, of $\sim 10^{-8}$ s. Therefore, the structure of the double layer has the capability to respond rapidly to potential changes in the same time frame. The process involves only a charge rearrangement, not a chemical reaction. This rapid response to change is in contrast to the situation with the redox electrode reactions in batteries and fuel cells. The time constant for the redox reactions is much slower and in the range of $10^{-2}-10^{-4}$ s related to the impedance of the reaction. The redox reactions contribute to "polarization capacitance" associated with the electrode reactions. The other main difference between supercapacitors and batteries and fuel cells is the reversibility (short time constant) of the EDL process compared to the longer time constant of the redox reactions and the stress from detrimental side reactions, which reduce the cycle life and long-term stability of the device. Whereas cycle life and stability of the double layer electrochemical capacitor can easily exceed 1 million cycles, battery electrodes can reach this level only if charged and discharged at a low depth of discharge.

When carbons are placed in an electrolyte, they generally assume a voltage near the zero point of charge of the EDL. In aqueous solutions, this is near 0 V versus hydrogen. By applying an external voltage, many more additional ions and electrons can be moved to the double layer, increasing the capacitance C (= charge per applied voltage, $C = Q/U$). As a rule of thumb, carbons and metals typically have a double-layer capacitance in the range of $10-40 \ \mu F/cm^2$. The exact values depend mainly on the voltage and the extent of participation of the IHP in the electrical double layer. A high-surface-area carbon electrode can yield a capacitance of ~ 4 F/g.

4.3. EC Operation

As noted above, electrochemical capacitors are close cousins to batteries. The simple circuit shown illustrates their basic operation.
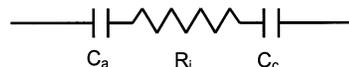
Here, C_a and C_c are the double-layer capacitances of the anode and cathode, respectively. R_i is the internal
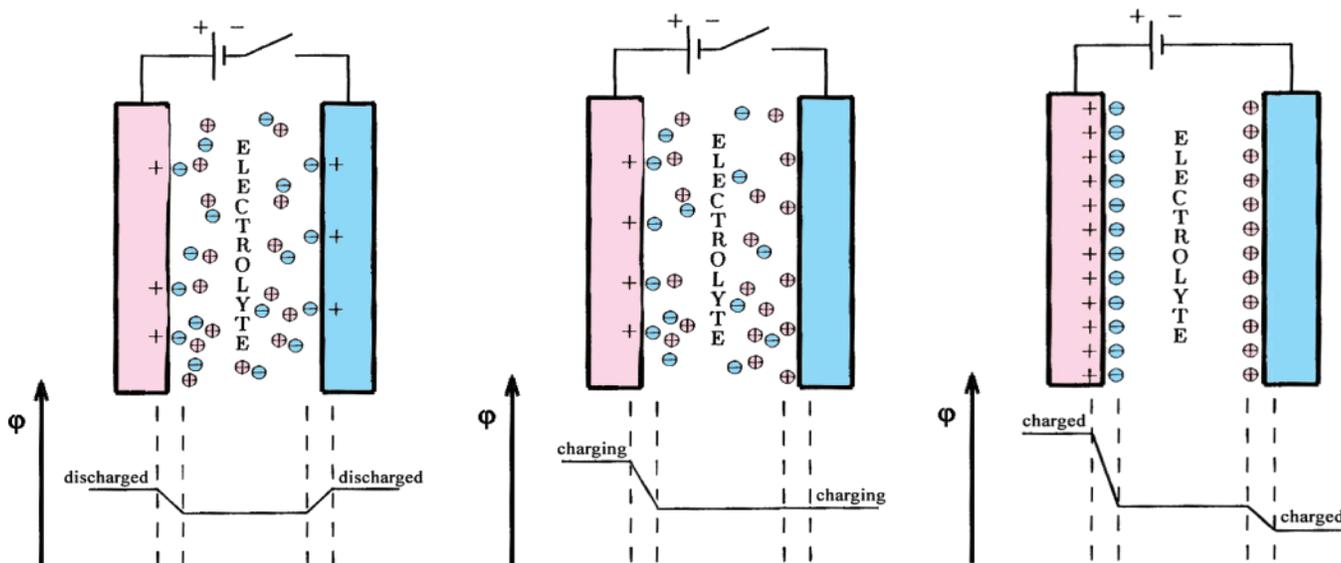
Figure 29. Depiction of the charging process of a symmetric capacitor.

resistance of the cell. For capacitors in series

$$1/C = 1/C_a + 1/C_c \qquad (42)$$

If $C_a = C_c$, as would be expected for an ultracapacitor, then

$$C = {}^1\!/_2 C_a \qquad (43)$$

High-surface-area carbon is the material of choice, as it combines a large surface area wetted by the electrolyte, high electronic conductivity, and chemical and electrochemical stabilities with low cost. The capacitance of these devices can be orders of magnitude larger than those of conventional dry and electrolytic capacitors. The voltage for electrochemical capacitors with aqueous electrolytes is ~1 V, limited by the voltage stability of the electrolyte. By switching to an organic-based electrolyte, voltages of up to 2.7 V can be found in practice. However, the organic electrolytes have lower double-layer capacitance and poorer conductivity. Because the energy storage is given by energy = $^1\!/_2 Q V^2$, the higher voltage permitted by an organic electrolyte significantly increases the energy storage capability of the EC. Because the resistivity is ~100 times larger than for aqueous electrolytes, the time constant for response to a large pulse is slower for the nonaqueous electrolyte-based ECs.

The charge–discharge of a symmetric EC composed of two carbon electrodes with approximately the same mass immersed in an aqueous or nonaqueous electrolyte is shown in Figure 29. With zero applied charge Q, both electrodes of a cell are at the same voltage. The potential of the electrodes increases in opposite directions during charge, as each has approximately the same capacitance. Maximum cell operating voltage is reached when one of the electrodes reaches the stability limit of the electrolyte.

The asymmetric type of EC incorporates a battery electrode as one of the electrodes. The battery electrode has a capacitance associated with the redox
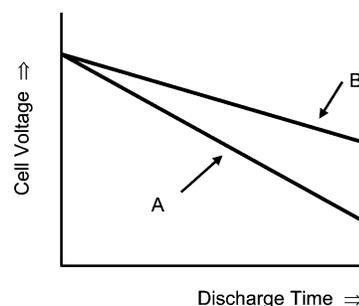

Figure 30. Operation principle of an EC in the discharged state, during charging, and in the charged state: (A) for a symmetric construction and (B) for an asymmetric construction.

battery reaction of ~10 times the capacitance of the electrical double layer. For instance, if the nickel battery cathode is substituted for the cathode in a symmetric capacitor, for example, NiOOH for carbon, then substituting $C_c = 10 C_a$ in eq 42, the capacitance of the EC is essentially doubled.

$$1/C = 1/C_a + 1/10 C_a \qquad (44)$$

$$C \approx C_a \qquad (45)$$

This asymmetric type of EC is often termed a "hybrid" capacitor. The typical discharge curve for this hybrid EC is shown in Figure 30. Because the battery electrode has a capacity of 3–10 times that of the double-layer electrode, it remains at an invariant voltage during charge and discharge. As a result, the discharge voltage of the hybrid capacitor falls more slowly than that of the carbon–carbon EDL capacitor.

In some cases, the kinetics of the redox charge–discharge reactions can proceed almost as quickly and reversibly as EDL charging. Thin film redox electrodes, based on the lithium intercalation/insertion principle such as $Li_4Ti_5O_{12}$, exhibit high reversibility and fast kinetics. The RuO_2 materials deposited on carbon show "pseudo-capacitive" charge–

discharge behavior as do polymeric materials such as polyaniline, polypyrrole, and polydiaminoanthraquinone (DAAQ). These have facile kinetics and have shown high capacitance and long life. The insertion of anions and cations into their structure can yield capacitances of up to 200 μF/cm² and, moreover, they can be easily fabricated as thin films.

5. Summary

Electrochemical energy conversion devices are pervasive in our daily lives. Batteries, fuel cells and supercapacitors belong to the same family of energy conversion devices. They are all based on the fundamentals of electrochemical thermodynamics and kinetics. All three are needed to service the wide energy requirements of various devices and systems. Neither batteries, fuel cells nor electrochemical capacitors, by themselves, can serve all applications.

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