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Lithium metal battery

Lithium metal batteries are primary batteries that have metallic lithium as an anode. The name intentionally refers to the metal as to distinguish them from lithium-ion batteries, which use lithiated metal oxides as the cathode material.^[1] Although most lithium metal batteries are non-rechargeable, rechargeable lithium metal batteries are also under development. Since 2007, Dangerous Goods Regulations differentiate between lithium metal batteries (UN 3090) and lithium-ion batteries (UN 3480).^[2]

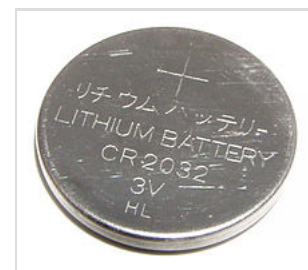
They stand apart from other batteries in their high charge density and high cost per unit. Depending on the design and chemical compounds used, lithium cells can produce voltages from 1.5 V (comparable to a zinc–carbon or alkaline battery) to about 3.7 V.

Disposable primary lithium batteries must be distinguished from secondary lithium-ion or a lithium-polymer,^[3] which are rechargeable batteries and contain no metallic lithium. Lithium is especially useful, because its ions can be arranged to move between the anode and the cathode, using an intercalated lithium compound as the cathode material but without using lithium metal as the anode material. Pure lithium will instantly react with water, or even moisture in the air; the lithium in lithium-ion batteries is a less reactive compound.

Lithium batteries are widely used in portable consumer electronic devices. The term "lithium battery" refers to a family of different lithium-metal chemistries, comprising many types of cathodes and electrolytes but all with metallic lithium as the anode. The battery requires from 0.15 to 0.3 kg (5 to 10 oz) of lithium per kWh. As designed these primary systems use a charged cathode, that being an electro-active material with crystallographic vacancies that are filled gradually during discharge.

The most common type of lithium cell used in consumer applications uses metallic lithium as the anode and manganese dioxide as the cathode, with a salt of lithium dissolved in an organic solvent as the electrolyte.^[4]

History



CR2032 lithium button cell battery



Lithium 9 volt, AA, and AAA sizes. The top object is a battery of three lithium-manganese dioxide cells; the bottom two are lithium-iron disulfide cells and are compatible with 1.5-volt alkaline cells.

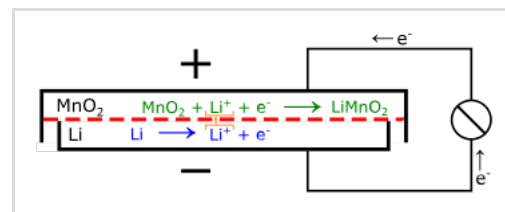


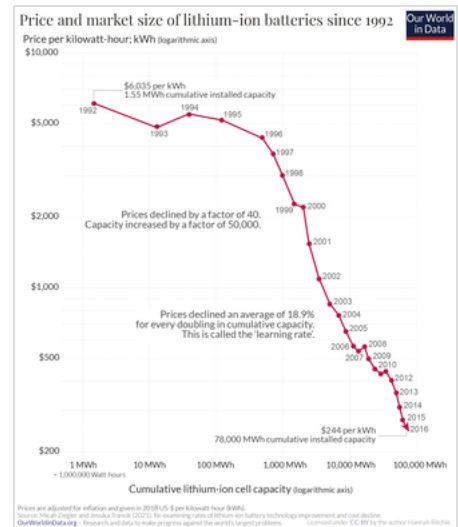
Diagram of lithium button cell battery with MnO₂ (manganese dioxide) at cathode

Lithium is the alkali metal with lowest density and with the greatest electrochemical potential and energy-to-weight ratio. The low atomic weight and small size of its ions also speeds its diffusion, likely making it an ideal battery material.^[5] Experimentation with lithium batteries began in 1912 under American physical chemist Gilbert N. Lewis, but commercial lithium batteries did not come to market until the 1970s in the form of the lithium-ion battery.^{[6][7]} Three volt lithium primary cells such as the CR123A type and three volt button cells are still widely used, especially in cameras and very small devices.



Lithium-ion battery

Three important developments regarding lithium batteries occurred in the 1980s. In 1980, an American chemist, John B. Goodenough, discovered the LiCoO_2 (Lithium cobalt oxide) cathode (positive lead) and a Moroccan research scientist, Rachid Yazami, discovered the graphite anode (negative lead) with the solid electrolyte. In 1981, Japanese chemists Tokio Yamabe and Shizukuni Yata discovered a novel nano-carbonaceous-PAS (polyacene)^[8] and found that it was very effective for the anode in the conventional liquid electrolyte.^{[9][10]} This led a research team managed by Akira Yoshino of Asahi Chemical, Japan, to build the first lithium-ion battery prototype in 1985, a rechargeable and more stable version of the lithium battery; Sony commercialized the lithium-ion battery in 1991.^[11] In 2019, John Goodenough, Stanley Whittingham, and Akira Yoshino, were awarded the Nobel Prize in Chemistry, for their development of lithium-ion batteries.^[12]



Curve of price and capacity of lithium-ion batteries over time; the price of these batteries declined by 97% in three decades.

In 1997, the lithium polymer battery was released by Sony and Asahi Kasei. These batteries hold their electrolyte in a solid polymer composite instead of in a liquid solvent, and the electrodes and separators are laminated to each other. The latter difference allows the battery to be encased in a flexible wrapping instead of in a rigid metal casing, which means such batteries can be specifically shaped to fit a particular device. This advantage has favored lithium polymer batteries in the design of portable electronic devices such as mobile phones and personal digital assistants, and of radio-controlled aircraft, as such batteries allow for a more flexible and compact design. They generally have a lower energy density than normal lithium-ion batteries.

High costs and concerns about mineral extraction associated with lithium chemistry have renewed interest in sodium-ion battery development, with early electric vehicle product launches in 2023.^[13]

Chemistries

Chemistry	Cathode	Electrolyte	Nominal voltage	Open-circuit voltage	Wh/kg	Wh/L
Li–MnO ₂ (IEC code: C), "CR"	Heat-treated manganese dioxide	Lithium perchlorate in an organic solvent (propylene carbonate and dimethoxyethane in many common cells ^{[14][15][16]})	3 V	3.3 V	280	580
	"Li–Mn". The most common consumer-grade lithium 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. Operational temperature ranges from -30 °C to 60 °C. Can deliver high pulse currents. ^[17] With discharge, the internal impedance rises and the terminal voltage decreases. High self-discharge at high temperatures. 1,2-Dimethoxyethane is a REACH candidate substance of very high concern.					
Li–(CF) _x (IEC code: B), "BR"	Carbon monofluoride	Lithium tetrafluoroborate in propylene carbonate, dimethoxyethane, or gamma-butyrolactone	3 V	3.1 V	360–500	1,000
	Cathode material formed by high-temperature intercalation of fluorine gas into graphite powder. Compared to manganese dioxide (CR), which has the same nominal voltage, it provides more reliability. ^[17] Used for low to moderate current applications in memory and clock backup batteries. Used in aerospace applications, qualified for space since 1976, military applications both terrestrial and marine, in missiles, and in artificial cardiac pacemakers. ^[18] Operates up to around 80 °C. Very low self-discharge (<0.5%/year at 60 °C, <1%/yr at 85 °C). Developed in the 1970s by Matsushita. ^[19]					
Li–FeS ₂ (IEC code: F), "FR"	Iron disulfide	Propylene carbonate, dioxolane, dimethoxyethane	1.4–1.6 V	1.8 V	297 ^[20]	
	"Lithium-iron", "Li/Fe". Called "voltage-compatible" lithium, it can work as a replacement for alkaline batteries with its 1.5 V nominal voltage. As such, Energizer lithium cells of AA ^[21] and AAA size employ this chemistry. 2.5 times higher lifetime for high current discharge regime than alkaline batteries, better storage life due to lower self-discharge(10–20 years). FeS ₂ is cheap. Cathode is often designed as a paste of iron sulfide powder mixed with powdered graphite. Variant is Li–CuFeS ₂ .					
Li–SOCl ₂ (IEC code: E)	Thionyl chloride	Lithium tetrachloroaluminate in thionyl chloride	3.5 V	3.65 V	500–700	1,200
	Liquid cathode. For low-temperature applications. Can operate down to –55 °C, where it retains over 50% of its rated capacity. A negligible amount of gas generated in nominal use, a 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 are used for portable electronics and memory backup. High-current cells are used in military applications. In long storage, forms passivation layer on the 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 a trained technician for the replacement of these batteries. Hazardous waste, Class 9 Hazmat shipment. ^[22] Not used for consumer or general-purpose batteries.					
Li–SOCl ₂ , BrCl, Li–BCX (IEC code: E)	Thionyl chloride with bromine chloride	Lithium tetrachloroaluminate in thionyl chloride	3.7–3.8 V	3.9 V	350	770
	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 the discharge. The cells with added bromine chloride are thought to be safer when abused.					

Li-SO ₂ Cl ₂ (IEC code: Y)	Sulfuryl chloride	Lithium tetrachloroaluminate in sulfuryl chloride	3.7 V	3.95 V	330	720
	Liquid cathode. Similar to thionyl chloride. Discharge does not result in a build-up of elemental sulfur, which is thought to be involved in some hazardous reactions, therefore sulfuryl chloride batteries may be safer. Commercial deployment is hindered by the tendency of the electrolyte to 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. ^[23]					
Li-SO ₂ (IEC code: W)	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. ^[24] Used in military applications. Addition of bromine monochloride can boost the voltage to 3.9 V and increase energy density. ^[25]					
Li-I ₂	Iodine that has been mixed and heated with poly-2-vinylpyridine (P2VP) to form a solid organic charge transfer complex.	A solid monomolecular layer of crystalline Lithium iodide that conducts lithium ions from the anode to the cathode but does not conduct iodine. ^[26]	2.8 V	3.1 V		
	Solid electrolyte. Very high reliability and low self-discharge rate. Used in medical applications that need a long life, e.g. pacemakers. Does not generate gas even under a short circuit. Solid-state chemistry, limited short-circuit current, suitable only for low-current applications. Terminal voltage decreases with the degree of discharge due to precipitation of lithium iodide.					
Li-Ag ₂ CrO 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 a certain percentage of discharge provides early warning of impending discharge. Developed specifically for medical applications, for example, implanted pacemakers.					
Li-Ag ₂ V ₄ O ₁₁ , Li-SVO, Li-CSVO	Silver oxide+vanadium pentoxide (SVO)	lithium hexafluorophosphate or lithium hexafluoroarsenate in propylene carbonate with dimethoxyethane				
	Used in medical applications, like implantable defibrillators, neurostimulators, and drug infusion systems. Also projected for use in other electronics, such as emergency locator transmitters. High energy density. Long shelf life. Capable of continuous operation at a nominal temperature of 37 °C. ^[27] Two-stage discharge with a plateau. Output voltage decreases proportionally to the degree of discharge. Resistant to abuse.					
Li-CuO (IEC code:)	Copper(II) oxide	Lithium perchlorate dissolved in dioxolane	1.5 V	2.4 V		

G), "GR"	Can operate up to 150 °C. Developed as a replacement of zinc–carbon and alkaline batteries. "Voltage up" problem, the high difference between open-circuit and nominal voltage. Produced until the mid-1990s, replaced by lithium–iron sulfide. Current use is limited.					
Li– Cu ₄ O(PO ₄) ₂	Copper oxyphosphate					
	See Li–CuO					
Li–CuS	Copper sulfide	Lithium salt or a salt such as a tetraalkylammonium chloride dissolved in LiClO ₄ in an organic solvent that is a mixture of 1,2-dimethoxy ethane, 1,3-dioxolane and 2,5-dimethyloxazole as a stabilizer ^[28]	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. See lithium-iron disulfide.					
Li–Bi ₂ Pb ₂ O 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 ₂ O ₃	Bismuth trioxide		1.5 V	2.04 V		
Li–V ₂ O 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–CuCl ₂	Copper chloride	LiAlCl ₄ or LiGaCl ₄ in SO ₂ , a liquid, inorganic, non-aqueous electrolyte.				
	Rechargeable. This cell has three voltage plateaus as it discharges (3.3 V, 2.9 V, and 2.5 V). ^[29] Discharging below the first plateau reduces the life of the cell. ^[29] The complex salt dissolved in SO ₂ has a lower vapor pressure at room temperature than pure sulfur dioxide, ^[30] making the construction simpler and safer than Li–SO ₂ batteries.					
Li/Al–MnO ₂ , "ML"	Manganese dioxide		3 V ^[31]			
	Rechargeable. Anode is a Lithium-Aluminum alloy. ^{[31][32]} Mainly marketed by Maxell.					
Li/Al–V ₂ O ₅ , "VL"	Vanadium pentoxide		3 V ^[33]			
	Rechargeable. Anode is a Li–Al alloy. ^[34]					
Li–Se	Selenium	non-aqueous carbonate electrolytes	1.9 V ^[35]			
Li–air	Porous carbon	Organic, aqueous, glass–ceramic (polymer–ceramic			1,800–660 ^[36]	1,600–600 ^[36]

		composites)				
		Rechargeable. As of 2012, no commercial implementation is available due to difficulties in achieving multiple discharge cycles without losing capacity. ^[36] There are multiple possible implementations, each having different energy capacities, advantages and disadvantages. In November 2015, a team of University of Cambridge researchers furthered work on lithium-air batteries by developing a charging process capable of prolonging the battery life and battery efficiency. Their work resulted in a battery that delivered high energy densities, more than 90% efficiency, and could be recharged for up to 2,000 times. The lithium-air batteries are described as the "ultimate" batteries because they propose a high theoretical energy density of up to ten times the energy offered by regular lithium-ion batteries. They were first developed in a research environment by Abraham & Jiang in 1996. ^[37] Toyota promoted a vehicle with a working solid-state battery in September 2021; due to cost, the company plans to use it in a hybrid vehicle in 2025, before scaling up to fully electric vehicles. ^[38] Other companies working on commercialization include <u>QuantumScape</u> and <u>Solid Power</u> (funded by <u>Ford Motor Company</u> and <u>BMW</u>). ^[38]				
<u>Li-FePO₄</u>	<u>Lithium iron phosphate</u>	ethylene carbonate–dimethyl carbonate (EC–DMC) 1–1 lithium perchlorate (LiClO ₄) 1M	3.0 ~ 3.2 V	3.2 V	90–160 ^{[39][40]}	325 Wh/L (1,200 kJ/L) ^[40]
	The specific capacity of LiFePO ₄ is higher than that of the related <u>lithium cobalt oxide</u> (LiCoO ₂) chemistry, but its <u>energy density</u> is less due to its lower operating voltage. The main drawback of LiFePO ₄ is its low electrical conductivity. Because of low cost, low toxicity, well-defined performance, long-term stability, etc. LiFePO ₄ is finding a number of roles in vehicle use, utility scale stationary applications, and backup power.					

University of California San Diego have developed an electrolyte chemistry that allows lithium batteries to run at temperatures as low as -60 °C. The electrolytes also enable electrochemical capacitors to run as low as -80 °C. Previous low-temperature limit is -40 °C. High performance at room temperature is still maintained. This may improve energy density and safety of lithium batteries and electrochemical capacitors.^[41]

Applications

Lithium batteries find application in many long-life, critical devices, such as 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.

Lithium batteries also prove valuable in oceanographic applications. While lithium battery packs are considerably more expensive than standard oceanographic packs, they hold up to three times the capacity of alkaline packs. The high cost of servicing remote oceanographic instrumentation (usually by ships) often justifies this higher cost.

Sizes and formats

Small lithium batteries are very commonly used in small, portable electronic devices, such as PDAs, watches, camcorders, digital cameras, thermometers, calculators, personal computer BIOS (firmware),^[42] 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. The common CR2032 battery is 20 mm diameter and 3.2 mm thick, where the first two digits is the diameter and the last two digits are thickness. A CR2025 is the same 20 mm diameter but 2.5 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.

Popularity

Lithium primary batteries account for 28% of all primary battery sales in Japan but only 1% of all battery sales in Switzerland. In the EU only 0.5% of all battery sales including secondary types are lithium primaries.^{[43][44][45][46]}

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.

Rapid-discharge problems

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 – especially if cobalt is present in the cells' design – can result in overheating of the battery (that lowers the electrical resistance of any cobalt content within the cell), rupture, and even an explosion. Lithium-thionyl chloride batteries are particularly susceptible to this type of discharge. Consumer batteries usually incorporate overcurrent or thermal protection or vents to prevent an explosion.

Air travel

From January 1, 2013, much stricter regulations were introduced by IATA regarding the carriage of