

Chapter 9

Batteries for Implants

Abstract Batteries for implants must possess characteristics such as safety, reliability, high volumetric energy density, low self-discharge, and long duration of service, which represent essential commitments from manufacturers. The state of discharge must be indicated. In the primary batteries, lithium metal anodes are used. The cathode systems include iodine, manganese oxide, carbon monofluoride, silver vanadium oxide, and crossbreed or hybrid cathodes. This choice of batteries caters to the power levels required by implantable devices, which are spread over a broad range of current values from microampere to ampere levels. Limited battery life is a major impediment to the development of advanced medical implant devices, e.g., when a pacemaker battery runs out, it has to be replaced by surgery. With progressive shrinkage of implant size, more emphasis is laid on building smaller, longer-lasting batteries. Applications involving high power usage rates such as neurostimulators working at milliwatt powers employ secondary rechargeable batteries to achieve longer life span with reduced size.

Keywords Battery • Lithium battery • Iodine cathode • Manganese dioxide cathode • Carbon monofluoride cathode • Silver vanadium oxide cathode • Lithium-ion battery

9.1 Introduction

The battery is a system for storing electrochemical energy. Strictly speaking, the battery comprises a multitude of interconnected cells, joined together in a series combination to yield the necessary voltage, and in a parallel connection for achieving the desired current capacity. Each cell comprises two electrodes: a positive electrode and a negative one. These electrodes are separated by a solution of an electrolyte, usually a salt which dissociates into constituent ions, to allow transference of ions from one electrode to the other. Upon connecting these electrodes electrically, the chemical reactions advance in tandem at the two electrodes. These chemical reactions, occurring at the same time, release electrons and enable the valving of current, either its controlling or halting, by the device connected to battery. To facilitate understanding, the battery terminology is briefly presented in Table 9.1.

Table 9.1 Battery terminology

Sl. No.	Term	Meaning	Unit/measure (if applicable)
1.	Battery	A device used for transformation of chemical energy into electrical energy in the form of direct current and, conversely, electrical energy into chemical energy	–
2.	Primary battery	A non-rechargeable or non-reenergizeable battery	–
3.	Secondary battery	A rechargeable or reenergizeable battery	–
4.	State of charge (SOC)	Available battery capacity expressed as a fraction of its rated capacity	%
5.	Depth of discharge (DOD)	Complement of SOC, it expresses how deeply a battery is depleted. Specified as a fraction of battery capacity that has been discharged/ its maximum capacity	%
6.	Terminal voltage	Output voltage determined across the poles of the battery when load is applied	V
7.	Open-circuit voltage	Output voltage ascertained across the poles of the battery without application of load	V
8.	Nominal voltage	Reported or imprinted voltage of the battery	V
9.	Cutoff voltage	Voltage defining the fully discharged state of the battery	V
10.	Capacity/nominal capacity/ coulometric capacity	Electric charge stored in the battery = current drawn from a battery × the number of hours the current flows	Ah or mAh
11.	Gravimetric energy density/ specific energy	Energy storage efficiency expressed as nominal battery energy per unit mass; energy-to-weight ratio	W/kg
12.	Volumetric energy density	Energy storage efficiency expressed as nominal battery energy per unit volume; energy-to-volume ratio	W/L
13.	Power density	Maximum available power per unit volume	W/L
14.	Shelf life	Period during which a battery preserves a certain fraction of its capacity when not being used	Hours

Table 9.2 Some lithium-based batteries

Sl. No.	Battery	Anode	Cathode	Electrolyte	Open-circuit potential (V)
1.	Li/ I ₂ -PVP	Lithium	I ₂ /PVP = 30:1 to 50:1	Lithium iodide	2.8
2.	Li- MnO ₂	Lithium	MnO ₂ + conductive agents	Organic solvent mixture	3.1–3.3
3.	Li/CF _x	Lithium	CF _x	LiBF ₄ dissolved in γ -butyrolactone or GBL (C ₄ H ₆ O ₂)	3.1
4.	Li/ SVO	Lithium	SVO	Propylene carbonate or PC having formula CH ₃ C ₂ H ₃ O ₂ CO and dimethoxyethane (C ₄ H ₁₀ O ₂) with a lithium salt in the form of a solution	3.2
5.	Li-ion	Graphite (Carbon)	Lithiated cobalt oxide	Lithium salts, such as LiPF ₆ , LiBF ₄ , or LiClO ₄ , dissolved in ether (C ₄ H ₁₀ O)	3.7

Because of their capability to provide high energy density and afford wide design flexibility, Li-based batteries (Table 9.2) have superseded other battery systems. Today, they lead in portable battery sales worldwide [1]. Primary and secondary lithium batteries have already become the premier prototypical sources of power. They offer opportunities for uncontaminated and efficient storage as well as conversion of electrochemical energy. Every day, they are getting more importance for powering modern society. The term “lithium batteries” encompasses the entire gamut of battery systems in which lithium is used as the anode material. However, these batteries differ in features such as cathode material, electrolyte, cell design, and other mechanical aspects. Further, these batteries are wrapped in an assortment of form factors such as coin, cell, and film or prismatic. Each lithium system is distinguished by its inherent characteristics, e.g., electrical properties, energy density, operating temperature, reliability, and safety.

A fundamental reason for the use of lithium is that it is the lightest metal. It has a density about half that of water = 0.534 g/cm³. Hence, if lithium was not so reactive, a chunk of lithium metal will float on water. However, it reacts vigorously with water. Other notable features of lithium are that it is the third element in the periodic table. Lithium has the smallest atomic number of any metal = 3. So, the number of protons in the lithium atom = 3. Electronic configuration of lithium is 1s²2s¹. It belongs to the alkali metal group, the Group 1 of the periodic table of chemical elements. It is soft, silver-white in color, and flammable.

A lithium atom loses one electron in its outermost shell to acquire a stable atomic configuration. In chemistry, this tendency is described as an electropositive behavior. Electropositive elements are those which lose electrons to become positively charged. Lithium is one of the highly electropositive elements. In aqueous solution,

the standard potential for the cathode half-reaction Li^+ (aqueous) + e^- (electron) = Li (solid) versus the hydrogen electrode is -3.04 V. The negative sign indicates that Li has a tendency to be oxidized rather than reduced in comparison with hydrogen. In other words, lithium is a reducing agent. The standard potential of lithium far exceeds that of magnesium, calcium, and sodium. The extreme lightness of lithium combined with its electropositive character has led to its prolific use in battery technology. Due consideration is taken of its reactivity. Among the other properties that speak in favor of lithium for use in batteries may be mentioned its low volume resistivity ($9.5 \times 10^{-6} \Omega \text{ cm}$), high ionization energy (5.39 eV), and low melting or liquefaction point ($180.5 \text{ }^\circ\text{C}$). Its comparative plentitude (0.0017% in earth's crust), as shown by its occurrence in several materials, further strengthens its case. Examples of these materials are continental, geothermal, and oilfield brines. The spectacular electrochemical equivalent of lithium is 0.259 g/Ah . It clearly overrides all other contestants. Notably, Mg, Ca, and Na have electrochemical equivalents of 0.45 g/Ah , 0.75 g/Ah , and 0.86 g/Ah , respectively. Although Al is a close follower with 0.34 g/Ah , its low standard potential of -1.7 V leads to its exclusion from the race.

Lithium shows almost ideal fundamental properties, amply justifying its use as the anode in both primary and rechargeable batteries. Therefore, scientists have associated the well-accepted and voguish lithium anode with a large number of cathode materials and different electrolytic solutions. This pairing has resulted in the spacious choice of various chemistries. Lithium batteries are subdivided into two classes: primary cells for one-time use and secondary or rechargeable cells for multiple usages. The primary cells contain lithium metal anodes. They represent the preferred battery for cardiac pacemakers. Secondary cells exploit lithium-ion chemistry. They are used with neurostimulators [2].

9.2 Lithium/Iodine–Polyvinylpyridine Battery

Beginning from the work of Gutmann et al. [3] in 1967, patented by Schneider and Moser in 1972 and Moser in 1972, it supplies current in the microampere range. It is the favorite choice for implantable cardiac pacemakers. Since 1972, the battery has undergone drastic improvement. Its energy has reached three times that of the first battery. It has an exemplary track record of reliability and safety [4].

The anode of this battery is made of lithium (Fig. 9.1). The cathode is formed by the thermal reaction of iodine and polyvinylpyridine, $(\text{C}_6\text{H}_9\text{NO})_n$, a water-soluble polymer made from *N*-vinylpyrrolidone, $\text{C}_6\text{H}_9\text{NO}$. The (I_2/PVP) ratio varies from 30:1 to 50:1. The reaction between iodine and PVP is accompanied by evolution of heat. It is a highly exothermic reaction. This reaction starts a little below the melting point of iodine ($113.5 \text{ }^\circ\text{C}$). In the resulting polymeric structure, one iodine molecule is attached with nitrogen atom on the pyridine ring (an aromatic heterocyclic compound characterized by a 6-membered ring structure composed of 5 carbon atoms and 1 nitrogen atom; chemical formula $\text{C}_5\text{H}_5\text{N}$), and an iodine atom substitutes the

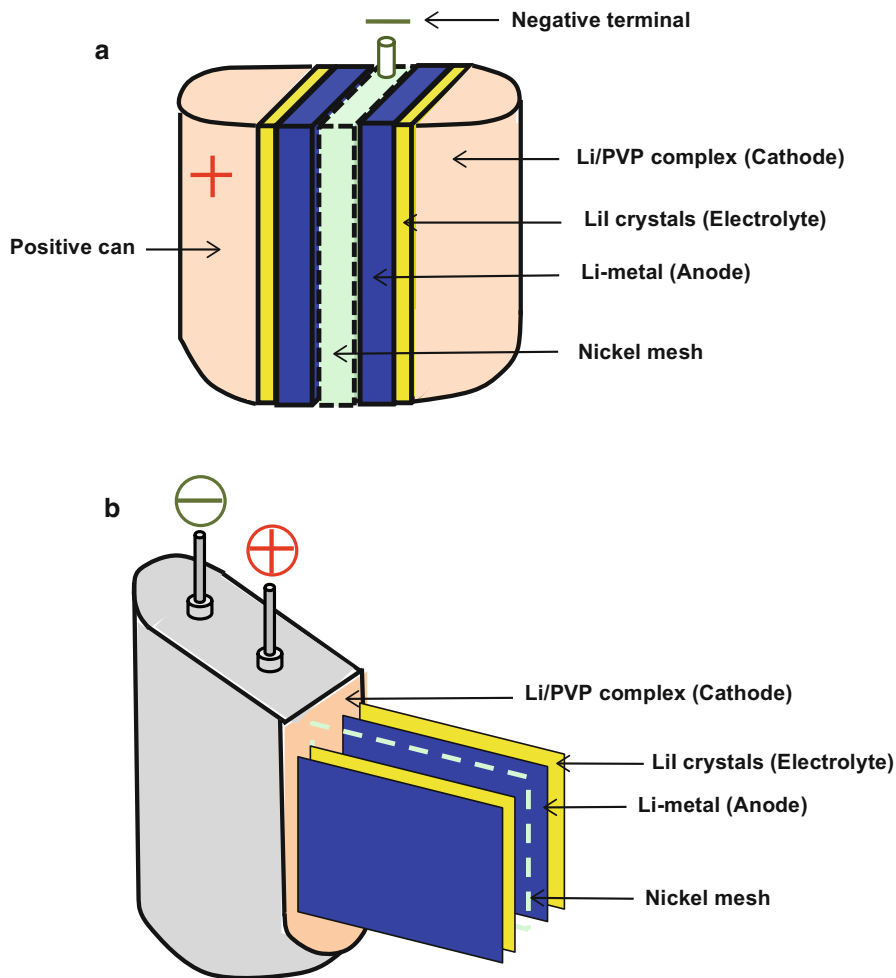


Fig. 9.1 Layers in the Li/I₂-PVP battery consisting of two cells: (a) front view of the cell (b) cutaway view of cell opened from side to show the layers

alpha hydrogen atom (a hydrogen atom on an alpha carbon, i.e., a carbon atom directly bonded to an atom, group, functional group, or other moiety in an organic molecule) on the polymer chain. This polymeric structure is a conductor showing electronic conductivity. The conductivity varies with the I₂/PVP ratio. The peak value of conductivity occurs at the I₂/PVP weight ratio of 8:1. Since the starting value of this ratio is considerably higher, the electronic conductivity increases until it attains a weight ratio of 8:1. Subsequently, it begins to decrease with the progression of cell reaction.

The electrolyte in this battery is lithium iodide. It is a solid electrolyte or superionic conductor showing a high ionic conductivity due to the fast diffusion of one ionic species in a framework or lattice constituted by ions of opposite sign. The

electrolyte also functions as a cell separator. It is a product of the basic cell reaction between lithium and elemental iodine: $\text{Li} + \frac{1}{2}\text{I}_2 \rightarrow \text{LiI}$. The Gibb's free energy of this reaction, i.e., the energy that can be used to do work, is -64.45 kCal/mol. The resultant open-circuit voltage from the cell is 2.8 V. The construction of the battery involves formation of a LiI layer at the anode by the addition of molten cathode material (I_2 -PVP) to the Li anode. In one time-consuming method, a solution of the organic material in a solvent is carefully smeared on the anode by painting or brushing. In another method, a sheet of the organic material is preformed by hot pressing. The sheet is applied to the anode surface using an adhesive. This requires a greater amount of organic material. Also, it is difficult to retain flexibility of the sheet under dry conditions. In a further improved method [5], the substrate material is flexible. It is preferably a synthetic open mesh fabric. The applied film is also flexible. It can be applied over a smooth or irregular surface. The method provides greater manufacturing efficiency, better uniformity, and reduced cell-to-cell variability.

Discharging of the battery is accompanied by growth and thickening of the LiI layer. Exhaustion of Li and I_2 takes place. The cell impedance increases. The battery voltage decreases. The same is easily detected by the electronic circuit in the pacemaker. Thus the discharge profile of the battery is an indicator of its condition. It allows the doctor to know the end-of-service point of the battery. The doctor can therefore plan timely preventive scheduling of the surgery for battery replacement.

Historically, the first commercially triumphant Li/ I_2 -PVP battery was large in size (14 mm \times 45 mm \times 52 mm). It had a capacity of 3.5 Ah. The second smaller size design had a capacity of 1.4 Ah. As mentioned in Table 9.1, the ampere-hour (Ah) representing a unit of electric charge, is the rating of the battery capacity. A battery which is able to supply a current of 1 A to a load nonstop for 1 h is said to have a capacity of 1 Ah.

The first case-grounded battery was produced in 1975. Also, noting that stainless steel was not attacked in absence of water, the unrequired inert material was eliminated from the design. The energy density was thereby tripled. Subsequent improvements included the increase of I_2 -PVP ratio from 10:1 to 30:1 for achieving higher energy density. The use of a grooved, wrinky anode enlarged the surface area and hence the capability of the battery for delivering current.

9.3 Lithium–Manganese Dioxide Battery

Launched into commercial market by Ikeda et al. (1977, 1978), this battery is used for medium rate applications. Some of the applications are additional functionality pacemakers, neurostimulators, and drug delivery systems. These devices/systems require power at milliwatts level. Li– MnO_2 system offers a good balance of performance and safety for consumer applications.

The anode is made of pure lithium metal. The cathode is a high conductivity mixture of heat-treated electrolytic manganese dioxide (MnO_2) with conductive agents. The electrolyte is an organic solvent mixture. The mixture contains mainly

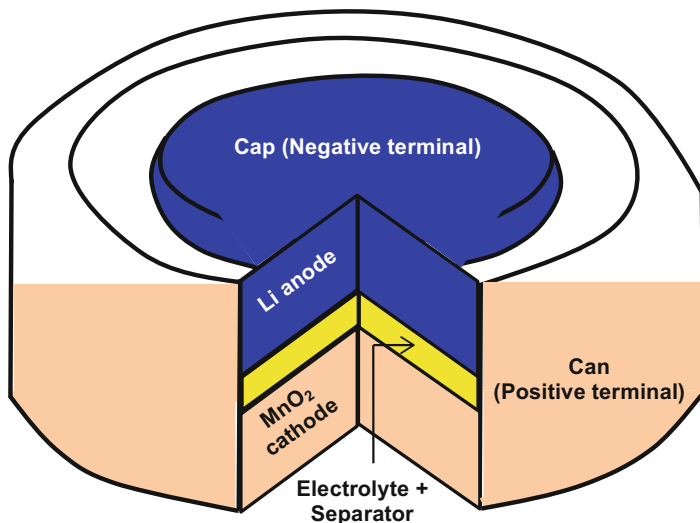


Fig. 9.2 Li–MnO₂ button cell

ethers, with an alkali metal salt dissolved in it (Fig. 9.2). This electrolyte is liquid at room temperature and normal pressure. It is nontoxic and noncorrosive. Electrolyte filling is done by creating a vacuum inside the cell. The cell is hermetically sealed. There is no internal cell pressure. The safety vent opens if the internal temperature or pressure of the cell exceeds predefined limits. A separator is placed between the anode and the cathode. In one version of separator, a polyethylene layer is sandwiched between two polypropylene layers.

A larger battery voltage in the initial stage as well as during discharge is possible due to the high conductivity of the cathode. Also, reliable performance after long storage periods is assured by the thermodynamically stable MnO₂. The cell has a long shelf life up to 10 years. High ionic conductivity together with low viscosity of the electrolyte permits efficient utilization of cathode over varying temperatures and during rapid discharge periods.

At the anode, lithium is oxidized to Li⁺ ions: $\text{Li} \rightarrow \text{Li}^+ + e^-$ (electron). Inside the cell, the Li⁺ ion diffuses through the electrolyte and separator towards the cathode. Outside the cell, the electron moves from anode to cathode. At the cathode, Li⁺ ion, tetravalent MnO₂, and electron combine. Tetravalent MnO₂ is reduced to trivalent MnO₂. The solid product formed during the discharge reaction is left behind in the cathode. The discharge reaction is not accompanied by the liberation of any gaseous product. Hence, there is no buildup of pressure inside the cell. So, a pressurized situation does not develop, increasing the safety. The cell reaction is $\text{Li} + (\text{MnO}_2)^{4+} \rightarrow \text{Li}^+ + e^- + (\text{MnO}_2)^{3+} \rightarrow \text{Li}^+ (\text{MnO}_2)^{3+}$. Open-circuit voltage of the cell ranges from 3.1 to 3.3 V. Therefore, a single Li–MnO₂ cell replaces two conventional cells.

The voltage profile during discharge comprises three distinctive regions. The first region is characterized by a gradually decreasing voltage. The second relatively long-duration region is marked by a flat voltage–time graph showing constancy of voltage. In the third region, the voltage slowly decreases towards the end of cell life [6–8]. These three regions correspond to the three stages of insertion of lithium into the manganese dioxide lattice. The first and the third regions represent the insertion of lithium into the MnO_2 lattice via a homogeneous reaction, i.e., one that occurs in a single phase. The second region pertains to a two-phase reaction.

Lithium batteries are made in either of the two versions: solid core (Fig. 9.3) or wound (Fig. 9.4).

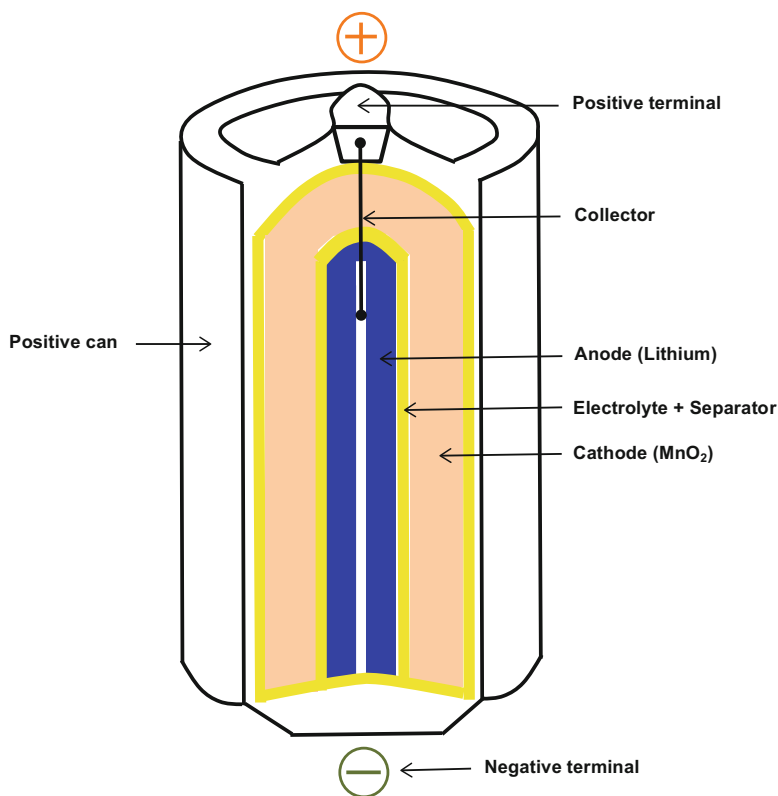


Fig. 9.3 The basic components of a lithium solid-core battery

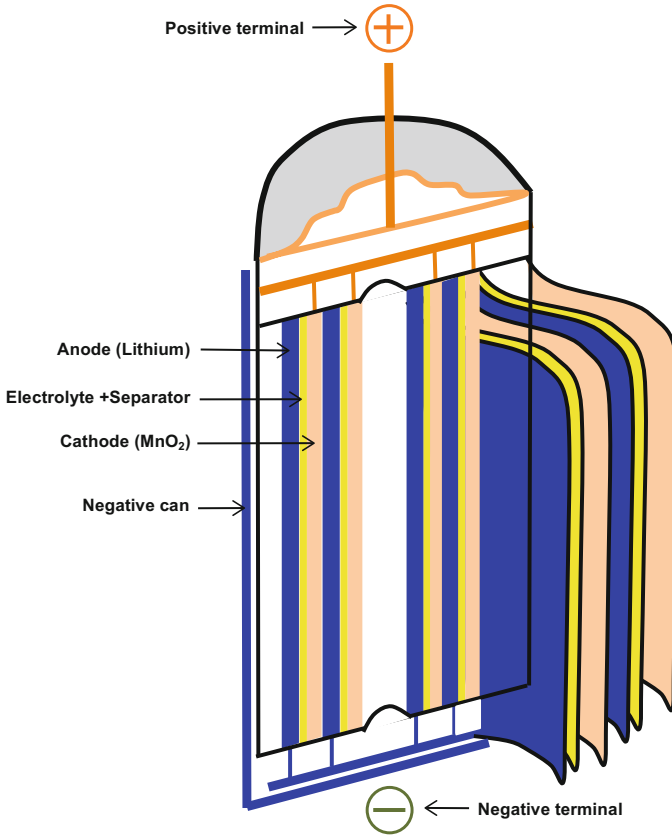


Fig. 9.4 A wound lithium cylindrical battery

9.4 Lithium/Carbon Monofluoride Battery

This battery is an alternative choice for milliwatt power range because of its low internal impedance. Its high energy density guarantees long life operation for implantable devices working at medium rate currents. Predictability of its discharge profile allows electronic determination of end point. Low self discharge and reliable cell chemistry are additional benefits.

The cell is made of a lithium anode, a carbon monofluoride (CF_x) cathode, and lithium tetrafluoroborate ($LiBF_4$) electrolyte dissolved in γ -butyrolactone. Highly stable carbon monofluoride is obtained by fluorination of carbon with fluorine at 400–600 °C. Usually, a carbon substrate such as graphite powder is exposed to fluorine gas at high temperature. This exposure creates a material where fluorine is intermixed with carbon at a molar ratio near 1:1, but generally not precisely 1:1 [9]. These materials are collectively referred to as carbon monofluoride. They often range from $CF_{0.68}$ to $CF_{1.12}$. The structure of CF_x contains sp^3 hybridized layers of carbon in which

the fluorine atoms are covalently bonded to carbon. A higher fluorine percentage decreases the electrical conductivity of CF_x . Therefore, a conductive additive is included along with a binder to allow pressing of the cathode pellet. Li/CF_x batteries permit customization or tuning of the cathode according to specific applications. Variation of the incorporation of fluorine inside the carbon structure at the atomic scale at the time of bulk production leads to these changes conforming to individual or personal specifications. Thus properties of the battery are modified to obtain higher energy densities. By such customization process, characteristics of the battery can also be altered in other ways to achieve the performance desired by the user.

The cell operates through the chemical reaction: $x\text{Li} + \text{CF}_x \rightarrow x\text{LiF} + \text{C}$. It gives an open-circuit potential of 3.1 V [10]. The discharge occurs initially through inclusion of solvated Li^+ ions within the fluoride stratum. Consequently, a transitional phase is formed. This phase consists of carbon, fluoride, and lithium ions. It is a diffusion layer which slowly decomposes into LiF , C , and solvent molecules.

The discharge potential of the cell increases by heat treatment of CF_x at a temperature lower than that causing its decomposition [11]. Carbothermal treatment using a combination of heat with carbon black increases the discharge performance [12].

Comparing $\text{Li}-\text{MnO}_2$ battery with Li/CF_x type, $\text{Li}-\text{MnO}_2$ batteries have lower gravimetric and volumetric energy densities, typically 200 W/kg and 550 W/L than Li/CF_x contenders whose values are ~ 700 W/kg and 850 W/L. Ranges of working temperature for the $\text{Li}-\text{MnO}_2$ and Li/CF_x batteries are -20 to -60 °C and -60 to -160 °C, respectively. Corresponding shelf life ranges are 5–10 years and 15 years. The only disadvantage of Li/CF_x battery is its moderately higher price. This higher price far outweighs its superior performance.

Rangasamy et al. [13] found that a new solid, bifunctional electrolyte Li_3PS_4 (LPS) can generate 26 % higher capacity than the theoretical maximum if each component acted independently. It also extends the life span of the device. The increase in capacity is caused by the supportive interactions between the electrolyte and cathode. The solid electrolyte serves as the chemically inactive electrolyte at the anode. It also acts as an active ingredient at the cathode. With the discharging of the battery, a lithium fluoride salt is produced. This salt promotes the electrochemical activity of the electrolyte. It converts the electrolyte from an inactive to an active component of the battery. This finding supersedes the hitherto prevalent belief that in a battery the anode, cathode, and the electrolyte can play only single roles. This is because of the dual role shown for the electrolyte. The revolutionary idea will help in designing batteries of unparalleled energy densities.

9.5 Lithium/Carbon Monofluoride–Silver Vanadium Oxide Hybrid Battery

This battery supplies superior capability for pulsatile current flow than a Li/CF_x battery can do on its own. Besides supplying a higher power density than Li/CF_x cells, the provision of a broad high-level region or tableland at a lower potential towards the completion of discharge affords easier end point detection. It has mixed-breed

cathodes conglomerated from CF_x and silver vanadium oxide (SVO), $\text{Ag}_2\text{V}_4\text{O}_{11}$. In one design, the two are physically mixed together. In the other design for high current pulses, a laminated cathode is used. In the physically mixed hybrid cell, at low current rates, first the partial reduction of SVO takes place. In the next stage, CF_x is completely discharged. Finally, the residual SVO is reduced [14]. At higher rates of current, SVO delivers a major portion of energy. The reason is its high current-carrying capability. This decreases its potential with respect to CF_x . So, it is recharged by CF_x . By that means, the potentials of SVO and CF_x are in equilibrium. Depending on the application, the composition of the mixture is varied to fulfill the desired capacity or power density need.

9.6 High-Rate Lithium/Silver Vanadium Oxide Battery

This battery has the capability to supply intermittent current pulses of magnitudes 2–3 A for charging the capacitors of implantable cardioverter defibrillators as well as supplying a continuous current of small value for pacing the cardiac system. Therefore, it is commonly used in defibrillators. The cell has a Li anode. The silver vanadium oxide cathode is prepared by a solid-state synthesis route. Its layered structure embodies edge and corner sharing, distorted, octahedral VO_6 structures. The electrolyte consists of propylene carbonate ($\text{C}_4\text{H}_6\text{O}_3$) and dimethoxyethane ($\text{C}_4\text{H}_{10}\text{O}_2$) with a lithium salt in solution. There are two cell designs: (1) either multi-plate cathode type in which several cathodes are parallelly connected to increase the output or (2) a flattened coil in which the anode and cathode strips are wound together. The discharge reaction is: $7\text{Li} + \text{Ag}_2\text{V}_4\text{O}_{11} \rightarrow 2\text{Ag}^0 + \text{Li}_7\text{V}_4\text{O}_{11}$. It provides an open-circuit potential of 3.2 V [15, 16]. The discharge product is $\text{Li}_x\text{Ag}_2\text{V}_4\text{O}_{11}$, where x denotes the number of moles of lithium intercalated into SVO. Intercalation is the reversible insertion of a material between layers in a lattice. The Ag^+ ion is reduced to Ag^0 from $0 < x < 2.4$. Crystallinity is lost during this process. Silver reduction improves the capacity. So, high-rate applications are catered to. Earlier in the discharge process, vanadium reduction takes place. But from $2.4 < x < 3.8$, the reduction of V^{5+} to V^{4+} dominates. At $x > 3.8$, during further reduction, V^{4+} changes to V^{3+} . Thus, mixed valence materials containing V^{3+} , V^{4+} , V^{5+} ions are formed. Due to this multistage reduction, the potential profile is a stepped one. This profile is beneficial for fibrillator use. It allows physicians to envisage the terminal stage of battery.

The superior electrochemical performance of nanostructured SVO as compared to bulk SVO can be utilized to enhance the battery function [17]. If nanoscale SVO particles are used, the movement of Ag^+ and Li^+ ions in the SVO skeleton becomes faster. The transport becomes faster due to their shorter diffusion lengths. In addition, the exceptional electronic properties of nanoparticles result in higher capacities and cell voltages.

9.7 High-Rate Lithium–Manganese Dioxide Battery

This battery has the capability to deliver current pulses of large magnitudes. It is a useful optional choice for implantable cardioverter defibrillators. Here, the cathode is a mixture of MnO_2 with chromium oxide and lead oxides. This mixture produces a profile of battery discharge, which clearly signposts the point at which cell replacement is warranted [18]. Augmentation of cell performance is achieved by employing a double cell design [19]. In this design, two cathode-limited series-connected cells are employed in a single battery enclosure for reducing the volume. Still further performance amelioration is accomplished by integrating cathode-limited double cells into a mixed structure. Consequently, a greater value of low rate capacity is obtained at a reduced consumption of volume. There is a trivial deterioration in the capability to provide pulsed power. Pulsed power is provided by storing energy for a long time and releasing it suddenly in the form of a high-energy pulse so that instantaneous power delivered has a very high value [20]. The discharge curve of Li–MnO_2 cell for use in defibrillator devices has been mathematically modeled [21]. The model enables prediction of cell behavior.

9.8 High-Rate Lithium/Carbon Monofluoride–Silver Vanadium Oxide Hybrid Battery

It can deliver high current pulses like Li–MnO_2 and $\text{Li/CF}_x\text{–SVO}$ batteries and serves identical function. A novel electrode design-based $\text{Li/CF}_x\text{–SVO}$ hybrid cell gives high current pulse output for defibrillation. It employs a cathode consisting of CF_x juxtaposed between two SVO layers [22]. The cells exhibit a stepped discharge profile with plateaus at 3.2, 2.8, and 2.6 V. These plateaus pertain to the discharging of SVO, CF_x , and SVO layers, respectively. At the beginning, SVO is reduced. Then CF_x supplies a major portion of energy for low rate currents. But in the event of heavy load pulsing of the cell, preferential discharging of SVO takes place. Then the resultant potential of silver vanadium oxide is less than that of carbon monofluoride. The profile of cell discharge has the shape of a series of steps; hence, it is called a stepped profile. This kind of profile readily signifies the condition when the battery is down.

9.9 Secondary Lithium-Ion Battery

It is a battery for milliwatt power level. It can be recharged in the implanted state to the original pre-charge condition. It is used in neurostimulators working in the milliwatt power range. As for primary batteries, essential qualities expected for these batteries are also safety and reliability. Over and above, the battery must have high

energy density. Low self-discharge is another virtue. These qualities cannot be least compromised with for implantable devices.

The working of secondary cells is based on lithium-ion cell technology [23]. Early efforts to produce lithium batteries that could be recharged for reuse were frustrated by their substandard cycling characteristics. Problems concerning safe handling of metallic lithium, a reactive caustic metal, further aggravated the issue. These attempts were not successful until a carbon anode was used. This anode permitted the intercalation (insertion) of ionic lithium and its pairing with a high-voltage cathode. This was done using lithiated cobalt oxide. A substitute cathode material is lithium iron phosphate (LiFePO_4). It has a marginally lower capacity as rivaled against lithium cobalt oxide (LiCoO_2). But its conductivity is appreciably lower. It is inexpensive and also displays lower chemical reactivity.

The Li-ion cells have a carbonaceous anode. The cathode is made of a metal oxide (Fig. 9.5). The electrolyte is a mixture of lithium salts, e.g., LiPF_6 , LiBF_4 , or LiClO_4 . These salts are dissolved in an organic solvent like ether. In these cells, both the electrode materials can intercalate lithium ions reversibly. Materials used in cathode manufacture are nickel-, manganese-, and cobalt-based oxides. LiCoO_2 is very frequently used. Its structure is composed of interspersed layers of LiCoO_2 , interchanging repetitively with one another [24]. The layered structure facilitates the intercalation of lithium ions. The cell construction involves the use of a discharged cathode as the Li^+ ion source. Initial charging digs out lithium from the cathode and infuses it into anode (Fig. 9.6). Upon discharging (Fig. 9.7), a reversal of this process occurs. Unnecessary heating and rupturing of the cell may take place on over charging the cell. The same happens in case of a short-circuiting incident. Such an incident must be always avoided. A high energy density is obtained from cells using LiCoO_2 . The cycle life is ~ 500 to 700 discharge cycles. These cycles are of deep discharge nature.

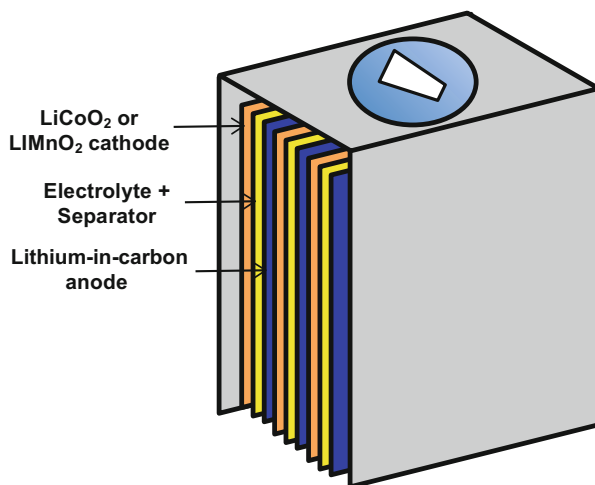


Fig. 9.5 Lithium-ion battery

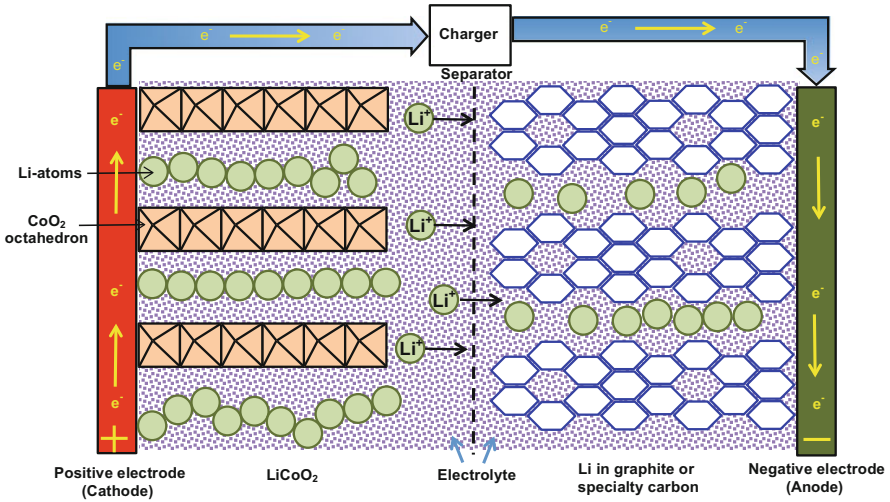


Fig. 9.6 Flow of current through a lithium-ion battery during charging. In LiCoO_2 , layers of lithium are placed between broad flat pieces of octahedrons formed by cobalt and oxygen atoms

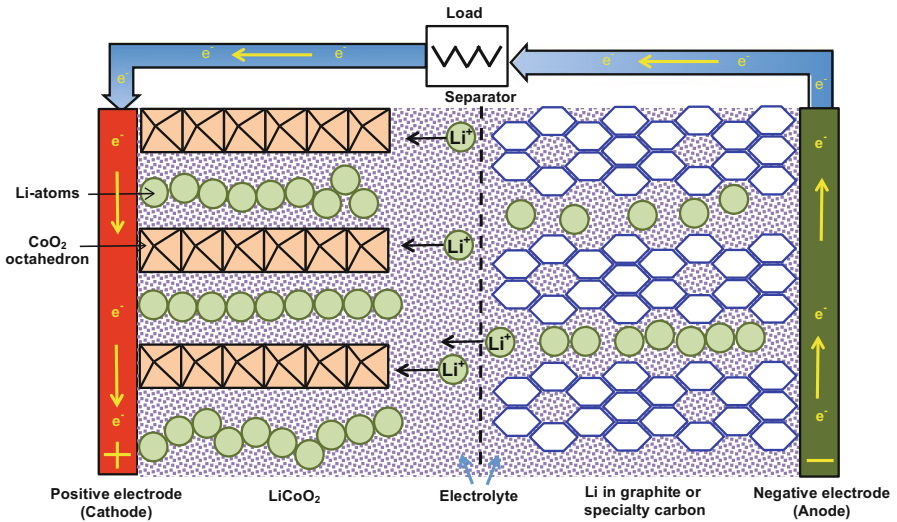


Fig. 9.7 Flow of current through a lithium-ion battery during discharging

9.10 Discussion and Conclusions

A broad panorama of primary cells has been developed for implantable devices. These primary cells use lithium anodes in combination with various cathode materials. They are distinguished by their capabilities to deliver currents ranging from microamperes to a few amperes in magnitude. Single-ingredient cathodes include

those made of I_2 , MnO_2 , CF_x , and $Ag_2V_4O_{11}$. Among cathodes of hybridized variety, mention may be made of cathodes made by interleaving CF_x and $Ag_2V_4O_{11}$ layers. Apart from the aforesaid primary cells, which are not chargeable, there exist secondary rechargeable cells based on Li^+ -ion chemistry. These can be recharged from outside while remaining implanted in the human body.

Irrespective of the technology used, performance parameters of the battery such as cell potential, capacity, or energy density depend upon the deep-rooted, innate properties of the formative materials of the anodes and cathodes. The lifetime is a function of the properties of interfacial regions separating the electrodes from the electrolyte. Safety is determined by the stability of the constructional materials used for making electrodes and also depends on the nature of interfaces within the cell. Improvements can be made by changes in chemical design of the battery and engineering of the cell structure. The optimum performing electrode/electrolyte/electrode combination is found through the selective use of prevailing and up-and-coming materials to fabricate the two electrodes of the cell. Suitable electrolyte arrangement is one that minimizes adverse reactions occurring at the confluence and interaction planes between the electrode and the electrolyte.

Review Exercises

- 9.1 What is a battery? How does it differ from a cell? Define the following terms for a battery: (1) nominal voltage, (2) open-circuit voltage, and (3) cutoff voltage.
- 9.2 What are primary and secondary batteries? Are secondary batteries indefinitely rechargeable?
- 9.3 What is meant by capacity of a battery? Explain the meanings of the terms, “gravimetric energy density” and “volumetric energy density”.
- 9.4 Name the lightest metal. To which group of the periodic table does it belong?
- 9.5 What are the reasons for the widespread use of lithium in batteries? Is lithium an electropositive element? What is its standard electrode potential? Explain the significance of the negative sign in the electrode potential.
- 9.6 Is “lithium battery” same as “lithium-ion battery”? If not, what is the difference? Which one is discarded after one-time use?
- 9.7 Name the anode, cathode, and electrolyte materials in the following batteries: (1) Li/I_2 -PVP, (2) $Li-MnO_2$, and (3) Li/CF_x .
- 9.8 How is the I_2 /PVP cathode made in the lithium battery? How does the I_2 /PVP ratio influence the conductivity of the electrolyte?
- 9.9 What is the basic cell reaction in a Li/I_2 -PVP battery? What value of open-circuit potential is obtained?

(continued)

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- 9.10 What charge carrier processes occur in a Li–MnO₂ cell at different locations: (1) at the anode, (2) inside the cell, (3) at the cathode, and (4) outside the cell.
- 9.11 What is the chemical reaction through which a Li/CF_x cell operates? Prepare a comparative chart highlighting the relative advantages and disadvantages of Li–MnO₂ and Li/CF_x cells.
- 9.12 How is it possible to cross the theoretical barrier of capacity of a Li/CF_x cell using a bifunctional electrolyte? What are the two roles played by the electrolyte?
- 9.13 What hybrid batteries have been developed with capability of supplying higher values of pulsed currents than CF_x alone? What other notable advantage is offered by these batteries?
- 9.14 Describe the discharge behavior and characteristics of Li/CF_x–SVO hybrid cells using the physically blended cathode model.
- 9.15 Point out the constructional difference of a (Li/CF_x–SVO) hybrid battery from a simple Li/CF_x battery? What significant advantage is derived by this difference?
- 9.16 What is the discharge reaction taking place in a Li/SVO battery? In what ways does the use of SVO nanoparticles help in improving the battery performance?
- 9.17 Which battery is able to comply with the high power demands of ICDs for supplying high current pulses of magnitudes 2–3 A to rapidly charge the capacitors of the device? How is the SVO cathode material prepared? Why is the discharge profile of this battery a stepped one? How is it beneficial?
- 9.18 How does a high-rate Li–MnO₂ battery differ from a simple Li–MnO₂ battery?
- 9.19 Explain the origin of plateaus in the stepped discharge profile of a Li/CF_x–SVO hybrid battery.
- 9.20 What is the typical application of a lithium-ion battery? Of what materials are the anode and cathode made? What is the source of lithium ions?

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