Lithium Batteries

(Types, Components & Technology)

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Lithium Battery and Components

CR2032 lithium button cell battery

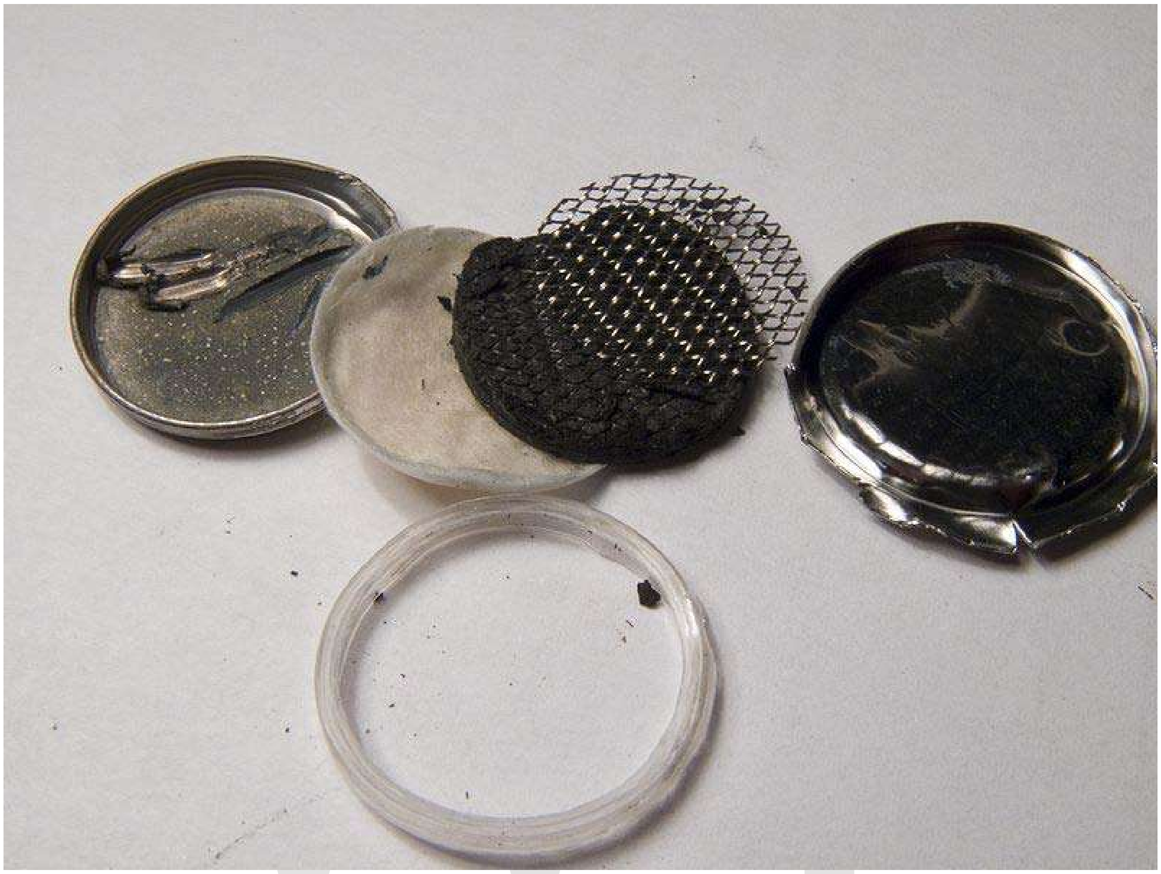
Lithium 9 volt, AA, & AAA sizes

Lithium batteries are disposable (primary) batteries that have lithium metal or lithium compounds as an anode. Depending on the design and chemical compounds used, lithium cells can produce voltages from 1.5 V to about 3.7 V, over twice the voltage of an ordinary zinc-carbon battery or alkaline cell battery. Lithium batteries are widely used in products such as portable consumer electronic devices.

Description

The term "lithium battery" refers to a family of different chemistries, comprising many types of cathodes and electrolytes.

The most common type of lithium cell used in consumer applications uses metallic lithium as anode and manganese dioxide as cathode, with a salt of lithium dissolved in an organic solvent.



Disassembled CR2032 battery From left — negative cup from inner side with layer of lithium (oxidized in air), separator(porous material), cathode (manganese dioxide), metal grid — current collector, metal casing (+)(damaged during opening the cell), on the bottom is plastic sealing ring

Another type of lithium cell having a large energy density is the **lithium-thionyl chloride cell**. Lithium-thionyl chloride batteries are generally not sold to the consumer market, and find more use in commercial/industrial applications, or are installed into devices where no consumer replacement is performed. In this cell, a liquid mixture of thionyl chloride ($SOCl_2$) and lithium tetrachloroaluminate ($LiAlCl_4$) acts as the electrolyte and cathode respectively. A porous carbon material serves as a **cathode current collector** which receives electrons from the external circuit. Lithium-thionyl chloride batteries are well suited to extremely low-current applications where long life is necessary, e.g. wireless alarm systems.

Chemistries

<table>
<tr><th>Chemistry</th><th>Cathode</th><th>Electrolyte</th><th>Nominal voltage</th><th>Open-circuit voltage</th><th>Wh/kg</th><th>Wh/dm^3</th></tr>
<tr><td rowspan="2">Li-MnO_2 (Li-Mn, "CR")</td><td>Heat-treated manganese dioxide</td><td>Lithium perchlorate in propylene carbonate and dimethoxyethane</td><td>3 V</td><td>3.3 V</td><td>280</td><td>580</td></tr>
<tr><td colspan="6">The most common consumer grade battery, about 80% of the lithium battery market. Uses inexpensive materials. Suitable for low-drain, long-life, low-cost applications. High energy density per both mass and volume. Can deliver high pulse currents. Wide temperature range. With discharge the internal impedance rises and the terminal voltage decreases. Maximum temperature limited to about 60 °C. High self-discharge at high temperatures.</td></tr>
<tr><td rowspan="2">Li-$SOCl_2$</td><td>Thionyl chloride</td><td>Lithium tetrachloroaluminate in thionyl chloride</td><td>3.5 V</td><td>3.65 V</td><td>290</td><td>670</td></tr>
<tr><td colspan="6">Liquid cathode. For low temperature applications. Can operate down to -55 °C, where it retains over 50% of its rated capacity. Negligible amount of gas generated in nominal use, limited amount under abuse. Has relatively high internal impedance and limited short-circuit current. High energy density, about 500 Wh/kg. Toxic. Electrolyte reacts with water. Low-current cells used for portable electronics and memory backup. High-current cells used in military applications. In long storage forms passivation layer on anode, which may lead to temporary voltage delay when put into service. High cost and safety concerns limit use in civilian applications. Can explode when shorted. Underwriters Laboratories require trained technician for replacement of these batteries. Hazardous waste, Class 9 Hazmat shipment.</td></tr>
<tr><td rowspan="2">Li-$SOCl_2$,BrCl, Li-BCX</td><td>Thionyl chloride with bromine chloride</td><td>Lithium tetrachloroaluminate in thionyl chloride</td><td>3.7-3.8 V</td><td>3.9 V</td><td>350</td><td>770</td></tr>
<tr><td colspan="6">Liquid cathode. A variant of the thionyl chloride battery, with 300 mV higher voltage. The higher voltage drops back to 3.5 V soon as the bromine chloride gets consumed during the first 10-20% of discharge. The cells with added bromine chloride are thought to be safer when abused.</td></tr>
<tr><td rowspan="2">Li-SO_2Cl_2</td><td>Sulfuryl chloride</td><td></td><td>3.7</td><td>3.95</td><td>330</td><td>720</td></tr>
<tr><td colspan="6">Liquid cathode. Similar to thionyl chloride. Discharge does not result in buildup of elemental sulfur, which is thought to be involved in some hazardous reactions, therefore sulfuryl chloride batteries may be safer. Commercial deployment hindered by tendency of the electrolyte to</td></tr>
</table>

	corrode the lithium anodes, reducing the shelf life. Chlorine is added to some cells to make them more resistant to abuse. Sulfuryl chloride cells give less maximum current than thionyl chloride ones, due to polarization of the carbon cathode. Sulfuryl chloride reacts violently with water, releasing hydrogen chloride and sulfuric acid.					
Li-SO_2	Sulfur dioxide on teflon-bonded carbon	Lithium bromide in sulfur dioxide with small amount of acetonitrile	2.85 V	3.0 V	250	400
	Liquid cathode. Can operate down to -55 °C and up to +70 °C. Contains liquid SO_2 at high pressure. Requires safety vent, can explode in some conditions. High energy density. High cost. At low temperatures and high currents performs better than Li-MnO_2. Toxic. Acetonitrile forms lithium cyanide, and can form hydrogen cyanide in high temperatures. Used in military applications. Addition of bromine monochloride can boost the voltage to 3.9 V and increase energy density.					
Li-$(CF)_x$ ("BR")	Carbon monofluoride	Lithium tetrafluoroborate in propylene carbonate, dimethoxyethane, and/or gamma-butyrolactone	2.8 V	3.1 V	360	680
	Cathode material formed by high-temperature intercalation of fluorine gas into graphite powder. High energy density (250 Wh/kg), 7 year shelf life. Used for low to moderate current applications, eg. memory and clock backup batteries. Very good safety record. Used in aerospace applications, qualified for space since 1976. Used in military applications both terrestrial and marine, and in missiles. Also used in cardiac pacemakers. Maximum temperature 85 °C. Very low self-discharge (<0.5%/year at 60 °C, <1%/yr at 85 °C). Developed in 1970s by Matsushita.					
Li-I_2	Iodine	solid organic charge transfer complex (eg. poly-2-vinylpyridine, P2VP)	2.8 V	3.1 V		
	Solid electrolyte. Very high reliability. Used in medical applications. Does not generate gas even under short circuit. Solid-state chemistry, limited short-circuit current, suitable only for low-current applications. Terminal voltage decreases with degree of discharge due to precipitation of lithium iodide. Low self-discharge.					
Li-Ag_2CrO_4	Silver chromate	Lithium perchlorate solution	3.1/2.6 V	3.45 V		

	Very high reliability. Has a 2.6 V plateau after reaching certain percentage of discharge, provides early warning of impending discharge. Developed specifically for medical applications, eg. implanted pacemakers.				
Li-$Ag_2V_4O_{11}$, Li-SVO, Li-CSVO	Silver oxide+vanadium pentoxide (SVO)	lithium hexafluorophosphate or lithium hexafluoroarsenate in propylene carbonate with dimethoxyethane			
	Used in medical applications, eg. implantable defibrillators, neurostimulators, and drug infusion systems. Also projected for use in other electronics, eg. emergency locator transmitters. High energy density. Long shelf life. Capable of continuous operation at nominal temperature of 37 °C. Two-stage discharge with a plateau. Output voltage decreasing proportionally to the degree of discharge. Resistant to abuse. Addition of copper(II) oxide to the cathode material results in the Li-CSVO variant.				
Li-CuO	Copper(II) oxide	Lithium Perchlorate dissolved in Dioxolane	1.5 V	2.4 V	
	Can operate up to 150 °C. Developed as a replacement of zinc-carbon and alkaline batteries. "Voltage up" problem, high difference between open-circuit and nominal voltage. Produced until mid-1990s, replaced by lithium-iron sulfide. Current use limited.				
Li-$Cu_4O(PO_4)_2$	Copper oxyphosphate				
Li-CuS	Copper sulfide		1.5 V		
Li-PbCuS	Lead sulfide and copper sulfide		1.5 V	2.2 V	
Li-FeS	Iron sulfide	Propylene carbonate, dioxolane, dimethoxyethane	1.5-1.2 V		
	"Lithium-iron", "Li/Fe". used as a replacement for alkaline batteries.				
$Li-FeS_2$	Iron disulfide	Propylene carbonate, dioxolane, dimethoxyethane	1.6-1.4 V	1.8 V	297
	"Lithium-iron", "Li/Fe". Used in Energizer lithium cells as a replacement for alkaline zinc-manganese chemistry. Called "voltage-compatible" lithiums. 2.5 times higher lifetime for high current discharge regime than				

	alkaline batteries, better storage life in e.g. cars in summer due to lower self-discharge, 10 years storage time. FeS_2 is cheap. Some types rechargeable. Cathode often designed as a paste of iron sulfide powder mixed with powdered graphite. Variant is Li-$CuFeS_2$.					
Li-$Bi_2Pb_2O_5$	Lead bismuthate		1.5 V	1.8 V		
	Replacement of silver-oxide batteries, with higher energy density, lower tendency to leak, and better performance at higher temperatures.					
Li-Bi_2O_3	Bismuth trioxide		1.5 V	2.04 V		
Li-V_2O_5	Vanadium pentoxide		3.3/2.4 V	3.4 V	120/260	300/660
	Two discharge plateaus. Low-pressure. Rechargeable. Used in reserve batteries.					
Li-CoO_2	Cobalt dioxide					
Li-$CuCl_2$	Copper chloride					
	Rechargeable.					
Li/Al-MnO_2	Manganese dioxide					
	Rechargeable.					
Li/Al-V_2O_5	Vanadium pentoxide					
	Rechargeable.					
Li-ion	carbon	liquid				
	Rechargeable.					
Li-poly	polymer	solid				
	Rechargeable.					

The liquid organic electrolyte is usually a solution of an ion-forming inorganic lithium compound in a mixture of a high-permittivity solvent (eg. propylene carbonate) and a low-viscosity solvent (eg. dimethoxyethane).

Applications

Lithium batteries find application in many long-life, critical devices, such as artificial pacemakers and other implantable electronic medical devices. These devices use specialized lithium-iodide batteries designed to last 15 or more years. But for other, less critical applications such as in toys, the lithium battery may actually outlast the device. In such cases, an expensive lithium battery may not be cost-effective.

Lithium batteries can be used in place of ordinary alkaline cells in many devices, such as clocks and cameras. Although they are more costly, lithium cells will provide much longer life, thereby minimizing battery replacement. However, attention must be given to the higher voltage developed by the lithium cells before using them as a drop-in replacement in devices that normally use ordinary zinc cells.

Small lithium batteries are very commonly used in small, portable electronic devices, such as PDAs, watches, camcorders, digital cameras, thermometers, calculators, laptop BIOS, communication equipment and remote car locks. They are available in many shapes and sizes, with a common variety being the 3 volt "coin" type manganese variety, typically 20 mm in diameter and 1.6–4 mm thick. The heavy electrical demands of many of these devices make lithium batteries a particularly attractive option. In particular, lithium batteries can easily support the brief, heavy current demands of devices such as digital cameras, and they maintain a higher voltage for a longer period than alkaline cells.

Some other lithium batteries use a platinum-iridium alloy instead of more usual compounds. These batteries are generally not preferred, as their cost is high and they tend to be fragile.

Safety issues and regulation

The computer industry's drive to increase battery capacity can test the limits of sensitive components such as the membrane separator, a polyethylene or polypropylene film that is only 20-25 µm thick. The energy density of lithium batteries has more than doubled since they were introduced in 1991. When the battery is made to contain more material, the separator can undergo stress.

Ingestion and choking hazard

Button cell batteries are attractive to small children and often ingested. In very small children, they are a choking hazard. Lithium coin batteries lodged in the esophagus should be removed immediately. Leakage, chemical burns and potential perforation can occur within hours of ingestion.

Rapid-discharge issues

Lithium batteries can provide extremely high currents and can discharge very rapidly when short-circuited. Although this is useful in applications where high currents are required, a too-rapid discharge of a lithium battery can result in overheating of the battery, rupture, and even explosion. Lithium-thionyl chloride batteries are particularly susceptible to this type of discharge. Consumer batteries usually incorporate overcurrent or thermal protection or vents in order to prevent explosion.

Air travel

Because of the above risks, shipping and carriage of lithium batteries is restricted in some situations, particularly transport of lithium batteries by air.

The United States Transportation Security Administration announced restrictions effective January 1, 2008 on lithium batteries in checked and carry-on luggage. The rules forbid lithium batteries not installed in a device from checked luggage and restrict them in carry-on luggage by total lithium content.

Australia Post prohibited transport of lithium batteries in air mail during 2010.

Lithium batteries and methamphetamine labs

Unused lithium batteries provide a convenient source of lithium metal for use as a reducing agent in methamphetamine labs. Some jurisdictions have passed laws to restrict lithium battery sales or asked businesses to make voluntary restrictions in an attempt to help curb the creation of illegal meth labs. In 2004 Wal-Mart stores were reported to limit the sale of disposable lithium batteries to three packages in Missouri and four packages in other states. High demand for lithium batteries for use in power-hungry devices such as digital cameras conflicts with such restrictions in stores, but internet retailers are an alternate source.

Transportation

UK regulations for the transport of lithium batteries were amended by the National Chemical Emergency Centre in 2009.

On 2009 fall, at least some postal administrations restricted airmail shipping (including EMS) of lithium batteries, lithium-ion batteries and products containing these (e.g. laptops, cell phones etc). Among these countries are Hong Kong, USA and Japan.

Lithium (Component)

Appearance

silver-white (seen here floating in oil)

General properties

Name, symbol, number	lithium, Li, 3
Element category	alkali metal
Group, period, block	1, 2, s
Standard atomic weight	6.941g·mol^{-1}
Electron configuration	1s^2 2s^1
Electrons per shell	2, 1 (Image)

Physical properties

Phase	solid
Density (near r.t.)	0.534 g·cm^{-3}
Liquid density at m.p.	0.512 g·cm^{-3}
Melting point	453.69 K180.54 ° ,C356.97 ° ,F
Boiling point	1615 K1342 ° ,C2448 ° ,F
Critical point	(extrapolated) 3223 K, 67 MPa
Heat of fusion	3.00 kJ·mol^{-1}
Heat of vaporization	147.1 kJ·mol^{-1}
Specific heat capacity	(25 °C) 24.860 J·mol^{-1}·K^{-1}

Vapor pressure

P (Pa)	1	10	100	1 k	10 k	100 k
at T (K)	797	885	995	1144	1337	1610

Atomic properties

Oxidation states	**+1**, -1 (strongly basic oxide)

Electronegativity	0.98 (Pauling scale)
Ionization energies	1st: 520.2 kJ·mol^{-1}
	2nd: 7298.1 kJ·mol^{-1}
	3rd: 11815.0 kJ·mol^{-1}
Atomic radius	152 pm
Covalent radius	128±7 pm
Van der Waals radius	182 pm
Miscellanea	
Crystal structure	body-centered cubic
Magnetic ordering	paramagnetic
Electrical resistivity	(20 °C) 92.8 nΩ·m
Thermal conductivity	(300 K) 84.8 W·m^{-1}·K^{-1}
Thermal expansion	(25 °C) 46 µm·m^{-1}·K^{-1}
Speed of sound (thin rod)	(20 °C) 6000 m/s
Young's modulus	4.9 GPa
Shear modulus	4.2 GPa
Bulk modulus	11 GPa
Mohs hardness	0.6
CAS registry number	7439-93-2

Most stable isotopes

iso	NA	half-life	DM	DE (MeV)	DP
^{6}Li	7.5%	^{6}Li is stable with 3 neutrons			
^{7}Li	92.5%	^{7}Li is stable with 4 neutrons			

^{6}Li content may be as low as 3.75% in natural samples. ^{7}Li would therefore have a content of up to 96.25%.

Lithium is a soft, silver-white metal that belongs to the alkali metal group of chemical elements. It is represented by the symbol **Li**, and it has the atomic number 3. Under standard conditions it is the lightest metal and the least dense solid element. Like all alkali metals, lithium is highly reactive and flammable. For this reason, it is typically stored in mineral oil. When cut open, lithium exhibits a metallic luster, but contact with moist air corrodes the surface quickly to a dull silvery gray, then black, tarnish. Because of its high reactivity, lithium never occurs free in nature, and instead, only appears in compounds, usually ionic ones. Lithium occurs in a number of pegmatitic minerals, but is also commonly obtained from brines and clays. On a commercial scale, lithium is isolated electrolytically from a mixture of lithium chloride and potassium chloride.

The nuclei of lithium are not far from being unstable, since the two stable lithium isotopes found in nature have among the lowest binding energies per nucleon of all stable nuclides. As a result, they can be used in fission reactions as well as fusion reactions of nuclear devices. Due to its near instability, lithium is less common in the solar system than 25 of the first 32 chemical elements even though the nuclei are very light in atomic weight. For related reasons, lithium has important links to nuclear physics. The transmutation of lithium atoms to tritium was the first man-made form of a nuclear fusion reaction, and lithium deuteride serves as a fusion fuel in staged thermonuclear weapons.

Trace amounts of lithium are present in the oceans and in all organisms. The element serves no apparent vital biological function, since animal and plants survive in good health without it. Nonvital functions have not been ruled out. The lithium ion Li^+ administered as any of several lithium salts has proved to be useful as a mood-stabilizing drug due to neurological effects of the ion in the human body. Lithium and its compounds have several industrial applications, including heat-resistant glass and ceramics, high strength-to-weight alloys used in aircraft, lithium batteries and lithium-ion batteries. These uses consume more than half of lithium production.

Characteristics

Atomic and physical

Lithium pellets covered in white lithium hydroxide (above) and ingots with a thin layer of black oxide tarnish (below)

Like the other alkali metals, lithium has a single valence electron that is easily given up to form a cation. Because of this, it is a good conductor of heat and electricity as well as a highly reactive element, though the least reactive of the even-more highly reactive alkali metals. Lithium's low reactivity compared to other alkali metals is thought to be due to the proximity of its valence electron to its nucleus (the remaining two electrons in lithium's 1s orbital and are much lower in energy, and therefore they do not participate in chemical bonds).

Lithium metal is soft enough to be cut with a knife. When cut, it possesses a silvery-white color that quickly changes to gray due to oxidation. While it has one of the lowest melting points among all metals (180 °C), it has the highest melting point of the alkali metals.

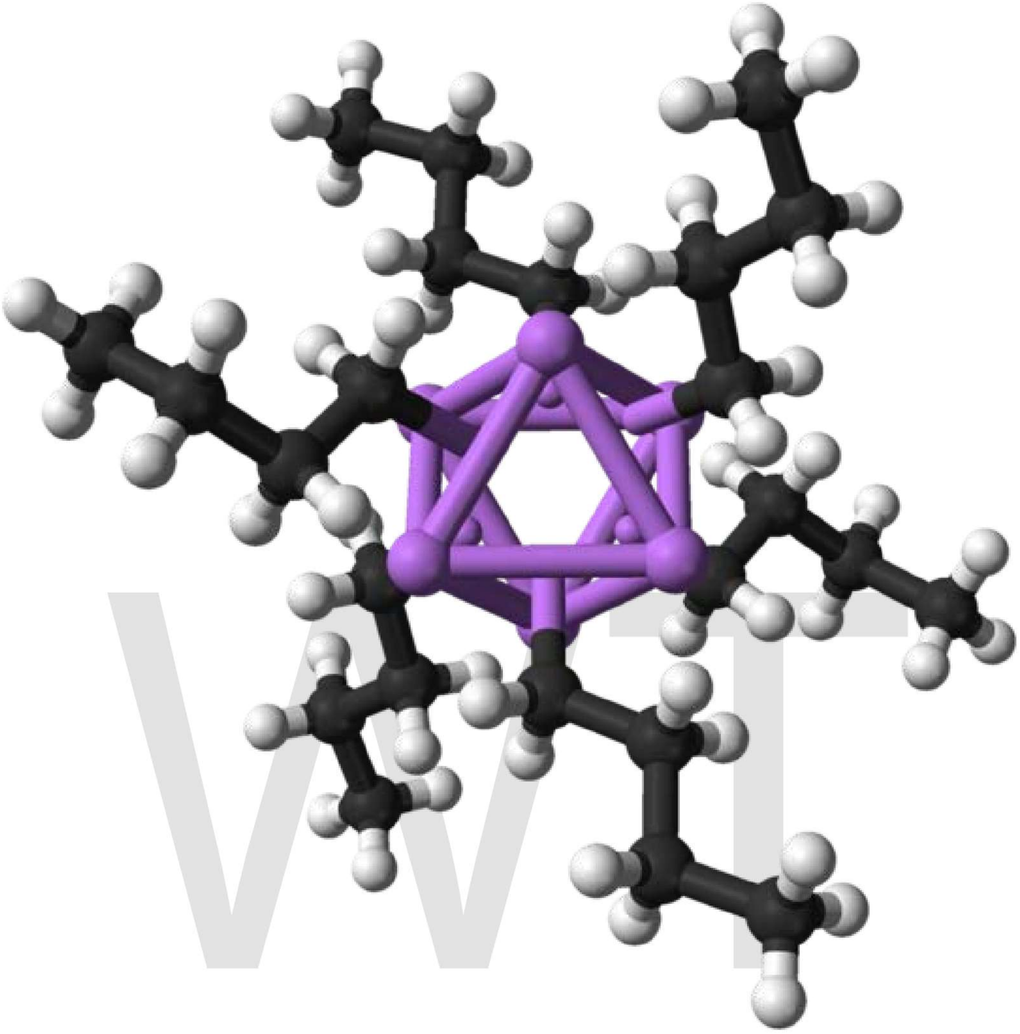
It is the lightest metal in the periodic table. It has a very low density, of approximately 0.534 g/cm^3, which gives sticks of the metal a similar heft to dowels of a medium density wood, such as pine. It floats on water but also reacts with it. It is the least dense of all elements that are not gasses at room temperature. The next lightest element is over 60% more dense (potassium, at 0.862 g/cm^3). Furthermore, aside from helium and hydrogen, it is the least dense element in a solid or liquid state, being only 2/3 as dense as liquid nitrogen (0.808 g/cm^3).

Lithium's coefficient of thermal expansion is twice that of aluminum and almost four times that of iron. It has the highest specific heat capacity of any solid element. Lithium is superconductive below 400 μK at standard pressure and at higher temperatures (more than 9 K) at very high pressures (>20 GPa) At temperatures below 70 K, lithium, like sodium, undergoes diffusionless phase change transformations. At 4.2 K it has a rhombohedral crystal system (with a nine-layer repeat spacing); at higher temperatures it transforms to face-centered cubic and then body-centered cubic. At liquid-helium temperatures (4 K) the rhombohedral structure is the most prevalent. Multiple allotropic forms have been reported for lithium at high pressures.

Chemistry and compounds

Lithium reacts with water easily, but with noticeably less energy than other alkali metals do. The reaction forms hydrogen gas and lithium hydroxide in aqueous solution. Because of its reactivity with water, lithium is usually stored under cover of a viscous hydrocarbon, often petroleum jelly. Though the heavier alkali metals can be stored in less dense substances, such as mineral oil, lithium is not dense enough to be fully submerged in these liquids. In moist air, lithium rapidly tarnishes to form a black coating of lithium hydroxide ($LiOH$ and $LiOH \cdot H_2O$), lithium nitride (Li_3N) and lithium carbonate (Li_2CO_3, the result of a secondary reaction between $LiOH$ and CO_2).

When placed over a flame, lithium compounds give off a striking crimson color, but when it burns strongly the flame becomes a brilliant silver. Lithium will ignite and burn in oxygen when exposed to water or water vapors. Lithium is flammable, and it is potentially explosive when exposed to air and especially to water, though less so than the other alkali metals. The lithium-water reaction at normal temperatures is brisk but not violent, though the hydrogen produced can ignite. As with all alkali metals, lithium fires are difficult to extinguish, requiring dry powder fire extinguishers, specifically Class D type. Lithium is the only metal which reacts with nitrogen under normal conditions.



Hexameric structure of the LiBu fragment in a crystal

Lithium has a diagonal relationship with magnesium, an element of similar atomic and ionic radius. Chemical resemblances between the two metals include the formation of a nitride by reaction with N_2, the formation of an oxide (Li_2O) and peroxide (Li_2O_2) when burnt in O_2, salts with similar solubilities, and thermal instability of the carbonates and nitrides. The metal reacts with hydrogen gas at high temperatures to produce lithium hydride (LiH).

Other known binary compounds include the halides (LiF, LiCl, LiBr, LiI), and the sulfide (Li_2S), the superoxide (LiO_2), carbide (Li_2C_2). Many other inorganic compounds are known, where lithium combines with anions to form various salts: borates, amides, carbonate, nitrate, or borohydride ($LiBH_4$). Multiple organolithium reagents are known where there is a direct bond between carbon and lithium atoms effectively creating a carbanion that are extremely powerful bases and nucleophiles. In many of these organolithium compounds, the lithium ions tend to aggregate into high-symmetry clusters by themselves, which is relatively common for alkali cations.

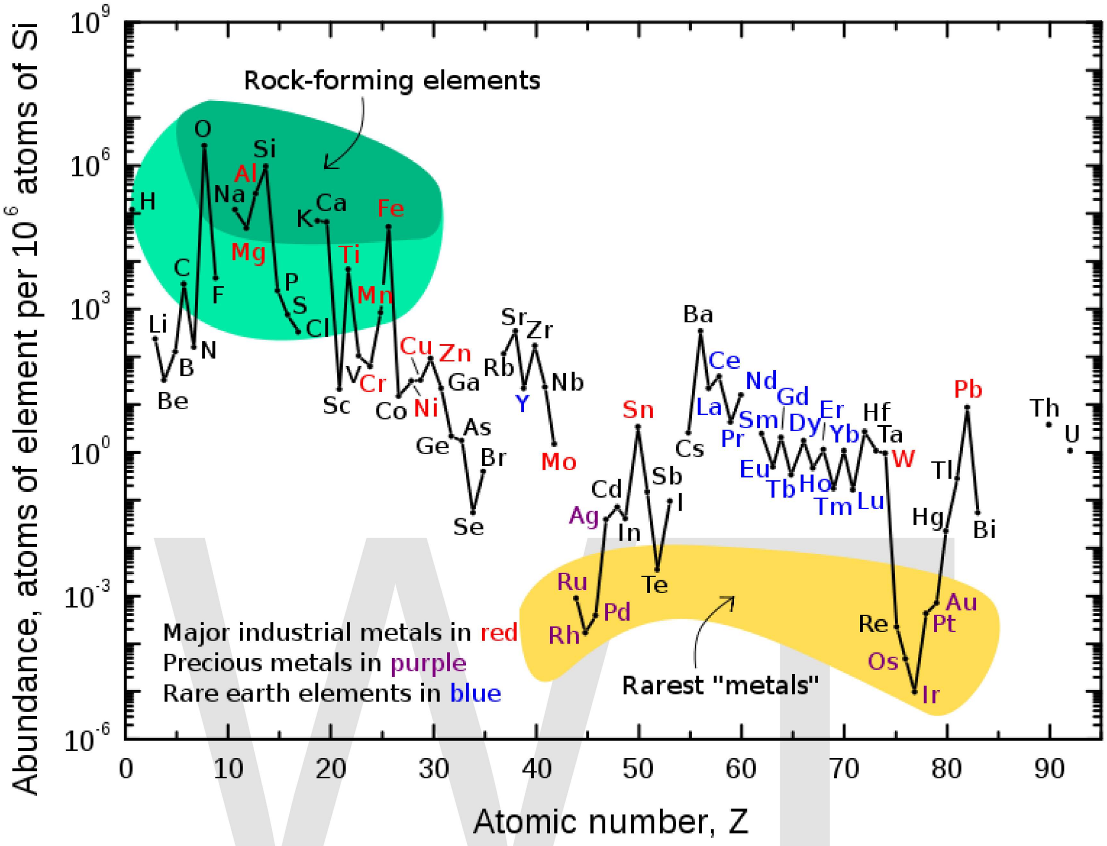
Isotopes

Naturally occurring lithium is composed of two stable isotopes, ^{6}Li and ^{7}Li, the latter being the more abundant (92.5% natural abundance). Both natural isotopes have anomalously low nuclear binding energy per nucleon compared to the next lighter and heavier elements, helium and beryllium, which means that alone among stable light elements, lithium can produce net energy through nuclear fission. The two lithium nuclei have lower binding energies per nucleon than any other stable compound nuclides other than deuterium, and helium-3. As a result of this, though very light in atomic weight, lithium is less common in the solar system than 25 of the first 32 chemical elements. Seven radioisotopes have been characterized, the most stable being ^{8}Li with a half-life of 838 ms and ^{9}Li with a half-life of 178 ms. All of the remaining radioactive isotopes have half-lives that are shorter than 8.6 ms. The shortest-lived isotope of lithium is ^{4}Li, which decays through proton emission and has a half-life of 7.6×10^{-23} s.

^{7}Li is one of the primordial elements (or, more properly, primordial nuclides) produced in Big Bang nucleosynthesis. A small amount of both ^{6}Li and ^{7}Li are produced in stars, but are thought to be burned as fast as produced. Additional small amounts of lithium of both ^{6}Li and ^{7}Li may be generated from solar wind, cosmic rays hitting heavier atoms, and from early solar system ^{7}Be and ^{10}Be radioactive decay. While lithium is created in stars during the Stellar nucleosynthesis, it is further burnt. ^{7}Li can also be generated in carbon stars.

Lithium isotopes fractionate substantially during a wide variety of natural processes, including mineral formation (chemical precipitation), metabolism, and ion exchange. Lithium ions substitute for magnesium and iron in octahedral sites in clay minerals, where ^{6}Li is preferred to ^{7}Li, resulting in enrichment of the light isotope in processes of hyperfiltration and rock alteration. The exotic ^{11}Li is known to exhibit a nuclear halo. The process known as laser isotope separation can be used to separate lithium isotopes.

Occurrence



Lithium is about as common as chlorine in the Earth's upper continental crust, on a per-atom basis.

Astronomical

According to modern cosmological theory, lithium—as both of its stable isotopes lithium-6 and lithium-7—was among the 3 elements synthesized in the Big Bang. Though the amount of lithium generated in Big Bang nucleosynthesis is dependent upon the number of photons per baryon, for accepted values the lithium abundance can be calculated, and there is a "cosmological lithium discrepancy" in the Universe: older stars seem to have less lithium than they should, and some younger stars have far more. The lack of lithium in older stars is apparently caused by the "mixing" of lithium into the interior of stars, where it is destroyed. Furthermore, lithium is produced in younger stars. Though it transmutes into two atoms of helium due to collision with a proton at temperatures above 2.4 million degrees Celsius (most stars easily attain this temperature in their interiors), lithium is more abundant than predicted in later-generation stars, for causes not yet completely understood.

Though it was one of the three first elements (together with helium and hydrogen) to be synthesized in the Big Bang, lithium, together with beryllium and boron are markedly less abundant than other nearby elements. This is a result to the low temperature necessary to destroy lithium, and a lack of common processes to produce it.

Lithium is also found in brown dwarf stars and certain anomalous orange stars. Because lithium is present in cooler, less-massive brown dwarf stars, but is destroyed in hotter red dwarf stars, its presence in the stars' spectra can be used in the "lithium test" to differentiate the two, as both are smaller than the Sun. Certain orange stars can also contain a high concentration of lithium. Those orange stars found to have a higher than usual concentration of lithium (such as Centaurus X-4) orbit massive objects—neutron stars or black holes—whose gravity evidently pulls heavier lithium to the surface of a hydrogen-helium star, causing more lithium to be observed.

Terrestrial

Lithium mine production (2009) and reserves in tonnes

Country	Production	Reserves
Argentina	2,200	800,000
Australia	4,400	580,000
Brazil	110	190,000
Canada	480	180,000
Chile	7,400	7,500,000
People's Republic of China	2,300	540,000
Portugal	490	Not available
United States	Withheld	38,000
Zimbabwe	350	23,000
World total	**18,000**	**9,900,000**

Although lithium is widely distributed on Earth, it does not naturally occur in elemental form due to its high reactivity. The total lithium content of seawater is very large and is estimated as 230 billion tonnes, where the element exists at a relatively constant concentration of 0.14 to 0.25 parts per million (ppm), or 25 micromolar; higher concentrations approaching 7 ppm are found near hydrothermal vents.

Estimates for crustal content range from 20 to 70 ppm by weight. In keeping with its name, lithium forms a minor part of igneous rocks, with the largest concentrations in granites. Granitic pegmatites also provide the greatest abundance of lithium-containing minerals, with spodumene and petalite being the most commercially viable sources. A newer source for lithium is hectorite clay, the only active development of which is through the Western Lithium Corporation in the United States. At 20 mg lithium per kg of Earth's crust, lithium is the 25th most abundant element. Nickel and lead have about the same abundance.

Lithium is found in trace amount in numerous plants, plankton, and invertebrates, at concentrations of 69 to 5,760 parts per billion (ppb). In vertebrates the concentration is slightly lower, and nearly all vertebrate tissue and body fluids have been found to contain lithium ranging from 21 to 763 ppb. Marine organisms tend to bioaccumulate lithium more than terrestrial ones. It is not known whether lithium has a physiological role in any of these organisms.

According to the *Handbook of Lithium and Natural Calcium*, "Lithium is a comparatively rare element, although it is found in many rocks and some brines, but always in very low concentrations. There are a fairly large number of both lithium mineral and brine deposits but only comparatively a few of them are of actual or potential commercial value. Many are very small, others are too low in grade."

The largest reserve base of lithium is in the Salar de Uyuni area of Bolivia, which has 5.4 million tonnes. US Geological Survey, estimates that in 2009 Chile had the largest reserves by far (7.5 million tonnes) and the highest annual production (7,400 tonnes). Other major suppliers include Australia, Argentina and China. Other estimates put Argentina's reserve base (7.52 million tonnes) above that of Chile (6 million).

In June 2010, the New York Times reported that American geologists were conducting ground surveys on dry salt lakes in western Afghanistan believing that large deposits of lithium are located there. "Pentagon officials said that their initial analysis at one location in Ghazni Province showed the potential for lithium deposits as large of those of Bolivia, which now has the world’s largest known lithium reserves." These estimates are "based principally on old data, which was gathered mainly by the Soviets during their occupation of Afghanistan from 1979–1989" and "Stephen Peters, the head of the USGS’s Afghanistan Minerals Project, said that he was unaware of USGS involvement in any new surveying for minerals in Afghanistan in the past two years. 'We are not aware of any discoveries of lithium,' he said."

History

Johan August Arfwedson is credited with the discovery of lithium in 1817

Petalite ($LiAlSi_4O_{10}$) was discovered in 1800 by the Brazilian chemist José Bonifácio de Andrada e Silva in a mine on the island of Utö, Sweden. However, it was not until 1817 that Johan August Arfwedson, then working in the laboratory of the chemist Jöns Jakob Berzelius, detected the presence of a new element while analyzing petalite ore. This element formed compounds similar to those of sodium and potassium, though its carbonate and hydroxide were less soluble in water and more alkaline. Berzelius gave the alkaline material the name "*lithion*/*lithina*", from the Greek word *λιθος* (transliterated as *lithos*, meaning "stone"), to reflect its discovery in a solid mineral, as opposed to potassium, which had been discovered in plant ashes, and sodium which was known partly for its high abundance in animal blood. He named the metal inside the material as "*lithium*".

Arfwedson later showed that this same element was present in the minerals spodumene and lepidolite. In 1818, Christian Gmelin was the first to observe that lithium salts give a bright red color to flame. However, both Arfwedson and Gmelin tried and failed to isolate the pure element from its salts. It was not isolated until 1821, when William Thomas Brande obtained it by electrolysis of lithium oxide, a process that had previously been employed by the chemist Sir Humphry Davy to isolate the alkali metals potassium and sodium. Brande also described some pure salts of lithium, such as the chloride, and, estimating that lithia (lithium oxide) contained about 55% metal, estimated the atomic weight of lithium to be around 9.8 g/mol (modern value ~6.94 g/mol). In 1855, larger quantities of lithium were produced through the electrolysis of lithium chloride by Robert Bunsen and Augustus Matthiessen. The discovery of this procedure henceforth led to commercial production of lithium, beginning in 1923, by the German company Metallgesellschaft AG, which performed an electrolysis of a liquid mixture of lithium chloride and potassium chloride.

The production and use of lithium underwent several drastic changes in history. The first major application of lithium became high temperature grease for aircraft engines or similar applications in World War II and shortly after. This small market was supported by several small mining operations mostly in the United States. The demand for lithium increased dramatically during the Cold War with the production of nuclear fusion weapons. Both lithium-6 and lithium-7 produce tritium when irradiated by neutrons, and are thus useful for the production of tritium by itself, as well as a form of solid fusion fuel used inside hydrogen bombs in the form of lithium deuteride. The United States became the prime producer of lithium in the period between the late 1950s and the mid 1980s. At the end the stockpile of lithium was roughly 42,000 tonnes of lithium hydroxide. The stockpiled lithium was depleted in lithium-6 by 75%.

Lithium was used to decrease the melting temperature of glass and to improve the melting behavior of aluminium oxide when using the Hall-Héroult process. These two uses dominated the market until the middle of the 1990s. After the end of the nuclear arms race the demand for lithium decreased and the sale of Department of Energy stockpiles on the open market further reduced prices. But in the mid-1990s, several companies started to extract lithium from brine which proved to be a less expensive method than underground or even open pit mining. Most of the mines closed or shifted their focus to other materials as only the ore from zoned pegmatites could be mined for a competitive price. For example, the US mines near Kings Mountain, North Carolina closed before the turn of the century. The use in lithium ion batteries increased the demand for lithium and became the dominant use in 2007. With the surge of lithium demand in batteries in to 2000s, new companies have expanded brine extraction efforts to meet the rising demand.

Production

Satellite images of the Salar del Hombre Muerto, Argentina (above), and Uyuni, Bolivia (below), salt flats are rich in lithium. The lithium-rich brine is concentrated by pumping it into solar evaporation ponds (visible in above image).

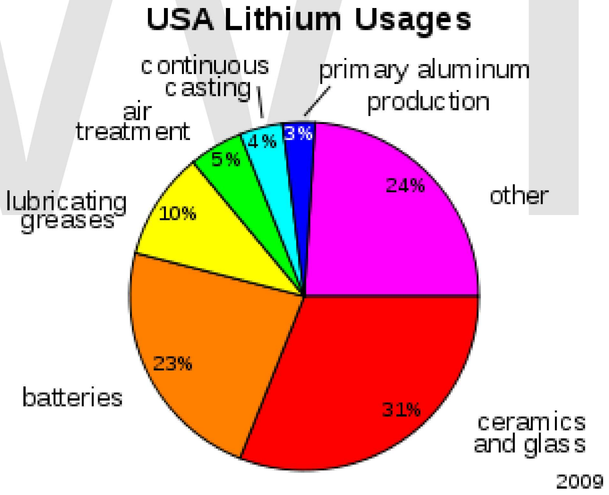
Since the end of World War II lithium production has greatly increased. The metal is separated from other elements in igneous minerals such as those above. Lithium salts are extracted from the water of mineral springs, brine pools and brine deposits. The metal is produced electrolytically from a mixture of fused lithium chloride and potassium chloride. In 1998 it was about 95 US$ / kg (or 43 US$/pound).

There are widespread hopes of using lithium ion batteries in electric vehicles, but one study concluded that "realistically achievable lithium carbonate production will be sufficient for only a small fraction of future PHEV and EV global market requirements", that "demand from the portable electronics sector will absorb much of the planned production increases in the next decade", and that "mass production of lithium carbonate is not environmentally sound, it will cause irreparable ecological damage to ecosystems that should be protected and that LiIon propulsion is incompatible with the notion of the 'Green Car'".

Deposits of lithium are found in South America throughout the Andes mountain chain. Chile is the leading lithium producer, followed by Argentina. Both countries recover the lithium from brine pools. In the United States lithium is recovered from brine pools in Nevada. Nearly half the world's known reserves are located in Bolivia, a nation sitting along the central eastern slope of the Andes. In 2009 Bolivia is negotiating with Japanese, French, and Korean firms to begin extraction. According to the US Geological Survey, Bolivia's Uyuni Desert has 5.4 million tonnes of lithium, which can be used to make batteries for hybrid and electric vehicles. China may emerge as a significant producer of brine-source lithium carbonate around 2010. There is potential production of up to 55,000 tonnes per year if projects in Qinghai province and Tibet proceed.

Worldwide reserves of lithium are estimated to be 23 million tonnes. Using the battery efficiency figure of 400 g of lithium per kWh, this gives a total maximum lithium battery capacity of 52 billion kWh which, assuming it is used exclusively for car batteries, is enough for approximately 2 billion cars with a 24 kWh battery (like a Nissan Leaf).

Applications



Usage of lithium in the USA in 2009

Electrical and electronics

In the later years of the 20th century lithium became important as an anode material. Used in lithium-ion batteries because of its high electrochemical potential, a typical cell can generate approximately 3 volts, compared with 2.1 volts for lead/acid or 1.5 volts for zinc-carbon cells. Because of its low atomic mass, it also has a high charge- and power-to-weight ratio. Lithium batteries are disposable (primary) batteries with lithium or its compounds as an anode. Lithium batteries are not to be confused with lithium-ion batteries, which are high energy-density rechargeable batteries. Other rechargeable batteries include the lithium-ion polymer battery, lithium iron phosphate battery, and the nanowire battery. New technologies are constantly being announced.

Lithium niobate is used extensively in telecommunication products such as mobile phones and optical modulators, for such components as resonant crystals. Lithium applications are used in more than 60% of mobile phones. Because of its specific heat capacity, the highest of all solids, lithium is often used in coolants for heat transfer applications.

Medicinal

Lithium salts were used during the 19th century to treat gout. Lithium salts such as lithium carbonate (Li_2CO_3), lithium citrate, and lithium orotate are mood stabilizers. They are used in the treatment of bipolar disorder since, unlike most other mood altering drugs, they counteract both depression and mania (though more effective for the latter). Lithium continues to be the gold standard for the treatment of bipolar disorder. It is also helpful for related diagnoses, such as schizoaffective disorder and cyclic major depression. In addition to watching out for the well-known complications of lithium treatment—hypothyroidism and decreased renal function—health care providers should be aware of hyperparathyroidism. Lithium can also be used to augment antidepressants. Because of Lithium's nephrogenic diabetes insipidus effects, it can be used to help treat the syndrome of inappropriate antidiuretic hormone hypersecretion (SIADH). It was also sometimes prescribed as a preventive treatment for migraine disease and cluster headaches.

The active principle in these salts is the lithium ion Li^+. Although this ion has a smaller diameter than either Na^+ or K^+, in a watery environment like the cytoplasmic fluid, Li^+ binds to the oxygen atoms of water, making it effectively larger than either Na^+ or K^+ ions. How Li^+ works in the central nervous system is still a matter of debate. Li^+ elevates brain levels of tryptophan, 5-HT (serotonin), and 5-HIAA (a serotonin metabolite). Serotonin is related to mood stability. Li^+ also reduces catecholamine activity in the brain (associated with brain activation and mania), by enhancing reuptake and reducing release. Therapeutically useful amounts of lithium (1.0 to 1.2 mmol/L) are only slightly lower than toxic amounts (>1.5 mmol/L), so the blood levels of lithium must be carefully monitored during treatment to avoid toxicity.

Common side effects of lithium treatment include muscle tremors, twitching, ataxia, and hypothyroidism. Long term use is linked to hyperparathyroidism, hypercalcemia (bone loss), hypertension, damage of tubuli in the kidney, nephrogenic diabetes insipidus (polyuria and polydipsia) and/or glomerular damage – even to the point of uremia, seizures and weight gain. According to a study in 2009 at Oita University in Japan and published in the British Journal of Psychiatry, communities whose water contained larger amounts of lithium had significantly lower suicide rates, but did not address whether lithium in drinking water causes the negative side effects associated with higher doses of the element.

Chapter- 2

Lithium-Ion Battery

Lithium-ion battery

Nokia Li-ion battery for powering a mobile phone

specific energy	100-250 W·h/kg (0.36-0.90 MJ/kg)
energy density	250-620 W·h/L (0.90-2.23 MJ/L)
specific power	~250-~340 W/kg
Charge/discharge efficiency	80-90%
Energy/consumer-price	2.5 Wh/US$
Self-discharge rate	8% at 21 °C 15% at 40 °C 31% at 60 °C (per month)
Cycle durability	400-1200 cycles

Nominal cell voltage	3.6 / 3.7 V

A **lithium-ion battery** (sometimes **Li-ion battery** or **LIB**) is a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge, and back when charging. Chemistry, performance, cost, and safety characteristics vary across LIB types. Unlike lithium primary batteries (which are disposable), lithium-ion electrochemical cells use an intercalated lithium compound as the electrode material instead of metallic lithium.

Lithium-ion batteries are common in consumer electronics. They are one of the most popular types of rechargeable battery for portable electronics, with one of the best energy densities, no memory effect, and a slow loss of charge when not in use. Beyond consumer electronics, LIBs are also growing in popularity for military, electric vehicle, and aerospace applications. Research is yielding a stream of improvements to traditional LIB technology, focusing on energy density, durability, cost, and intrinsic safety.

Charge and discharge

During discharge, lithium ions Li^+ carry the current from the negative to the positive electrode, through the non-aqueous electrolyte and separator diaphragm.

During charging, an external electrical power source (the charging circuit) applies a higher voltage (but of the same polarity) than that produced by the battery, forcing the current to pass in the reverse direction. The lithium ions then migrate from the positive to the negative electrode, where they become embedded in the porous electrode material in a process known as intercalation.

Construction

Cylindrical 18650 cell before closing

The three primary functional components of a lithium-ion battery are the anode, cathode, and electrolyte. The anode of a conventional lithium-ion cell is made from carbon, the cathode is a metal oxide, and the electrolyte is a lithium salt in an organic solvent.

The most commercially popular anode material is graphite. The cathode is generally one of three materials: a layered oxide (such as lithium cobalt oxide), a polyanion (such as lithium iron phosphate), or a spinel (such as lithium manganese oxide).

The electrolyte is typically a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing complexes of lithium ions. These non-aqueous electrolytes generally use non-coordinating anion salts such as lithium hexafluorophosphate ($LiPF_6$), lithium hexafluoroarsenate monohydrate ($LiAsF_6$), lithium perchlorate ($LiClO_4$), lithium tetrafluoroborate ($LiBF_4$), and lithium triflate ($LiCF_3SO_3$).

Depending on materials choices, the voltage, capacity, life, and safety of a lithium-ion battery can change dramatically. Recently, novel architectures using nanotechnology have been employed to improve performance.

Pure lithium is very reactive. It reacts vigorously with water to form lithium hydroxide and hydrogen gas is liberated. Thus a non-aqueous electrolyte is typically used, and a sealed container rigidly excludes water from the battery pack.

Lithium ion batteries are more expensive than NiCd batteries but operate over a wider temperature range with higher energy densities, while being smaller and lighter. They are fragile and so need a protective circuit to limit peak voltages.

Formats

Nissan Leaf's lithium-ion battery pack

Li-Ion cells are available in various formats, which can generally be divided into four groups:

- Small cylindrical (solid body without terminals, such as those used in laptop batteries)
- Large cylindrical (solid body with large threaded terminals)
- Pouch (soft, flat body, such as those used in cell phones)
- Prismatic (semi-hard plastic case with large threaded terminals, often used in vehicles' traction packs)

The lack of case gives pouch cells the highest energy density; however, pouch cells (and prismatic cells) require an external means of containment to prevent expansion when their SOC level is high.

History

Varta Lithium-ion battery, Museum Autovision, Altlussheim, Germany

Lithium-ion batteries were first proposed by M.S. Whittingham at Binghamton University, at Exxon, in the 1970s. Whittingham used titanium(II) sulfide as the cathode and lithium metal as the anode.

The electrochemical properties of lithium intercalation in graphite were first discovered in 1980 by Rachid Yazami et al., at the Grenoble Institute of Technology (INPG) and French National Centre for Scientific Research (CNRS) in France. They showed the reversible intercalation of lithium into graphite in a lithium/polymer electrolyte/graphite half cell. Their work was published in 1982 and 1983. It covered both thermodynamics (staging) and kinetics (diffusion) together with reversibility.

Primary lithium batteries in which the anode is made from metallic lithium pose safety issues. As a result, lithium-ion batteries were developed in which both anode and cathode are made of a material containing lithium ions. In 1981, Bell Labs developed a workable graphite anode to provide an alternative to the lithium metal battery. Following cathode research performed by a team led by John Goodenough, in 1991 Sony released the first commercial lithium-ion battery. Their cells used layered oxide chemistry, specifically lithium cobalt oxide.

In 1983, Dr. Michael Thackeray, Goodenough, and coworkers identified manganese spinel as a cathode material. Spinel showed great promise, given low-cost, good electronic and lithium ion conductivity, and three-dimensional structure which gives it good structural stability. Although pure manganese spinel fades with cycling, this can be overcome with chemical modification of the material. Manganese spinel is currently used in commercial cells.

In 1989, Goodenough and Arumugam Manthiram of the University of Texas at Austin showed that cathodes containing polyanions, e.g. sulfates, produce higher voltages than oxides due to the inductive effect of the polyanion.

In 1996, Goodenough, Akshaya Padhi and coworkers identified lithium iron phosphate ($LiFePO_4$) and other phospho-olivines (lithium metal phosphates with olivine structure) as cathode materials.

In 2002, Yet-Ming Chiang and his group at MIT showed a substantial improvement in the performance of lithium batteries by boosting the material's conductivity by doping it with aluminum, niobium and zirconium. The exact mechanism causing the increase became the subject of a debate.

In 2004, Chiang again increased performance by utilizing iron-phosphate particles of less than 100 nanometers in diameter. This decreased particle density by almost one hundredfold, increased the cathode's surface area and improved capacity and performance. Commercialization led to a competitive market and a patent infringement battle between Chiang and Goodenough.

Electrochemistry

The three participants in the electrochemical reactions in a lithium-ion battery are the anode, cathode, and electrolyte.

Both the anode and cathode are materials into which, and from which, lithium can migrate. During *insertion* (or *intercalation*) lithium moves into the electrode. During the reverse process, *extraction* (or *deintercalation*), lithium moves back out. When a lithium-based cell is discharging, the lithium is extracted from the anode and inserted into the cathode. When the cell is charging, the reverse occurs.

Useful work can only be extracted if electrons flow through a closed external circuit. The following equations are in units of moles, making it possible to use the coefficient *x*.

The positive electrode half-reaction (with charging being forwards) is:

$$\mathrm{LiCoO_2} \leftrightarrows \mathrm{Li_{1-\mathit{x}}CoO_2} + x\mathrm{Li^+} + x\mathrm{e^-}$$

The negative electrode half-reaction is:

$$x\mathrm{Li^+} + x\mathrm{e^-} + 6\mathrm{C} \leftrightarrows \mathrm{Li_xC_6}$$

The overall reaction has its limits. Overdischarge supersaturates lithium cobalt oxide, leading to the production of lithium oxide, possibly by the following irreversible reaction:

$$\mathrm{Li^+} + \mathrm{LiCoO_2} \rightarrow \mathrm{Li_2O} + \mathrm{CoO}$$

Overcharge up to 5.2 Volts leads to the synthesis of cobalt(IV) oxide, as evidenced by x-ray diffraction

$$\mathrm{LiCoO_2} \rightarrow \mathrm{Li^+} + \mathrm{CoO_2}$$

In a lithium-ion battery the lithium ions are transported to and from the cathode or anode, with the transition metal, cobalt (Co), in $\mathrm{Li_{\mathit{x}}CoO_2}$ being oxidized from $\mathrm{Co^{3+}}$ to $\mathrm{Co^{4+}}$ during charging, and reduced from $\mathrm{Co^{4+}}$ to $\mathrm{Co^{3+}}$ during discharge.

Positive electrodes

Electrode material	Average potential difference	Specific capacity	Specific energy
$\mathrm{LiCoO_2}$	3.7 V	140 mA·h/g	0.518 kW·h/kg
$\mathrm{LiMn_2O_4}$	4.0 V	100 mA·h/g	0.400 kW·h/kg
$\mathrm{LiNiO_2}$	3.5 V	180 mA·h/g	0.630 kW·h/kg
$\mathrm{LiFePO_4}$	3.3 V	150 mA·h/g	0.495 kW·h/kg
$\mathrm{Li_2FePO_4F}$	3.6 V	115 mA·h/g	0.414 kW·h/kg
$\mathrm{LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2}$	3.6 V	160 mA·h/g	0.576 kW·h/kg
$\mathrm{Li(Li_{\mathit{a}}Ni_{\mathit{x}}Mn_{\mathit{y}}Co_{\mathit{z}})O_2}$	4.2 V	220 mA·h/g	0.920 kW·h/kg

Negative electrodes

Electrode material	Average potential difference	Specific capacity	Specific energy
Graphite (LiC_6)	0.1-0.2 V	372 mA·h/g	0.0372-0.0744 kW·h/kg
Hard Carbon (LiC_6)	? V	? mA·h/g	? kW·h/kg
Titanate ($Li_4Ti_5O_{12}$)	1-2 V	160 mA·h/g	0.16-0.32 kW·h/kg
Si ($Li_{4.4}Si$)	0.5-1 V	4212 mA·h/g	2.106-4.212 kW·h/kg
Ge ($Li_{4.4}Ge$)	0.7-1.2 V	1624 mA·h/g	1.137-1.949 kW·h/kg

Electrolytes

The cell voltages given in the Electrochemistry section are larger than the potential at which aqueous solutions can electrolyze, in addition lithium is highly reactive to water, therefore, nonaqueous or aprotic solutions are used.

Liquid electrolytes in lithium-ion batteries consist of lithium salts, such as $LiPF_6$, $LiBF_4$ or $LiClO_4$ in an organic solvent, such as ethylene carbonate, dimethyl carbonate, and diethyl carbonate. A liquid electrolyte conducts lithium ions, acting as a carrier between the cathode and the anode when a battery passes an electric current through an external circuit. Typical conductivities of liquid electrolyte at room temperature (20 °C (68 °F)) are in the range of 10 mS/cm (1 S/m), increasing by approximately 30–40% at 40 °C (104 °F) and decreasing by a slightly smaller amount at 0 °C (32 °F)

Unfortunately, organic solvents easily decompose on anodes during charging. However, when appropriate organic solvents are used as the electrolyte, the solvent decomposes on initial charging and forms a solid layer called the solid electrolyte interphase (SEI), which is electrically insulating yet provides sufficient ionic conductivity. The interphase prevents decomposition of the electrolyte after the second charge. For example, ethylene carbonate is decomposed at a relatively high voltage, 0.7 V vs. lithium, and forms a dense and stable interface.

A good solution for the interface instability is the application of a new class of composite electrolytes based on PEO (poly(oxyethylene)) developed by Syzdek et al. It can be either solid (high molecular weight) and be applied in dry Li-polymer cells, or liquid (low molecular weight) and be applied in regular Li-ion cells.

Another issue that Li-ion technology is facing is safety. Large scale application of Li cells in Electric Vehicles needs a dramatic decrease in the failure rate. One of the solutions is the novel technology based on reversed-phase composite electrolytes, employing porous ceramic material filled with electrolyte.

Advantages and disadvantages

Note that both advantages and disadvantages depend on the materials and design that make up the battery. This summary reflects older designs that use carbon anode, metal oxide cathodes, and lithium salt in an organic solvent for the electrolyte.

Advantages

A lithium-ion battery from a laptop computer

- Wide variety of shapes and sizes efficiently fitting the devices they power.
- Much lighter than other energy-equivalent secondary batteries.
- High open circuit voltage in comparison to aqueous batteries (such as lead acid, nickel-metal hydride and nickel-cadmium). This is beneficial because it increases the amount of power that can be transferred at a lower current.
- No memory effect.
- Self-discharge rate of approximately 5-10% per month, compared to over 30% per month in common nickel metal hydride batteries, approximately 1.25% per month for Low Self-Discharge NiMH batteries and 10% per month in nickel-cadmium batteries. According to one manufacturer, lithium-ion cells (and, accordingly, "dumb" lithium-ion batteries) do not have any self-discharge in the usual meaning of this word. What looks like a self-discharge in these batteries is a permanent loss of capacity. On the other hand, "smart" lithium-ion batteries do self-discharge, due to the drain of the built-in voltage monitoring circuit.
- Components are environmentally safe as there is no free lithium metal.

Disadvantages

Cell life

- Charging forms deposits inside the electrolyte that inhibit ion transport. Over time, the cell's capacity diminishes. The increase in internal resistance reduces the cell's ability to deliver current. This problem is more pronounced in high-current applications. The decrease means that older batteries do not charge as much as new ones (charging time required decreases proportionally).
- High charge levels and elevated temperatures (whether from charging or ambient air) hasten capacity loss. Charging heat is caused by the carbon anode (typically replaced with lithium titanate which drastically reduces damage from charging, including expansion and other factors).
- A Standard (Cobalt) Li-Ion cell that is full most of the time at 25 °C (77 °F) irreversibly loses approximately 20% capacity per year. Poor ventilation may increase temperatures, further shortening battery life. Loss rates vary by temperature: 6% loss at 0 °C (32 °F), 20% at 25 °C (77 °F), and 35% at 40 °C (104 °F). When stored at 40%–60% charge level, the capacity loss is reduced to 2%, 4%, and 15%, respectively. In contrast, the calendar life of LiFePO4 cells is not affected by being kept at a high state of charge.

Internal resistance

- The internal resistance of standard (Cobalt) lithium-ion batteries is high compared to both other rechargeable chemistries such as nickel-metal hydride and nickel-cadmium, and LiFePO4 and lithium-polymer cells. Internal resistance increases with both cycling and age. Rising internal resistance causes the voltage at the terminals to drop under load, which reduces the maximum current draw. Eventually increasing resistance means that the battery can no longer operate for an adequate period.

- To power larger devices, such as electric cars, connecting many small batteries in a parallel circuit is more effective and efficient than connecting a single large battery.

Safety requirements

If overheated or overcharged Li-ion batteries may suffer thermal runaway and cell rupture. In extreme cases this can lead to combustion. Deep discharge may short-circuit the cell, in which case recharging would be unsafe. To reduce these risks, Lithium-ion battery packs contain fail-safe circuity that shuts down the battery when its voltage is outside the safe range of 3–4.2 V per cell. When stored for long periods the small current draw of the protection circuitry itself may drain the battery below its shut down voltage; normal chargers are then ineffective. Many types of lithium-ion cell cannot be charged safely below 0°C.

Other safety features are required in each cell:

- shut-down separator (for overtemperature)
- tear-away tab (for internal pressure)
- vent (pressure relief)
- thermal interrupt (overcurrent/overcharging)

These devices occupy useful space inside the cells, add additional points of failure and irreversibly disable the cell when activated. They are required because the anode produces heat during use, while the cathode may produce oxygen. These devices and improved electrode designs reduce/eliminate the risk of fire or explosion.

These safety features increase costs compared to nickel metal hydride batteries, which require only a hydrogen/oxygen recombination device (preventing damage due to mild overcharging) and a back-up pressure valve.

Specifications and design

- Specific energy density: 150 to 250 W·h/kg (540 to 900 kJ/kg)
- Volumetric energy density: 250 to 620 W·h/l (900 to 1900 J/cm^3)
- Specific power density: 300 to 1500 W/kg (@ 20 seconds and 285 W·h/l)

Because lithium-ion batteries can have a variety of cathode and anode materials, the energy density and voltage vary accordingly.

Lithium-ion batteries with a lithium iron phosphate cathode and graphite anode have a nominal open-circuit voltage of 3.2 V and a typical charging voltage of 3.6 V. Lithium nickel manganese cobalt (NMC) oxide cathode with graphite anodes have a 3.7 V nominal voltage with a 4.2 V max charge. The charging procedure is performed at constant voltage with current-limiting circuitry (i.e., charging with constant current until a voltage of 4.2 V is reached in the cell and continuing with a constant voltage applied until the current drops close to zero). Typically, the charge is terminated at 3% of the initial charge current. In the past, lithium-ion batteries could not be fast-charged and needed at least two hours to fully charge. Current-generation cells can be fully charged in 45 minutes or less. Some lithium-ion varieties can reach 90% in as little as 10 minutes.

Charging procedure

Stage 1: Apply charging current until the voltage limit per cell is reached.

Stage 2: Apply maximum voltage per cell limit until the current declines below 3% of rated charge current.

Stage 3: Periodically apply a top-off charge about once per 500 hours.

The charge time is about three to five hours, depending on the charger used. Generally, cell phone batteries can be charged at 1*C* and laptop-types at 0.8*C*, where *C* is the current that would discharge the battery in one hour. Charging is usually stopped when the current goes below 0.03*C* but it can be left indefinitely depending on desired charging time. Some fast chargers skip stage 2 and claim the battery is ready at 70% charge. Laptop battery chargers sometimes gamble, and try to charge up to 4.35 V then disconnects the battery. This helps to compensate for the battery's internal resistance and charges up to 100% in short time.

Top-off charging is recommended when voltage goes below 4.05 V/cell.

Typically, lithium-ion cells are charged with 4.2 ± 0.05 V/cell, except for military long-life cells where 3.92 V is used for extending battery life. Most protection circuits cut off if either 4.3 V or 90 °C is reached. If the voltage drops below 2.50 V per cell, the battery protection circuit may also render it unchargeable with regular charging equipment. Most battery protection circuits stop at 2.7–3.0 V per cell.

For safety reasons it is recommended the battery be kept at the manufacturer's stated voltage and current ratings during both charge and discharge cycles.

Variations in materials and construction

The increasing demand for batteries has led vendors and academics to focus on improving the power density, operating temperature, safety, durability, charging time, output power, and cost of LIB solutions.

LIB types

Area	Technology	Researchers	Target application	Date	Benefit
Cathode	Manganese spinel (LMO)	Lucky Goldstar Chemical, NEC, Samsung, Hitachi, Nissan/AESC	Hybrid electric vehicle, cell phone, laptop	1996	durability, cost
	Lithium iron phosphate	University of Texas/Hydro-Québec,/Phostech Lithium Inc., Valence Technology, A123Systems/MIT	Segway Personal Transporter, power tools, aviation products, automotive hybrid systems, PHEV conversions	1996	moderate density (2 A·h outputs 70 amperes) operating temperature >60 °C (140 °F)
	Lithium nickel manganese cobalt (NMC)	Imara Corporation, Nissan Motor		2008	density, output, safety

	LMO/NMC	Sony, Sanyo			power, safety (although limited durability)
	Lithium iron fluorophosphate	University of Waterloo		2007	durability, cost (replace Li with Na or Na/Li)
	Lithium air	University of Dayton Research Institute	automotive	2009	density, safety
	5% Vanadium-doped Lithium iron phosphate olivine	Binghamton University		2008	output
Anode	Lithium-titanate battery (LT)	Altairnano	automotive (Phoenix Motorcars), electrical grid (PJM Interconnection Regional Transmission Organization control area, United States Department of Defense), bus (Proterra)	2008	output, charging time, durability (20 years, 9,000 cycles), safety, operating temperature (-50–70 °C (-58–158 °F)
	Lithium vanadium oxide	Samsung/Subaru.	automotive	2007	density (745Wh/l)
	Cobalt-oxide nano wires from genetically modified virus	MIT		2006	density, thickness
	Iron-phosphate nano wires from genetically modified virus	MIT		2009	density, thickness
	Silicon/titanium dioxide composite nano wires from genetically modified	University of Maryland	explosive detection sensors, biomimetic structures, water-repellent	2010	density, low charge time

	tobacco virus		surfaces, micro/nano scale heat pipes		
	Porous silicon/carbon nanocomposite spheres	Georgia Institute of Technology	portable electronics, electrical vehicles, electrical grid	2010	high stability, high capacity, low charge time
	nano-sized wires on stainless steel	Stanford University	wireless sensors networks,	2007	density (shift from anode- to cathode-limited), durability (wire cracking)
	Metal hydrides	Laboratoire de Réactivité et de Chimie des Solides, General Motors		2008	density (1480 mA·h/g)
Electrode	LT/LMO	Ener1/Delphi,		2006	durability, safety (limited density)
	Nanostructure	Université Paul Sabatier/Université Picardie Jules Verne		2006	density

Usage guidelines

Prolonging battery pack life

- Depletion below the low-voltage threshold (2.4 to 2.8 V/cell, depending on chemistry) results in a dead battery which does not even appear to charge because the protection circuit (a type of electronic fuse) disables it. This can be reversed in many modern batteries, especially single-cell ones, by applying a charging voltage for long enough to make the cell voltage rise above the low-voltage threshold; however this behaviour varies by manufacturer.
- Lithium-ion batteries should be kept cool; they may be stored in a refrigerator.
- The rate of degradation of Lithium-ion batteries is strongly temperature-dependent; they degrade much faster if stored or used at higher temperatures.

Multicell devices

Li-Ion batteries require a Battery Management System to prevent operation outside each cell's Safe Operating Area (over-charge, under-charge, safe temperature range) and to balance cells to eliminate SOC mismatches, significantly improving battery efficiency and increasing overall capacity. As the number of cells and load currents increase, the potential for mismatch also increases. There are two kinds of mismatch in the pack: state-of-charge (SOC) and capacity/energy ("C/E") mismatch. Though SOC is more common, each problem limits pack capacity (mA·h) to the capacity of the weakest cell.

Safety

Lithium-ion batteries can rupture, ignite, or explode when exposed to high temperature. Short-circuiting a battery will cause the cell to overheat and possibly to catch fire. Adjacent cells may also then heat up and fail, in some cases, causing the entire battery to ignite or rupture. In the event of a fire, the device may emit dense irritating smoke.

Replacing the lithium cobalt oxide cathode material in lithium-ion batteries with a lithium metal phosphate such as lithium iron phosphate, improves cycle counts, shelf life and safety, but lowers capacity. Currently, these 'safer' lithium-ion batteries are mainly used in electric cars and other large-capacity battery applications, where safety issues are critical.

Lithium-ion batteries normally contain safety devices to protect the cells from disturbance. However, contaminants inside the cells can defeat these safety devices.

Recalls

In March 2007, Lenovo recalled approximately 205,000 batteries at risk of explosion. In August 2007, Nokia recalled over 46 million batteries at risk of overheating and exploding. One such incident occurred in the Philippines involving an Nokia N91, which uses the BL-5C battery.

In December 2006, Dell recalled approximately 22,000 laptop batteries from the U.S. market. Approximately 10 million Sony batteries used in Dell, Sony, Apple, Lenovo/IBM, Panasonic, Toshiba, Hitachi, Fujitsu and Sharp laptops were recalled in 2006. The batteries were found to be susceptible to internal contamination by metal particles. Under some circumstances, these particles could pierce the separator, causing a short-circuit.

In October 2004, Kyocera Wireless recalled approximately 1 million mobile phone batteries to identify counterfeits.

Transport restrictions

In January 2008, the United States Department of Transportation ruled that passengers on board commercial aircraft could carry lithium batteries in their checked baggage if the batteries are installed in a device. Types of batteries affected by this rule are those containing lithium, including Li-ion, lithium polymer, and lithium cobalt oxide chemistries. Lithium-ion batteries containing more than 25 grams (0.88 oz) equivalent lithium content (ELC) are exempt from the rule and are forbidden in air travel. This restriction greatly reduces the chances of the batteries short-circuiting and causing a fire.

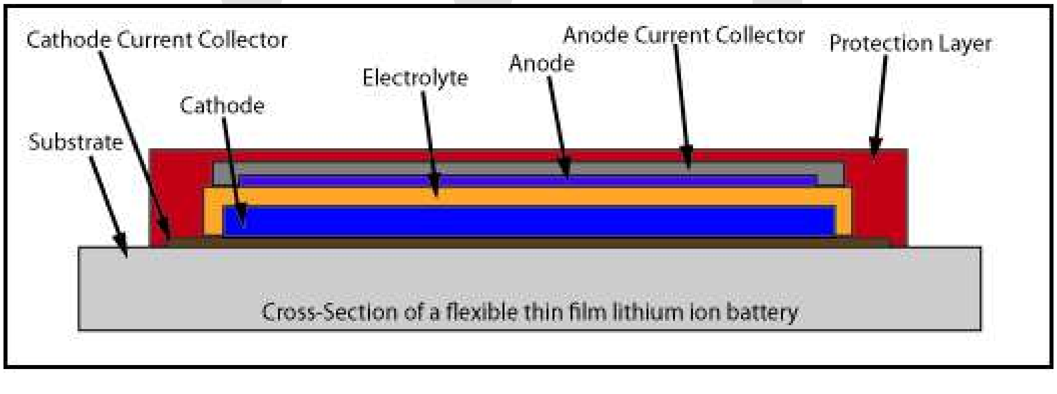
Additionally, a limited number of replacement batteries may be transported in carry-on luggage. Such batteries must be sealed in their original protective packaging or in individual containers or plastic bags.

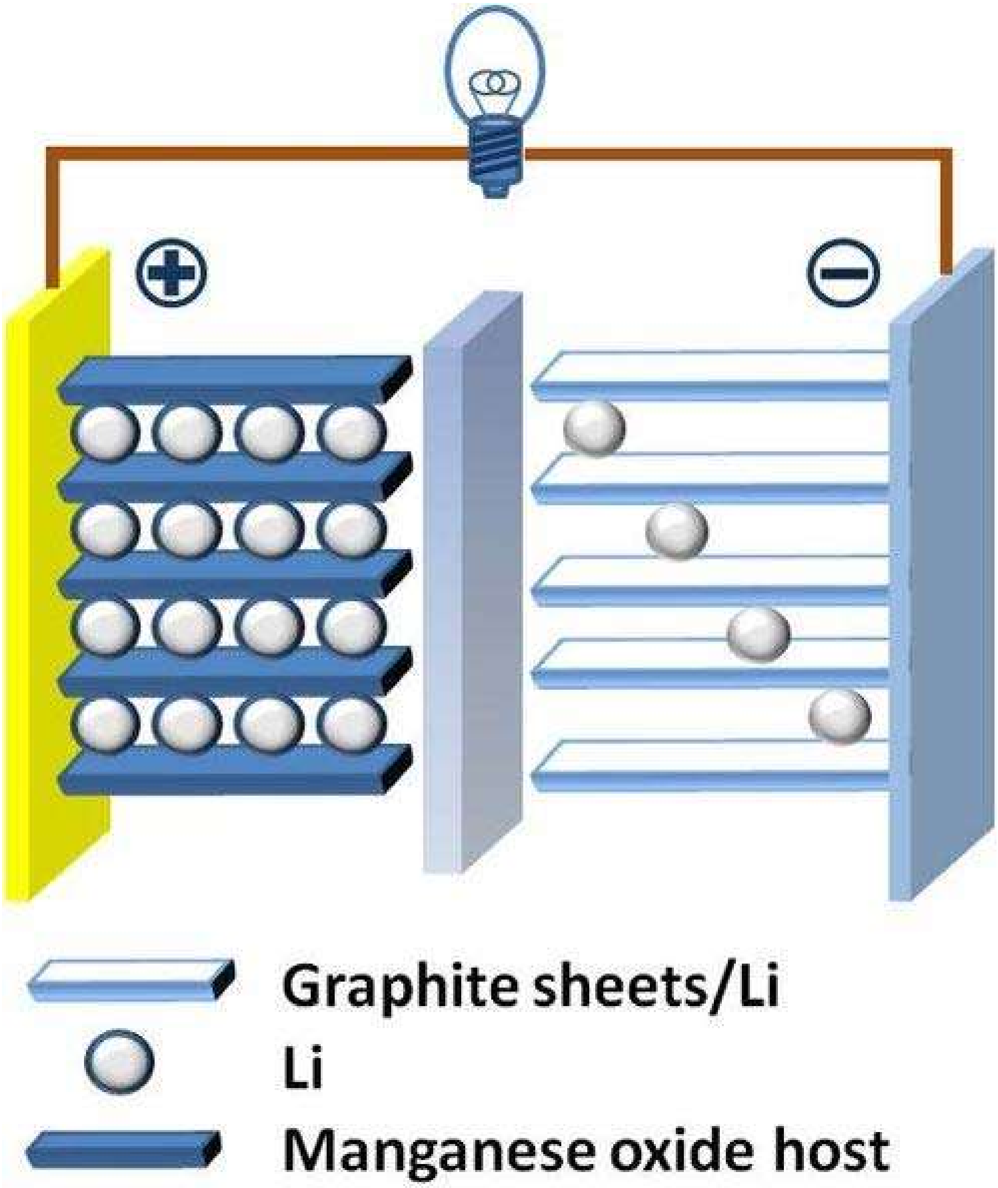
Some postal administrations restricted air shipping (including EMS) of lithium and lithium-ion batteries, and products containing these (e.g. laptops, cell phones etc.). Among these countries and regions are Hong Kong, Australia and Japan.

Chapter- 3

Thin Film Rechargeable Lithium Battery

Thin film lithium ion batteries are similar to lithium-ion batteries, but they are composed of thin materials, some only nanometers or micrometers thick, which allow for the finished battery to be just millimeters thick. They have been developed and advanced primarily within the last decade. These batteries consist of a substrate, electrolyte, current collector, anode, cathode, and a charge separator. There has been much research into the determination of the most effective components for this type of battery. It has been shown recently that even ordinary printer paper can be used as a charge separator and a substrate. . These thin film batteries are an improvement on the common secondary, or rechargeable, lithium ion batteries in many ways. These batteries exhibit the same voltage and current as their bulky counterparts, but their thinner dimensions allow for greater applications such as making thinner electronic devices, like cell phones and laptops and even implantable medical devices and reducing the weight of common devices that are run on battery power because of the batteries' high energy density. These batteries can be formed into any shape and they can be stacked, to be used in parallel, thus even further reducing the space needed for a battery.





Lithium Ion Battery Cell

Background

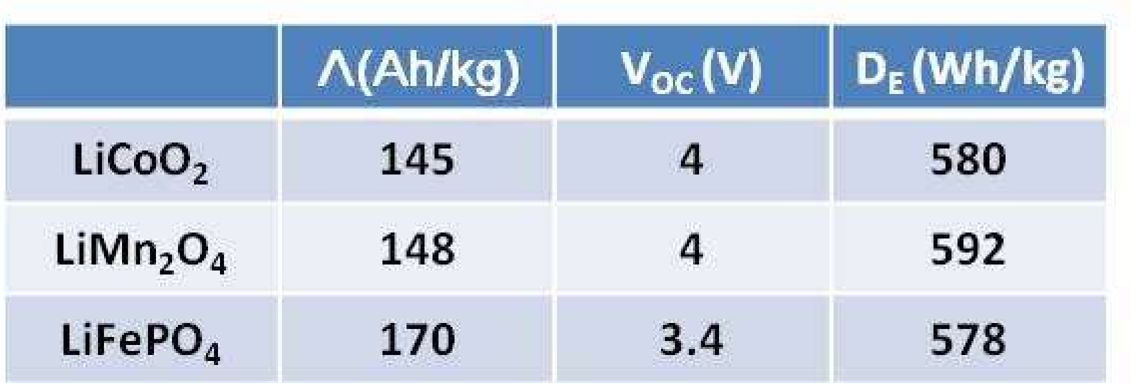
Lithium-ion batteries are a newer battery technology that is preferable due to their ability to be recharged. Also they have high energy density and last longer than many similar battery technologies. In the battery cell lithium ions flow through the electrolyte from the anode to the cathode while the battery is being discharged. Upon recharging the battery the lithium ions move back to the anode. This Li-ion battery design is effective for large devises. However, as a more mobile, technology driven society we rely heavily on portable electronics, which require thin batteries for power. Research into thin film batteries has developed over the recent years to accommodate for this demand.

Components of Thin Film Battery

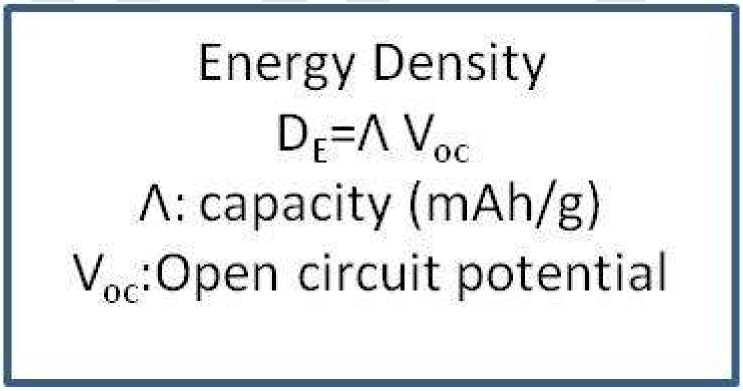
Cathode materials

Cathode materials in thin film lithium ion batteries are the same of what is seen in classical lithium ion batteries. They are normally metal oxides that are deposited as a film by various methods.

Metal oxide materials are shown below as well as their relative specific capacities (Λ), open circuit voltages (V_{oc}), and energy densities (D_E).



	Λ(Ah/kg)	V_{OC} (V)	D_E (Wh/kg)
$LiCoO_2$	145	4	580
$LiMn_2O_4$	148	4	592
$LiFePO_4$	170	3.4	578



Energy Density

$D_E = \Lambda V_{oc}$

Λ: capacity (mAh/g)

V_{oc}:Open circuit potential

Deposition methods for cathode materials

There are various methods being used in order to deposit a thin film cathode material onto the current collector.

Pulsed Laser Deposition (PLD)

In Pulsed Laser Deposition materials are fabricated with varying parameters such as laser energy and fluence, substrate temperature, background pressure, and target-substrate distance.

Magnetron Sputtering

In Magnetron Sputtering the substrate is cooled for deposition.

Chemical Vapor Deposition (CVD)

In Chemical Vapor Deposition volatile precursor materials is deposited onto a substrate material.

Sol-Gel Processing

Sol-gel processing allows for homogeneous mixing of precursor materials at the atomic level.

Electrolyte

The greatest difference between classical lithium ion batteries and thin, flexible, lithium ion batteries is in the electrolyte material used. Progress in lithium ion batteries relies as much on improvements in the electrolyte as it does in the electrode materials, as the electrolyte plays a major role in safe battery operation. The concept of thin film lithium ion batteries was increasingly motivated by manufacturing advantages presented by the polymer technology for their use as electrolytes. Lipon, lithium phosphorus oxynitride, is an amorphous polymer material used as an electrolyte material in thin film flexible batteries. Layers of Lipon are deposited over the cathode material at ambient temperatures by RF magnetron sputtering. This forms the solid electrolyte used for ion conduction between anode and cathode. Solid polymer electrolytes offer several advantages in comparison to a classical liquid lithium ion battery. Rather than having separate components of electrolyte, binder, and separator, these solid electrolytes can act as all three. This increases the overall energy density of the assembled battery because the constituents of the entire cell are more tightly packed.

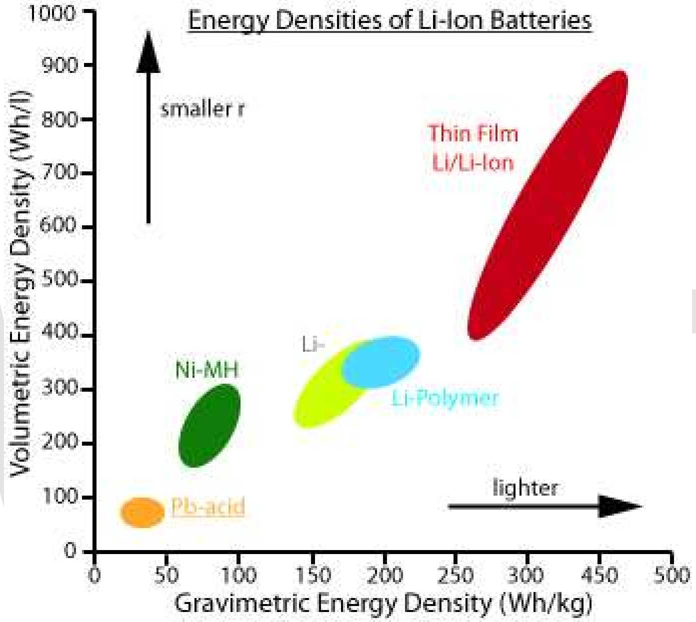
Separator Material

Separator materials in lithium ion batteries must have the ability to transport ions through their porous membranes while maintaining a physical separation between the anode and cathode materials in order to prevent short-circuiting. In a thin film based system, the electrolyte is normally a solid electrolyte, capable of conforming to the shape of the battery. Typically this material is a polymer based material and as mentioned above, this polymer commonly acts as both the separator and electrolyte. Since thin film batteries are made of all solid materials, this affords to use of simpler separator materials in these systems such as Xerox paper rather than in liquid based Li-ion batteries.

Current Collector

Current collectors in thin film batteries must be flexible, have high surface area, and cost-effective. Silver nanowires with improved surface area and loading weight have been shown to work as a current collector in these battery systems, but still are not as cost-effective as desired. Extending graphite technology to lithium ion batteries, solution processed carbon nanotubes (CNT) films are being looked into for use as both the current collector and anode material. CNTs have the ability to intercalate lithium and maintain high operating voltages, all with low mass loading and flexibility.

Advantages and Challenges



Thin film lithium ion batteries offer improved performance by having a higher average output voltage, lighter weights thus higher energy density, and longer cycling life than typical rechargeable batteries. In the thin film lithium ion battery, both electrodes are capable of reversible lithium insertion, thus forming a Li-ion transfer cell. Li-ion transfer cells are the most promising systems for satisfying the demand of high specific energy and high power. In order to construct a thin film battery it is necessary to fabricate all the battery components, as an anode, a solid electrolyte, a cathode and current leads into multi-layered thin films by suitable technologies.

In a thin film based system, the electrolyte is normally a solid electrolyte, capable of conforming to the shape of the battery. This is in contrast to classical lithium ion batteries, which normally have liquid electrolyte material. Liquid electrolytes can be challenging to utilized if they are not compatible with the separator. Also liquid electrolytes in general call for an increase in the overall volume of the battery, which is not ideal for designing a system that has high energy density. Additionally, in a thin film flexible Li-ion battery, the electrolyte, which is normally polymer-based, can act as the electrolyte, separator, and binder material. This provides the ability to have flexible systems since the issue of electrolyte leakage is circumvented. Finally, solid systems can be packed together tightly which affords an increase in energy density when compared to classical lithium ion batteries.

Separator materials in lithium ion batteries must have the ability to transport ions through their porous membranes while maintaining a physical separation between the anode and cathode materials in order to prevent short-circuiting. Furthermore, the separator must be resistant to degradation during the battery's operation. In a thin film Li-ion battery, the separator must be a thin and flexible solid. Typically today, this material is a polymer-based material. Since thin film batteries are made of all solid materials, allows one to use simpler separator materials in these systems such as Xerox paper rather than in liquid based Li-ion batteries.

Scientific Development

Development of thin solid state batteries allows for roll to roll type production of batteries which would decrease production costs. Solid-state batteries can also afford increased energy density due to decrease in overall device weight. Where as the flexible nature allows for novel battery design and incorporation into electronics. Development is still required in cathode materials which will resist decreased capacity due to cycling.

Prior Technology	Replacement Technology	Result
Solution based electrolyte	Solid state electrolyte	Increased safety and cycle life
Polymer separators	Paper separator	Decreased cost increased increased rate of ion conduction
Metalic current collectors	Carbon nanotube current collectors	Decreased device weight, increased energy density
Graphite anode	Carbon nanotube anode	Decreased device complexity

Applications

The advancements made to the thin film lithium ion battery have allowed for many potential applications. The majority of these applications are aimed at improving the currently available consumer and medical products. Thin film lithium ion batteries can be used to make thinner portable electronics, because the thickness of the battery required to operate the device can be reduced greatly. These batteries have the ability to be an integral part of implantable medical devices, such as defibrillators and neural stimulators, "smart" cards , radio frequency identification, or RFID, tags and wireless sensors. They can also serve as a way to store energy collected from solar cells or other harvesting devices . Each of these applications is possible because of the flexibility in the size and shape of the batteries. The size of these devices doesn't have to revolve around the size of the space needed for the battery anymore. The thin film batteries can be attached to the inside of the casing or in some other convenient way. The opportunities in which to use this type of batteries are endless.

Solar Cell Storage Devices

The thin film lithium ion battery can serve as a storage device for the energy collected from a solar cell. These batteries can be made to have a low self discharge rate, which means that these batteries can be stored for long periods of time without a major loss of the energy that was used to charge it. These fully charged batteries could then be used to power some or all of the other potential applications listed below.

Smart Cards

Smart cards are basically the same size as a credit card, but they contain a microchip that can be used to access information, give authorization, or process an application. These cards can go through harsh production conditions, with temperatures in the range of 130 to 150°C, in order to complete the high temperature, high pressure lamination processes . These conditions can cause other batteries to fail because of degassing or degradation of organic components within the battery. Thin film lithium ion batteries have been shown to withstand temperatures of -40 to 150°C . This use of thin film lithium ion batteries is hopeful for other extreme temperature applications.

RFID tags

Radio Frequency Identification (RFID) tags can be used in many different applications. These tags can be used in packaging, inventory control, used to verify authenticity and even allow or deny access to something. These ID tags can even have other integrated sensors to allow for the physical environment to be monitored, such as temperature or shock during travel or shipping. Also, the distance required to read the information in the tag depends on the strength of the battery. The farther away you want to be able to read the information, the stronger the output will have to be and thus the greater the power supply to accomplish this output. As these tags get more and more complex, the battery requirements will need to keep up. Thin film lithium ion batteries have shown that they can fit into the designs of the tags because of the flexibility of the battery in size and shape and are sufficiently powerful enough to accomplish the goals of the tag. Low cost production methods, like roll to roll lamination, of these batteries may even allow for this kind of RFID technology to be implemented in disposable applications.

Implantable Medical Devices

Thin films of $LiCoO_2$ have been synthesized in which the strongest x ray reflection is either weak or missing, indicating a high degree of preferred orientation. Thin film solid state batteries with these textured cathode films can deliver practical capacities at high current densities. For example, for one of the cells 70% of the maximum capacity between 4.2 V and 3 V (approximately 0.2 mAh/cm^2) was delivered at a current of 2 mA/cm^2. When cycled at rates of 0.1 mA/cm^2, the capacity loss was 0.001%/cycle or less. The reliability and performance of Li $LiCoO_2$ thin-film batteries make them attractive for application in implantable devices such as neural stimulators, pacemakers, and defibrillators.

Implantable medical devices require batteries that can deliver a steady, reliable power source for as long as possible. These applications call for a battery that has a low self-discharge rate, for when it's not in use, and a high power rate, for when it needs to be used, especially in the case of an implantable defibrillator. Also, users of the product will want a battery that can go through many cycles, so these devices won't have to be replaced or serviced often. Thin film lithium ion batteries have the ability to meet these requirements. The advancement from a liquid to a solid electrolyte has allowed these batteries to take almost any shape without the worry of leaking, and it has been shown that certain types of thin film rechargeable lithium batteries can last for around 50,000 cycles . Another advantage to these thin film batteries is that they can be stacked and used in parallel to give a larger voltage equal to the sum of the individual battery voltages. This fact can be used in reducing the "footprint" of the battery, or the size of the space needed for the battery, in the design of a device.

Wireless Sensors

Wireless sensors need to be in use for the duration of their application, whether that may be in package shipping or in the detection of some unwanted compound, or controlling inventory in a warehouse. If the wireless sensor can't transmit its data due to low or no battery power, the consequences could potentially be severe based on the application. Also, the wireless sensor must be adaptable to each application. Therefore the battery must be able to fit within the designed sensor. This means that the desired battery for these devices must be long-lasting, size specific, low cost, if they are going to be used in disposable technologies, and must meet the requirements of the data collection and transmission processes. Once again, thin film lithium ion batteries have shown the ability to meet all of these requirements.

Thinner Electronics

The reduction of the battery footprint can be the foothold to thinner and lighter electronics based on these thin film flexible lithium ion batteries. Since the batteries have such a high energy density in such a thin film, a thin film battery can replace a thicker, heavier, less energy dense battery in order to accomplish the same task. Today's society is fast-moving, technology driven and ever interconnecting. These thinner, lighter electronic devices can help shape the future of the way we use and think about technology. With other technological advancements being made, the possibility of even smaller, thinner and lighter electronic devices than those currently found today is not as far away as was once thought. These developments may be the step that leads to some part of the technology seen in futuristic television shows and movies, like Avatar, for example.

Chapter- 4

Nanoarchitectures for Lithium-Ion Batteries

Efforts in lithium-ion batteries research have been to improve two distinct characteristics: capacity and rate. The capacity of the battery to store energy can be improved through the ability to insert/extract more lithium ions from the electrode. Electrodes capacities are compared through three different measures, based upon capacity per weight, gravimetric capacity, capacity per volume or volumetric capacity, and area normalized specific capacity, areal capacity. Also efforts have focused on improving the rate of discharge, which is based upon the mass and charge transport, electronic and ionic conductivity, and electron-transfer kinetic; easy transport through shorter distance and greater surface area improve the rate performance of the battery.

Anodes of carbon were chosen because of the ability of lithium to intercalate without excess volumetric expansion. High volumetric expansion causes degradation of the battery and a large amount of irreversibility rendering the battery useless for any application with a need for rechargeable energy storage. However the small amount of lithium-ion intercalation into carbonaceous electrodes limits the ultimate capacity of batteries, carbon based anodes have a gravimetric capacity of 372 mAh/g for LiC_6

Silicon has been considered as electrode materials because of its ability to have larger amounts of lithium-ion intercalation; the capacity of these batteries is approximately ten times greater than carbon. Considering that that atomic radius of Si is 1.46 angstroms and the atomic radius of Li is 2.05 angstroms, the formation of $Li_{3.75}Si$ during intercalation of the lithium will cause a significant volumetric expansion of the host material . One approach to solve this problem was to create composite anodes of silicon with materials that are less reactive with lithium to limit destruction of the electrode; however, the inclusion of other materials limits the performance of the material . By reducing the size to the nanoscale numerous advantages are gained. At the nanoscale improved cycle life has been achieved, minimization of the size of silicon particles within a film of conductive binder to create films of active components that are below the critical flaw size minimizes crack propagation and failure . A reduction in transport lengths also improves efficiency by reducing ohmic losses. The high surface area at the nanoscale improves the charge and discharge rate of the battery; this is due to both an increase in the electrochemically active area and a reduction in ionic and electronic transportation lengths. However, the increase in surface area to volume ratio at the nanoscale also leads to increased side reactions of the electrode with the electrolyte causing higher self-discharge, poor cycling lifetime, and lower calendar life. Recent work to improve the performance has been focused on determining materials that are electrochemically active within the range where electrolyte decomposition or side reaction of the electrolyte with the electrode do not occur .

Nanostructured Architectures

For all the advancement of batteries within the past couple decades, a significant majority of battery designs are two –dimensional and rely on layer-by-layer construction . Recent research has taken the nanodes into fully three dimensional structures. Through novel architectures the nanoscale benefits are maintained while the battery is scaled up. This allows for significant improvements in battery capacity; a significant increase in areal capacity occurs between a 2d thick film electrode and a 3d array electrode .

Three dimensional Thin–Films

Solid state batteries are the most similar geometry to traditional thin-film batteries; three dimensional thin-films use the third dimension to increase the electrochemically active area in the battery. Since thin film two dimensional batteries are restricted to between 2-5 microns the areal capacity of the device is significantly below that of three dimensional geometries.

One approach achieves this through a perforated substrate. The perforations in the sample were created through inductive coupled plasma etching on silicon. Another approached used highly anisotropic etching of a silicon substrate through electrochemical or reactive ion etching to create deep trenches. The requisite layers, an anode, separator, and cathode, for a battery were then added by low-pressure chemical vapor deposition. In this geometry the battery consists of a thin active silicon layer separated from a thin cathodic layer by a solid-state electrolyte. Through this approach the electrochemically active area of the battery is significantly increased, and thus thin-film of silicon nanoparticles (50 nm) that remains below the critical size for crack propagation can provide enhanced capacity and reversibility

Interdigitated Electrodes

Another three dimensional battery architecture is a periodic grouping of anodic and cathodic poles. For this design the power and energy density of the battery is maximized by minimizing the separation between the anodes and cathodes; an innate non-uniform current density occurs, however, and will cause lower cell efficiencies, poorer stability, and non-uniform heating within the cell. Relative to a two dimensional battery the length scale that over which transport must occur is decreased by 350% which not only improves kinetics but also reduces ohmic loses. Furthermore optimization of L can lead to a significant improvement in areal capacity; an L on the size scale of 500 microns results in a 350% increase in capacity over a comparable two dimensional battery. However, ohmic loses will increase as L increase, eventually offsetting the enhancement achieved through increasing L. For this geometry, four main designs were originally proposed: rows of anodes and cathodes, alternating anodes and cathodes, hexagonal packing of 1:2 anodes:cathodes, and alternating anodic and cathodic triangular poles where the nearest neighbors in the row are rotated 180 degrees. The design using rows has a large non-uniform current distribution. The alternating design exhibits better uniformity than the row design since there are a high number of electrodes of opposite polarity. For systems with an anode or cathode that is sensitive to non-uniform current density non-equal numbers of cathodes and anodes can be used; the 2:1 hexagonal design allows for a uniform current density at the anode but has a severely non-uniform current distribution at the cathode. The performance of the battery can be increased through changing the shape of the poles; the triangular design improves cell capacity and power by sacrificing current uniformity. A similar system uses interdigitated plates instead of poles.

Concentric Electrodes

The concentric cylinder design is a similar architecture to the interdigitated poles. Instead of discrete anodes and cathodes poles, the anodes or the cathode is kept as a pole which is coated by electrolyte. The other electrode serves as the continuous phase in which the anode/cathode resides. The main advantage of this system is that the amount of electrolyte is reduced, and thus a higher energy density than for the interdigitated system is achieved. This design maintains short transport distance like the interdigitated system and thus has a similar benefit to charge and mass transport while minimizing ohmic loses.

Inverse Opal

A version of the concentric cylinder has been achieved through the packing of particles or close-packed polymer to create a three-dimensionally ordered macroporous (3DOM) carbon anode. In practice this system is fabricated by using colloidal crystal templating, electrochemical thin-film growth, and soft sol–gel chemistry. 3DOM materials have a unique structure of nanometer thick walls that surround interconnected and closed-packed sub-micrometer voids. When the 3DOM structure is coated with a thin polymer layer and then filled with second conducting phase, a lithium-ion battery can be formed. This method is advantageous because it leads to a lithium-ion battery with short transport lengths, high ionic conductivity, reasonable electrical conductivity, and removes the need for additives that do not contribute to the electrochemical performance of the battery. Performance of these devices can be improved through the coating of the sample with different materials. Coatings on the inverse opal structure can be used to improve the performance of the battery; the system has been coated with tin oxide nanoparticles to enhance the initial capacity . Batteries created by this method rely on the infiltration of the network formed by the 3DOM structure to produce uniform coatings.

Nanowires and Nanotubes

Nanowire and nanotubes have been integrated with numerous components of lithium-ion batteries. The reason for this interest in nanotubes and nanowires is because of the short transport lengths at the nanoscale, resistance to degradation, and ability to store lithium ions. For CNTs, lithium-ions can be stored on the exterior surface, in the interstitial sites between the nanotubes, and on the interior of the nanotube .

Numerous approaches have incorporated nanowires into lithium-ion batteries. The nanowires have been incorporated into the matrix with the anode and the cathode to create an anode / cathode with a built in conductive charge collector as well as enhancing capacity. The nanowires were incorporated into the anode / cathode through a solution based method that allows the active material to be printed on a substrate. The hope is that this architecture will allow for portable, lightweight, and disposable energy storage . Another approach uses a CNT-cellulose composite to form a lithium-ion battery. CNTs were grown on a silicon substrate by thermal-chemical vapor deposition and then embedded in cellulose. Finally in order to create the battery a lithium electrode is added on top the cellulose across from the CNTs. The result is the creation of a flexible lithium-ion battery. Recently Si nanowires have been fabricated on a steel substrate by a vapor-liquid solid growth method. These nanowires exhibited close to the theoretical value for silicon and showed only minimal fading after a 20% drop after the first cycle. This performance is attributed to the facile strain relaxation that allows for accommodations of large strains while maintaining good contact with the current collector and efficient 1d electron transport along the nanowire .

Aperoidic Electrodes

Every design so far has resulted in a periodic structure; however, as discussed earlier a periodic structure leads to non-uniform current densities which lower efficiency and decreases stability. The aperoidic structure is typically made of either aerogels or ambigels that form a porous aperiodic sponge. Aerogels and ambigels are formed from wet gels; aerogels are formed when wet gels are dried such that no capillary forces are established while ambigels are wet gels dried under conditions that minimize capillary forces . Aerogels and amigels are unique in that 75-99% of the material is ‘open’ but interpenetrated by a solid which is on the order of 10 nm resulting in pores on the order of 10 to 100 nm. Furthermore the solid is covalently networked and therefore is resistant to agglomeration and sintering. Beyond aperiodicity, the reason these structures are used in lithium-ion batteries is because the porous structure allows for rapid diffusion of material throughout the material, and the porous structure provides a high surface area for reactions. The fabrication of these batteries are through a coating the ambigel with a polymer electrolyte and then filling of the void space with RuO_2 colloids that act as an anode.

Conformal Coating of Nanoscale Electrodes

Nanoscale architectures for lithium-ion batteries are still mostly in the development phase. Very few of the batteries studied were more than half-cell experiments; usually the experiment only tests the anode or cathode. As geometries become more complex the need to develop non-line-of-sight methods to in-fill the complex geometries with materials that will act as electrolyte and oppositely charged electrodes becomes essential. These batteries can also be coated with various materials to improve their electrochemical performance and stability. However, chemical and physical heterogeneity in the samples cause molecular level control to still be a significant challenge, especially since the electrochemistry by which energy storage is not defect-tolerant .

Layer-by-Layer (LbL)

LbL is used to conformally coat within the 3d nanoarchitecture; through electrostatically binding a charged polymer to an oppositely charged surface the surface is coated with polymer. Repeated steps of oppositely charged polymer build up a well-controlled thick layer of polymer on the surface. Polyelectrolyte films and ultrathin, less than 5 nm, of electroactive polymers have been deposited on the have been deposited on planar substrates using this method. However, problems exist with the deposition of polymers in structures of complex geometries, e.g. pores, on the size scale of 50-300 nm that can result in defective coatings. A solution to this problem is to use self limiting approaches .

Atomic layer deposition (ALD)

Another approach to coating is ALD which coats the substrate layer-by-layer with atomic precision. The precision is due to reactions being confined to the surface containing an active chemical moiety that reacts with precursor; this limits the growth to one monolayer. This self-limiting growth is essential for fully coating the electrode since the deposition of the polymer does not inhibit the mobility of other polymeric units to non-coated sites. Thicker samples can be produced by cycling gases in a similar manner to alternating with oppositely charged polymers in LbL. In practice ALD may require a few cycles in order to achieve the desired coverage and can result in varied morphologies such as islands, isolated crystallites, or nanoparticles . As described previously morphology can alter electrochemical behavior and therefore must be carefully controlled.

Electropolymerization

Electropolymerization offers another approach to conformally coating architectures with a thin film, 10 to 100 nm, of polymer. The electropolymerization of an insulating polymer results in a self-limiting deposition as the active moiety is protected; the deposition can also be self-limiting if the polymer can block the solubilized monomer and prohibit continued growth. Through the control of electrochemical variables, polyaniline and polythiophene can be deposited in a controlled manner. Styrene, methyl methacrylate, phenols, and other electrically insulating polymers have been deposited on the electrode geometries to act as a separator that allows ionic transport but inhibits electrical transport to prevent shorting of the battery. Mesoporous manganese dioxide ambigels have been protected by thin films, 7-9 nm, of polymer such that the dissolution of the manganese dioxide in aqueous acid was avoided. In order to achieve uniform coatings the architecture must be wetted by the solution containing the monomer; this can be achieved through a solution which has a low viscosity or a similar surface energy to that of the porous solid. Furthermore, as the scale continuous to decrease and transport through the solid becomes more difficult, pre-equilibration is needed to ensure a uniform coating.

Chapter- 5

Lithium-Ion Polymer Battery

Lithium-ion polymer battery

A Lithium-Ion Polymer Battery used to power a mobile phone

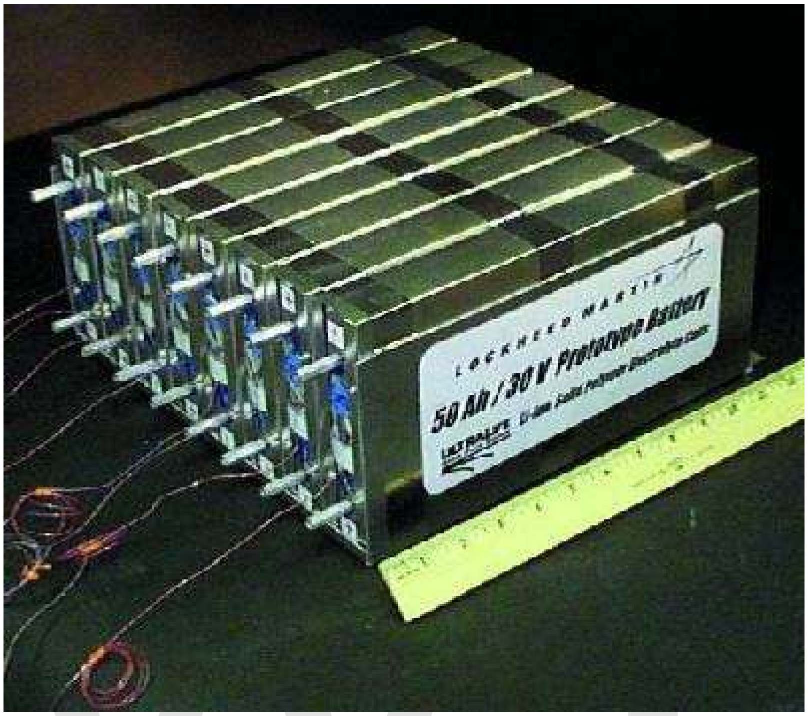
specific energy	130–200 W·h/kg
energy density	300 W·h/L
specific power	up to 7.1 kW/kg
Charge/discharge efficiency	99.8%
Energy/consumer-price	2.8–5 W·h/US$
Self-discharge rate	5%/month
Time durability	24–36 months
Cycle durability	>1000 cycles
Nominal cell voltage	3.7 V

Lithium-ion polymer batteries, **polymer lithium ion**, or more commonly **lithium polymer batteries** (abbreviated Li-poly, Li-Pol, LiPo, LIP, PLI or LiP) are rechargeable batteries (secondary cell batteries). Normally batteries are composed of several identical secondary cells in parallel addition to increase the discharge current capability.

Design origin

This type has technologically evolved from lithium-ion batteries. The primary difference is that the lithium-salt electrolyte is not held in an organic solvent but in a solid polymer composite such as polyethylene oxide or polyacrylonitrile. The advantages of Li-ion polymer over the lithium-ion design include potentially lower cost of manufacture, adaptability to a wide variety of packaging shapes, and ruggedness. Lithium-ion polymer batteries started appearing in consumer electronics around 1996.

Technology



An experimental Li Ion Polymer Battery made by Lockheed-Martin for NASA

Cells sold today as polymer batteries are pouch cells. Unlike lithium-ion cylindrical cells, which have a rigid metal case, pouch cells have a flexible, foil-type (polymer laminate) case. In cylindrical cells, the rigid case presses the electrodes and the separator onto each other; whereas in polymer cells this external pressure is not required because the electrode sheets and the separator sheets are laminated onto each other.

Since individual pouch cells have no strong metal casing, by themselves they are over 20% lighter than equivalent cylindrical cells. However, all Li-Ion cells expand at high levels of SOC; if uncontained, this may result in delamination, and reduction of reliability and cycle life; the case of cylindrical cells provides that containment, while pouch cells, by themselves, are not contained. Therefore, to achieve the rated performance, a battery composed of pouch cells must include an overall, strong, external casing to retain its shape.

The voltage of a Li-poly cell varies from about 2.7 V (discharged) to about 4.23 V (fully charged), and Li-poly cells have to be protected from overcharge by limiting the applied voltage to no more than 4.235 V per cell used in a series combination. Overcharging a Li-poly battery will probably cause explosion or fire. During discharge on load, the load has to be removed as soon as the voltage drops below approximately 3.0 V per cell (used in a series combination), or else the battery will subsequently no longer accept a full charge and may experience problems holding voltage under load. This can be achieved, as with other lithium-ion batteries, also harmed by under- and over-voltage, by circuitry that prevents overcharge and deep discharge.

Early in its development, lithium polymer technology had problems with internal resistance. Other challenges include longer charge times and slower maximum discharge rates compared to more mature technologies. Li-poly batteries typically require more than an hour for a full charge. Recent design improvements have increased maximum discharge currents from two times to 15 or even 30 times the cell capacity (discharge rate in amperes, cell capacity in ampere-hours). In December 2007 Toshiba announced a new design offering a much faster rate of charge (about 5 minutes to reach 90%). These cells were released onto the market in March 2008 and are expected to have a dramatic effect on the power tool and electric vehicle industries, and a major effect on consumer electronics.

When compared to the lithium-ion battery, Li-poly has a greater life cycle degradation rate. However, in recent years, manufacturers have been declaring upwards of 500 charge-discharge cycles before the capacity drops to 80%. Another variant of Li-poly cells, the "thin film rechargeable lithium battery", has been shown to provide more than 10,000 cycles.

Applications

A compelling advantage of Li-poly cells is that manufacturers can shape the battery almost however they please, which can be important to mobile phone manufacturers constantly working on smaller, thinner, and lighter phones.

3-Cell LiPo for RC-models

Li-poly batteries are also gaining favor in the world of radio-controlled aircraft as well as radio-controlled cars, where the advantages of both lower weight and greatly increased run times can be sufficient justification for the price. Some airsoft gun owners have switched to LiPo batteries due to the above reasons and the increased rate of fire they provide. However, lithium polymer-specific chargers are required to avoid fire and explosion. Explosions can also occur if the battery is short-circuited, as tremendous current passes through the cell in an instant. Radio-control enthusiasts take special precautions to ensure their battery leads are properly connected and insulated. Furthermore fires can occur if the cell or pack is punctured. Radio-controlled car batteries are often protected by durable plastic cases to prevent puncture. Specially designed electronic motor speed controls are used to prevent excessive discharge and subsequent battery damage. This is achieved using a low voltage cutoff (LVC) setting that is adjusted to maintain cell voltage greater than (typically) 3 V per cell.

Li-poly batteries are also gaining ground in PDAs and laptop computers, such as Apple's MacBook family, Amazon's Kindle, Lenovo's Thinkpad X300 and Ultrabay Batteries, the OQO series of palmtops, the HP Mini and Dell products featuring D-bay batteries. They can be found in small digital music devices such as iPods, Zunes, and other MP3 players and the Apple iPhone and iPad, as well as gaming equipment like Sony's Playstation 3 wireless controllers. They are desirable in applications where small form factors and energy density outweigh cost considerations.

Electric vehicles

These batteries may also power the next generation of battery electric vehicles. The cost of an electric car of this type is prohibitive, but proponents argue that with increased production, the cost of Li-poly batteries will go down.

Hyundai Motor Company plans to use this battery type in its hybrid electric vehicles. A Li-poly powered Audi A2 covered the record distance of 600 km without recharging on October 26, 2010.

Technical specifications

There are currently two commercialized technologies, both lithium-ion-polymer (where "polymer" stands for "polymer electrolyte/separator") cells. These are collectively referred to as "polymer electrolyte batteries".

The battery is constructed as:

- **Cathode**: $LiCoO_2$ or $LiMn_2O_4$
- **Separator**: Conducting polymer electrolyte
- **Anode**: Li or carbon-Li intercalation compound

Typical reaction:

- Anode: carbon–$Li_x \rightarrow C + xLi^+ + xe^-$
- Separator: Li+ conduction
- Cathode: $Li_{1-x}CoO_2 + xLi^+ + xe^- \rightarrow LiCoO_2$

Polymer electrolytes/separators can be solid polymers (e.g., polyethyleneoxide, PEO) plus $LiPF_6$, or other conducting salts plus SiO_2, or other fillers for better mechanical properties (such systems are not available commercially yet). Some manufacturers like Avestor (since merged with Batscap) are using metallic Li as the anode (these are the **lithium-metal-polymer batteries**), whereas others wish to go with the proven safe carbon intercalation anode.

Both currently commercialized technologies use PVdF (a polymer) gelled with conventional solvents and salts, like EC/DMC/DEC. The difference between the two technologies is that one (Bellcore/Telcordia technology) uses $LiMn_2O_4$ as the cathode, and the other the more conventional $LiCoO_2$.

Other, more exotic (although not yet commercially available) Li-polymer batteries use a polymer cathode. For example, Moltech is developing a battery with a plastic conducting carbon-sulfur cathode. However, as of 2005 this technology seems to have had problems with self-discharge and manufacturing cost.

Yet another proposal is to use organic sulfur-containing compounds for the cathode in combination with an electrically conductive polymer such as polyaniline. This approach promises high power capability (i.e., low internal resistance) and high discharge capacity, but has problems with cycleability and cost.

Prolonging life in multiple cells through cell balancing

Analog front ends that balance cells and eliminate mismatches of cells in series or parallel significantly improve battery efficiency and increase the overall pack capacity. As the number of cells and load currents increase, the potential for mismatch also increases. There are two kinds of mismatch in the pack: state-of-charge (SOC) and capacity/energy (C/E) mismatch. Though the SOC mismatch is more common, each problem limits the pack capacity (mA·h) to the capacity of the weakest cell.

Battery pack cells are balanced when all the cells in the battery pack meet two conditions:

- If all cells have the same capacity, then they are balanced when they have the same relative state of charge (SOC). In this case, the open circuit voltage (OCV) is a good measure of the SOC. If, in an out-of-balance pack, all cells can be differentially charged to full capacity (balanced), then they will subsequently cycle normally without any additional adjustments.

- If the cells have different capacities, they are also considered balanced when the SOC is the same. But, since SOC is a relative measure, the absolute amount of capacity for each cell is different. To keep the cells with different capacities at the same SOC, cell balancing must provide differential amounts of current to cells in the series string during both charge and discharge on every cycle.

Capacity rating

Cell capacities are rated in ampere hours (A·h) or milliampere hours (mA·h). A 1000 mA·h battery is the same as a 1 A·h battery: both will supply 1 A for 1 hour. The C rating commonly associated with lithium ion batteries refers to the maximum current supply capability as a multiple of the cell's capacity: for instance, a 1 A·h, 20 C battery should be able to supply 20 A continuously without damage (1 A·h x 20 C = 20 A). A useful way to calculate how long a battery will last for under heavy load is to multiply the A·h capacity by 60 min to give A·min, so a 1 A·h battery is a 60 A·min battery; to calculate how many minutes the battery will last, just divide by the average current drawn (e.g. a 10 A average current draw will mean that a 60 A·min battery will last for 60 A·min / 10 A = 6 minutes).

Charging

LiPoly batteries must be charged carefully. The basic process is to charge at constant current until each cell reaches 4.2 V; the charger must then gradually reduce the charge current while holding the cell voltage at 4.2 V until the charge current has dropped to a small percentage of the initial charge rate, at which point the battery is considered 100% charged. Some manufacturers specify 2%, others 3%, but other values are also possible. The difference in achieved capacity is minute.

Balance charging simply means that the charger monitors the voltage of each cell in a pack and varies the charge on a per-cell basis so that all cells are brought to the same voltage.

It is important to note that trickle charging is not acceptable for lithium batteries; Li-ion chemistry cannot accept an overcharge without causing damage to the cell, possibly plating out lithium metal and becoming hazardous. Most manufacturers claim a maximum and minimum voltage of 4.23 and 3.0 volts per cell. Taking any cell outside these limits can reduce the cell's capacity and ability to deliver full rated current.

Most dedicated lithium polymer chargers use a charge timer for safety; this cuts the charge after a predefined time (typically 90 minutes).

Storage

Unlike certain other types of batteries, lithium polymer batteries can be stored for one or two months without significantly losing charge. However, if storing for long periods, manufacturers recommend discharging the battery to 40% of full charge. In addition, other sources recommend refrigerating (but not freezing) the cell.

Chapter- 6

Lithium Air Battery and Lithium-Titanate Battery

Lithium air battery

A **lithium-air battery** is a battery in which a lithium anode is electrochemically coupled to atmospheric oxygen through an air cathode. During discharge, lithium cations flow from the anode through an electrolyte and combine with oxygen at the cathode (typically consisting of porous carbon) to form lithium oxide Li_2O or lithium peroxide Li_2O_2 which is inserted in the cathode; this is coupled to the flow of electrons from the battery's anode to the cathode through a load circuit.

Lithium air batteries have higher energy density than lithium ion batteries because of the lighter cathode and the fact that oxygen is freely available in the environment and does not need to be stored in the battery. Theoretically, with oxygen as an unlimited cathode reactant, the capacity of the battery is limited by the Li anode. Lithium air batteries are currently under development and are not yet commercially available.

History

In the mid-1990s, K.M. Abraham and co-workers demonstrated the first practical non-aqueous Li-air battery with the use of a Li negative electrode (anode), a porous carbon positive electrode (cathode), and a gel polymer electrolyte membrane that served as both the separator and ion-transporting medium. Oxygen from the atmosphere enters the pores of the carbon cathode to serve as the cathode active material. In the discharge of the Li-air battery, this oxygen is reduced and the products are stored in the pores of the carbon electrode. As a result, the cell capacity is expressed as ampere-hour per gram of the carbon in the cathode. The Li ion conducting gel polymer electrolytes used to construct polymer Li-air cells included those based on polyacrylonitrile (PAN) and polyvinylidene fluoride (PVdF). The electrolyte can also be organic liquid, dry organic polymer or inorganic solid electrolytes.

Properties of metal-air batteries

Of the various metal-air battery chemical couples (Table 1), the Li-air battery is the most attractive since the cell discharge reaction between Li and oxygen to yield Li_2O, according to $4Li + O_2 \rightarrow 2Li_2O$, has an open-circuit voltage of 2.91 V and a theoretical specific energy of 5200 Wh/kg. In practice, oxygen is not stored in the battery, and the theoretical specific energy excluding oxygen is 11140 Wh/kg, or 40.1 megajoules per kilogram. Compare this to the figure of 44 megajoules per kilogram for gasoline

Metal/air battery	**Calculated OCV, V**	**Theoretical specific energy, Wh/kg (including oxygen)**	**Theoretical specific energy, Wh/kg (excluding oxygen)**
Li/O_2	2.91	5210	11140
Na/O_2	1.94	1677	2260
Ca/O_2	3.12	2990	4180
Mg/O_2	2.93	2789	6462
Zn/O_2	1.65	1090	1350

The possible discharge cell reactions and the associated cell voltages in agreement with the experimental discharge data from the test cell are:

$2Li + O_2 \rightarrow Li_2O_2$; Go = -145 Kcal (Eo = 3.1 V)
$4Li + O_2 \rightarrow 2Li_2O$; Go = -268 Kcal (Eo = 2.91 V)

Indeed, Abraham et al showed using Raman spectroscopic analysis of the products that the main discharge reaction is the reduction of oxygen to form Li_2O_2.

Abraham and Jiang also demonstrated that the Li/oxygen battery is rechargeable when the carbon cathode contains catalysts derived from complexes or oxides of metals such as cobalt. The catalyst can be viewed as lowering the overvoltage for the oxidation of Li_2O_2 or Li_2O to form metallic Li and oxygen.

The non-aqueous metal-air batteries represent a class of potentially ultrahigh energy density power sources useful for a variety of applications. When fully developed these batteries are expected to exhibit practical specific energies of over 1000 Wh/kg (3.6 MJ/kg).

Abraham and co-workers also showed that a magnesium/oxygen battery can be constructed with a Mg ion conducting polymer electrolyte of the composition, 30PVdF-HFP-62.5 EC/PC-7.5$Mg(ClO_4)_2$, with a conductivity of 1.2×10^{-3} S/cm at 20 °C (68 °F). This Mg/O_2 cell showed an open circuit potential of about 1.2 V at room temperature, lower than the calculated value of 2.93 V, and its discharge voltage ranged between 0.7 to 1.1 V depending on the current density, carbon cathode and electrolyte composition.

Lithium-titanate battery

The **Lithium-titanate battery** is a type of rechargeable battery, which has the advantage of being faster to charge than other lithium-ion batteries. Some analysts speculate that lithium-titanate batteries will power electric cars of the future.

A lithium-titanate battery is a modified lithium-ion battery that uses lithium-titanate nanocrystals on the surface of its anode instead of carbon. This gives the anode a surface area of about 100 square meters per gram, compared with 3 square meters per gram for carbon, allowing electrons to enter and leave the anode quickly. This makes fast recharging possible and provides high currents when needed. The disadvantage is that lithium-titanate batteries have a lower voltage and capacity than conventional lithium-ion battery technologies.

Brands and uses

Altairnano

Altairnano produce lithium-titanate batteries under the "Nanosafe" line, mainly for battery electric vehicles. Some vehicle manufacturers which announced plans to use Altairnano batteries includes Lightning Car Company, which plan to use them for Lightning GT, an all-electric sports car, Phoenix Motorcars, in its electric sport-utility vehicles, and Proterra, in its all-electric EcoRide BE35 vehicle, a lightweight 35-foot bus.

Altairnano has also deployed their lithium-titanate energy storage systems for electric grid ancillary services and in various military applications.

Toshiba

An example of a SCiB cell

Toshiba released a lithium-titanate battery, dubbed Super Charge Ion Battery (SCiB). The battery is designed to offer 90% charge capacity in just 10 minutes.

SCiB batteries are used in the Schwinn Tailwind electric bike. Toshiba has also demonstrated its use as a laptop battery. Toshiba announced plans to bring the SCiB battery to electric vehicles.