

Lithium Batteries: The Latest Variant of Portable Electrical Energy

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18.1 INTRODUCTION

During the last two decades of the 20th century the lithium battery technique played a more and more important part in the market,¹ at first for the more expensive special applications as, e.g. the military and air- and spacecraft technologies. Its technique is one of the more recent results of research and development in the fields of applied electrochemistry. New products like lithium batteries were accessible because of the progress in chemistry, physics, materials sciences, analytics, measurement and control technology, and finally production technology, leading to something new even if this was based on old ideas.²

An important stimulus for the new batteries was the need for small and lightweight energy sources for portable electronic devices, which have become smaller and smaller by the tremendous progress of miniaturization in our electronic age. So the scientifically and technically manageable product found its wide market. The miniaturization of consumer electronics and their mechanical parts has to be addressed first.

¹ The extensive overviews of Refs. 1, 5, 6, and 9 are recommended to everybody who is interested in more electrochemical and technical details. In the past the battery industry regularly reported on lithium batteries in Boca Raton, Florida, too (10).

² The history of the lithium technology was described in more detail by Klaus Eberts in Ref. 11. Several of his figures have been adopted in this article.

Some desirable or necessary applications became accessible for the first time by lithium batteries: e.g. the cardiac pacemaker requires batteries with negligible self-discharge and extremely high reliability for service periods of 5 to 10 years. A control and display unit may be powered for all its service life of about 10 years by only one (primary) battery, which needs not to be changed before the whole unit is replaced at the end. Lithium batteries are able to power portable radio transceivers under deep arctic temperature conditions for weeks and months. Modern handheld mobile phones and computers are usable for (many) hours with their lightweight and small rechargeable lithium accumulators.

In the following article we are first going to define what “lithium battery” means. The general advantages of its technology will then be presented. Related mainly to the non-rechargeable lithium batteries, the chemistry and physics of anode, cathodes, and electrolytes are described showing the details of the specific lithium technology. Selected examples of lithium primary batteries, which have been on the market for a long time, allow us to explain the details of the various technical ways of their realization.

Following the primary batteries we deal with (rechargeable) secondary lithium batteries, which within the last decade found their specific markets. Examples of them will be described. Finally we will see which special components within the battery system are needed, preferably when high rate versions are called for, which procure the desired reliability and safety, and how – according to the battery type – suitable ways are used for their disposal after the end of their life.

18.2 THE NAME “LITHIUM BATTERY”

The lithium battery family got its name from the metal of the anode (negative electrode), lithium, which is the most lightweight metal, the third element of the periodic system just behind hydrogen and helium. The Li/Li^+ electrode is positioned at the extreme negative end of the system of electrochemical elements. If combined with counter-electrodes of a far positive potential, the lithium electrode produces a very high open circuit voltage (OCV) and thus also a very high energy content in the respective galvanic cells. Lithium is used for anodes as pure metal, alloyed with other suitable metals, and as intercalation compounds. In practice, together with lithium, a multiplicity of cathodic (positive electrode) materials (see [Table 18.1](#)) can build an electrochemical energy store, whereas the requirements for primary and secondary applications are different only in part. [Figure 18.1](#) shows the discharge curves of a selection of primary systems, which were then commercially available. Some of them reached an enduring market position; others were hardly more than prototypes or small series products.

The variety of electrolytes and electrolytic mixtures is comparable to that of the cathodes they are used for. The wide variety of applications may be recognized from the capacity range of industrialized products that reaches from a few mAh up to 10,000 Ah ([Figure 18.2](#)). The voltage of lithium cells is found between 1.5 and 4 V depending on the cathodic material used ([Figure 18.1](#)).

Production and handling of lithium batteries require special techniques on account of the specific features of the lithium metal and of some of the related cathodic substances. Here one has to deal primarily with the reactivity of lithium

Table 18.1 Classification of lithium primary batteries according to cathodes and electrolytes.

Classification	Electrolyte	Power	Capacity (Ah)	Temperature range (°C)	Shelf life (years)	Typical cathodes	Voltage (V)	Characteristics
Solved cathodes (fluid, gas)	Organic or inorganic	Medium to high W	0.5–20,000	–55–70 (150)	8–10	SO ₂	3.0	High energy, high power, good deep temperature capability, long life
Solid state cathodes	Organic	Low to medium, mW	0.01–10	–40–55 (200)	5–8	SOCl ₂	3.6	
						SO ₂ Cl ₂	3.9	
						CrO ₂	3.6	High energy, medium to low power, no internal overpressure
						V ₂ O ₅	3.3–2.3	
						Ag ₂ CrO ₄	3.1	
						MnO ₂	3.0	
						(CF) _x	2.6	
						S	2.2	
						Cu ₄ O(PO ₄) ₂	2.2	
						CuS	1.7	
						FeS ₂	1.6	
						FeS	1.5	
						CuO	1.5	
						Bi ₂ Pb ₂ O ₃	1.5	
						Bi ₂ O ₃	1.5	
Solid electrolyte	Solid	Very low μW	0.003–5	0–100	10–25	J ₂	2.8	Very long life, very safe, very low power
						PbJ ₂	1.8	
						PbS	1.8	

Source: Ref. 3.

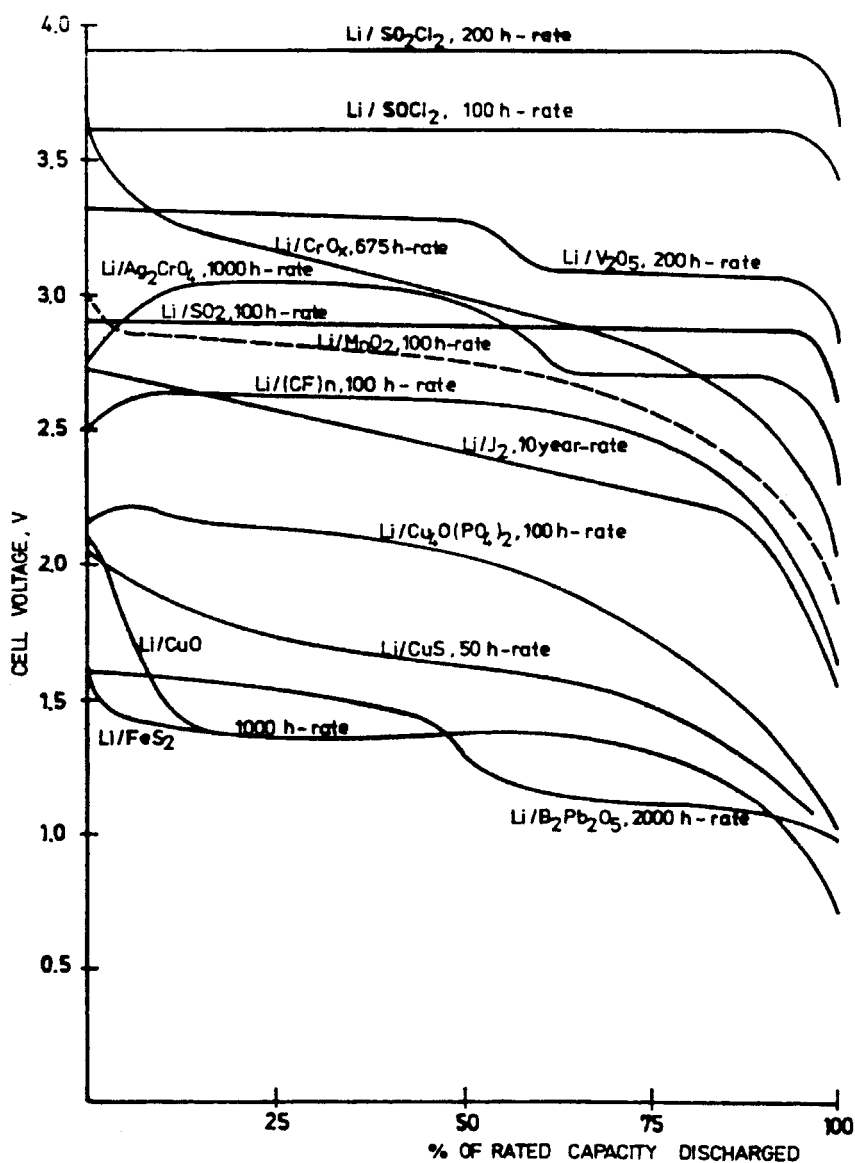


Figure 18.1 Discharge graphs of various lithium primary batteries. (From Ref. 3.)

with humidity and the main constituents of the atmosphere, i.e. nitrogen, carbon dioxide, and oxygen.

18.3 THE LITHIUM BATTERY'S SPECIAL ADVANTAGES

For defined applications lithium batteries show remarkable advantages if compared with traditional primary and secondary batteries.

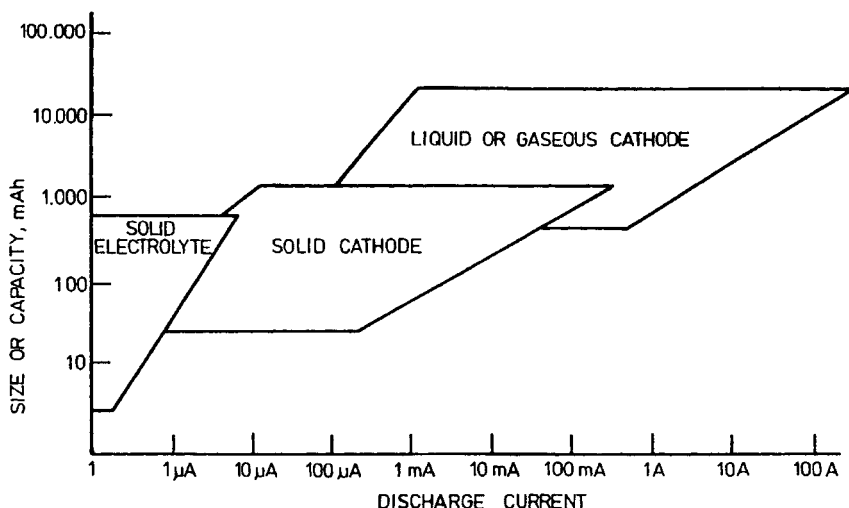


Figure 18.2 Typical regions of performance of lithium primary batteries by type of electrolyte and cathode (the upper right region has to be broadened up to 10,000,000 mAh at 10,000 A.) (From Ref. 3.)

18.3.1 High Cell Voltage

Most lithium battery systems show a cell voltage in the upper range of 1.5 to 4.0 V or even higher. This alone is an advantage with regard to the energy density and specific energy of those cells. So in many cases only one lithium cell suffices where otherwise two or three conventional Leclanché or alkaline cells are necessary.

18.3.2 Energy Content by Weight: Specific Energy

The mass related (gravimetric) energy content, the ‘specific energy’ (SE) of lithium batteries, is 100 to 500 Wh per kg depending on system and cell type. Preferably portable devices profit from a lithium power supply. For comparison: classic lead-acid batteries show a specific energy between 35 and 55 Wh/kg and NiCd batteries, a bit more powerful, from 50 to 70 Wh/kg. The said higher (lithium) values have, however, been only realized by primary systems until now.

18.3.3 Energy Content by Volume: Energy Density

The volumetric energy content, mostly understood as the ‘energy density’ (ED), goes from 300 to 1300 Wh/L. Lithium batteries therefore require less space than conventional battery systems. Leclanché cells, for example, deliver 165 and alkaline cells 330 Wh/L.

18.3.4 Loadability

One can choose between lithium primary batteries tailor-made as high rate batteries with a very low resistance for high loads or with a high resistance for low rate long-time applications. Until now secondary systems have been available only in the low capacity range for small and medium loads, i.e. with higher resistance.

18.3.5 Discharge Characteristic

Some lithium systems show an especially flat and stable curve (voltage against time) for the discharge of the whole capacity. This supports electronic devices which are designed for little tolerances of their feeding voltages.

18.3.6 Deep Temperature Capability

These batteries may be stored and operated within an extremely wide temperature range. For the first time especially the deep temperature range of -10 to -40 and even -55°C can be supported by them without any additional means such as heaters or special insulation.

18.3.7 Shelf Life

Most of the lithium primary batteries may be stored for over 10 up to 20 years with negligible self-discharge, so that they still deliver most of their nominal capacity. They are continuously active, i.e. at all time ready for service. At normal temperature storage only 5 to 10% self-discharge after 10 years is typical.

18.3.8 Environmental Compatibility

If compared to metals used for common batteries such as lead or nickel and cadmium, lithium is not as poisonous as these to biological systems. Disposal of used lithium batteries is therefore a smaller problem.

18.4 CHEMISTRY AND PHYSICS OF LITHIUM PRIMARY BATTERIES

18.4.1 Properties of Anodic Metal Lithium

As can be seen by comparison with some other anodically used metals, lithium metal is the anodic material with the highest capacity and energy contents related to weight (Ah/kg and Wh/kg). It is number three in the periodic system of elements after hydrogen and helium. It is the most lightweight of the lightweight metals, the alkali metals. According to the rules of chemistry it behaves similarly as the other metals of the same column of the periodic system, sodium and potassium. In the electrochemical series of elements, which represents a measure of how 'easily' metals and other redox systems may offer or attract electrons, lithium occupies the extreme left, or negative, position. The electrical potential of the redox system Li/Li^{+} related

to the standard hydrogen electrode is -3.040 V .³ That means that the lithium atom most readily gives up its outer valence electron. Combined with a suitable cathodic, i.e. electron-attracting, material it results in a high cell voltage. The complete cell reaction delivers an especially high amount of energy per formula turnover. So lithium batteries are 'high energy' batteries.

The silver-white lithium metal is soft and ductile, similar to lead and can be extruded or rolled into thin foils very easily. As long as it is not covered too much by passivation layers it may be welded simply by pressure in cold state and also onto copper as necessary, for example, for attachment of current collector tabs to the lithium electrode. Lithium readily reacts with water and air, similar to the other alkali metals, but not exactly as spontaneously and vigorously as its homologize sodium and potassium. Nonetheless the pure metal requires climate chambers of extremely dry air for handling.⁴ In normal atmosphere on a fresh metallic surface of lithium a protective layer grows up from lithium hydroxide, lithium oxides, and lithium carbonate and – at normal humidity (water acts here in a catalytic manner) – mostly from the nitrogen compound Li_3N . These lithium compounds generate an extremely dense reaction layer, a so-called passivation layer, which is generally well known especially from aluminium and which in turn gives the essential condition for the technical applicability of aluminium. Without that passivation layer, a component made of aluminium would be destroyed very quickly under atmospheric conditions.⁵ The lithium's capability for passivation is advantageous for the said long shelf-life of lithium (primary) batteries. Also the concept of the fluid cathodes is possible only by passivation. Of course lithium as the pure soft metal is of no common mechanical use as aluminium.

So the very important advantage of the long shelf-life of lithium batteries depends on both its passivation ability not only in atmosphere, but also in suitable electrolytes. In spite of the passivation film the lithium electrode may be 'activated' quickly and easily: On an electrical load the layer breaks down very quickly within seconds or fractions thereof. High current densities may then be realized. On the other hand the passivation film in a cell without load hinders self-discharge by unwanted side reactions of the anodic metal with components (or even contaminants) of the electrolyte. This strongly hindered but not absolutely excluded self-discharge of cells not under load during shelf-life has to be understood as the further growth of the passivation layer, which proceeds as a solid-state reaction only extremely slowly. So shelf-lives of 10 to 20 years are possible under consumption of only 10 to 20% of the active metal. Depending on the special battery system, the

³ The potential of a single electrode is defined as the energy or work to be done for the transport of an elementary electrical charge (massless) from the virtual free space into the phase under consideration. This cannot be measured, as everybody knows. It normally is handled as the difference between the potentials of the electrode and a reference electrode, most often the standard hydrogen electrode (SHE).

⁴ The standard condition is at a dew point (water) of -30°C . This corresponds to water in air concentration of less than 2% of relative humidity at normal temperature.

⁵ A passivation layer is a dense mechanically stable layer from compounds of the metal being protected and, e.g., oxygen, hydroxyl ions – from water – carbon dioxide CO , sulfuric acid H_2SO_4 , and other components, preferably from the air. This passive layer – once grown – keeps off the said reactants from further direct access to the metal. Further reaction is possible only as 'solid state reaction', which proceeds by several powers of ten more slowly than the first or 'direct' reaction of the unprotected surface.

passivation layer consists of lithium chloride, lithium dithionite, lithium hydroxide, or also of lithium alcoholates, carbonate, and others, i.e. generally lithium and parts of the actual electrolyte mix.

Lithium is most often refined from the mineral spodumen.⁶ Similarly to aluminium the refinement is done by electrolysis. It is consequently rather expensive but until now its availability has not been limited.

The energy density, measured as Wh/L, of the lithium electrode alone is not especially high. It is even slightly lower than the corresponding value of the classic battery material lead and remarkably lower than that of aluminum.⁷ The reason is that even at extremely different atomic weights the atomic volumes of these three are relatively similar at about 10 to 20 cm³/g atom, but during discharge lithium provides only one, lead two, and aluminium three electrons per metal atom. For comparison [Table 18.2](#) gives a collection of the so-called equivalent volumes⁸ of lithium and some other anodic metals which were used traditionally for batteries and accumulators. On the other hand the specific energy of lithium, measured as Wh/kg, is on top of the anodic materials considered. The energy content – both ED and SE – of a complete cell depends of course on the particular cathodic partner and type of housing and packing. So the theoretical data of the anode alone may not be overestimated.

18.4.2 Electrolytes for Lithium Batteries

18.4.2.1 Organic Solvents with Ionic Salts

The electrolyte of a battery⁹, or rather of an electrochemical cell, is the mediator between the reactions in parts which proceed at the two electrodes and which deliver electrical energy out of the combined chemical process. Via the electrolyte the different levels of electrical charge at cathode and anode in a cell under load are levelled out. Its conductivity essentially contributes to the cell's energetic efficiency. For many lithium systems the electrolyte is made from an organic solvent and a salt solved in it (electrolyte salt) – usually a lithium salt. The following requirements rule the choice of the electrolyte for a lithium battery (see [Table 18.3](#)):

The dielectric constant (dc) of the solvent has to be as high as possible. The higher the dc, the better the electrolyte salt is solvated, i.e. solved and dissociated.

In order to have solvated ions of the electrolyte salt as mobile as possible and so to get a resistance for the current flow as low as possible, the viscosity of the electrolytic fluid has to be as low as possible.

⁶ Spodumen or triphane $\text{LiAl}(\text{SiO}_3)_2$ belongs to the catena silicates or pyroxenes. It is found in pegmatites in the United States and also in Scotland and Austria.

⁷ Aluminum as an anode for battery applications in the field of marine and standby power was only experimentally investigated recently.

⁸ The equivalent mass of an ion is defined as the fraction of the atomic or molecular weight of this ion which carries one electrochemical equivalent, i.e. 96,450 Coulomb (Asec) of electrical charge. The equivalent volume is defined correspondingly.

⁹ According to the official version the smallest unit of an electrochemical storage medium is a (galvanic) 'cell'. Several cells make a 'battery'. In this article 'battery' is often used colloquially when the term 'cell' would be more correct.

Table 18.2 Specific data to determine the equivalent volumes of some anodic metals for batteries.

Anodic metal Maximal oxidation state	Li Li ⁺	Pb Pb ²⁺	Al Al ³⁺	Zn Zn ²⁺	Na Na ⁺	Cd Cd ²⁺
Atomic weight (g)	6.939	207.19	26.98	65.37	22.99	112.40
Equivalent weight (g)	6.939	103.60	8.99	32.69	22.99	56.20
Specific gravity (g/ccm)	0.534	11.34	2.702	7.14	0.97	8.642
Equivalent volume (ccm/equiv.)	12.99	9.14	3.33	4.58	23.70	6.50

Generally the electrolyte of an electrochemical cell must not be electrolyzed, i.e. degraded by the potential difference, the voltage between the electrodes. Aqueous electrolytes with the degradation voltage of 1.23 V for the water molecule have to be excluded regularly from use in lithium cells with cell voltages between 2.5 and nearly 4.5 V. The scheme of [Figure 18.3](#) explains this with the model of the molecular orbital (MO) and band theory¹⁰. The oxidation potential of the electrolyte has to be higher than the potential of the anode (or than the Fermi energy of the anodic metal) and the reduction potential has to be lower than the corresponding potential of the cathode (Fermi edge of the cathodic material). Where this requirement is not fulfilled, the thermodynamically demanded reaction between electrolyte and electrodes has to be blocked at least kinetically as realized in the lead-acid accumulator with its aqueous sulfuric acid electrolyte. The reactivity of the electrolyte's components against lithium (and the cathodic counterpart) has to be negligible to use the electrode quantitatively for its electrochemical purpose and not to get it consumed in a useless manner by self-discharge. A special case is the passivation of lithium in some systems under open circuit conditions (cell without load) and its electrochemical reactivity, i.e. discharge ability under load. This passivation is maintained by a very thin but very stable layer of reaction products between the lithium and one of the electrolyte's components. This layer then protects the bulk metal against further reaction. The passivation's barrier can be overcome only very slowly as is normal for a solid-state reaction. The electrochemical efficiency of the lithium anode for some lithium primary systems is within 60 to 90%. In any case water and alcohols, i.e. all protic solvents, have to be excluded from lithium cells, because they are not able to produce a sufficiently stable and really passivating layer.

The electrolyte should show a melting or solidification point as low as possible together with low viscosity even at low temperatures for high conductivity and high power. Typical limits for discharge of lithium batteries are between -40 and -55 °C.

Conductive salts for the electrolyte mixture are to be chosen with preferably low lattice energy. So solvation is easy and a high percentage of the solute might be dissociated in the solution. For most systems salts of lithium are chosen which are combined with big complex anions such as, e.g. lithium perchlorate LiClO₄, lithium tetrafluoroborate LiBF₄, lithium hexafluoroarsenate LiAsF₆, lithium hexafluoropho-

¹⁰ HOMO = highest occupied molecular (or atomic) orbital – here of oxygen, LUMO = lowest unoccupied molecular (or atomic) orbital – here of hydrogen. The difference between them is the decomposition voltage – here of water.

Table 18.3 Physical data of pure solvents used for lithium cells.

Name	Abbreviation	Boiling point (°C)	Melting point (°C)	Dielectric constant	Spec. gravity (g cm ⁻³)	Viscosity (cP)
Acetonitrile	AN	81.6	−45.7	35.95	0.777	0.34
γ-butyrolactone	BL	202	−43	39.1	1.13	1.75
1,2-dimethoxyethane	DME	83	−58	7.2	0.859	0.46
N,N-dimethyl formamide	DMF	153	−61	36.7	0.94	0.80
Dimethyl sulfoxide	DMSO	189	18,5	46.6	1.10	1.96
1,3-dioxolane		78	−95		1.06	
Ethylenecarbonate	EC	248	36	89	1.32	1.90 (40 °C)
Methyl formiate	MF	31.5	−99	8.5	0.974 (20 °C)	0.35 (20.15 °C)
Nitromethane	NM	101	−29	36	1.13	0.63
Propylene carbonate	PC	241	−49	64	1.19	2.53
Phosphoroxichloride		105	1.2	13.7	1.645	1.06
Thionylchloride		78.8	−105	9.05 (22 °C))	1.63	0.60
Sulfurylchloride		69.4	−54.1	9.15 (22 °C)	1.65	0.67
Tetrahydrofurane	THF	66	−65	7.6	0.89	0.46

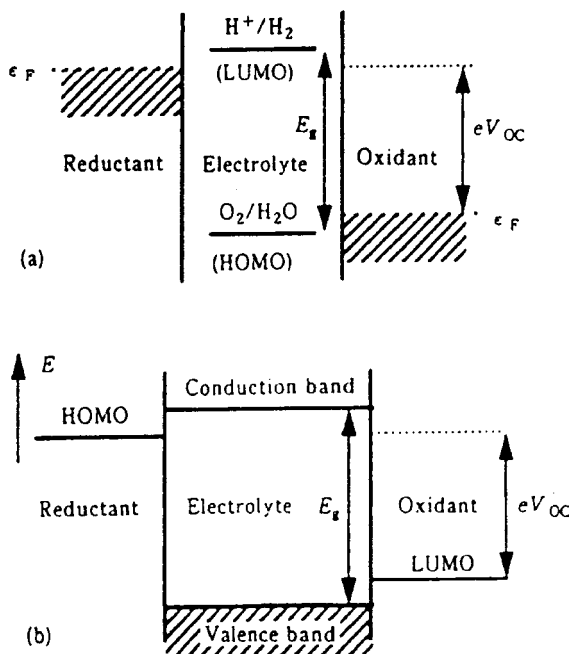


Figure 18.3 Position of the decomposition energies of electrolytes relative to the potentials of the anode (reductant is oxidized by discharge) and the cathode (oxidant is reduced by discharge) of a galvanic cell for (a) solid electrodes with fluid electrolyte and (b) fluid electrodes with solid electrolyte. (From Goodenough in Ref. 1.)

sphate LiPF_6 , lithium tetrachloroaluminate LiAlCl_4 . These anions seem to be big ones according to the simple formula. But in the solution these negatively charged ions are nonetheless relatively small because they are able to attract only a thin layer of “solvate ions”. Consequently they show a high mobility and hence a good conductivity. The contrary is valid for the small central ion of lithium that is surrounded by an over-proportionally thick layer of solvate molecules, thus showing a reduced mobility and conductivity. In practice often electrolyte solutions with 1 mole electrolyte salt per liter are used.

But also under optimal conditions these electrolytes based on organic solvents yield a conductivity of about $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$, which is by more than one power of ten lower than in alkaline or acidic aqueous solutions.

18.4.2.2 Inorganic Electrolytes Acting as Cathodes

This class of electrolytes gives the technology of lithium primary batteries a special exotic attraction. The fluid electrolyte mixture acts as the media of transfer of electric charges between anode and cathode as described above. In addition it also contains the cathodic active substance, which is in direct contact to the anodic counterpart, the lithium metal, but nonetheless reacts separately in a distance from the anode at a cathodic support electrode by consumption of electrons from the outer circuit. This paradoxical behavior is possible because of the “cathode’s” ability to create a

passivation layer on the lithium surface, which protects the metal against further attack of the spontaneously (thermodynamically favored) reacting “cathode” and against quantitative self-discharge. On the other hand the passivation layer cracks if the cell is electrically loaded.

Also these inorganic electrolytes or their mixtures with organic solvents have to be polar, i.e. be constituted from molecular dipoles, and to show a high dielectric constant, again for a high ability to solve and dissociate the lithium electrolyte salt and the products of the discharge reaction.

The electrolytes acting as cathodes are mixed with a suitable electrolyte salt and with or without an organic co-solvent. The most important examples are thionylchloride with lithium chloride and sulfur dioxide with acetonitrile and lithium bromide. The organic co-solvent again ensures low viscosity and low melting points for good deep temperature operation.

With highly porous cathodic conductors battery systems with inorganic cathodic electrolytes may deliver especially high power. These systems, which have been proved for years, are operated under moderate (SOCl_2 : about 0.5 to 5 bars) and high overpressure (SO_2 : 4 to 32 bars) in the cells.

18.4.2.3 Solid Electrolytes

Solid electrolytes generally have a far lower conductivity than fluids because of the low ionic mobility, also in specially selected ionic crystals and other solids. The higher resistance in such a cell allows therefore only very low loads. But otherwise side reactions such as self-discharge – provided anode and cathode are also in the solid state – run only extremely slowly if at all. From this basic low reactivity such battery systems show especially high reliability also during shelf-lives and operational times of many years.

One example is the lithium iodide electrolyte in a typical cardiac pacemaker battery. Another one is the mixture of lithium halides with – for immobilization – magnesium oxide in some thermal batteries, and a further one a mixture of lithium iodide with aluminium oxide or silica for some memory back-up systems.

18.4.2.4 Electrolytes from Molten Salts

A difference between a molten substance and another fluid chemical of course simply depends on the standpoint: Here we deal with substances which at normal conditions – such as normal temperature – are in the solid state and are fluid only at elevated temperatures when the battery is to operate. So we get battery systems whose electrolyte in the solid state at normal temperature shows an extremely low conductivity so that all self-discharge and other undesired side reactions are in fact frozen in.

With ‘thermal batteries’ such electrolytes are used combined with a tailor-made rapidly acting pyrotechnic heating device. Typical temperatures of operation lie between 200 and 500 °C, depending on the system. A molten salt electrolyte is used, for example, in the lithium iron disulfide battery which is described below.

18.4.3 Cathodic Materials

Some substances commonly used for cathodes are shown in [Table 18.4](#) explaining some important features.

18.4.3.1 Solid Cathodes: Intercalation Compounds and Others

Lithium intercalation compounds are preferably suitable for use as cathodes. The tiny lithium ion is easily inserted into and released from a certain number of inorganic solids at a potential that lies at positive values on the electrochemical series far away from the Li/Li^+ electrode. The lithium ion's small volume affects the host structure only slightly. The intercalation is merely not hindered so that this process is mostly reversible and hence suitable for rechargeable batteries.

18.4.3.2 Fluid Depolarizers

Table 18.4 also contains those substances, which are used in the fluid state at normal temperatures for cathodes. Their features were already described when we dealt with them as electrolytes. They are used with and without a co-solvent, they build up on the lithium metal's surface stable passivation layers which are cracked only under electrical load when during discharge lithium ions leave the surface. These "cathodes" are especially powerful if combined with highly porous cathodic conductors.

When a co-solvent is not needed – as in thionylchloride batteries – the system with the fluid depolarizer realizes an especially high energy density because this electrochemically non-active component of the co-solvent is avoided.

18.5 DESIGNS AND TECHNOLOGY OF PRIMARY LITHIUM BATTERIES

Lithium cells have to be hermetically sealed. Intrusion of atmospheric humidity is not allowed. On the other hand some of the cell components are not allowed to escape because of their aggressiveness and their high vapor pressure. This is obvious for sulfur dioxide for instance. The cell geometry is governed by mechanical requirements both from the standpoint of the manufacturing technique and the application. There are prismatic, cubic, and flat formats in different dimensions with cubic or circle shaped electrode stacks. There are preferably round cells, which contain the electrodes either in cylindrically wound or bobbin versions. In the case of the pressurized cell types, the round can is of course the most economic version of a pressure vessel.

The lithium anode is used in the pure metallic state as thin extruded or rolled foil with a thickness down to $25\text{ }\mu\text{m}$ or as a massive block, depending on the load to be applied. In special cases the lithium is applied also in alloys or, as in rechargeable batteries, in intercalation¹¹ compounds.

¹¹ See also the description of the rechargeable lithium batteries in Section 18.7.

Table 18.4 Physical and electrochemical data of some cathodic materials for lithium batteries.

Cathodic material	Molecular weight	Valences involved	Specific gravity (g cm^{-3})	Electrochemical equivalent			Calc. cell voltage (against Li) (V)
				(Ah g^{-1})	(Ah cm^{-3})	(g Ah $^{-1}$)	
SO ₂	64	1	1.37	0.419	—	2.39	3.1
SOCl ₂	119	2	1.63	0.450	—	2.22	3.65
SO ₂ Cl ₂	135	2	1.66	0.397	—	2.52	3.91
Bi ₂ O ₃	466	6	8.5	0.35	2.97	2.86	2.0
Bi ₂ Pb ₂ O ₅	912	10	9.0	0.29	2.64	3.41	2.0
(CF) _n	(31) _n	1	2.7	0.86	2.32	1.16	3.1
CuCl ₂	134.5	2	3.1	0.40	1.22	2.50	3.1
CuF ₂	101.6	2	2.9	0.53	1.52	1.87	3.54
CuO	79.6	2	6.4	0.67	4.26	1.49	2.24
CuS	95.6	2	4.6	0.56	2.57	1.79	2.15
FeS ₂	119.9	4	4.9	0.89	4.35	1.12	1.8
MnO ₂	86.9	1	5.0	0.31	1.54	3.22	3.5
MoO ₃	143	1	4.5	0.19	0.84	5.26	2.9
Ag ₂ CrO ₄	331.8	2	5.6	0.16	0.90	6.25	3.35
V ₂ O ₅	181.9	1	3.6	0.15	0.53	6.66	3.4

Source: Ref. 8.

For separation many systems with fluid electrolytes use a micro-porous foil from polypropylene known as Celgard[®]. Alternatives are fluorinated hydrocarbons (e.g. Halar[®]) or glass fiber nonwovens.

Cathodes are made from a paste of the cathodic active material with binders and electronically conductive additives, which are rolled onto metallic foils or exmets from nickel or aluminium. These cathodes are used as flat electrodes or in spirally wound form. The bobbin form realizes the same design in principle, but the layers of the active materials are much thicker, which in turn reduces the typical load to be applied to these bobbin cells. For fluid depolarizers the cathodic conductor often carries a mixture of carbon black with Teflon[®] binder, which is impregnated with catalytically active substances.

Containers of lithium batteries are mostly made from stainless steel. Depending on the internal pressure of the system, the containers are round cells of IEC standard formats or of proprietary geometry or with prismatic rectangular geometry (also button cells and circle shaped bigger cells and special geometries as for cardiac pacemakers have been realized). These cells are mostly hermetically sealed by welding or – in case of negligible inner pressure – crimp-sealed with polymer gaskets.

For the electrical contacts in many cases the metallic container is one pole and a glass-to-metal seal (or ceramic-to-metal seal) the other. The container may also have to be potential free; then both contacts are made from the glass-to-metal seals.

For batteries under overpressure and/or for high power, a pressure vent is integrated into the cell case. Additionally melting fuses or back-setting fuses – so-called thermo switches – are used. All this protects the system against overheating and uncontrolled pressure rise in case of a short.

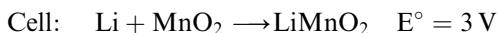
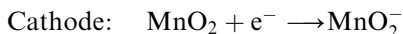
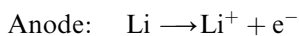
18.6 EXAMPLES OF LITHIUM PRIMARY BATTERY SYSTEMS

Figure 18.1 and Table 18.1 give an overview on the wide variety of lithium primary systems which have been at least temporarily introduced into the market. This variety gets remarkably wider if one takes into account also all those systems which were tested on the laboratory scale but not fully developed for practical applications. A small selection of lithium primary batteries which were successful in their special markets shall be described in detail here to show some design and building principles.

18.6.1 The System Lithium/Manganese Dioxide

For this cell type the pure metallic lithium electrode – mostly as a foil – is combined with a porous manganese dioxide electrode. Therefore the cathodic mass of a specially treated manganese dioxide MnO_2 together with a binder and some carbon black for improvement of the conductivity is pasted on a metallic carrier foil. The reaction scheme shows in a simplified manner that during discharge the positively charged lithium ions set free at the anode are built into the manganese dioxide's lattice, whereas the manganese formally changes its oxidation state from positive

four to three:



In most cases a mixture of propylene carbonate and dimethoxy methane with lithium perchlorate¹² or lithium trifluoromethane sulfonate¹³ as electrolyte salt is applied. Mixtures of tetrahydrofuran, butyrolactone, and dioxolane are used also. As an example of a passivation layer on the lithium metal anode in a cell with a solid cathode and a fluid organic electrolytic solvent we see here the dense and stable layer of lithium carbonate as the reaction product of lithium with propylene carbonate.

The manganese dioxide – well known already from Leclanché and alkaline cells and also existing as spinel in nature – has to be dried thoroughly for application in lithium cells. At the elevated temperatures used for the drying operation two modifications of the spinel structure can be generated: up to 250 °C the γ -phase is preferred, between 250 and 350 °C both the γ - and β -phase coexist, and beyond 350 °C the β -phase alone is stable. The geometry of both structures may be recognized in [Figures 18.4 and 18.5](#). The intercalation of the small Li^+ ion is supported by the wider channel structure of the γ -phase. So a γ -rich substance is preferred.

Lithium/manganese dioxide cells are manufactured as button cells, round cells of the spirally wound and bobbin type, and according to the customer's requirements combined to power modules fitting individually into diverse appliances. They are delivered in steel cases in welded and crimp-seal versions. High rate types are equipped with back-setting thermo fuses and burst vents. [Figure 18.6](#) shows a cut through of a button cell (Varta) and [Figure 18.7](#) of a round cell (Eveready).

The batteries are applied to watches, calculators, memories, sensors, hearings aids, cameras, radios, razors, torches, and radio trancivers and in safety and rescue equipment. Combined with lithium iodide cells (see [Section 18.6.5](#)) they also serve in the medical field for defibrillation in case of heart irregularities. Typical discharge curves for a 190-mAh button cell (Union Carbide) are shown in [Figure 18.8](#). [Figure 18.9](#) presents discharge curves of equivalent cells and batteries of the Leclanché (zinc/carbon), alkaline, and lithium/manganese dioxide types. Versions A and B require two cells to deliver an overall voltage of about 3 V comparable with that of one single lithium cell. Here the advantage of the higher specific energy of lithium cells is obvious besides the relatively stable voltage level during the major part of the discharge. The cells are leakproof even when crimp-sealed. The shelf-life is given as the self-discharge rate: It is about 1% per year for the crimped and 0.5% per year for the welded version. Cells and batteries may be used from –40 to +80 °C.

The lithium/manganese technology is based on the research work of Sanyo in 1975. In addition to this company and the other ones cited above we have to mention, as suppliers, all well-known Japanese companies and Rayovac, Varta, Berec, Friwo, Litronic, and Renata.

¹² Typical data are conductivity $> 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ and viscosity $< 3 \text{ cP}$.

¹³ LiCF_3SO_3 .

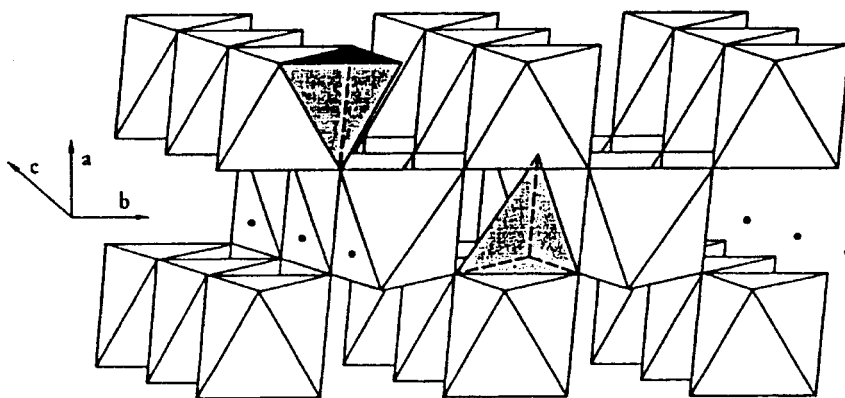
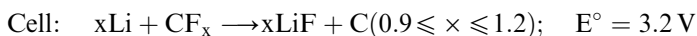
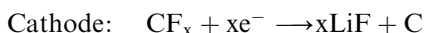
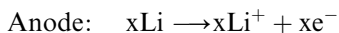


Figure 18.4 Manganese dioxide β -phase (high temperature) with single channels for incorporation of lithium. (From Ref. 2.)

18.6.2 The System Lithium/Carbon Monofluoride

The design principle of lithium/carbon monofluoride cells is comparable to that of the LiMnO_2 cells. The cathode however uses as its active material the said carbon monofluoride. The reaction scheme



shows that during discharge the lithium ion from the anode formally reacts with the fluoride of CF_x to produce LiF and carbon. Electrons for charge equalization are provided by the outer part of the circuit for the CF system. The reaction product carbon is finally divided in the cathode. So the cathode's electronic conductivity is improved during discharge.

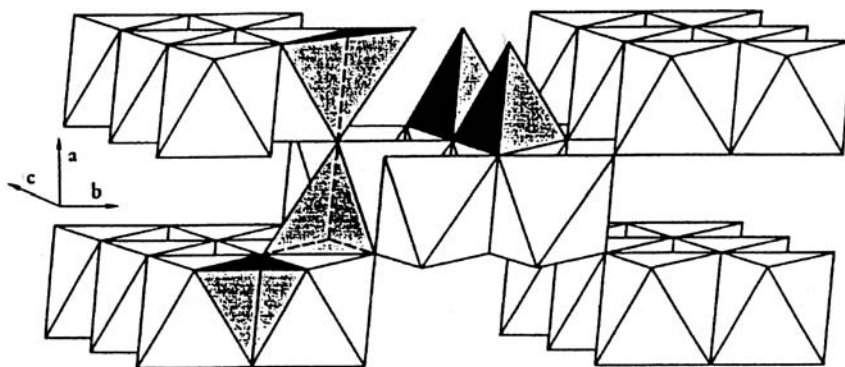


Figure 18.5 Manganese dioxide γ -phase (deep temperature) with double channels for incorporation of lithium. (From Ref. 2.)

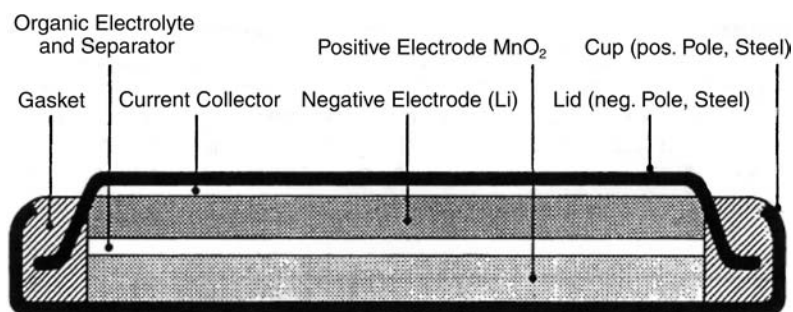


Figure 18.6 Cross-section of a lithium/manganese dioxide cell (Varta).

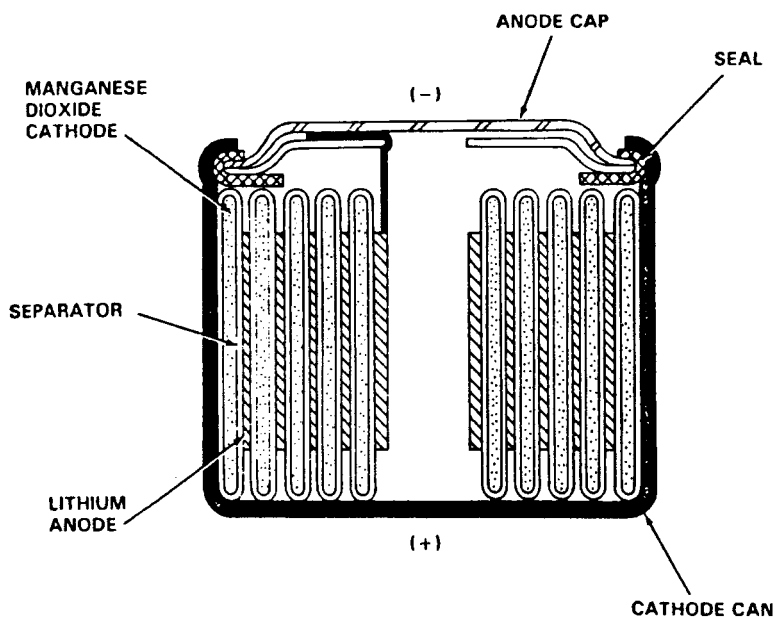


Figure 18.7 Cross-section of a lithium/manganese dioxide round cell (Eveready).

Most often a 1:1 mixture of propylene carbonate and dimethoxyethane with the conducting salt lithium tetrafluoroborate is used for the electrolyte. An alternative is lithium hexafluoroarsenate in γ -butyrolactone.

The cathodic material carbon monofluoride CF_x is made from graphite, coke, or active coal by fluorination at 200 to 800 °C as black $\text{CF}_{0.5}$ or white $\text{CF}_{1.0}$.¹⁴ Thereby to each second or each single carbon atom one F atom is bound according to a ratio of C:F from 1:0.5 to 1:1. These substances behave similarly to PTFE. So CF_x is also used as a thermo-resistant lubricant and coating. The first cell with this

¹⁴ The literature refers to CF_x as compositions with $0.13 < x < 2.0$. Matsushita uses CF_x with $0.9 < x < 1.2$.

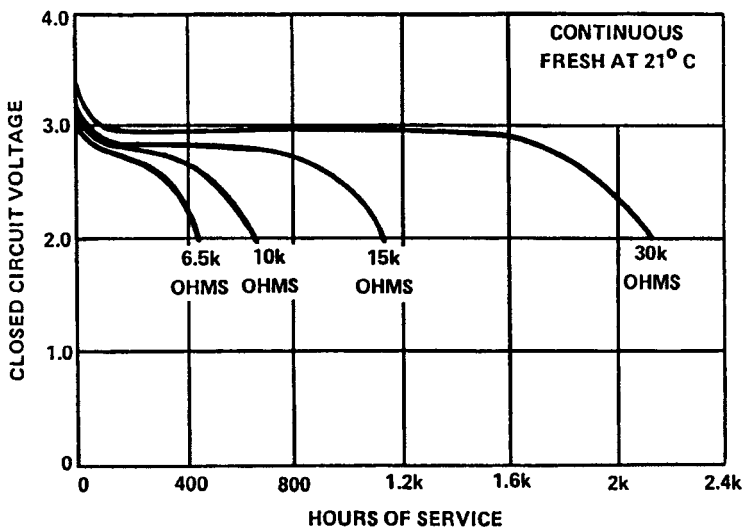


Figure 18.8 Discharge graph of a 190-mAh lithium/manganese dioxide button cell under various loads (Union Carbide).

cathodic material was developed in the early seventies by Matsushita. The capacity of a cell is proportional to the degree of fluorination. As carbon monofluoride, contrary to graphite, is a very bad electronic conductor, carbon black with some PTFE binder is added to the active CF_x mass for an enhanced conductivity. The structure of CF_x as compared to the graphitic structure is shown in [Figure 18.10](#).

Lithium carbon monofluoride cells are manufactured as button cells, also as ultra-thin discs, as round cells, or as small “pins”. Such pins (e.g. with a diameter of 2.2mm, a length of 115mm) are used for fishing line floats. The round cells are mostly designed as bobbin cells for low rate applications.

Indeed carbon monofluoride cells preferentially are suitable for low rate discharge as in memory back-up and other memory applications. Compared to the

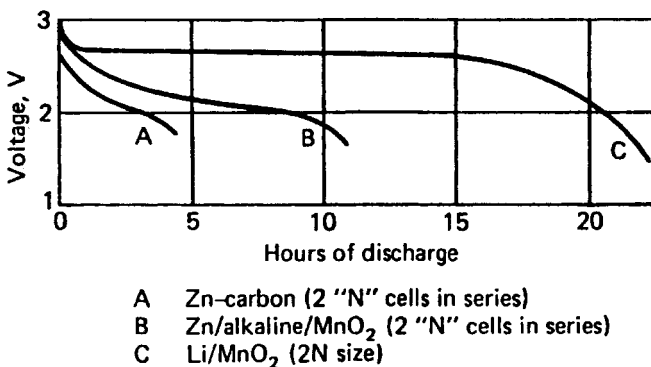


Figure 18.9 Discharge graph of old and new primary batteries: A = Leclanché, B = alkaline, C = lithium/manganese dioxide. (From Ref. 3.)

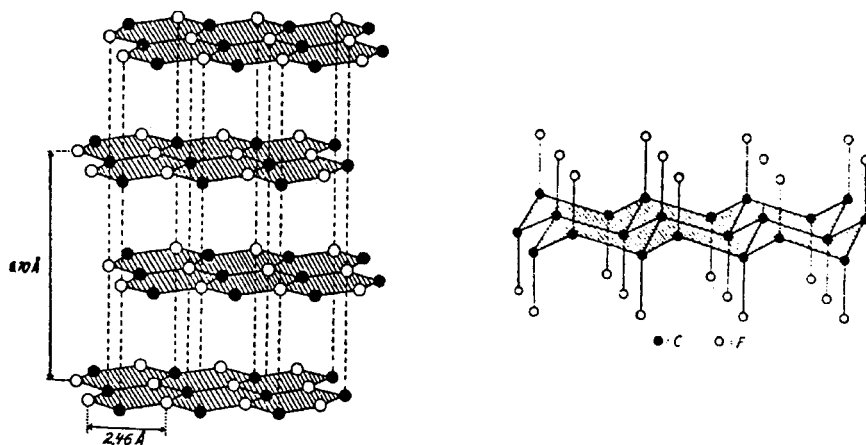


Figure 18.10 Comparison of the structures of (hexagonal) graphite and carbon monofluoride. (From Ref. 4.)

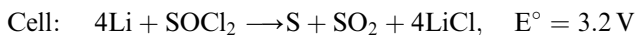
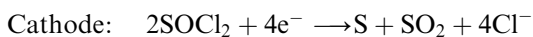
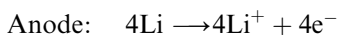
MnO₂ technology the CF_x technique is favored by a clearly higher specific capacity and energy. For CF_x a specific capacity of 2.380 Ah/L and a specific energy of 350 Wh/L are reported, whereas for MnO₂: 1.550 Ah/L and 200 Wh/L. This might be understood from the pairing of lithium and fluorine as the most extreme partners in electrochemical series. That system can also be designed especially compact. It may normally be applied from −40 to +85 °C, but cells are also known with special equipment for use at up to 150 °C. The reliability and environmental acceptability are excellent. The discharge characteristic is flat and ‘hard’. So this system is a considerable competitor for the MnO₂ technique, apart from lower loadability.

A collection of typical discharge curves of a CF_x cell (C size, Matsushita) can be recognized from [Figure 18.11](#). [Figure 18.12](#) demonstrates how little discharge time or capacity depends on the operational temperature. The closed circuit voltages (CCV) as function of temperature, however, vary widely between 2.9 V (60 °C) and 1.8 V (−40 °C). Lithium CF_x cells are produced by Matsushita (Panasonic) and under their license by Eveready, Eagle Picher, Rayovac, Wilson Greatbatch, Duracell, and others.

18.6.3 The System Lithium/Thionylchloride

The battery system lithium/thionylchloride is the most important system with a fluid depolarizer, i.e. with a fluid cathodic substance, which offers an outstanding practical energy density and specific energy at especially high loadability.

Within the cell reaction



as reaction products in addition to lithium chloride also sulfur and sulfur dioxide are

found. The sulfur is mostly related to the aspects of safe handling of these high energy and high rate systems (see below). The thionylchloride in this case is both electrolyte and cathodic material combined with lithium tetrachloroaluminate salt with concentrations between 1.0 and 1.8 molar for improved ionic conductivity. The thionylchloride itself is an acridly smelling colorless liquid, which heavily attacks the breathing system. It boils at 76 °C. It is applied in an anhydrous and pure state as for gas chromatography. The system is based on the already described paradox of the direct contact between anode and “cathode” because of the passivation layer between them. The growth of the passivation layer depends both on temperature and concentration of the electrolyte salt. It is supposed that on a very thin and homogeneous primary layer of lithium oxide or lithium carbonate the bulk reaction product of the contact with the electrolyte, lithium chloride, grows in a more porous structure as a secondary layer. Figure 18.13 shows the measured and expected capacity conservation during shelf-life of up to 10 years at 23 and 72 °C, respectively. One may see the very low effect of self-discharge, which is caused by the solid-state reaction of the passivation layer’s growth. It is provided here that during the whole shelf-life there is indeed no interruption of the passivation layer by short periods of discharge.

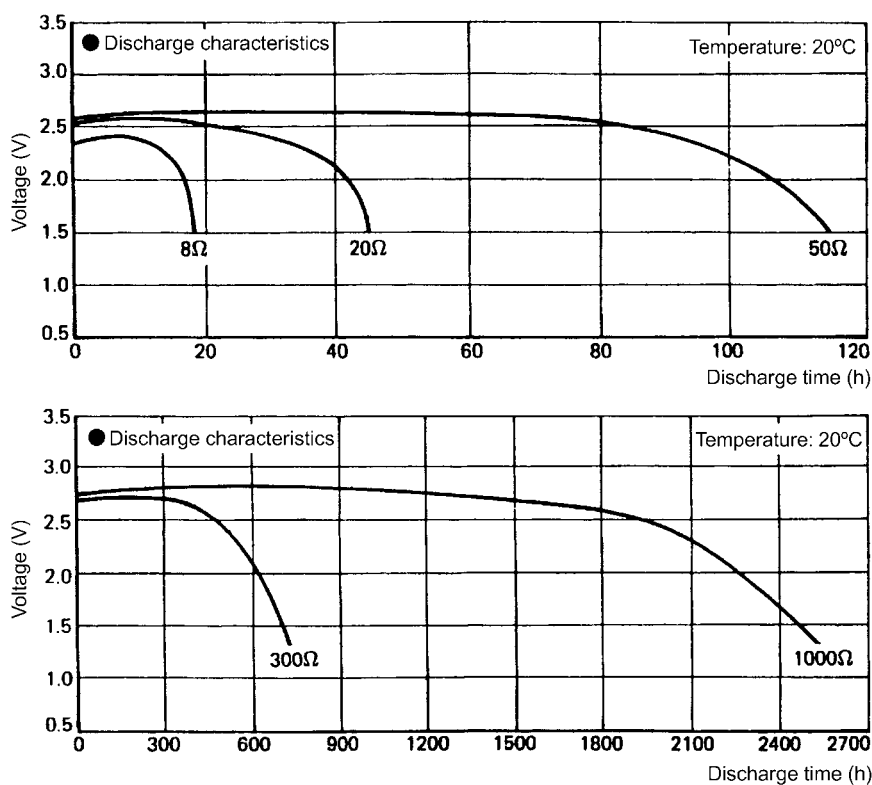


Figure 18.11 Discharge graphs of lithium/carbon monofluoride cells (C size) depending on the load (Matsushita).

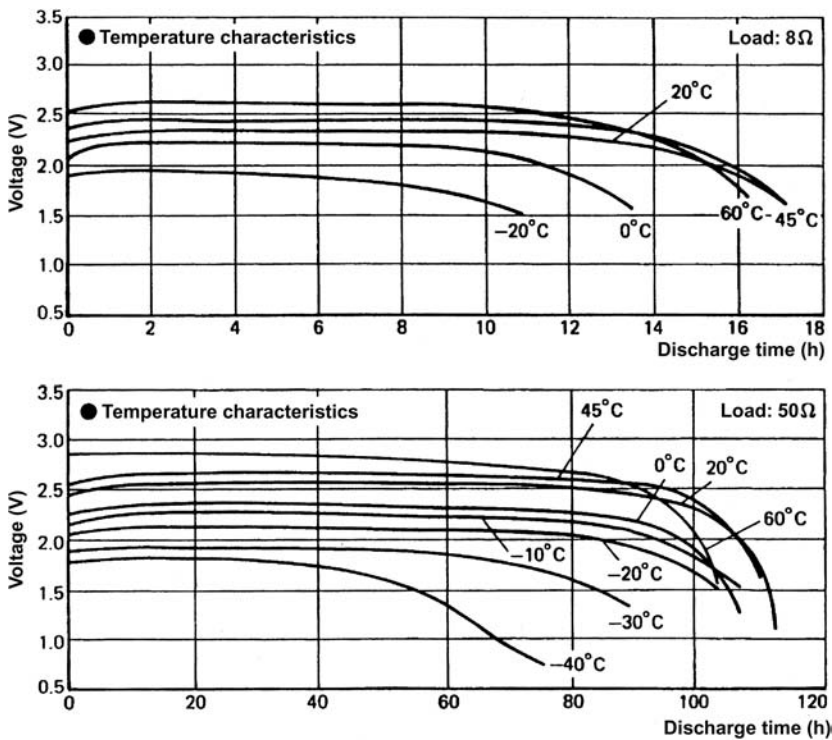


Figure 18.12 Discharge graphs of lithium/carbon monofluoride cells (C Size) depending on the temperature (and load) (Matsushita).

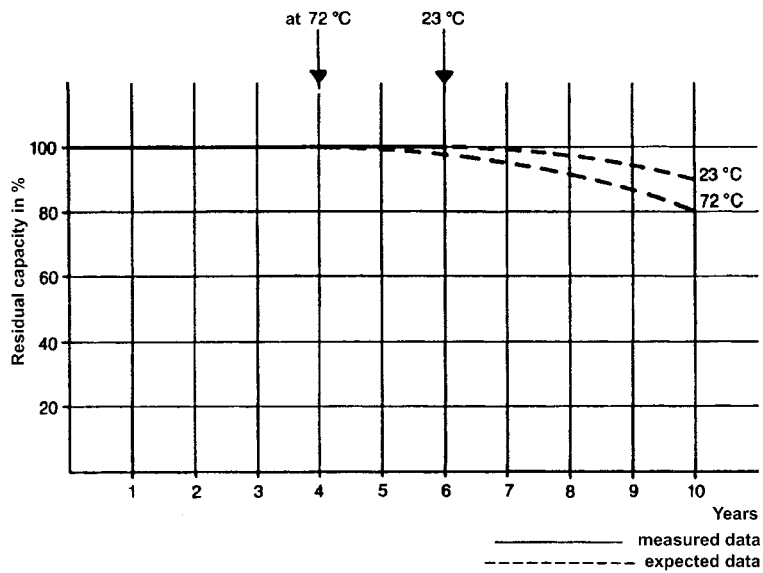


Figure 18.13 Retention of capacity of lithium/thionylchloride cells during storage at normal temperature and 72 °C (Sonnenschein).

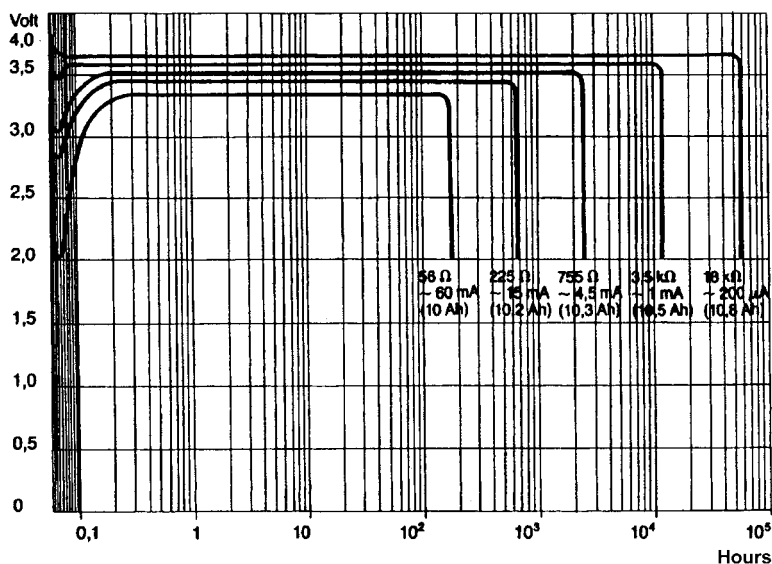


Figure 18.14 Discharge graphs at various loads of lithium/thionylchloride cells (10.5 Ah, bobbin type) after 1 year storage at normal temperature (Sonnenschein).

The useful stability of the passivation layer with respect to shelf-life and low self-discharge on the other hand causes a shorter or longer breakdown of the cell voltage at the beginning of a high rate discharge – the ‘voltage delay’. This holds especially after longer shelf-lives. In Figure 18.14 from the discharge curves of a 10.5-Ah bobbin type cell (Sonnenschein) after one year’s storage at 25 °C, the voltage delay can be seen preferably at higher rates. The passivation layer can be influenced by addition of lithium oxide Li_2O or sulfur dioxide SO_2 for shorter and shallower voltage delays, but only at the expense of shelf-life. Figure 18.15 shows the positive influence of an additive not described by the manufacturer – it may be PVC from other hints in literature – on the voltage delay that is here to be attributed clearly to the anode.

The cathodic current collector is made from carbon black – sometimes also from carbon fibers – with PTFE and a catalyst¹⁵ on a substrate of nickel foil. Here the pore volume and geometry govern loadability and capacity of the system. Figure 18.16 shows some discharge curves of a cell of the spirally wound form (Saft) which can be compared to those of Figure 18.14. The former may obviously be loaded higher than the latter. The spirally wound electrodes are especially thin and provide a large surface both macroscopically and microscopically.

For the separation glassy nonwovens are used. They are not expensive and yield a low resistivity. For high rate cells which are also loaded mechanically a porous foil of Tefzel[®] is used, too, but on account of the higher resistance the deep temperature capacity is reduced.

¹⁵ For example, the cobalt compound cobalt tetramethoxyphenylene porphyrine.

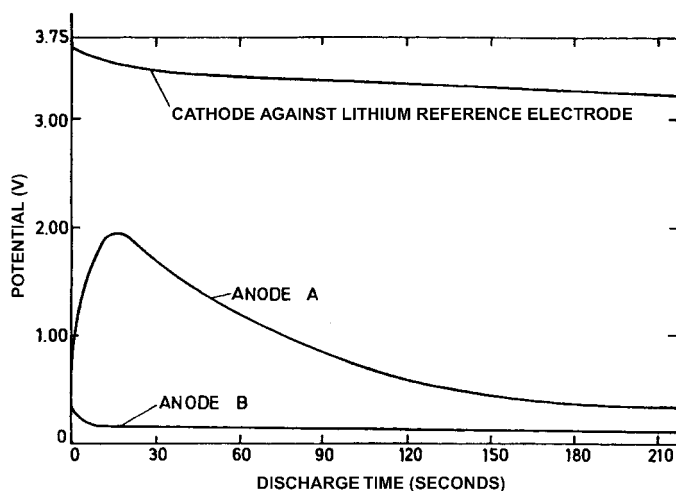


Figure 18.15 Suppression of the voltage delay at the beginning of the discharge of a lithium/thionylchloride cell: effect of an additive (GTE).

The OCV of 3.66 V per cell enables CCV values of 2.8 to 3.6 V, depending on design and load. With various design versions these cells may be operated between -55°C and more than $+150^{\circ}\text{C}$.

Until now thionylchloride cells have been produced – within wide boundaries of sizes and with capacities ranging from a few mAh up to 20,000 Ah – in the form of round cells of the bobbin, spirally wound, and flat electrode types. Flat electrodes are also used for prismatic geometries. These prismatic cells and also bigger round cells

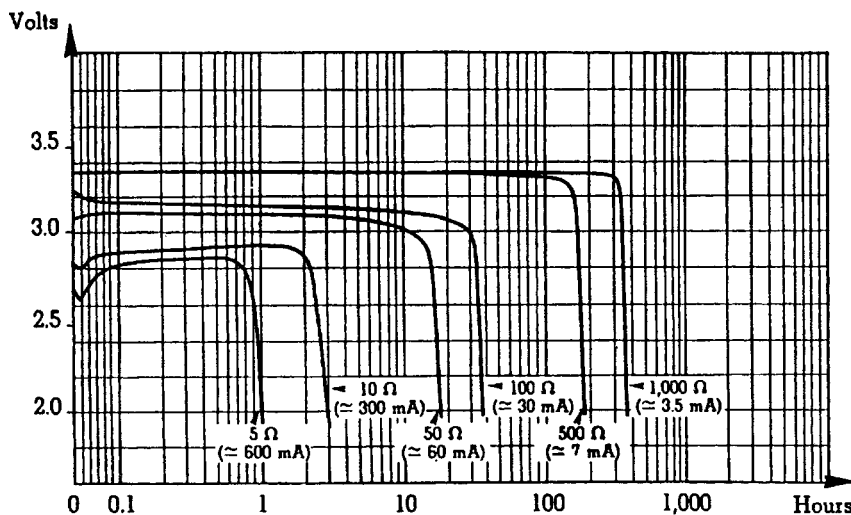


Figure 18.16 Discharge graphs of 1-Ah lithium/thionylchloride cells (spirally wound) (Saft).

with relatively thin walls are possible because of the “reduced” overpressure in these cells under operational conditions – at least if compared to the sulfur dioxide system (see next section). Nonetheless cells bigger than 1 Ah and all high rate versions are to be equipped with a burst vent as part of the cell case with the aim of opening only in a controlled manner when overheated.

For military applications also ‘activateable’ batteries were developed whose electrolyte during shelf-life is separated from the electrode stack and pushed into the cell within seconds only just before use of the battery.¹⁶ Of course the shelf-life of such batteries is still longer than that of “active” batteries of the thionylchloride type with their capacity loss of 10% during 10 years of storage. But for military purposes the reliability of the improved system and the avoidance of the initial voltage delay make the activateable technology more attractive than the reduction of self-discharge.

On account of the especially high energy density, the necessarily hard cell cases and the poisonous components, the handling and the use of Li-SOCl₂ cells ought to be carried out only according to the following safety instructions:

- Do not recharge!
- Protect parallel strings with diodes!
- Do not short!
- Do not assemble with reversed polarity!
- Do not open, puncture, or crush!
- Do not throw into fire!
- Assemble batteries only after contacting the cell supplier!
- Use cells and batteries only in containers that are not blocking the escape of gases!

Li-SOCl₂ cells are applied to memory back-ups, to radio transceivers, and to emergency or safety power supplies. Figure 18.17 shows the discharge curve of a special military emergency power supply of 200-Ah capacity with a 350-hour low rate discharge and short high rate pulses. Even under high rate load the voltage level remains constant until shortly before the end of discharge.

In the former Minuteman missile silos, thionylchloride batteries of 10,000-Ah cells were used as the redundant and grid- (mains)-independent power supply. From Figure 18.18 one may see the especially flat and constant curve of the voltage-time graph of this type of battery during a low rate discharge lasting longer.

Thionylchloride cells are manufactured in Germany by Sonnenschein Lithium and FRIWO, worldwide by Eagle Picher, Saft, Honeywell, Power Conversion, Philips USFA, and others.

18.6.4 The System Lithium/Sulfur Dioxide

This system operates with sulfur dioxide SO₂; this is also a fluid depolarizer from which the thionylchloride is deduced chemically. Design and mechanisms of both

¹⁶ The cell of PCI – 5.1 g of weight delivering 280 mAh of capacity – contains the electrolyte within a glass ampoule, which is broken under operation so that the electrolyte is able to fill the space between the electrodes.

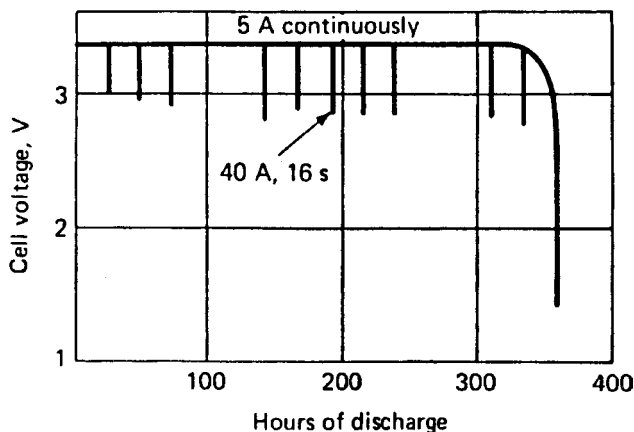
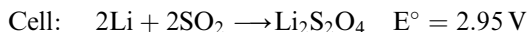
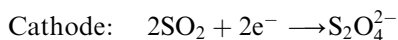
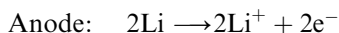


Figure 18.17 Discharge graph of a 200-Ah lithium/thionylchloride cell under mixed continuous and pulse load: 5 A continuously, several pulses of 40 A and 16 sec (GTE).

systems are identical to a large extent. In the 1970s based on research activities at American Cyanamid during the 1960s the SO_2 system was the first lithium high-energy product being manufactured in series.¹⁷ The following reaction equations show lithium dithionite $\text{Li}_2\text{S}_2\text{O}_4$ as the (main) discharge product, which is a colorless substance, also being the main component of the passivation layer on lithium in this cell type:



Under normal conditions sulfur dioxide SO_2 is a colorless acridly smelling gas that is a strong poison when breathed similar to thionylchloride SOCl_2 . It condenses at -10°C and solidifies at -73.5°C . To be put into the Li- SO_2 cells it has to be liquefied and kept in the cells under its own vapor pressure of 3 to 4 bars at normal temperature.

The twofold function of SO_2 as electrolyte and cathode is possible because of the passivation layer built up on the lithium surface as in the SOCl_2 cells. Although being its own solvent SO_2 is combined with a co-solvent of acetonitrile (AN) or propylene carbonate (PC) and with lithium bromide as electrolyte salt which has to be pure to a high degree and water free (H_2O content ≤ 100 ppm). The salt is solved (solvated) mostly by the SO_2 , whereas the acetonitrile – building a compound-like complex with the SO_2 – serves for low viscosity and consequently for good conductivity also at low temperatures.¹⁸ But nonetheless the vapor pressure of SO_2 mixed with acetonitrile is lowered only slightly.

¹⁷ The technical realization was achieved by the companies Duracell, Honeywell, and PCI. With know-how from PCI the German FRIWO installed a production since 1978.

¹⁸ A typical SO_2 -AN-LiBr electrolyte shows a conductivity of $5 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 20°C and of $2.2 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at -50°C .

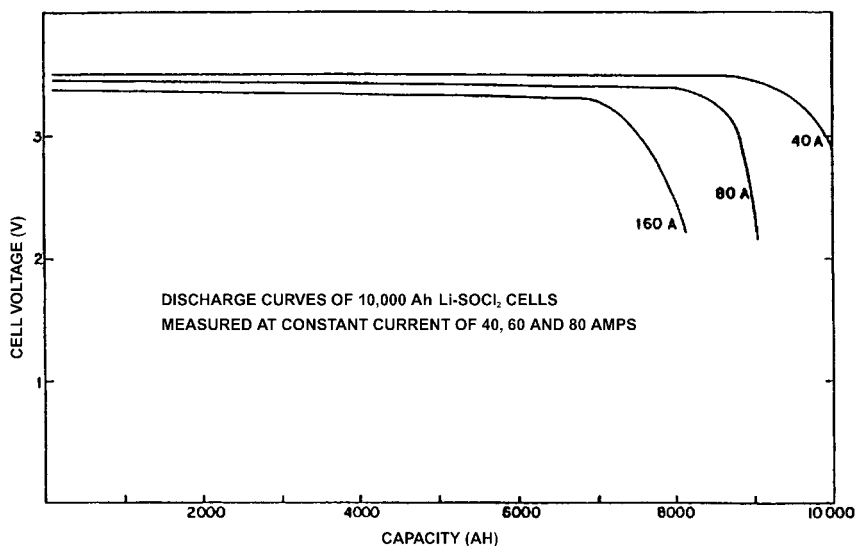


Figure 18.18 Discharge graph of the 10,000-Ah Minuteman lithium/thionylchloride cells under various loads (GTE).

Concerning the cell design it was found that Li and SO₂ have to be used as close to the 1:1 ratio as possible. Under an excess of lithium – which, however, is useful for high rate pulses¹⁹ – the danger prevails that at the end of discharge, i.e. complete consumption of SO₂, the remaining Li metal depassivates and then reacts vigorously with the co-solvent AN producing lithium cyanide and methane. Once the cell after warming up opens under the overpressure, the escaping methane may catch fire spontaneously. Therefore the balanced design is required for multicell batteries where one or the other cell may be deeply discharged – even into reversal, which means a recharge of the single cell under reversed polarity – because of the unavoidable, production-based fluctuations of the capacities of the single cells.

The passivation layer of lithium dithionide breaks down easily also at the first load after a longer period of storage. The cell shows only a very short voltage delay which is less deep than with the “early” SOCl₂ product. This can be recognized from the characteristic discharge curves of [Figure 18.19](#) together with the especially stable and constant discharge voltage. Compared to the SOCl₂ system, however, the self-discharge effect also at lower temperatures is a little faster with SO₂ cells, the reason being the faster growth of the passivation layer (see [Figure 18.20](#), Duracell). To get extreme long shelf-lives one should avoid checking the OCV from time to time because the disturbed passivation layer would then have to recover again repeatedly, which would mean an acceleration of the self-discharge rate.

At least for high rate discharges the cathodic current collector may also limit the capacity of the system. It is made of a highly porous mixture of carbon black, Teflon[®], and a catalyst pasted on an aluminum-expanded metal. It is plausible that

¹⁹ Special cells are applied for radio buoys, which operate indeed with some excess lithium, but this is a safety risk that can be borne in the buoys’ environment.

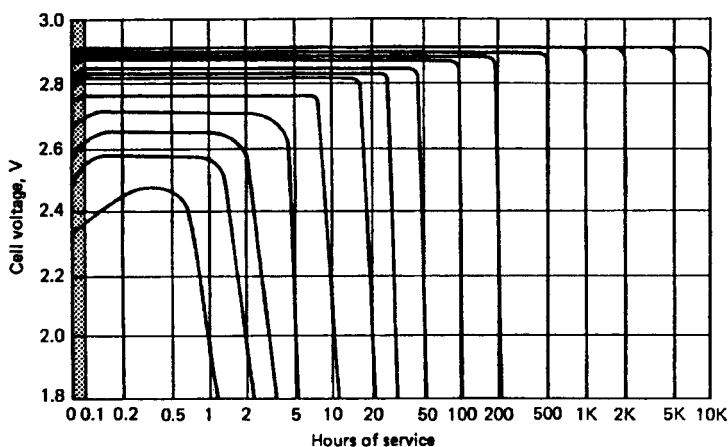


Figure 18.19 Discharge graphs of lithium/sulfur dioxide cells of the spirally wound technique under various loads (Duracell).

the use of the pore volume of the current collector by the deposition of the reaction product lithium dithionite depends mostly on the current density during discharge. In the geometric model of those pores, formed like bottles, preferably the bottlenecks are covered with the reaction product under high rate conditions. Already after a partial discharge the depth of the pore's bottle is no more available for the reaction and the reaction product's disposal on account of the blocked bottleneck. In this way the (high rate) discharge has ended prematurely. Deep temperatures enhance this effect. Both influences are documented in [Figure 18.21](#).

At higher temperatures the internal pressure of SO_2 cells is also high, up to 30 bar and more. So the geometry of these cells is restricted to round tubes, which may be easily and economically used as pressure vessels. They are manufactured in standard or customized sizes from stainless steel – exclusively hermetically welded

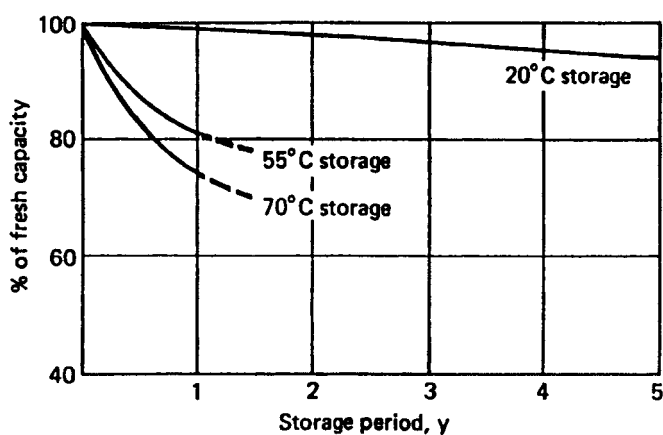


Figure 18.20 Retention of capacity of lithium/sulfur dioxide cells during storage at various temperatures (Duracell).

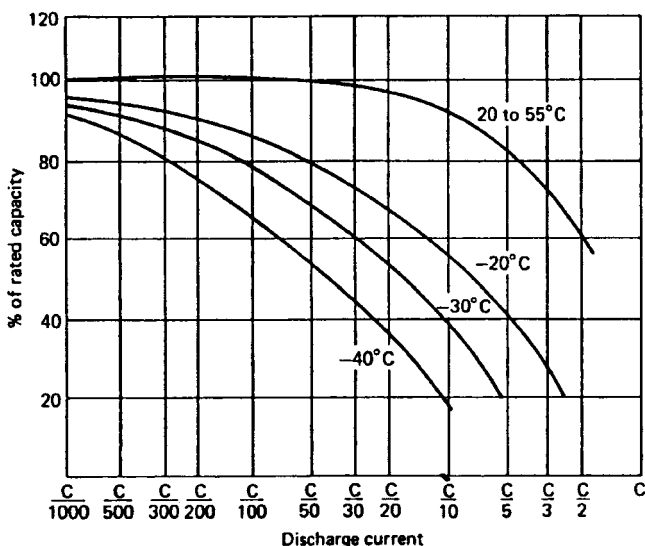


Figure 18.21 Dischargeable capacity of lithium/sulfur dioxide cells depending on their discharge temperature (Duracell).

with glass-to-metal seals from special glasses²⁰, which have to be resistant against electrochemical corrosion under these conditions. The electrodes for high rates are of the spirally wound type. Because of the high SO₂ gas pressure, a safety vent is an absolute must. During discharge, however, the internal pressure is gradually reduced as shown in Figure 18.22 at various temperatures. Nonetheless the safety layout of course has to suffice also for fresh cells with their high-energy content and high internal pressure.

The OCV of the system is about 2.95 V. SO₂ cells may be heavily loaded: A standard D cell with 7 to 8 Ah nominal capacity may be discharged by 2 A continuous current and 30 A pulses. Its specific energy of about 275 Wh/kg is lower than that of the competing SOCl₂ cells. The shelf-life is very good with a self-discharge rate of about 10% after 10 years (see Figure 18.20).

The SO₂ cells are applied as single cells or battery packs to radio transceivers, to emergency equipment with long shelf-lives, to memory back-ups, to film and video cameras, and others. The most important customer is the military, which is especially concerned in long shelf-life, high energy density, and applicability for all climatic zones.

The SO₂ cells are often equipped with back-setting thermo switches as protection against overload and to avoid an action of the safety (bursting) vent. Battery packs often have a built-in resistor, which may be switched on for safe discharge of capacity rests before final disposal (see Figure 18.23).

The SO₂ cells are manufactured in Germany by FRIWO, worldwide by Honeywell, PCI, and Duracell.

²⁰ Under the influence of an electric field also glasses, depending on their composition, may relatively easily corrode.

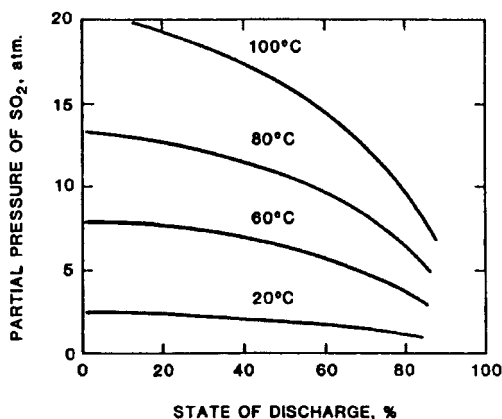


Figure 18.22 Pressure drop in lithium/sulfur dioxide cells during discharge at various temperatures (from P. Bro).

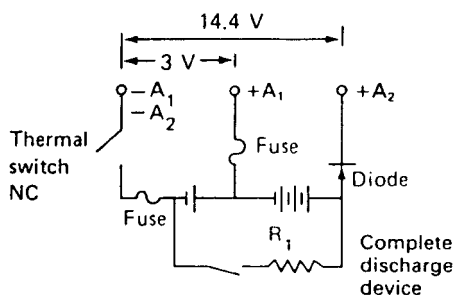


Figure 18.23 Electric circuit of the lithium/sulfur dioxide battery pack BA-5598 equipped with various safety components. (From Reddy in Ref. 5.)

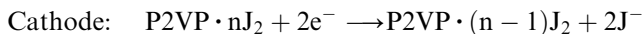
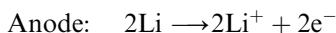
18.6.5 The System Lithium/Iodine

The first lithium/iodine cardiac pacemaker battery was implanted in 1972. This type of battery proved to be very successful in this field²¹ and for other applications, too. The special features of this solid state battery are explained with its technique, which is limited with its extremely high energy density and reliability, especially for low rate applications. This technique is based firstly on the electrode couple of lithium and iodine with its high energy content²² – the OCV of the lithium/iodine cell is 2.80 V – and secondly on the favorable fact that the product of the cell reaction, the lithium iodide (LiI), forms very tight and continuous layers between the active material of the electrodes, which are acceptable ionic conductors with negligible electronic

²¹ Until 1990 about 2 million batteries were used for cardiac pacemakers exclusively of the LiI type.

²² Iodine belongs to the chemical elements of the 7th column of the periodic system, to the halogens. By reaction between the halogens and the alkaline metals, e.g. lithium, especially high energy is released.

conductivity. The cell reaction follows the reaction scheme



In this way the reaction product lithium iodide represents the electrolyte as well as the separator for this cell simultaneously. It is being created already as a thin reaction layer between the electrode materials once the active materials of anode and cathode are brought into contact during the manufacturing process without any additional separator. This solid electrolyte layer grows during discharge more and more with the consequence of an enhanced resistivity of the cell. The early pacemaker batteries therefore showed a markedly declined discharge characteristic. [Figure 18.24](#) shows this for a pacemaker battery (Medtronic), whose second half of capacity could be discharged only with continuously lowered CCV because of the exponentially rising resistance.

The cathodic material is a mixture of iodine with poly-2-vinylpyridine (abbreviated as P2PV).²³ The P2PV acts as a stabilizer for the iodine and as conducting agent. The high vapor pressure of pure iodine is thereby reduced remarkably. The cathodic mixture was poured into the early pacemaker batteries as a fluid. During discharge there was a volume contraction on account of the generation of the separating electrolyte salt LiJ. It was accompanied by the solidification of the electrolyte-cathode system. Then the components were solidified but not tightly packed within the cathode. So the inner resistance of the cell was comparable to that shown in [Figure 18.24](#). The further development introduced thoroughly compressed cathodic pellets, which reduced the rise of the inner resistance during discharge noticeably. [Figure 18.25](#) shows some discharge curves of a lithium iodine button cell manufactured that way (Catalyst Research). But even with this improvement these cells fit only best for low rate long-time applications with μA currents for a couple of years. The CCV of cells being used for medical purposes is around 2.7 V. Pacemaker batteries are used starting at 2.8 to 2.7 V and are replaced at the latest at 2.3 to 2.0 V. For the pacemaker application a flatter curve is appreciated at the end of discharge to keep a safety reserve before the battery's final exchange.

The iodine cathode is the capacity-limiting partner of this system. It is especially reliable and safe (this means 'good tempered') and gives no problems when mishandled. The operational temperature is between -55°C and $+125^\circ\text{C}$.

The system's theoretical energy density is 1930 Wh/L. Practically it amounts to 1000 to 1300 Wh/l. The practical specific energy is about 300 Wh/kg.

Lithium iodine batteries are available mostly in the pacemaker shape, i.e. in that flat nearly semicircle geometry of, e.g. $5 \times 30 \times 40 \text{ mm}$, with 1 to 3 Ah capacity at a weight of 10 to 30 g. For industrial applications flat rectangular formats are made with contact pins that make them mountable onto electronic boards. Button cells are also realizable. All cells have glass-to-metal seals for both polarities or for the negative one only. A button cell's cross-section is shown in [Figure 18.26](#)

²³ Iodine and P2VP are mixed at a ratio of 20:1 to 30:1. They react to form a complex compound.

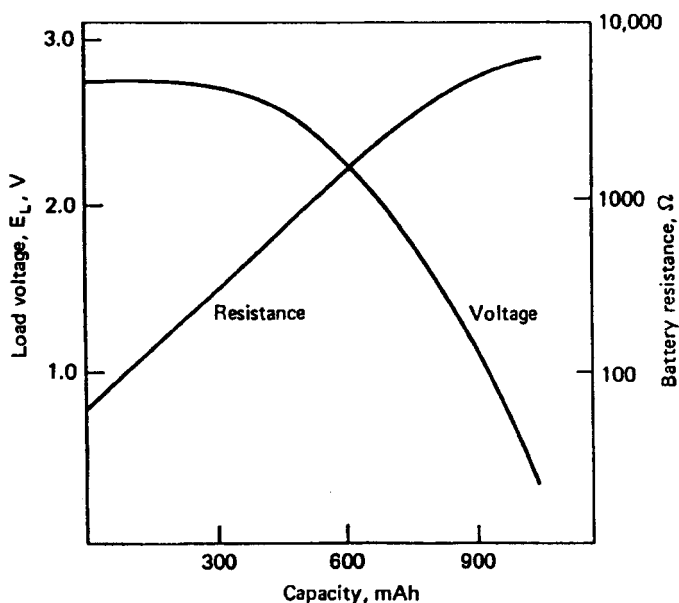


Figure 18.24 Discharge graph of voltage and inner resistance of an early lithium/iodine pacemaker battery, discharged with the relatively high current of 100 mA (Medtronic).

(Catalyst Research). It is applied to typical low rate systems as memories, sensors, and monitoring devices, but preferably as cited above in pacemakers. So they were used more recently combined with lithium/manganese dioxide cells (earlier also with vanadium oxide cells) in so-called pacemaker defibrillators, too.²⁴ Although other lithium systems were also used for pacemakers, the lithium iodine technique had the major market share.

The efforts for quality control of the production of pacemaker batteries and others for medical applications, which may remain implanted for 5 to 10 years or longer, are very intensive. They amount to a multiplicity of the value of the material used.²⁵ That explains the high prices (several hundreds of DM). The design of a typical pacemaker battery is shown in Figure 18.27.

Manufacturers of lithium iodine batteries are Catalyst Research, who developed the technique originally, Wilson Greatbatch, and Medtronic (in Germany Litronic).

18.6.6 The System Lithium-Aluminum/Iron Disulfide

The so-called ‘thermal batteries’ belong to the family of ‘activateable’ batteries, which are put into activity by a defined physical process if they are to become dischargeable. For thermal batteries this process means their being heated up by several hundred degrees centigrade. At normal temperatures the active components

²⁴ Defibrillation serves to counteract ventricular fibrillation, i.e. to re-establish the correct heartbeat.

²⁵ Pacemaker batteries, e.g., are checked 100% during several weeks at 37 °C (body temperature) for their function and are only then released for service.

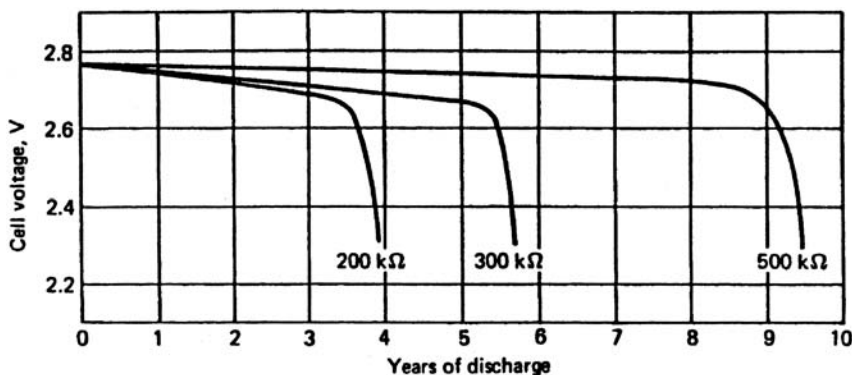


Figure 18.25 Discharge graphs of a lithium/iodine button cell at long time discharge (Catalyst Research).

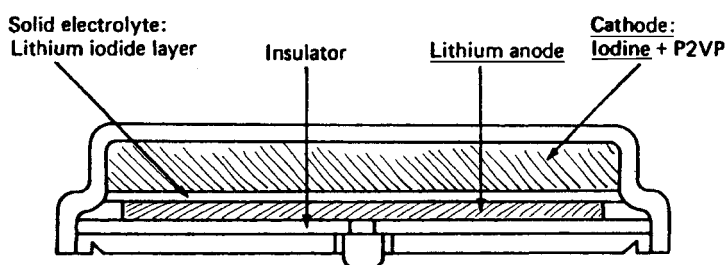
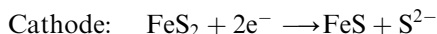
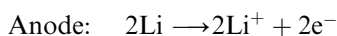


Figure 18.26 Cross-section of a lithium/iodine button cell (Catalyst Research).

of these batteries are in the solid state. So virtually no reaction takes place between them. But at the operating temperature of between 400 and 500 °C the salt mixture acting as the electrolyte is molten and the electrode materials – still being solid – are sufficiently reactive to let them react with the required speed.

For a long time thermal batteries were available for discharge times of several minutes. The relatively new thermal battery system lithium-aluminum/iron disulfide makes the thermal technology also applicable for discharges lasting several hours with acceptable voltage time curves. For this system the energy conversion is based on the discharge of the lithium anode against the cathode of iron disulfide to produce iron sulfide – pyrite – and lithium sulfide according to the reaction scheme



²⁶ This unusually high OCV is related to traces of heavy metals like Ni, Co, and Cr in the FeS_2 . On load the voltage falls below 2 V.

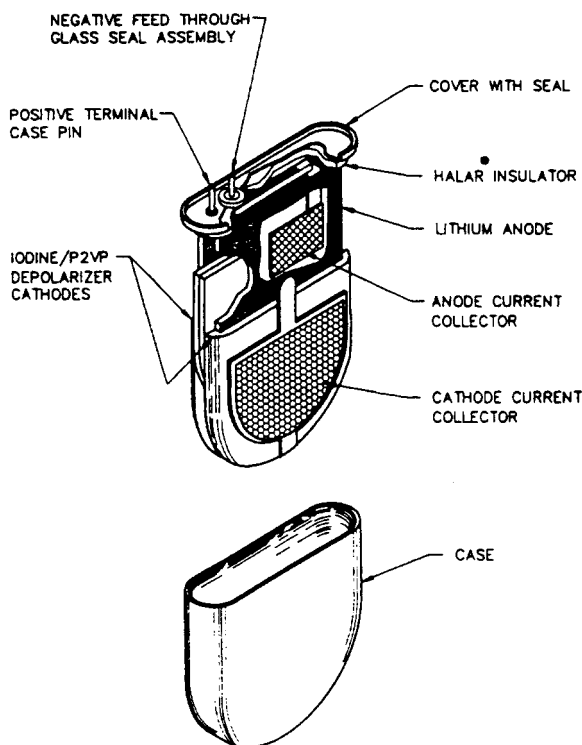


Figure 18.27 Pacemaker battery with pressed cathode and double anode. (From Jolson et al. in Ref. 5.)

The effective CCV for this discharge process is only 1.5 to 1.8 V depending on the design of the system.²⁷ The ternary system lithium-iron-sulfur is far more complex than can be recognized from the reaction scheme. In [Figure 18.28](#) one can see the two iron-sulfur phases FeS and FeS_2 and additionally also the phase FeS_{1-x} together with several areas of coexistence of the species being involved. The iron sulfide can be discharged indeed beyond the stage of FeS : The discharge of the first species FeS_2 is done with a relatively constant CCV. After complete consumption of the FeS_2 , the discharge voltage declines by discharge of FeS step by step over several reduction states of iron down to pure metallic iron as the final cathodic reaction product. Usually only the first discharge step of the system is used. FeS_2 shows sufficient electronic conductivity. So conductors as additives to the cathode are not necessary. FeS_2 decomposes above 550°C into FeS and S . Therefore the operating temperature should not exceed this temperature level. The cathodic discs (see below) are compressed from powder mixtures of FeS_2 and LiCl-KCl eutectic – for improvement of reactivity and loadability – together with some SiO_2 (silica).

²⁷ This cell voltage is not so favorable if compared to that of other lithium systems. But we have to take into account those other characteristics explained below which are desirable for the special applications of these thermal batteries.

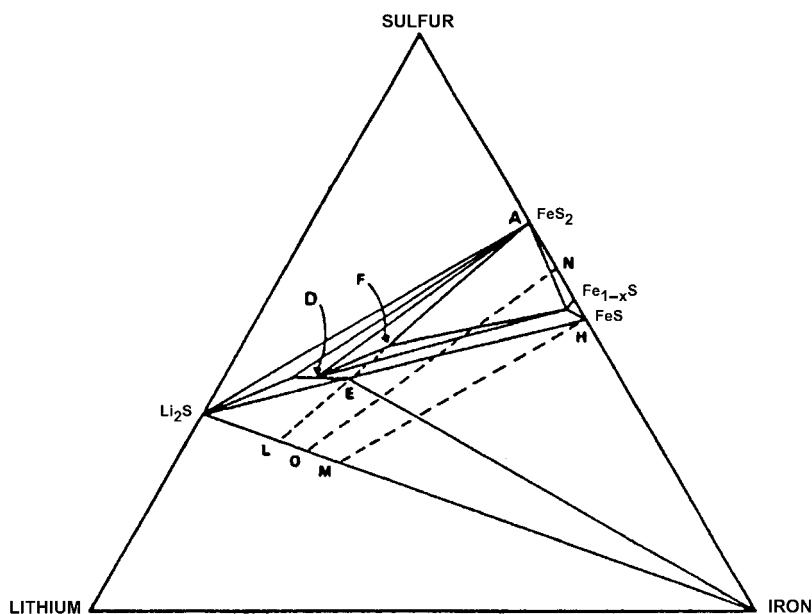


Figure 18.28 The lithium/sulfur-iron phase diagram.

The anode is made from the LiAl β -alloy (see [Figure 18.29](#)), which contains both components nearly at a ratio of 1 to 1. Its melting point is about 690 °C. These anodes are compression moulded from the pure alloy powder. The potential of this lithium electrode remains constant during the discharge, provided one does not leave the coexistence region of 8 to 47% lithium content between the β -phase and the Al α -phase, which is poor in lithium. Li-Fe and Li-Si mixtures are also used as anodes with a sufficiently stable potential during discharge.

It applies for both electrodes of the lithium/iron disulfide cell that the active materials can be used up during discharge only to a small extent.

Suitable electrolytes for the lithium thermal batteries may be chosen from the low melting eutectics²⁸ of the lithium halides. Their melting points are from 300 to 350 °C. For improved stability they are mixed with magnesia and compressed to flat discs for assembly into the cell stacks. The eutectic point of the LiCl-KCl electrolyte is at 352 °C and that of a LiCl-LiBr-KBr electrolyte is at 310 °C.

For most military applications the thermal batteries are to be heated up and activated as quickly as possible. This is done by heat-generating tablets made from ‘Thermit’-like²⁹ mixtures of iron powder Fe and potassium perchlorate KClO_4 . This

²⁸ Mixtures of at least two components with a defined mix ratio, which are completely immiscible in the solid state and completely miscible in the liquid state, are called ‘eutectic’. The eutectic mix ratio is defined by the minimum melting point of all possible mixtures (combinations) of the components. It means in practice that at temperatures exceeding the eutectic one at least a part of the mixture is liquid. In the solid state the eutectic is a mixture of finely divided tiny crystals of – in most cases – two different compositions.

²⁹ The Thermit or aluminothermic process for constructing railways by welding the rails in place: A powder mixture of FeO and Al is ignited by BaO_2 . The heat of reaction is sufficient to let the iron as the reaction product liquefy and flow into the welding gap.

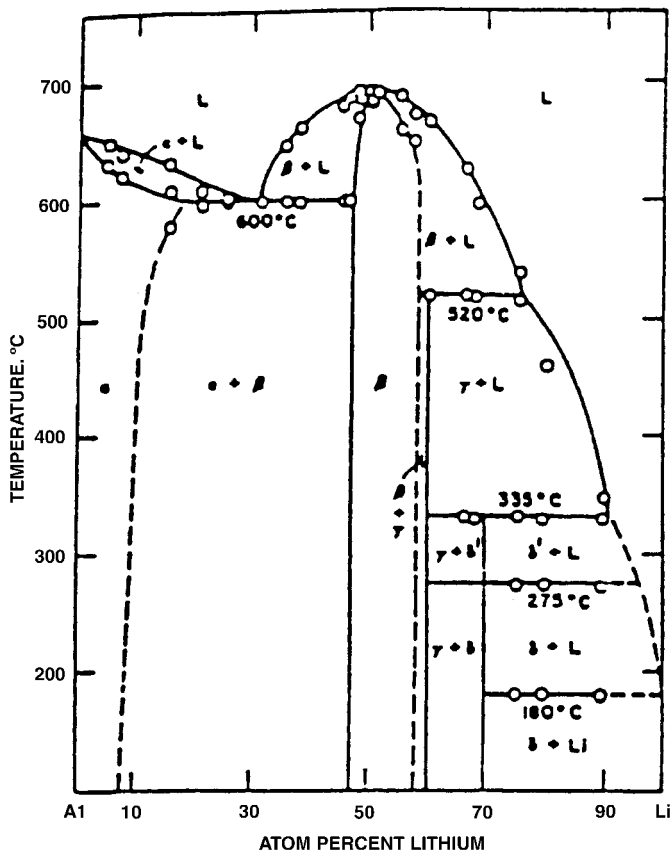


Figure 18.29 The lithium-aluminum phase diagram.

mixture is ignited via firing strips made from paper being pyrotechnically impregnated. The paper consists of zirconium Zr and barium chromate (VI) BaCrO_4 combined with a suitable fiber material. The firing strips themselves are ignited by electrically fired ignite pills. The burning front of the firing strips proceeds with a speed of about 250 mm/sec. So depending on the battery size they get heated up within 100 msec to 2 sec.

Typically thermal batteries are constructed as stacks or 'piles', according to [Figures 18.30](#) and [18.31](#). Usually multiples of circle-shaped cell units of anode, electrolyte separator, cathode, and heating tablet are stacked one on top of the other according to the required operating overall voltage. The total unit is placed into a pressure-proof stainless steel container that thermally insulated as well as possible. These batteries are produced in controlled rooms with dry air, as normally used for the production of lithium batteries. All battery components have to be extremely dry.

Lithium thermal batteries are produced mostly for military applications to support control and trigger functions within weapon systems such as aircraft, missiles, and high-caliber gun ammunition. They are offered for power requirements

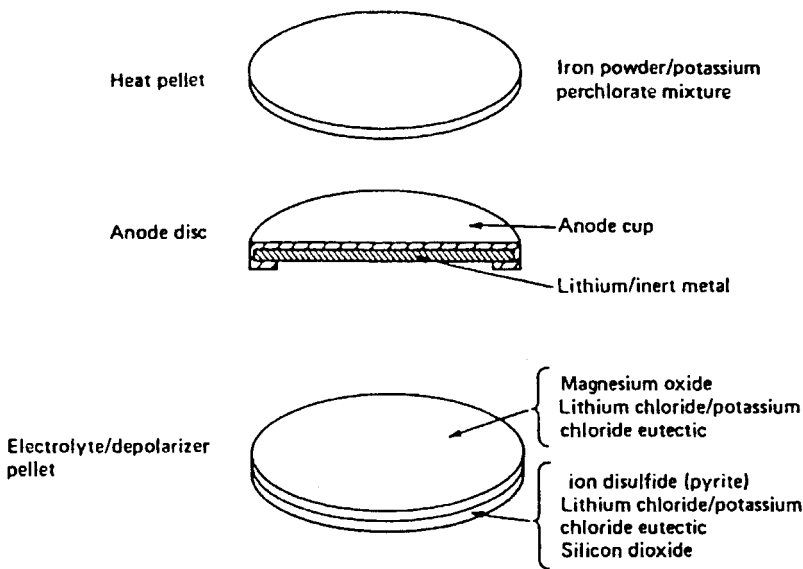


Figure 18.30 The pile structure of a single lithium/aluminum/iron disulfide thermal cell. (From Ref. 3.)

ranging from 1 W for 10 ms to several kW for up to two hours. [Figure 18.32](#) shows the relation between volume, power, and available discharge time for typical lithium thermal batteries. In spite of the built-in insulation, it is the rapid cooling down that limits the operational time. If the temperature falls below the working temperature

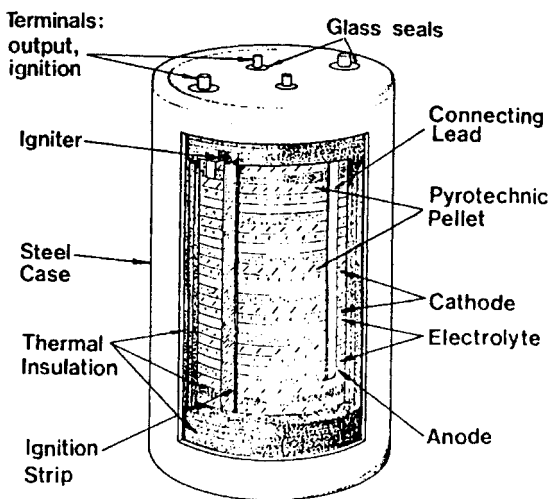


Figure 18.31 Inner structure of a multi-cell thermal battery. (From Ref. 5.)

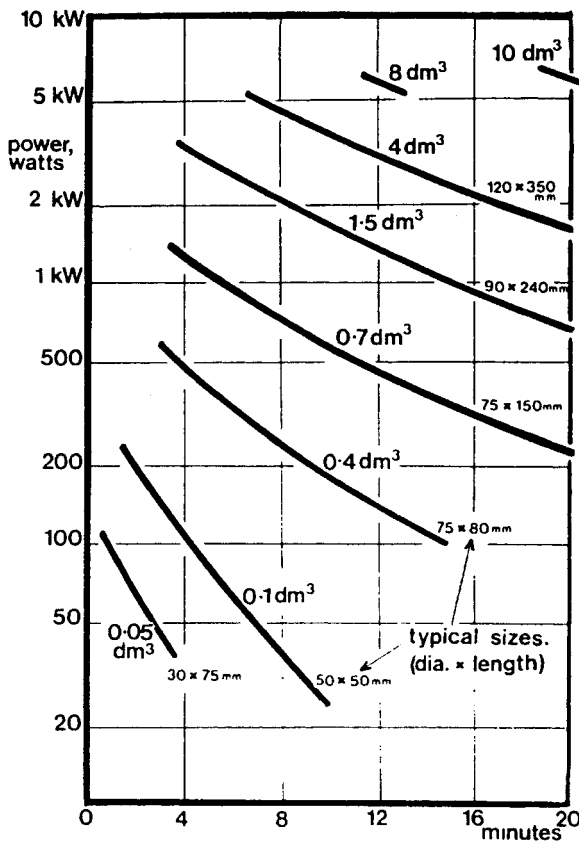


Figure 18.32 Relation between volume, power, and operation time of various Li-FeS₂ thermal battery sizes. (From Attewell in Ref. 5.)

of 400 °C and eventually below the eutectic point of the electrolyte, the battery becomes – even if not fully discharged – highly resistive.

Older versions of thermal batteries use calcium or magnesium anodes with cathodes from alkaline metal chromates, tungstates, ferrates, or vanadates. Figure 18.33 presents discharge curves of three different thermal battery systems of comparable construction size but varying voltage levels and discharge times. Discharge over longer periods of time than shown is impossible with all three systems because of the thermal losses and – with the Ca/Mg systems – because of several side reactions.

From environmental temperatures between –40 and +70 °C thermal batteries may be activated and used indiscriminately. Their extremely good storability in the “frozen” state at normal temperatures makes them especially suitable for military applications in weapons and equipment whose system shelf-life in total is often shorter than that of the integrated batteries. Because of their compactness thermal batteries are particularly resistant against shock, vibration, acceleration, and spin.

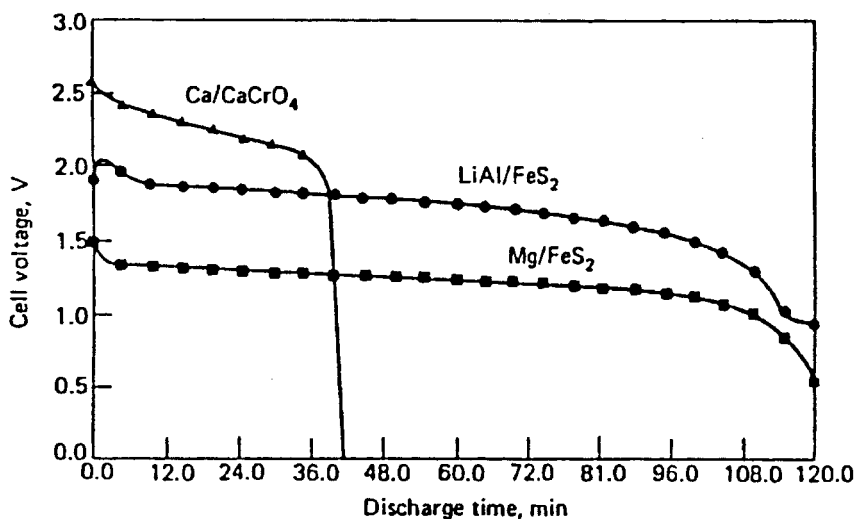


Figure 18.33 Discharge graphs of old (Ca-Ca-chromate, Mg-FeS₂) and new thermal batteries (Li-Al-FeS₂). (From Ref. 3.)

At least temporarily a lithium/aluminum/iron disulfide battery was also under development as a rechargeable high temperature system for use in electric submarine vehicles.³⁰

The roots of the thermal battery technology go back to German research and development efforts at the end of World War II. Today thermal batteries are manufactured by MSA, Eagle Picher, PCI, Leclanché, and SAFT.

18.7 SECONDARY LITHIUM BATTERIES

Soon after the introduction of the first primary lithium batteries into the market in the 1980s, it was attempted to develop also rechargeable lithium cells. These first approaches were based on pure metallic lithium anodes. It was simply an attempt to make existing primary systems rechargeable. The first secondary battery on the market was a Canadian product (Moli Industries) – a lithium/molybdenum disulfide system. This and other concepts were not successful, however. The reason was mainly the impossibility to deposit the lithium anode during recharge in such a compact and stable way that the lithium advantages of the primary systems – low self-discharge and few side reactions – could be maintained. This goal was not achieved at that time.³¹ The first secondary lithium batteries had some safety problems because of the uncontrolled deposition of the lithium metal yielding large microscopic surfaces of high reactivity.

³⁰ Lithium/iron disulfide batteries were also made as active primary systems for normal operating temperatures with a metallic lithium anode and one of the well-known conducting salt-solvent mixtures as their electrolyte. The product, as button or cylindrical cell, with its CCV of about 1.5 V was thought to become a cheaper competitor to the AgO-Zn cell. But they were not successful in the market.

³¹ The only exception was a rechargeable Li-MnO₂ battery of Tadiran for very special applications.

A tricky approach was more successful, which has already been explained together with the thermal system Li(Al)/iron disulfide:³² A stable inert matrix which does not react with other cell components was offered to the anodic lithium to be built into it repeatedly during recharge in an unchanged manner. In such a way and with precise charging and voltage control safe rechargeable lithium batteries could be introduced also for the consumer market. The best known and most widely spread system today (2002) is that of the lithium-ion battery as described below, which operates with a lithium-carbon intercalation compound as an anode.

18.7.1 The Special Aspects of a Secondary Lithium Battery Technology

Whoever has knowledge about batteries from application of lead-acid or nickel/cadmium batteries must consider several specifics of the rechargeable lithium batteries to understand their technology. These specifics are a consequence of the simple fact that during discharge the reactive agent of the anode – the lithium – not only changes its oxidation state, but also migrates quantitatively to the cathode. So the structure of the anode is totally decomposed during discharge and built up again during recharge. This central problem been solved by the development and realization of the secondary lithium cell.

- In lithium cells the current between the electrodes, i.e. through the electrolyte and the separators, is fully maintained by migration of positively charged lithium ions, independent from the primary or secondary mode of operation. The lithium metal is solved during discharge losing one electron per lithium atom and thus yielding a lithium cation, which migrates through the electrolyte and is finally incorporated in the cathode under charge equilibration by intake of an electron, which in turn is part of the current flow through the outer circuit.³³ In contrast to this the cadmium metal in the NiCd accumulator's anode and also the lead metal in the lead-acid accumulator's anode does not leave the electrode during discharge. The metal atoms here also change their oxidation state but stay at their place by taking in hydroxide and sulfate ions for charge equilibration. In both systems the charge transfer, the current, is maintained by ions from the aqueous electrolyte: the hydroxide ion in the NiCd and the sulfate and the hydrogen ion in the lead-acid batteries. The lithium electrode by contrast is an electrode whose metal atoms are dissolved ('solvation electrode', the potential of the electrode is controlled by the dissolved cations) or an electrode of the 'first type', whereas the traditional secondary batteries operate with anodes of the second type (cadmium) or pseudo second type (lead-acid) (the potential of which is controlled by the corresponding anion in the electrolyte). Here the electrodes undergo the same states from cycle to cycle and virtually maintain their constant

³² The lithium has also to be stabilized for the operation of the Li(Al)/iron disulfide thermal battery at over 300 °C. Otherwise because of its low melting point of only 180 °C, the lithium would vigorously react already during the short pyrotechnic heat-up period.

³³ The mechanism is in more detail explained below.

macroscopic geometry. So they are also geometrically cyclable. But if the pure metallic lithium anode, after its discharge normally as a compact foil, should be recharged, it would not yield a smooth and compact foil again but a mossy structure of dendrites, i.e. microscopically thin crystal fibers, which have a far larger surface than at the beginning. So the lithium electrode does not work reversibly in the sense of the required macroscopic structure, even if it is reversible thermodynamically because of the relatively low negative potential of deposition.

- For cyclic operation a large microscopic surface is not desirable indeed because during each cycle active lithium is lost and efficiency and cyclability of the system are severely affected. That is why the dendritically deposited lithium metal reacts at the surface also with the normally used aprotic solvents of the electrolyte to form the required compact reaction layer, which slows down the further attack to such a degree that the electrode can be regarded as stable (passive) at least temporarily. This passivation, however, irreversibly consumes active material, and this happens again and again during each new cycle. This of course makes the rechargeability the poorer, the higher its amount counts per cycle. The lithium consumed by passivation during recharge can't really be regenerated. The passivation reaction occasionally also strangles whole dendritic crystallites. Consequently their metallic remainders – not yet consumed by the reaction with the electrolyte's components – cannot be used any longer electrochemically because they have lost their metallic electronically conducting contact to the bulky mass of the electrode. A far quicker decay of capacity during cycling is the consequence.
- The capacity losses on account of the lithium's side reactions are increasing with the depth of discharge (DOD) per cycle. There are secondary lithium systems that reach many cycles only under very shallow discharge conditions. But there are also applications where secondary cells with such characteristics prove useful.
- Dendritic³⁴ metal deposition during recharge might also generate a metallic short through the pores of the separator between anode and cathode. This might end disastrously for the cell because of the afore-emphasized high reactivity of the lithium.
- For these reasons, as explained, the rate of self-discharge in secondary lithium cells might be higher than in the primary cells described earlier.
- Just as for primary systems the electrolyte mixture for secondary cells should be chosen with respect to stability against the high voltage of the cell. The electrolyte does not withstand cell voltages of more than about 4.0 to 4.8 V. Of course this also holds for the even more-or-less higher charging voltages: It must not lead to any decomposition reaction.

Today rechargeable lithium batteries – up from a few 100 mAh capacity – based on the reasons given have an anode from a lithium alloy or, more often, a nonmetallic

³⁴ A dendrite is a tiny needle-like crystal with ramifications like a tree. It develops when a crystal during deposition preferably grows in the direction of only one crystallographic plane and branches out here and there.

but very good electronically conducting carbon matrix of various crystallinity. The potential level of both types of electrodes differs only little from that of the pure metallic lithium anode. The electrode reactions are sufficiently reversible needing only low overvoltages. Consequently the values of the discharge and charge voltages of most of these cells are comparable.

In all cases a matrix is also used for the cathode, where the small lithium is inserted and released easily. The prototype of these matrices is the manganese dioxide, already well known from the primary technology.³⁵ With the proper choice of crystal structure the lithium ions are inserted or intercalated and released easily here. From this ability the name 'intercalation compounds' has been chosen for this type of crystalline material.

Electrolytes are mixtures of suitably selected organic solvents – as already well known from the primary cells – which should be good solvation (solving) agents, should show low viscosity and should be combined with effective conducting salts (see Section 18.4.2).

A number of different lithium secondary systems serve for very low energy demands of electronic modules as memories and clocks. The batteries for these fields of application are manufactured as button cells. These cells are described first. Then for medium and high energy requirements lithium-ion batteries are explained. Today they are widely applied for portable electronic devices such as cellular phones and notebooks, which need much more energy than the aforementioned components for as many hours as possible (practically today up to 4 hours in notebooks). On the developmental stage it has been attempted to apply the lithium-ion technology also for much bigger accumulators, e.g. for so-called hybrid vehicles with a combined combustion and electric propulsion system.³⁶

18.7.2 Rechargeable Lithium Batteries for Low Energy Applications (Button Cells)

Rechargeable lithium button cells are available at the market sized from 621 up to 3036³⁷ with typical weights of 0.3 to 6 g and with capacities of 0.010 to about 100 mAh. These very small accumulators are produced for applications with very shallow cycles, where a deeper discharge is possible from time to time but only as an exception. These button cells are for the support of memories and timers.

It is no surprise that the Japanese, who are the market leaders for electronic products for mass consumer articles, dominate the market for these very small accumulators. Manufacturers of these accumulators are Matsushita, Sanyo, Seiko,

³⁵ Complex compounds of lithium and heavy metal oxides as nickel oxide and cobalt oxide are working more effectively than the lithium/manganese oxide spinel which incorporates lithium ions into its tube-like voids whereas the former with their layered structure take up and release lithium ions more easily.

³⁶ Since 1997 the Japanese car manufacturer Toyota has offered the Prius as a hybrid-driven car produced in series. Today however it is still equipped with a nickel/metal hydride battery.

³⁷ Their type number describes the geometric dimensions of rechargeable lithium batteries systematically: It contains for the button and cylindrical types the diameter in mm and the height in 0.1 mm. The cell size 18650, e.g., has a diameter of 18 mm and a height of 65 mm. Cubic constructions are designated with the smallest dimension (height) in mm, with the next larger one (width) in mm, and with the largest one (length) in mm. The cell size 102248, e.g., is 10.5 mm high (flat), 22.5 mm wide, and 48 mm long.

and Toshiba. Some systems which are available on the market are described in the next section and a compilation is in Ref. 3.

18.7.2.1 The System Lithium-Aluminum/Manganese Dioxide

This product can be obtained in several button cell sizes. In the charged state the anode is a lithium-aluminum alloy with manganese and chromium additions. The manganese dioxide cathode is a crystalline mixture of lithium manganate (layered structure) and manganese dioxide (channel structure). This type of battery is able to deliver more than 500 shallow cycles – where “shallow” means a depth of discharge of about 10%. The electrolyte of this cell is a mixture of EC and BC³⁸ combined with one of the already cited conducting salts. The storability of these small accumulators is rather good: self-discharge being less than 5% per year. After deep discharge such a cell may also be stored for longer periods (see Figure 18.34 for a 14 month shelf-life in the deep discharge condition).

18.7.2.2 The System Lithium-Aluminum/Vanadium Oxide

This product of Matsushita operates similarly to the manganese dioxide cell described with a lithium-aluminum alloy anode, but with a cathode made from vanadium pentoxide. The discharge voltage's average value is about 3 V with a flat discharge characteristic as long as the cell is discharged slowly, i.e. with the 100-hour rate or even more slowly. This cell type is insensitive to overcharging. The energy density is between 100 and 140 Wh/L. The field of application is in memories.

18.7.2.3 The System Lithium Alloy/Polyaniline

This system, again with an alloy anode, is marketed by Seiko, the watch manufacturers. On the cathodic side the lithium ions are charged and discharged by the polymer polyaniline.³⁹ The discharge characteristic is strongly declining between 2 and 3 V. It depends on the concentration of lithium in the cathodic polyaniline. Small accumulators of this kind may be used for more than 1000 cycles with 20 to 30% DOD and low discharge currents of I_{500} or lower. The energy density is very low: it is 11 Wh/L. An important advantage of this accumulator is that it is free of heavy metals in the active parts and offers no environmental problems of disposal.

18.7.2.4 The System Lithium Alloy/Activated Carbon

Matsushita offers this rechargeable lithium battery system, which operates anodically with a host alloy for lithium containing bismuth, lead, tin, and cadmium. These components form low melting alloys with melting points – depending on the ratios of composition – between 60 and 120 °C. The Matsushita product uses the long- and well-known “wood” metal composed of bismuth, lead, tin, and cadmium at a ratio of 4:2:1:1 and melting at 70 °C. Accordingly the obviously low lattice energy of this alloy allows for easy implementation and release of lithium atoms/

³⁸ EC = ethylene carbonate; BC = butylene carbonate.

³⁹ Polyaniline is known as ‘conducting polymer’.

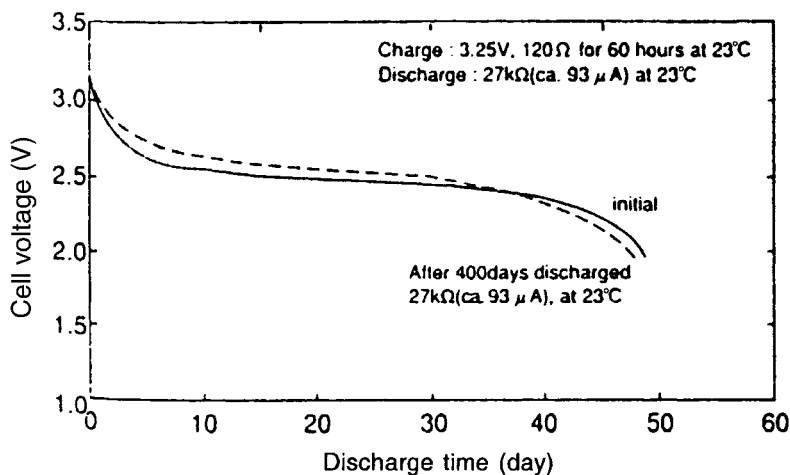


Figure 18.34 Storability of rechargeable lithium/manganese dioxide button cells (Sanyo ML2430) in the discharged condition (From Nishio/Furukawa in Ref. 6.)

ions. The especially low melting point however limits thermally the range of application and the size of those accumulators. The cathode consists of activated carbon with an inner microscopic surface of about $1000 \text{ m}^2/\text{g}$. Presumably the lithium ions are stored at those inner surfaces of the microporous structure of the carbon particles and not inserted into the graphitic layers⁴⁰ of the structure of these particles. The discharge characteristic drops comparatively quickly between 3 and 2 V. The energy density is only 4 Wh/L.

18.7.2.5 The System Lithium LGH/Vanadium Oxide

This system, offered by Toshiba, works with the so-called lithium LGH⁴¹ electrode, a graphitic intercalation electrode. The cathode is a mixture of vanadium pentoxide and phosphor pentoxide. The discharge characteristic of this cell declines progressively from 3 to 1.5 V. The energy density of the system is about 96 Wh/L.

18.7.2.6 The System Niobium Oxide/Vanadium Oxide

This cell type, marketed by Matsushita, operates with heavy metal oxide intercalation compounds on both the anodic (niobium oxide) and cathodic (vanadium oxide) side. The system is especially capable of rapid recharge. Deep discharge is tolerated well. With shallow discharges one may expect more than 700 cycles. The button cell size 1616 shows an energy density of 37 Wh/L.

⁴⁰ Various carbon materials are described more in detail in Section 18.7.3.1.

⁴¹ LGH = linear graphite hybrid is a special graphitic carbon preparation.

18.7.2.7 The System Titanium Oxide/Manganese Dioxide

This product is also marketed by Matsushita and contains anodically a lithium titanate of the spinel type and of the composition $\text{Li}_{1.33}\text{Ti}_{1.66}\text{O}_4$ that at 800°C forms a mixture of titanium oxide (anatase) and lithium hydroxide. The cathode is the manganese dioxide of “combined” structure as described in Section 18.7.2.1. For cycle life 400 cycles are reported. A typical average discharge voltage is 1.5 V. Compared to this, the only slightly higher charging voltage demonstrates the high reversibility of the electrode reactions. The energy density is 45 Wh/L. These batteries are applied to watches, memories, and small solar systems. The cells are offered with capacities between 1.2 and 3.0 mAh.

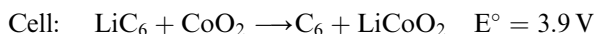
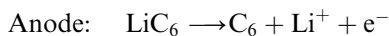
The rechargeable lithium button cells described so far are manufactured in sizes of 1 to 100 mAh of capacity being suitable for appliances which are shut off the grid during breaks and whose operation periods connected to the grid should suffice for recharge of the small accumulators, or for small devices which are equipped with solar cells for recharge during the periodically changing sunshine.

18.7.3 Lithium-Ion Batteries

In order to power appliances and applications of higher energy demand by rechargeable lithium batteries, the technology described so far had to be developed further on towards higher energy contents accompanied by improved specific energy and energy density values, i.e. towards more reactive mass in limited space – and towards better cyclability with 1000 cycles and more at 100% DOD (nominal). These requirements were to be fulfilled of course without any restriction to safety of operation.

Batteries of this quality have been available on the market since the beginning of the 1990s under the name ‘lithium-ion batteries’. A pioneer in developing and marketing of this product was Sony, which was able to realize batteries of about 1 Ah capacity in those days.

The lithium-ion technique operates with ‘host lattices’ for both anode and cathode, between which lithium (ions) are exchanged during discharge and charge. The anode of carbon in the graphitic or coke form contains the lithium in the charged state and delivers it to the cathode made from cobalt oxide CoO_2 during discharge where it is able to build in a maximum amount of lithium corresponding to the formula LiCoO_2 . The lithium ions migrate during cycling forth and back between the two host lattices of C_x and CoO_2 . The following reaction scheme shows this in a simplified manner:



For recharge the arrows have to be reversed. This back and forth of the lithium ions is named ‘rocking chair’ or ‘swing’ principle. The varieties and specialties of the electrodes and other cell components are investigated as follows.

18.7.3.1 Modifications of Carbon as Host Lattices for the Lithium Anode

Carbon is a candidate for anodic host lattices because of its ability to form small particles of graphitic-layered structures and to build stable, highly porous agglomerates from those particles, which easily incorporate lithium and show good electronic conductivity. The redox potential for the lithium incorporation is near to the potential of the electrochemical solution and deposition of the pure metallic lithium. Consequently, with secondary lithium-ion cells one can expect high cell voltages and energy densities or specific energies, respectively.

Pure carbon is found in nature as graphite and diamond – the two extremely different ideal modifications of this element. Graphite is soft, lubricious, and electronically conductive, whereas diamond is extremely hard, non-fissionable, and electrically insulating. Pure graphite is built from parallel staggered carbon layers (see [Figure 18.10](#)), whose carbon atoms are positioned at the corners of symmetrical hexagons, which represent a two-dimensional network like honeycombs. So each carbon atom is bound to the three nearest neighbors in its layer by equivalent forces/chemical bonds. It is formally a 1.5-fold bond between each pair of carbon atoms, a σ -plus a π -bond in part. This results in the significant honeycomb structure.⁴² The honeycomb layers can be staggered according to the scheme ABAB... (hexagonal graphite) or the scheme ABCABC... (rhombohedral graphite). The lattice energies, however, and the respective activation energies are so small that one structure may be transformed into the other very easily and in practice both structures are found in a graphite sample. The van der Waals forces⁴³ – no chemical bonds – between the carbon planes are comparatively weak so that the layers can be shifted easily against each other. Therefore graphite is a useful and well-known dry lubricant and the normal distance between the layers of 3.35 Angstrom may be widened by incorporation of foreign atoms, ions, and molecular components. This behavior is the basis to enable the use of natural graphite and many synthetic graphite and carbon modifications for intercalation of lithium and so as intercalation electrodes.

During the intercalation of lithium cations between the graphitic carbon layers, the accumulation of positive charge is compensated in part by the intake of electrons into the conducting band of the π -bonding system. In most cases the lithium ion electron household is not fully balanced so that a remarkable enhancement of the electronic conductivity follows by quasi-free electrons.⁴⁴ The capacity for intake of lithium ions is limited. It was found that lithium ions could be incorporated into

⁴² The chemical bond within the graphite layers is a combination of covalent single bonds – so-called σ -bonds and a delocalized π -bond system, which is found also in the benzene ring molecules. The π -system is distributed over the complete even honeycomb structure of each graphite layer and is responsible for its electronic conductivity because the electrons are free to “move” within the whole layer. Between adjacent graphite layers act no σ - or π -bonds but only weak van der Waals forces (see below), which let the layers glide easily one against the other. Compared with this the diamond crystal has to be understood as one huge three-dimensional molecule where the carbon atoms are connected to each other by four single σ -bonds per carbon atom being oriented into a tetrahedron’s edge. The diamond “molecule” (crystal) has no “free” electrons. That is why it is an insulator.

⁴³ The van der Waals forces by means of so-called dipole interactions make the cohesion between molecules and molecule clusters in fluids and solids which are not linked by chemical bonds in the true sense (ionic or covalent ones).

⁴⁴ These carbon intercalation compounds are also called ‘synthetic metals’.

regular undisturbed graphite structures under normal conditions up to the formula LiC_6 at the most⁴⁵ (Figure 18.35). Lithium can also be built as clusters into heavily disturbed carbon preparations (see below).

As already described the distances between the carbon layers have to be enhanced only slightly for that lithium incorporation as can be shown by x-ray analysis of lithium containing graphite and pure graphite. So only little activation energy is needed for that in-out migration of lithium, and consequently the closed circuit voltage (CCV) under load, when lithium leaves the anodic host, is only a little lower than the OCV and only a small overvoltage is needed for recharge – when lithium is inserted again.

During that incorporation of lithium the structure of the graphite crystallite is not only stretched into the direction of the c-axis, i.e. perpendicular to the honeycomb planes. The single layers are also slightly shifted within their planes against each other so that the ABAB order or the ABCABC order becomes an AAAA sequence. In the c-axis direction chains of $\text{C}_6\text{-Li-C}_6\text{-Li-C}_6\text{-Li-C}_6$ are generated that way. The ‘bond’ between the lithium ion and the nearest C_6 rings compensates for the loss of fit of the closest package of the carbon atoms in pure graphite. Graphitic carbons with a highly disturbed lattice, i.e. with chemical bonds also between the C planes, are not able to allow a total or perfect rearrangement of the carbon planes and hence not able to take lithium up to the maximum of the formula LiC_6 .

A graphite crystal gives access to the lithium incorporation only from the edges of the layered structure – as long as there is no disorder within the planes. The geometry of the edges is either of the ‘arm chair’ or of the ‘zigzag’ type (Figure 18.36). Here the carbon atoms themselves are also reactive to a certain extent leading to reactions with the electrolytic solvents (see below)⁴⁶. For the “charging” of lithium into the layered structure Figure 18.37 shows a stepwise response of its potential where each potential level or plateau corresponds to equilibrium between two ‘load’ levels. These load levels⁴⁷ thermodynamically represent different “phases” of the lithium carbon intercalation compound. From the more-or-less declined charge and discharge/time characteristic ($U=f(t/C)$) of a lithium-ion battery with graphite anode you can recognize this passing through those different charge and potential levels.

As can be seen in Figure 18.38 during the charging process, both charging and discharging proceed nearly at the same highly negative redox potential as the solvation and deposition of the pure lithium metal (see above), i.e. the energy contents of the pure lithium metal and the lithium intercalated into graphite differ only little. Consequently lithium ion cells deliver high CCV values similarly to lithium primary cells, which are based mostly on a pure metal anode. The usefully high CCV – with respect to the cell’s energy density – requires a very precise charging technique which assures that metallic lithium deposition does not happen

⁴⁵ Under high pressure (60 kbar) and high temperature (300 °C) conditions LiC_2 can be also prepared, but degrades then at normal conditions slowly again into LiC_6 and lithium.

⁴⁶ See also Section 18.7.3.3 about electrolytes.

⁴⁷ The load levels or phases of the lithium intercalation compound are called ‘step I’ to ‘step IV’ depending on the number of carbon layers between adjacent interlayers loaded with lithium.

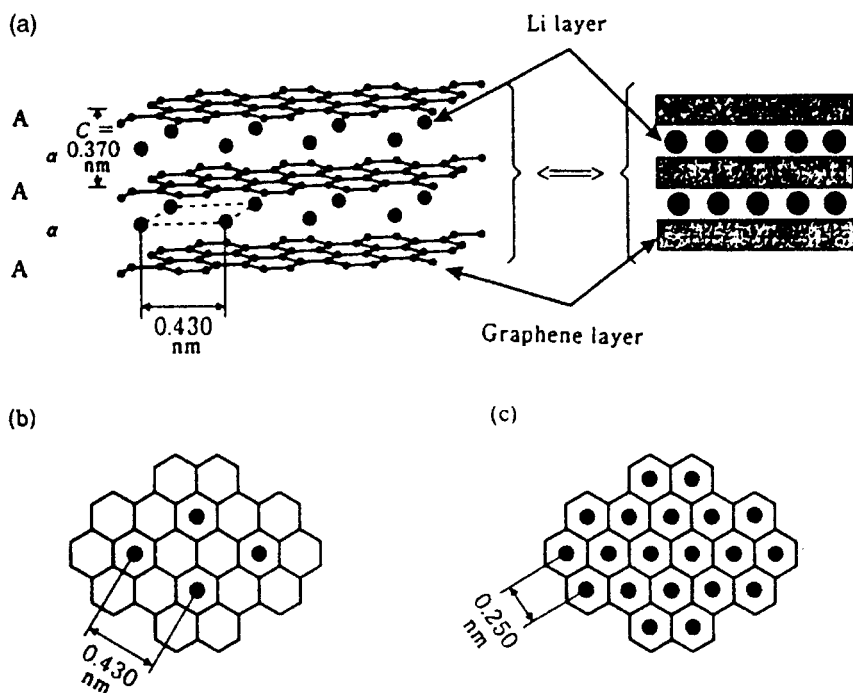


Figure 18.35 Incorporation scheme of lithium in graphite: (a) sequence of layers of LiC_6 ; (b) distribution of lithium within an interlayer in case of LiC_6 ; (c) distribution of lithium within an interlayer in case of LiC_2 . (From Winter and Besenhard in Ref. 1.)

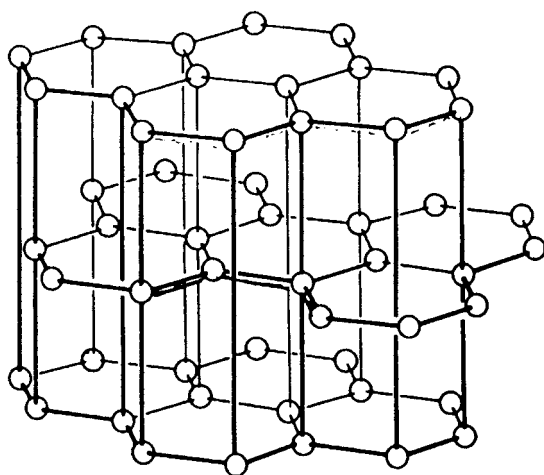


Figure 18.36 Geometry of the edges of hexagonal graphite, 'zig-zag' above and 'armchair' in the middle. In case of incorporation of lithium the ABAB sequence of layers is abandoned in favor of the AAA sequence. (From Ref. 7.)

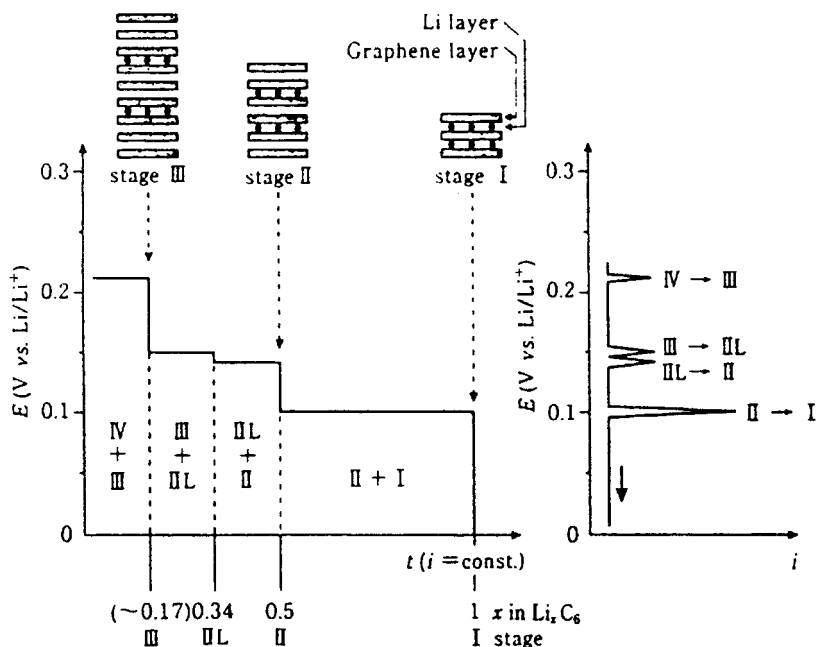


Figure 18.37 Stepwise electrochemical intercalation of lithium in graphite: shown on the left by $E = f(x)$, $i = \text{const.}$, in Li_xC_6 ; on the right by $i = f(E)$, $dE/dt = \text{const.}$ (From Winter and Besenhard in Ref. 1.)

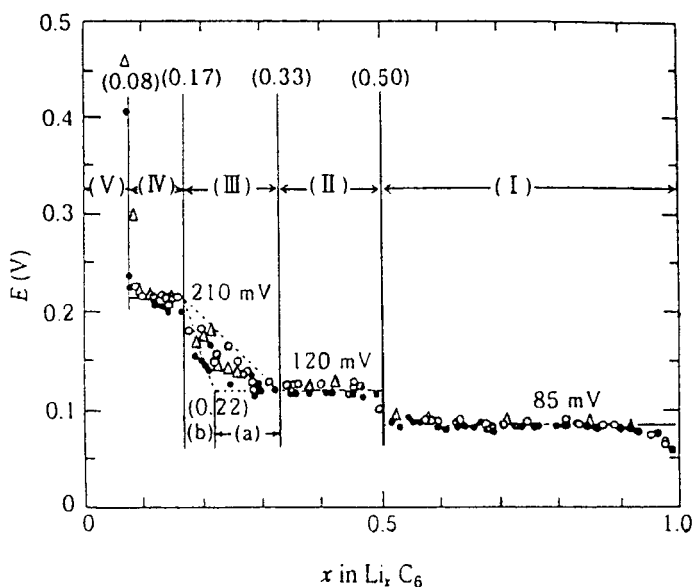


Figure 18.38 Reversible potential (against Li metal) of various Li-graphite intercalation compounds depending on their composition. (From Ohzuku from Besenhard in Ref. 1.)

simultaneously with its intercalation. The redox potentials of both processes are close together, with only 0.1 V difference between metal and full graphite electrode.

For the graphitic carbons as addressed above their 'crystallinity', i.e. their similarity to ideal graphite, is an important criterion for quality, which is described by the average thickness L of the graphite layers being staggered (more-or-less regularly) one upon the other. The degree of disturbance of the layered structure is measured as the deviation of that average distance between the carbon layers in real substances from the "ideal" value of $d = 3.35 \text{ \AA}$ in undisturbed graphite. For natural graphite one measures $L > 1.000 \text{ \AA}$ and $d = 3.354 \text{ \AA}$, and in artificial graphite produced at elevated temperatures it is $L < 1.000 \text{ \AA}$ and $d = 3.36 \text{ \AA}$. Both substances are really close to the ideal value of $d = 3.35 \text{ \AA}$. The degree of disturbance is far higher in various pitch cokes with smaller crystalline areas and wider plane distances: $L = 10\text{--}20 \text{ \AA}$ and $d = 3.38\text{--}3.80 \text{ \AA}$.

Graphite is a modification of carbon, which is found naturally in a high grade of purity. Far more carbon is found in nature as coal, which is not as pure as graphite. Both are degradation and metamorphic products of floral substances, which were secluded from the air and under high pressure underground for long periods of history (about 350 million years since the Carboniferous period). Coal contains pure carbon but also other elements, constituents of organic substance such as sulfur, oxygen, and hydrogen. The structure of the coal is similar to the graphitic one in tiny areas. The layered structure of coal is highly disturbed, partly already within the graphitic planes themselves because of the incorporation of those three foreign atoms whose bonding geometry is different to the symmetrical bonding of carbon in graphite. So small areas around the foreign atoms deviate from the honeycomb pattern. Practically most of the volatile foreign components of the coal can be withdrawn by high temperature treatment. Nearly pure carbon remains: coke, which is still far different from the said graphite. There are still only tiny areas of the ideal honeycomb and layer structure, which in turn are oriented irregularly to each other and interconnected chemically by 'bridging' atoms. The result is a three-dimensional structure which gives the coke its hardness and stability, which differs a lot from the soft and lubricant behavior of graphite based on the easy gliding of carbon planes against each other. Non-graphitic carbons can also be made from coal tar or pitch, the by-product of the coke "distillation", or from pitch-like high boiling fractions of petroleum or from organic polymers by heating up to 1500°C or higher under nitrogen atmosphere (pyrolysis). The materials thus prepared from all the various basic substances differ greatly from the highly crystalline graphite because of the said disturbances of the carbon lattice, which limit the carbon planes' sizes and widen the distances of the layers. The hotter, however, and the longer the transformation is carried through, the more graphite-like the product can become. This is valid especially with fluid base materials such as oil pitch, the high boiling fraction of petroleum and coal tar. The various carbon products (cokes) made by such dry distillation are also designated as 'hard' or 'soft' carbons depending on their similarity or dissimilarity to graphite and their mechanical behavior. Especially hard non-graphitic carbons are generated by heating phenolic resins or polymers of furfuryl alcohols up to the respective temperatures (1000 to 2000°C).

Depending on the solvent used within a lithium battery, graphitic anodes under cyclic operation tend more and more to get their layered structure distorted. This

happens when solvate⁴⁸ molecules from the electrolytic mix are inserted also into the carbon layers. It is the bigger volume of the solvated ions that destroys the connection between the carbon layers and hence its crystal lattice.⁴⁹ Because of its more-or-less poor cyclability, the graphitic carbon is mixed with hard non-graphitic ones. These varieties of coke (made at relatively high temperatures of about 1000 °C) stabilize the graphitic parts of this mixture against distortion. Even if it is accompanied with the loss of specific capacity, this is balanced by the gain in cycles. On the other hand the electrolytic solvent is chosen for the lowest possible degree of incorporation so that the degradation of the layered structure is minimized.

Hard carbons, which are produced mostly at higher temperatures beyond 1000 °C, partly show a remarkable higher specific capacity than the optimal natural graphite at the beginning of their cycle life. This behavior is explained by the “card house” structure of these substances, which can be understood as irregularly connected agglomerates of single carbon sheets or thin multilayer plates of graphitic carbon. These structures have very few regular graphitic interlayer sites for lithium insertion but present many tiny cavities of Ångstrom dimensions. The experts believe that lithium caught as clusters in these cavities and covering both sides of the carbon sheets may explain the high specific lithium capacity of these hard carbons. The potential however of this lithium charge and discharge is less favorable than for graphite and the high specific capacity of the first charges may be lost by cycling.

For battery applications the secondary structure of the carbons is relevant also. The preparations mostly used have a particle sizes of about 10 µm. Electrodes made from these particles together with carbon black⁵⁰ and binders⁵¹ are highly porous with an extremely big microscopic inner surface. Hence, even at low microscopic current densities the lithium anodes of the intercalation type can be loaded nearly as high as the very reactive but relatively small macroscopic surfaces of the compact pure metallic anodes of primary batteries.

Lithium ions may enter the intercalation structure only from the surrounding sides and edges of the carbon layers. For some products, to enhance the ratio of “accessible” graphitic edges and sides of the carbon particles’ total surface, synthetic microscopically small graphite balls⁵² are used which may be understood as turned (machined) from the layered graphitic structure. Micro-short carbon fibres are also successfully applied as anode hosts.

The most important parameter of a lithium ion accumulator, its specific energy, of course depends on how much – reversibly dischargeable – lithium is stored in the carbon host lattice. The ideal maximum charge of the sum formula LiC_6 corresponds to the specific capacity of 372 mAh g^{-1} . In practice natural graphite shows 330 to 350 mAh g^{-1} , artificial graphite a bit less.

⁴⁸ Solvate = dissolved, i.e. lithium ions surrounded by molecules of the solvent.

⁴⁹ See more details in Section 18.7.3.3 about electrolyte solutions.

⁵⁰ To increase the electronic conductivity.

⁵¹ For example, Teflon[®] particles.

⁵² MCMB = mesocarbon microbeads.

18.7.3.2 Transition Metal⁵³ Oxides as Host Lattices for the Lithium Battery Cathode

In lithium-ion batteries substances should be used as cathode material which can intercalate and discharge lithium ions at a highly positive potential⁵⁴ – compared to the intercalation into the carbon anode – and with only low kinetic hindrance, i.e. at low over-voltage or nearly reversible. The first requirement is fulfilled especially by transition metal oxides⁵⁵ and halides and also, to a lesser extent, by sulfides. The second requirement of low kinetic hindrance for insertion and release of lithium ions is meant as a requirement of high mobility of lithium ions and electrons within the cathodic lattice and of unhindered mass transfer across phase boundaries as far as phase transitions happen in the host lattice during in- and excorporation of lithium. As the transition metal halides are poorer electronic conductors than oxides, only the latter are used in practice.

The said components and structures are preferable because of the easy redox transition of valence electrons in the $3d^n$ bands of transition metals, which is necessary to compensate for the simultaneous intake or release of lithium ions (Figure 18.39): the metal atoms of these compounds easily change their valence whereas the geometry of their crystal structure is changed only slightly by the lithium in- and excorporation. The function of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ electrode during cycling is similarly based on the in and out of hydrogen atoms and acts also as intercalation compound.

Oxides of manganese, nickel, and cobalt have lattice structures, which fit to the requirements of intercalation of lithium. In practice LiCoO_2 , LiNiO_2 , and LiO_2O_4 have been proved as useful cathodic materials for lithium-ion batteries. The formulas above correspond more or less to the cathodes in the discharged condition of the cell when most of the lithium ions have migrated from the carbon anode to the oxide intercalation cathode. LiCoO_2 and LiNiO_2 have a layered structure being similar to that of sodium ferrate (III) NaFeO_2 (Figure 18.40), with a cubic closest package of its oxide layers. During discharge of the cell the Li^+ ions are inserted between those $(\text{MeO}_2)_x$ layers ($\text{Me} = \text{Co}, \text{Ni}$). The first commercial lithium-ion batteries were equipped with LiCoO_2 cathodes. One reason might have been that this substance can easily be made from a mixture of LiCO_3 and CoCO_3 by heating up to 850 to 950 °C for 20 hrs. This product made so easily can be improved only marginally by further treatment – curing at 850 °C in pure oxygen atmosphere. The critical parameter here is the specific – dischargeable – capacity, which for LiCoO_3 cathodes amounts to 150 to 160 mAh g⁻¹. The cobalt oxide delivers a good and relatively flat discharge characteristic of 4.0 to 3.9 V against the Li/Li^+ anode at limited rates.

⁵³ Chemistry calls the elements of groups 3 through 11 ‘transition metals’. They have an incomplete d shell or can generate cations with an incomplete d shell.

⁵⁴ The electrochemical potentials of the partners of the cell reaction describe the energy contents of the various species – ions and electrons – in the corresponding phases. The chemical and electrical components of these potentials can be separated and result then – after rearrangement in a suitable way – in the Nernst equation, which relates the measurable cell voltage to the reaction’s free enthalpy.

⁵⁵ Also transition metal sulfides as, e.g., TiO_2 are able to intercalate and were intensively investigated correspondingly. The specific redox potential however is much lower than for the oxides.

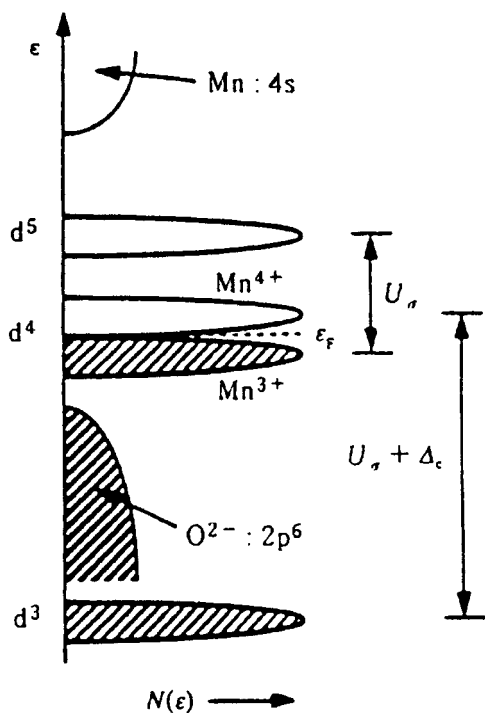


Figure 18.39 Electronic energy levels within the Mn_2O_4 spinel sublattice as given in LiMn_2O_4 . (From Goodenough in Ref. 1.)

Because of the relatively high cost of the cobalt this technique is not an especially satisfying lasting solution. Corresponding investigations on LiNiO_2 cathodes led to promising results. The more economic nickel compound, which by the analog heating resulted in the best capacities, is accessible from a mixture of LiOH and $\text{Ni}(\text{OH})_2$, the product giving a specific capacity of only 70 mAh g^{-1} in raw condition. An additional equalization at slightly lower temperatures of 750°C show practically the same specific capacity as with the cobalt compound – only the voltage declines a little faster during the second half of discharge. As an explanation for this it was found that at higher temperatures the oxide lattice in part of the nickel oxide is disturbed heavily so that far fewer lattice positions are available for lithium incorporation. It is also shown that the similar treatment at 750°C , but in a pure oxygen atmosphere, improves the compound's quality further, up to reported 190 mAh g^{-1} . Mixed oxides of cobalt and nickel were also investigated with acceptable results. Consequently one may expect that nickel or mixed oxide electrodes will be available for use in the future.

Mn_2O_4 is also less expensive than cobalt and nickel and is easily available as raw material; the manganese dioxide is also environmentally more tolerable than Ni or Co. Therefore, and also because manganese materials have a long tradition as active substances in batteries (more recently also in lithium primary batteries), its applicability for lithium-ion batteries is under investigation.

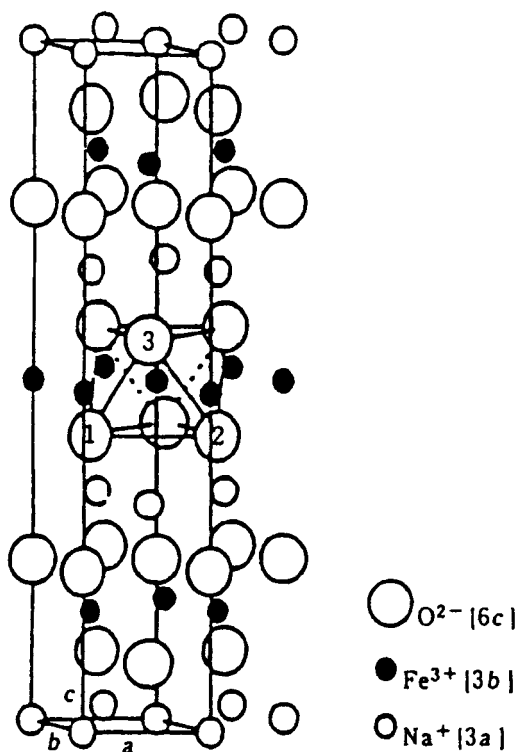
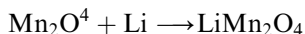
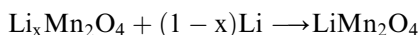


Figure 18.40 Layered structure of α -sodium ferrate (III) as analogy of lithium cobaltite and lithium nickelite. (From Goodenough, Ref. 1.)

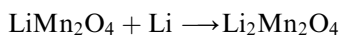
Mn_2O_4 , LiMn_2O_4 , and $\text{Li}_2\text{Mn}_2\text{O}_4$ have a structure of the spinel type with cubic symmetry. The $\text{Li}_2\text{Mn}_2\text{O}_4$ structure tends to change easily into the atacamite structure. The spinel structure resembles a three-dimensional system of tube-like voids made from the lattice of manganese and oxygen atoms. Here lithium is not only easily built into but also transported from one void to the other. So far with respect to the ionic conductivity the manganese structure exceeds the layered structures of the cobalt and nickel oxides. The cathodic discharge reaction (and, by reversal, charge reaction) roughly resembles the following equations:



or better



and



The first step of the lithium incorporation takes place at a cell voltage, against the lithium anode, of about 4 V, the second at about 3 V. Especially the second step suffers from very poor cyclability. So until now it has not been used for practical operation of a rechargeable battery. But also the energetically favored 4 V step shows

slow capacity decay during cycling: It amounts to about 40% up to the 100th cycle. For both cases this decay is explained by an irreversible spinel-to-atacamite transformation. Lithium manganese spinels are very promising. Here up to a sixth of the lattice's Mn position is replaced by Cr or better Co. The improved cathodic material delivers up to 400–500 cycles without remarkable loss of capacity (<10%). The endowment obviously hinders the said irreversible phase transition.

18.7.3.3 Electrolytes for Lithium-Ion Batteries

The quality criteria for lithium primary batteries, as far as organic solvents are used, also hold for the secondary cells.⁵⁶

For the application in a high-energy cell with a CCV of 3 to 4 V or higher a sufficient chemical and electrochemical stability of the electrolytic solvents is usually required which ensures that there is no degradation during operation.

The mixture of electrolytic salt and solvents must have a high dielectric constant and a low viscosity and, in most cases combined with it, a low freezing point.

From the cyclic application of a lithium-ion battery additional aspects must be considered for the right choice of the optimal electrolyte. This applies especially to the reactivity of the electrolyte's solvent with the carbon of the anodic host lattice.

The list of suitable solvents which were preferably used for primary cells contains a number of alkyl carbonates, of which the cyclic esters, propylene carbonate (PC), and ethylene carbonate (EC) excel by their high dielectric constant. This ensures the good solvation of the used electrolytic salts. Both, however, are highly viscous because of their polarity, EC higher than PC. To compensate for it, low viscous representatives of straight alkyl carbonates, e.g. the esters dimethyl carbonate (DMC) or diethyl carbonate (DEC), are added as well. These components are stable also at the negative potential of the anode, which does not hold as well for the ethers dimethoxyethane (DME) and tetrahydrofuran (THF). Today lithium-ion batteries with electrolyte mixtures of PC + DEC and EC + DMC are found in the market. As in primary systems lithium salts with voluminous anions are used as electrolyte salts: LiClO_4 , LiBF_4 , LiAsF_6 , LiPF_6 , and LiAlCl_4 (see Section 18.4.2). Lately even more spacious anions have been investigated for their applicability as electrolyte components, e.g. lithium perfluoromethylsulfonimide $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ and the corresponding lithium perfluoromethylsulfomethanide $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$ and lithium perfluoromethylsulfomethanide $\text{Li}(\text{CF}_3\text{SO}_2)_3\text{C}$.

The examples of the mixtures of PC/DME and PC/THF with LiClO_4 in [Figure 18.41](#) explicitly show that the 1:1 mixtures exhibit an optimum of the conductivity as a matter of fact. The optimal combination of dc and viscosity enhances the molar conductivity by nearly one order of magnitude compared to the data of the components alone. With each special mixture, however, you also have to take into account the kind of solvation of the electrolyte salt, showing total dissociation or perhaps generation of larger ion pairs, which might control the effective conductivity. It is the so-called donor or acceptor ability of the solvents which is responsible for an effective dissociation, depending on how the solvent molecule offers or accepts negative charge to or from the solved ion.

⁵⁶ See also Section 18.4.2 for electrolytes for primary lithium cells.

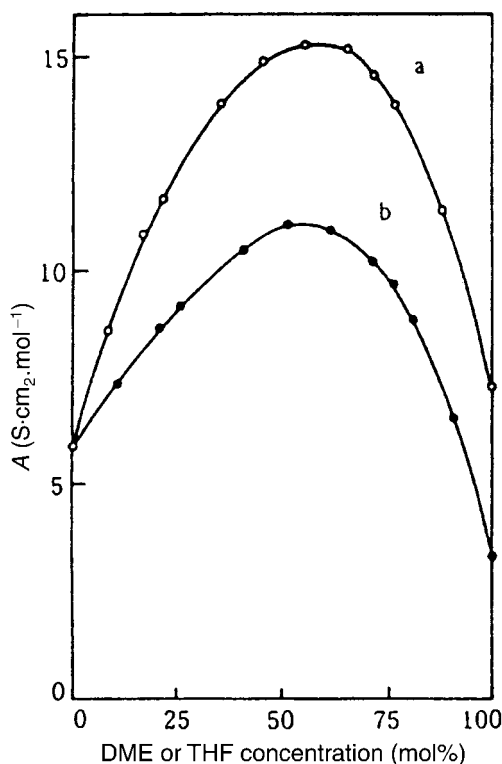


Figure 18.41 Molar conductivity of 1 molar lithium perchlorate solutions, in mixtures of (a) PC + DME and (b) PC + THF (From Matsuda in Ref. 1.)

Besides the optimization of the conductivity, the proper choice of suitable electrolytes depends on for how many cycles it remains stable against the anode. The way any reaction takes place (if at all) with the carbon of the anode determines the cyclability of the system in a crucial sense. The soft carbons, e.g. which were favored first for their good capacities, tend to decompose PC during the charging process: finally a film of lithium carbonate Li_2CO_3 deposits on the carbon surface. The cyclability of the anode now depends on its stability and permeability, differing with various carbon qualities and co-solvents. So for the use of graphitic carbons a mixture of LiAsF_6 in EC/DEC composed at a ratio of 3:1 has proved best.

The so-called ‘exfoliation’ is also based on interactions between carbon and solvent thus destroying the cohesion of the carbon layers during the discharge-charge cycles. Stepwise whole solvent molecules or fragments of it are inserted together with lithium ions by the charging step. These voluminous components are not “discharged” again as done with the lithium ions during the next discharging step and the graphitic interlayer distances do not return to the original values. The anode swells in this way to a macroscopically measurable extent. This problem may be overcome by using, at least in part, the less ideally structured but far more stable hard carbons for the intercalation anode or by application of solvents which can’t be inserted as easily.

18.7.4 The System Lithium (Carbon)/Lithium (Cobalt Oxide)

Since 1986 Sony had developed a rechargeable lithium battery, which in 1991 was introduced into the fast growing market of portable telephones, camcorders, CD players, and laptop computers. Based on a lithium carbon intercalation anode and a lithium cobaltite intercalation cathode it was the first product on the market which offered the lithium technology's advantages of light weight and high energy density in a rechargeable and safe version. From 1992 on a modified version with improved cyclability and a protective feature against overcharging has been provided for mobile phones and laptops. Stepwise the capacity was remarkably further enhanced in 1995 and 1997.

The early product was based on soft coke carbon with mostly graphitic structure as the anode. As explained before the lithium is inserted here as ions into the graphite interlayer gaps up to a maximum concentration corresponding to the formula LiC_6 and to a specific capacity of the carbon of 372 mAh.g^{-1} . The discharge characteristic of the complete cell was relatively hard with a high OCV even at the end of discharge. But it was recognized that the capacity soon declined during cycling. Computer tomograms of spirally wound cells showed that the anodes were visibly swollen already after about 100 cycles. This was interpreted as destruction of the graphitic structure by 'exfoliation'.

Now instead of soft carbons hard ones were introduced as anodes. The hard carbons have a more stable irregular structure consisting of very small and thin platelets of carbon which are interconnected. Within this network the lithium ions are no longer bound as the $\text{C}_6\text{-Li-C}_6\text{-Li-C}_6\text{-Li-C}_6$ chains perpendicular to the graphite planes already described, but are agglomerated on both sides of the C platelets and inside the cage-like submicroscopic voids of the irregular structure. Thus the specific capacity of the carbon can be enhanced to about 500 mAh.g^{-1} . Only beyond this value do NMR spectra show traces of lithium deposited as metallic clusters. With the help of Li NMR it can be shown that the lithium in both the graphite and the hard carbon is bound ionically at least below that mentioned threshold. Besides the higher specific capacity, compared to the soft carbons, the hard carbons are more stable and therefore have a longer cycle life. A disadvantage is the voltage time curve, which declines here earlier at the end of discharge. But this behavior may also be seen as an advantage because in that way it allows us to recognize the state of (residual) charge. The anodic mass is mixed with polyvinylidene fluoride (PVDF) as a binder and some solvent and pasted on both sides of a $10\text{-}\mu\text{m}$ collector foil.

Meanwhile specialists praise the even better features of the matrix of natural graphite for the anode. Now it seems to be possible to suppress the undesired interaction between graphite and solvent. So by Sony and Sanyo today 1.35 Ah and more than 1.000 cycles are claimed for the cell size 18650, whereas the former values were 0.9 (0.95) Ah and 500 cycles.

The Sony battery uses the intercalation compound LiCoO_2 for the cathode. The preparation of the lithium cobaltite (by dry heating of a one-to-one mixture of cobalt oxide or carbonate with lithium carbonate in an air stream up to 950°C) was modified twice. First to get larger particles of cobaltite, polyvinyl alcohol (PVA) is added to the powder mix of the two components during the mixing and granulating process before the heat treatment. The PVA is an organic compound being sometimes used as a glue

by battery makers. It burns and evaporates without residues in the heat. Instead of 1- to 5- μm granules made without glue the additive yields granules with 15- to 20- μm diameters. Electrodes made from this material react more inertly under short conditions and hence the cells are less prone to overheating. The second improvement concerns a safety feature built into the cathodic substance. We know that overcharging may deposit metallic lithium at the anode, which is dangerous because of its high reactivity. As a protective measure a slight excess of Li_2CO_3 is added to the cathode mix which is decomposed by overcharging at voltages of over 4.80 V and thus creates overpressure in the hermetically sealed cell by its gaseous reaction products. A suitably designed membrane bulges consequently and interrupts the contact between the cathode and the battery's positive pole. The cathodic material is mixed, in analogy to the anodic side, with PVDF and solvent, and pasted on both sides of an aluminum conducting foil.

The cathode manufacturing process as described here shows that the electrodes are prepared and assembled to complete cells in the discharged state. This is a basic requirement because of the sensitiveness and reactivity of the lithium-charged anode, which is charged best for the first time in situ, in the cell.

For the improved cell with hard carbon anode a 1-molar solution of LiPF_6 in a 1:1 mixture of PC/DEC was applied. The PC, which reacts by decomposition on graphite, is practically stable with hard carbon. With its relatively low viscosity (compared to EC) it enables good deep temperature discharge ability.

Twofold stretched polyethylene (PE) is used as separator. Stretching which lets the ionic current pass through the polymeric network generates the pores. The pore structure is stable, however, only at normal operating temperatures. With the temperature being enhanced beyond a defined threshold value, the separator "remembers" its state before the stretching and shrinks again, closing the pores. The separator becomes highly resistive and the discharge reaction is interrupted. Neither of the components can react in an uncontrolled way (any longer).

The lithium-ion cell is manufactured as a cylindrical round cell from a pair of electrode strips being spirally wound together with two separator foils. The electrode coil may also be flattened and put into a prismatic housing. The Sony (and Sanyo) round cells have steel containers and these are, e.g. with the sizes 18650 or 18500, negatively polarized. The lid is positive and is insulated electrically and sealed against the can by a plastic gasket. The lid contains (sandwich-like) the outer contact, a thermo switch foil (Polyswitch[®]) and that disconnecting membrane that might be activated by overpressure. The Polyswitch[®] is made of a polymer foil, which is conductive at normal temperature but becomes non-conductive at a defined threshold temperature, here at about 100 °C. In contrast to the separator's shutdown and the switch-off of the membrane the Polyswitch[®] is reset again by simply cooling down, i.e. the Polyswitch[®] foil becomes conductive again when the temperature drops.

The specific energy (Wh/kg) of this system and its energy density (Wh/L) are remarkably higher⁵⁷ than the traditional NiCd or nickel/metal hydride systems as we might expect and as it can be seen in [Figure 18.42](#). Therefore portable devices driven

⁵⁷ For the cited Sony cell 18650 (new design) the energy density is 295 Wh/L and the specific energy 120 Wh/kg.

Chemistry	ED (Wh/l)	SE (Wh/kg)
NiCd	120-150	40-50
NiMH	250-300	70-80
LiIon	280-320	110-130

Figure 18.42 Comparison of the energy contents of the competing battery systems nickel/cadmium, nickel/metal hydride, and lithium-ion (Energizer). (From Braun in Ref. 10.)

by it may operate far longer. The data of the nickel/metal hydride system were also improved recently.

Typical discharge curves of a lithium-ion battery of another producer are shown in [Figures 18.43](#) and 18.44 for various loads, from a 15-minute to a 5-hour discharge of the nominal capacity, and at normal and reduced or enhanced temperatures from -20 to $+60^{\circ}\text{C}$. A good discharge ability at high rates and at low temperatures is recognized here, too. The charging curve in [Figure 18.45](#) demonstrates how a lithium-ion battery is fully recharged within 3 hours and up to 95% within 1.5 hours. The charger, however, has to be a little sophisticated: The charging current and voltage are to be limited according to the shown I-U scheme. The side reactions which might occur otherwise (deposition of metallic lithium and decomposition of the electrolyte solvent) would jeopardize the safety and the cycle life of the battery.

But with controlled chargers, lithium-ion batteries are well cyclable. [Figure 18.46](#) shows how the usable capacity of an AA cell of Tadiran develops during 1000 cycles. More than 80% of the initial capacity is still available thereafter.

Batteries being assembled from a larger number of single cells as, for example, necessary for laptops ([Figure 18.47](#)) are equipped with an even more complicated

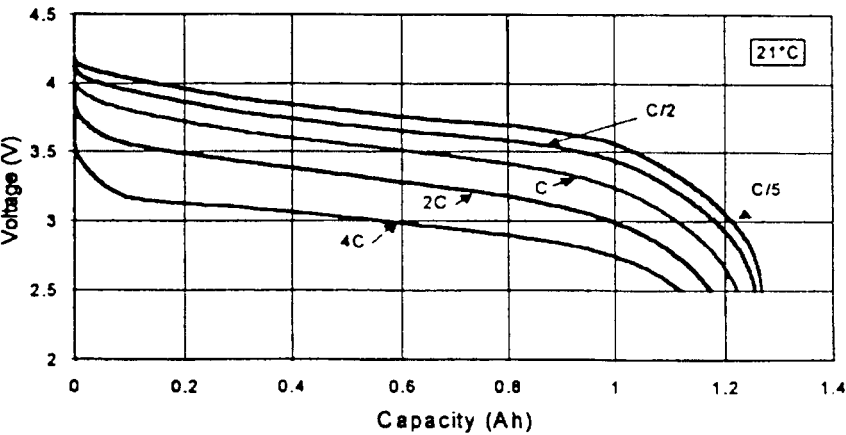


Figure 18.43 Discharge graphs of a lithium-ion cell 18650 at various loads (PolyStor), (From Juzkow in Ref. 10.)

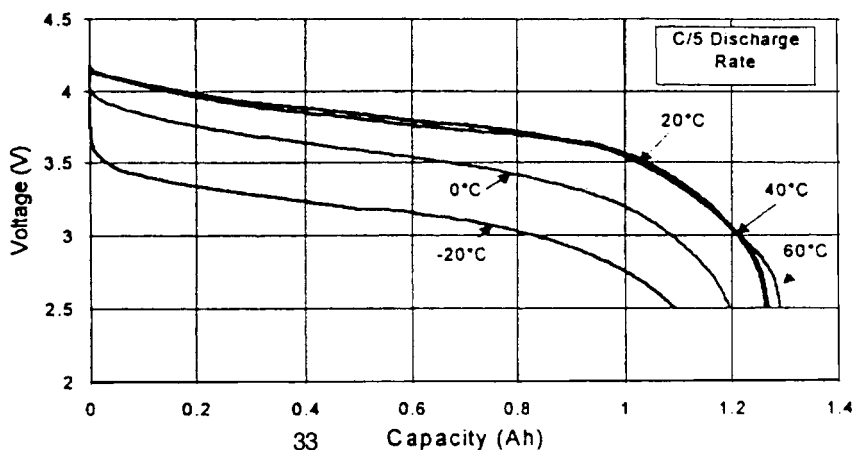


Figure 18.44 Discharge graphs of a lithium-ion cell 18650 at 5 hours discharge and various temperatures (PolyStor). (From Juzkow in Ref. 10.)

electronic device for control and safety. It protects the battery against too high currents during charge and discharge, against deep discharge, and it assists recharge after deep discharge on account of extended storage. Figure 18.48 contains a corresponding wiring scheme. A back-setting thermo switch (Polyswitch, PTC), a fuse, a safety vent, and a thermocouple (NTC) are the elements of the safety equipment in addition to safety components of each single cell.

The example of Sony in Figure 18.49 shows how a typical cylindrical cell is designed. Flat cubic cell formats are also supplied, e.g. the cell type UF 101248 of Sanyo with 750 mAh and dimensions of 10.5 mm × 22.5 mm × 48 mm.

Lithium-ion batteries were very carefully checked during development for their safety and reliability (see also Section 4.8). According to national and international

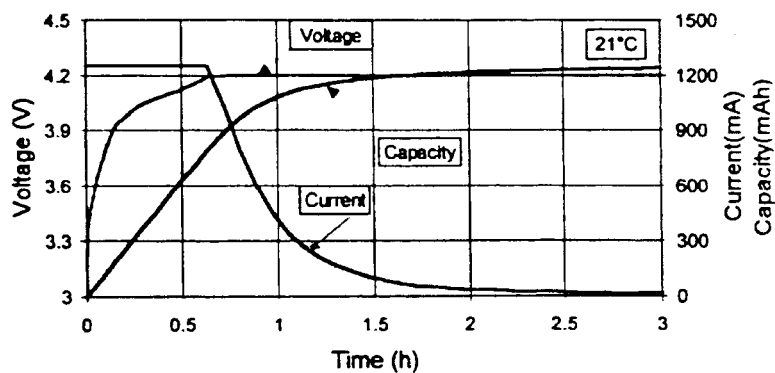


Figure 18.45 Charge characteristics of a lithium-ion cell 18650 (PolyStor). (From Juzkow in Ref. 10.)

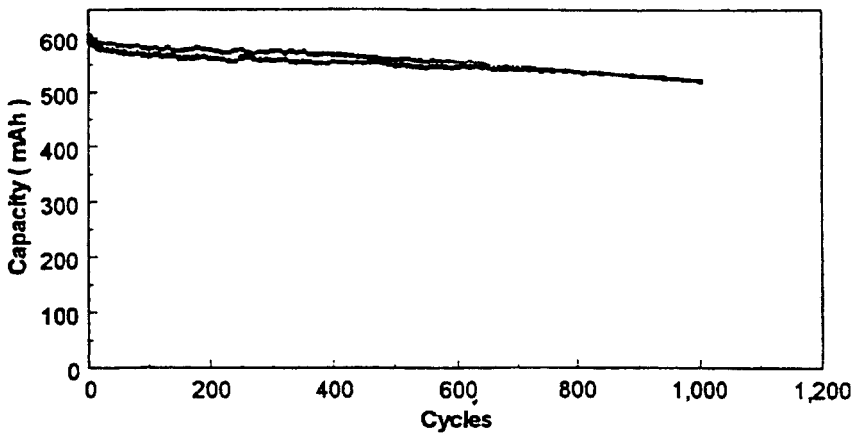


Figure 18.46 Dischargeable capacity during the cycle life of a lithium-ion battery (Tadiran). (From Luski et al. in Ref. 10.)

regulations the prototypes are investigated before official acknowledgment and release for the following impacts and environmental conditions:

- Continuous charging.
- Overcharging.
- (Forced) deep discharge.
- High rate discharge.
- External short.
- Shock and vibration.
- Changing pressure.
- Open fire.
- Heat.

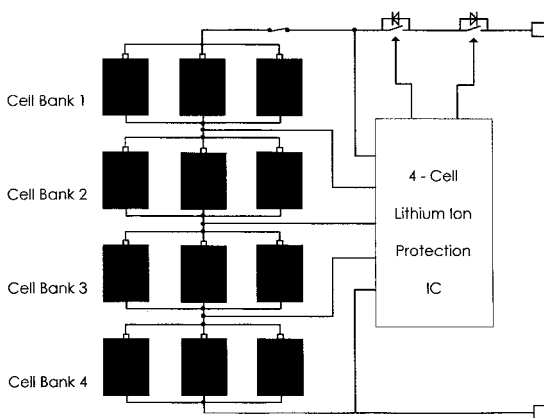


Figure 18.47 Circuit diagram in principle of a multi-cell lithium-ion battery with four groups in series of three cells in parallel each (Energizer) (From Braun in Ref. 10.)

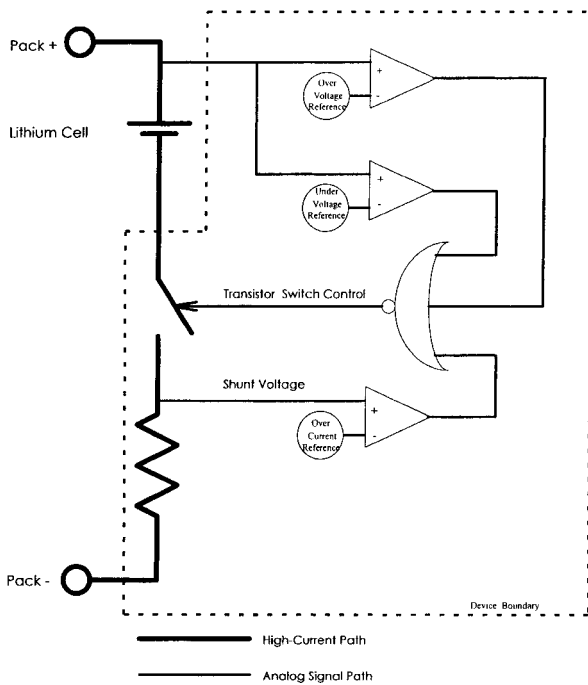


Figure 18.48 Circuit diagram of the surveillance and control electronics of a multi-cell lithium-ion battery (Energizer) (From Braun in Ref. 10.)

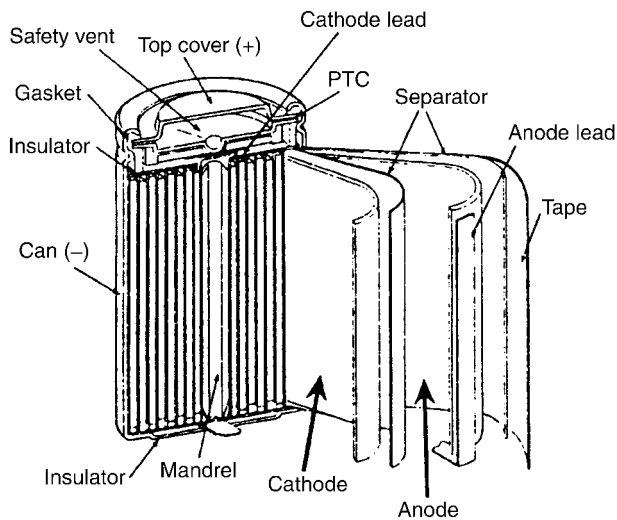


Figure 18.49 Design of the Sony lithium-ion cell. (From Nishi in Ref. 1.)

- Thermal shock.
- Mechanical damage, crushing.
- Puncture.

Sony, Sanyo, Panasonic, Eveready (Energizer), Tadiran, Yardney, and others nowadays produce lithium-ion batteries.

18.7.5 Other Rechargeable Lithium Batteries

The technology of rechargeable lithium batteries is being developed continuously. Goals are larger batteries, e.g. for the hybrid propulsion system of vehicles,⁵⁸ environmentally more compatible components, especially for the cathode, lower priced materials, longer cycle lives, more inert electrodes, etc. So-called solid-state batteries with polymeric electrolyte are also to be mentioned here. They are lithium-ion cells with an inert polymer matrix or a gel, which contains the electrolytic solvent-conductive salt mix.⁵⁹ Herewith, the use of the normal heavy steel containers, which cannot be manufactured with heavily reduced wall thickness anyway, can be abandoned; and a plastic laminated aluminum foil can be applied instead. In this way lightweight and very thin cells of a card format can be made.

The field of research and development is wide. The urge of competition is high and the preliminary results are promising.

18.7.6 Potential Safety Impacts

One substantial problem of the lithium technology is the fact of the lithium metal's melting point at 180°C. The liquid metal is highly reactive in contrast to the solid state. So within a cell it tends to react with the cathode material and the components of the electrolyte just when its melting point is reached. This reaction delivers a high amount of thermal energy. So in many cases the melting of lithium leads to the damage of the cell case.

The potential of rapid reaction is generally higher with primary cells of high loadability than with low rate types or secondary cells with alloy or intercalation anode. Primary reaction products can also initiate additional undesired reactions if they possess suitable reactivity. The sulfur which is released during the discharge of thionyl chloride cells belongs to this category.

Another risk is a rapid increase of the internal pressure following fast rise of temperature if there are low boiling components or reaction products in the cell (e.g. S_x, SO₂, SOCl₂).

⁵⁸ Since 1997 Toyota has been selling their hybrid passenger car Prius with growing success. Until now this car uses a nickel/metal hydride battery for buffering its energy.

⁵⁹ The principle is well known from sealed lead-acid batteries, which contain their electrolyte immobilized, by glass mats or silica gel. For lithium rechargeable batteries it is called SPE (solid polymer electrolyte) or gel technology.

18.7.7 Safety Measures

Lithium batteries ought to be intrinsically safe by layout and design: Here we mean, for example, the balanced cathode-anode design, the stabilization of the lithium metal by an alloying partner metal, or another solid state substratum, which all enhance the critical temperature significantly. They also comprise the thermally soft or weak separators, which close their pores at a defined (high) temperature and stop any further discharge reaction, and finally an electrode surface as small as possible which limits the discharge rate but also hinders the thermal runaway if the cell is shortened. The electrolyte solvents have to be chosen to minimize undesired reactions.

Special design features serve to gradually realize safety. If safety mechanisms operate early enough, a worse result can be avoided. These safety mechanisms are, e.g., bursting vents which open the hermetically sealed system instantaneously and thus release (as in the case of the sulfur dioxide system) a pressurized component that will not be able to react any longer. Secondary risks, e.g. release of sulfur dioxide in closed rooms, have to be taken into consideration, too.

All mechanisms which operate at a defined threshold temperature can be reckoned as built-in safety means. These are fuses for “single” applications or thermo switches which recover by cooling down again. Features like these are effective only with problems caused by the outer circuitry the cell or battery is embedded into.

The new secondary systems are mainly safety controlled by electronic charge and discharge control devices to avoid any damage by faulty operation. Here we mean the limitation of charge and discharge voltages, thermo control devices and switches, and membranes to avoid overpressure.

Eventually safe operation and handling of lithium batteries may be also based on observation of operation instructions; therefore at least the high power versions of lithium batteries have to be kept away from consumers, and the use of these batteries is only meant for experts who can abide by the necessary safety instructions.

As international safety standard IEC 60086-4, Primary Batteries, Part 4: Safety Standard for Lithium Batteries, is valid for lithium primary batteries and IEC 61960-1 and 61960-2, Secondary Lithium Cells and Batteries for Portable Applications, Part 1: Secondary Lithium Cells and Part 2: Secondary Lithium Batteries, apply to the secondary techniques. Here the details of test and approval procedures can be found.

18.8 DISPOSAL OF LITHIUM BATTERIES

Besides the risks for health and equipment, the question of environmental compatibility of the disposal of lithium batteries after use and of scrap of the production has to be answered. The entire chemical, thermal, electric, and toxic aspects of the lithium battery technology have to be considered. The lithium metal is far less harmful than the heavy metal mercury. On the other hand thermal decomposition of a lithium high rate battery might be locally much more disastrous than a bursting alkali manganese or lead-acid battery.

After the approaches in the German Federal Republic to a “free agreement” between manufacturers and traders of conventional batteries to minimize the problems of the poisonous metals mercury and cadmium, we consequently have to talk about lithium batteries, too. This will become difficult, because the large variety of different lithium battery systems hinders a quick and simple analysis of the battery scrap and an assessment of the related risks. This might be difficult to carry out at least for local environmental authorities.

The present situation is made easier by the comparably low turnover of lithium batteries. Partly batteries are disposed of as harmless in normal sanitary landfills (like primary lithium/manganese dioxide cells), partly more active systems are brought to special landfills (like lithium/sulfur dioxide together with neutralizing amounts of limestone), and partly batteries are burned in special ovens in combination with oil (like lithium/thionylchloride batteries).

Various domestic and external companies⁶⁰ offer the disposal and the recycling of lithium battery scrap. Most procedures comprise shredding, washing, recuperation of the cell case metals, and concentration and burning of those components that can't be reused. It is a basic requirement of all recycling methods that the user and consumer fully support all activities of collection and sorting of the batteries in question.

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⁶⁰ For LiMnO_2 : RVD process of Accurec, Mülheim, Germany; for lithium-ion batteries: S.N.A.M. in St. Quentin Fallavier, France. Also for all types of batteries: Batrec AG of Dietikon, Switzerland, Recymet S.A. of Nyon, Switzerland, Toxco of Trail, B.C., Canada.