

Lithium-ion battery

A **lithium-ion battery** or **Li-ion battery** is a type of rechargeable battery. Lithium-ion batteries are commonly used for portable electronics and electric vehicles and are growing in popularity for military and aerospace applications.^[9] A prototype Li-ion battery was developed by Akira Yoshino in 1985, based on earlier research by John Goodenough, M. Stanley Whittingham, Rachid Yazami and Koichi Mizushima during the 1970s–1980s,^{[10][11][12]} and then a commercial Li-ion battery was developed by a Sony and Asahi Kasei team led by Yoshio Nishi in 1991.^[13]

In the batteries, lithium ions move from the negative electrode through an electrolyte to the positive electrode during discharge, and back when charging. Li-ion batteries use an intercalated lithium compound as the material at the positive electrode and typically graphite at the negative electrode. The batteries have a high energy density, no memory effect (other than LFP cells)^[14] and low self-discharge. They can however be a safety hazard since they contain flammable electrolytes, and if damaged or incorrectly charged can lead to explosions and fires. Samsung was forced to recall Galaxy Note 7 handsets following lithium-ion fires,^[15] and there have been several incidents involving batteries on Boeing 787s.

Chemistry, performance, cost and safety characteristics vary across types of lithium-ion batteries. Handheld electronics mostly use lithium polymer batteries (with a polymer gel as electrolyte), a lithium cobalt oxide (LiCoO₂) cathode material, and a graphite anode, which together offer a high energy density.^{[16][17]} Lithium iron phosphate (LiFePO₄), lithium manganese oxide (LiMn₂O₄ spinel, or Li₂MnO₃-based lithium rich layered materials (LMR-NMC)), and lithium nickel manganese cobalt oxide (LiNiMnCoO₂ or NMC) may offer longer lives and may have better rate capability. Such batteries are widely used for electric tools, medical equipment, and other roles. NMC and its derivatives are widely used in electric vehicles.

Research areas for lithium-ion batteries include extending lifetime, increasing energy density, improving safety, reducing cost, and increasing charging speed,^[18] among others. Research has been under way in the area of non-flammable electrolytes as a pathway to increased safety based on the flammability and volatility of the organic solvents used in the typical electrolyte. Strategies include aqueous lithium-ion batteries, ceramic solid electrolytes, polymer electrolytes, ionic liquids, and heavily fluorinated systems.^{[19][20][21][22]}

Lithium-ion battery



A Li-ion battery from a Nokia 3310 mobile phone

Specific energy	100–265 W·h/kg ^{[1][2]} (0.36–0.875 MJ/kg)
Energy density	250–693 W·h/L ^{[3][4]} (0.90–2.43 MJ/L)
Specific power	~250 – ~340 W/kg ^[1]
Charge/discharge efficiency	80–90% ^[5]
Energy/consumer-price	6.4 Wh/US\$ ^[6]
Self-discharge rate	0.35% to 2.5% per month depending on state of charge ^[7]
Cycle durability	400–1,200 cycles ^[8]
Nominal cell voltage	3.6 / 3.7 / 3.8 / 3.85 V, LiFePO4 3.2 V

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Terminology

Battery versus cell

A *cell* is a basic electrochemical unit that contains the electrodes, separator, and electrolyte.^{[23][24]}

A *battery* or *battery pack* is a collection of cells or cell assemblies, with housing, electrical connections, and possibly electronics for control and protection.^{[25][26]}

Anode and cathode electrodes

For rechargeable cells, the term *anode* (or *negative electrode*) designates the electrode where *oxidation* is taking place during the *discharge cycle*; the other electrode is the cathode (or positive electrode). During the *charge cycle*, the positive electrode becomes the anode and the negative electrode becomes the cathode. For most lithium-ion cells, the lithium-oxide electrode is the positive electrode; for titanate lithium-ion cells (LTO), the lithium-oxide electrode is the negative electrode.

History

Background

Lithium batteries were proposed by British chemist M. Stanley Whittingham, now at Binghamton University. Whittingham started on the research that led to his breakthrough at Stanford University. Early in the 1970s, he discovered how to store lithium ions within the layers of a disulfide material. After getting hired by Exxon, he improved on this innovation.^[27] Whittingham used titanium(IV) sulfide and lithium metal as the electrodes. However, this rechargeable lithium battery could never be made practical. Titanium disulfide was a poor choice, since it has to be synthesized under completely sealed conditions, also being quite expensive (~\$1,000 per kilogram for titanium disulfide raw material in 1970s). When exposed to air, titanium disulfide reacts to form hydrogen sulfide compounds, which have an unpleasant odour and are toxic to most animals. For this, and other reasons, Exxon discontinued development of Whittingham's lithium-titanium disulfide battery.^[28] Batteries with metallic lithium electrodes presented safety issues, as lithium metal reacts with water, releasing flammable hydrogen gas.^[29] Consequently, research moved to develop batteries in which, instead of metallic lithium, only lithium compounds are present, being capable of accepting and releasing lithium ions.



Varta lithium-ion battery, Museum Autovision, Altussheim, Germany

Reversible intercalation in graphite^{[30][31]} and intercalation into cathodic oxides^{[32][33]} was discovered during 1974–76 by J. O. Besenhard at TU Munich. Besenhard proposed its application in lithium cells.^{[34][35]} Electrolyte decomposition and solvent co-intercalation into graphite were severe early drawbacks for battery life.

Development

- 1973 – Adam Heller proposed the lithium thionyl chloride battery, still used in implanted medical devices and in defense systems where a greater than 20-year shelf life, high energy

- density, and/or tolerance for extreme operating temperatures are required.^[36]
- 1977 – Samar Basu demonstrated electrochemical intercalation of lithium in graphite at the University of Pennsylvania.^{[37][38]} This led to the development of a workable lithium intercalated graphite electrode at Bell Labs (LiC_6)^[39] to provide an alternative to the lithium metal electrode battery.
 - 1979 – Working in separate groups, Ned A. Godshall et al.,^{[40][41][42]} and, shortly thereafter, John B. Goodenough (Oxford University) and Koichi Mizushima (Tokyo University), demonstrated a rechargeable lithium cell with voltage in the 4 V range using lithium cobalt dioxide (LiCoO_2) as the positive electrode and lithium metal as the negative electrode.^{[43][44]} This innovation provided the positive electrode material that enabled early commercial lithium batteries. LiCoO_2 is a stable positive electrode material which acts as a donor of lithium ions, which means that it can be used with a negative electrode material other than lithium metal.^[45] By enabling the use of stable and easy-to-handle negative electrode materials, LiCoO_2 enabled novel rechargeable battery systems. Godshall et al. further identified the similar value of ternary compound lithium-transition metal-oxides such as the spinel LiMn_2O_4 , Li_2MnO_3 , LiMnO_2 , LiFeO_2 , LiFe_5O_8 , and LiFe_5O_4 (and later lithium-copper-oxide and lithium-nickel-oxide cathode materials in 1985)^[46]
 - 1980 – Rachid Yazami demonstrated the reversible electrochemical intercalation of lithium in graphite,^{[47][48]} and invented the lithium graphite electrode (anode).^{[49][10]} The organic electrolytes available at the time would decompose during charging with a graphite negative electrode. Yazami used a solid electrolyte to demonstrate that lithium could be reversibly intercalated in graphite through an electrochemical mechanism. As of 2011, Yazami's graphite electrode was the most commonly used electrode in commercial lithium-ion batteries.
 - The negative electrode has its origins in PAS (polyacenic semiconductive material) discovered by Tokio Yamabe and later by Shizukuni Yata in the early 1980s.^{[50][51][52][53]} The seed of this technology was the discovery of conductive polymers by Professor Hideki Shirakawa and his group, and it could also be seen as having started from the polyacetylene lithium ion battery developed by Alan MacDiarmid and Alan J. Heeger et al.^[54]
 - 1982 – Godshall et al. were awarded U.S. Patent 4,340,652 (<https://patents.google.com/patent/US4340652>)^[55] for the use of LiCoO_2 as cathodes in lithium batteries, based on Godshall's Stanford University Ph.D. dissertation and 1979 publications.
 - 1983 – Michael M. Thackeray, Peter Bruce, William David, and John B. Goodenough developed manganese spinel, Mn_2O_4 , as a charged cathode material for lithium-ion batteries. It has two flat plateaus on discharge with lithium one at 4V, stoichiometry LiMn_2O_4 , and one at 3V with a final stoichiometry of $\text{Li}_2\text{Mn}_2\text{O}_4$.^[56]
 - 1985 – Akira Yoshino assembled a prototype cell using carbonaceous material into which lithium ions could be inserted as one electrode, and lithium cobalt oxide (LiCoO_2) as the other.^[57] This dramatically improved safety. LiCoO_2 enabled industrial-scale production and enabled the commercial lithium-ion battery.
 - 1989 – Arumugam Manthiram and John B. Goodenough discovered the polyanion class of cathodes.^{[58][59]} They showed that positive electrodes containing polyanions, e.g., sulfates, produce higher voltages than oxides due to the inductive effect of the polyanion. This polyanion class contains materials such as lithium iron phosphate.^[60]

Commercialization and advances

The performance and capacity of lithium-ion batteries increased as development progressed.

- 1991 – Sony and Asahi Kasei released the first commercial lithium-ion battery.^[61] The Japanese team that successfully commercialized the technology was led by Yoshio Nishi.^[13]
- 1996 – Goodenough, Akshaya Padhi and coworkers proposed lithium iron phosphate (LiFePO_4) and other phospho-olivines (lithium metal phosphates with the same structure as mineral olivine) as positive electrode materials.^[62] *Journal of the Electrochemical Society*, 144 (4), p. 1188-1194
- 1998 – C. S. Johnson, J. T. Vaughey, M. M. Thackeray, T. E. Bofinger, and S. A. Hackney report the discovery of the high capacity high voltage lithium-rich NMC cathode materials.^[63]
- 2001 – Arumugam Manthiram and co-workers discovered that the capacity limitations of layered oxide cathodes is a result of chemical instability that can be understood based on the relative positions of the metal 3d band relative to the top of the oxygen 2p band.^{[64][65][66]} This discovery has had significant implications for the practically accessible compositional space of lithium ion battery layered oxide cathodes, as well as their stability from a safety perspective.
- 2001 – Christopher Johnson, Michael Thackeray, Khalil Amine, and Jaekook Kim file a patent^{[67][68]} for lithium nickel manganese cobalt oxide (NMC) lithium rich cathodes based on a domain structure.
- 2001 – Zhonghua Lu and Jeff Dahn file a patent^[69] for the NMC class of positive electrode materials, which offers safety and energy density improvements over the widely used lithium cobalt oxide.
- 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^[70] with aluminium, niobium and zirconium. The exact mechanism causing the increase became the subject of widespread debate.^[71]
- 2004 – Yet-Ming Chiang again increased performance by utilizing lithium iron phosphate particles of less than 100 nanometers in diameter. This decreased particle density almost one hundredfold, increased the positive electrode's surface area and improved capacity and performance. Commercialization led to a rapid growth in the market for higher capacity lithium-ion batteries, as well as a patent infringement battle between Chiang and John Goodenough.^[71]
- 2005 – Y Song, PY Zavalij, and M. Stanley Whittingham report a new two-electron vanadium phosphate cathode material with high energy density.^{[72][73]}
- 2011 – Lithium nickel manganese cobalt oxide (NMC) cathodes, developed at Argonne National Laboratory, are manufactured commercially by BASF in Ohio.^[74]
- 2011 – Lithium-ion batteries accounted for 66% of all portable secondary (i.e., rechargeable) battery sales in Japan.^[75]
- 2012 – John Goodenough, Rachid Yazami and Akira Yoshino received the 2012 IEEE Medal for Environmental and Safety Technologies for developing the lithium ion battery.^[10]
- 2014 – John Goodenough, Yoshio Nishi, Rachid Yazami and Akira Yoshino were awarded the Charles Stark Draper Prize of the National Academy of Engineering for their pioneering efforts in the field.^[76]
- 2014 – Commercial batteries from Amprius Corp. reached 650 Wh/L (a 20% increase), using a silicon anode and were delivered to customers.^[77]
- 2016 – Koichi Mizushima and Akira Yoshino received the NIMS Award from the National Institute for Materials Science, for Mizushima's discovery of the LiCoO_2 cathode material for the lithium-ion battery and Yoshino's development of the lithium-ion battery.^[12]
- 2016 – Z. Qi, and Gary Koenig reported a scalable method to produce sub-micrometer sized LiCoO_2 using a template-based approach.^[78]
- 2019 – The Nobel Prize in Chemistry was given to John Goodenough, Stanley Whittingham and Akira Yoshino "for the development of lithium ion batteries".^[11]

In 2010, global lithium-ion battery production capacity was 20 gigawatt-hours.^[79] By 2016, it was 28 GWh, with 16.4 GWh in China.^[80] Production is complicated and requires many steps.^[81]

Market

Industry produced about 660 million cylindrical lithium-ion cells in 2012; the 18650 size is by far the most popular for cylindrical cells. If Tesla were to have met its goal of shipping 40,000 Model S electric cars in 2014 and if the 85-kWh battery, which uses 7,104 of these cells, had proved as popular overseas as it was in the United States, a 2014 study projected that the Model S alone would use almost 40 percent of estimated global cylindrical battery production during 2014.^[82] As of 2013, production was gradually shifting to higher-capacity 3,000+ mAh cells. Annual flat polymer cell demand was expected to exceed 700 million in 2013.^[83]

In 2015, cost estimates ranged from \$300–500/kWh.^[84] In 2016 GM revealed they would be paying US\$145/kWh for the batteries in the Chevy Bolt EV.^[85] In 2017, the average residential energy storage systems installation cost was expected to drop from 1600 \$/kWh in 2015 to 250 \$/kWh by 2040 and to see the price with 70% reduction by 2030.^[86] In 2019, some electric vehicle battery pack costs were estimated at \$150–200,^[87] and VW noted it was paying US\$100/kWh for its next generation of electric vehicles.^[88]

Batteries are used for grid energy storage and ancillary services. For a Li-ion storage coupled with photovoltaics and an anaerobic digestion biogas power plant, Li-ion will generate a higher profit if it is cycled more frequently (hence a higher lifetime electricity output) although the lifetime is reduced due to degradation.^[89]

Lithium nickel manganese cobalt oxide (NMC) cells come in several commercial types, specified by the ratio of component metals. NMC 111 (or NMC 333) have equal parts of nickel, manganese and cobalt, whereas NMC 532 has 5 parts nickel, 3 parts manganese and 2 parts cobalt. As of 2019, NMC 532 and NMC 622 were the preferred low-cobalt types for electric vehicles, with NMC 811 and even lower cobalt ratios seeing increasing use, mitigating cobalt dependency.^{[90][91][87]} However, cobalt for electric vehicles increased 81% from the first half of 2018 to 7,200 tonnes in the first half of 2019, for a battery capacity of 46.3 GWh.^[92]

Price-Fixing Cartel

An antitrust-violating Price-Fixing Cartel among 9 corporate families, including LG Chem, GS Yuasa, Hitachi Maxell, NEC, Panasonic/Sanyo, Samsung, Sony, and Toshiba was found to be rigging battery prices and restricting output between 2000 and 2011.^{[93][94][95][96]}

Construction

The three primary functional components of a lithium-ion battery are the positive and negative electrodes and electrolyte. Generally, the negative electrode of a conventional lithium-ion cell is made from carbon. The positive electrode is typically a metal oxide. The electrolyte is a lithium salt in an organic solvent.^[97] The electrochemical roles of the electrodes reverse between anode and cathode, depending on the direction of current flow through the cell.

The most commercially popular anode (negative electrode) is graphite, which in its fully lithiated state of LiC₆ correlates to a maximal capacity of 372 mAh/g.^[98] The positive electrode 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).^[99] Recently, graphene containing electrodes (based on 2D and 3D structures of graphene) have also been used as components of electrodes for lithium batteries.^[100]

The electrolyte is typically a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing complexes of lithium ions.^[101] 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, energy density, life, and safety of a lithium-ion battery can change dramatically. Current effort has been exploring the use of novel architectures using nanotechnology have been employed to improve performance. Areas on interest include nano-scale electrode materials and alternative electrode structures.^[102]

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

Lithium-ion batteries are more expensive than NiCd batteries but operate over a wider temperature range with higher energy densities. They require a protective circuit to limit the peak voltage.

The battery pack of a laptop computer, for each lithium-ion cell, will contain

- a temperature sensor
- a voltage regulator circuit
- a voltage tap
- a charge-state monitor
- a mains connector

These components

- monitor the charge-state and current flow
- record the latest, full-charge capacity
- monitor the temperature

Their design will minimize the risk of short circuits.^[103]

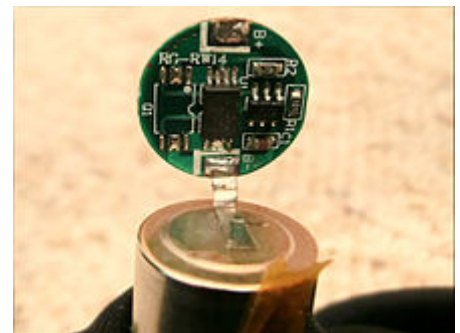
Shapes

Li-ion cells (as distinct from entire batteries) are available in various shapes, which can generally be divided into four groups:^[104]

- Small cylindrical (solid body without terminals, such as those used in older laptop batteries)
- Large cylindrical (solid body with large threaded terminals)
- Flat or pouch (soft, flat body, such as those used in cell phones and newer laptops; these are lithium-ion polymer batteries.^[105]



Cylindrical Panasonic 18650 lithium-ion battery cell before closing.



Lithium-ion battery monitoring electronics (over-charge and deep-discharge protection)



An 18650 size lithium ion battery, with an alkaline AA for scale. 18650 are used for example in notebooks or Tesla Model S

- Rigid plastic case with large threaded terminals (such as electric vehicle traction packs)

Cells with a cylindrical shape are made in a characteristic "swiss roll" manner (known as a "jelly roll" in the US), which means it is a single long 'sandwich' of the positive electrode, separator, negative electrode, and separator rolled into a single spool. The shape of the jelly roll in cylindrical cells can be approximated by an Archimedean spiral. One advantage of cylindrical cells compared to cells with stacked electrodes is the faster production speed. One disadvantage of cylindrical cells can be a large radial temperature gradient inside the cells developing at high discharge currents.



Nissan Leaf's lithium-ion battery pack.

The absence of a case gives pouch cells the highest gravimetric energy density; however, for many practical applications they still require an external means of containment to prevent expansion when their state of charge (SOC) level is high,^[106] and for general structural stability of the battery pack of which they are part. Both rigid plastic and pouch-style cells are sometimes referred to as prismatic cells due to their rectangular shapes.^[107] Battery technology analyst Mark Ellis of Munro & Associates sees three basic Li-ion battery types used in modern (~2020) electric vehicle batteries at scale: *cylindrical cells* (e.g., Tesla), *prismatic pouch* (e.g., from LG), and *prismatic can cells* (e.g., from LG, Samsung, Panasonic, and others). Each form factor has characteristic advantages and disadvantages for EV use.^[17]

Since 2011, several research groups have announced demonstrations of lithium-ion flow batteries that suspend the cathode or anode material in an aqueous or organic solution.^{[108][109]}

In 2014, Panasonic created the smallest Li-ion battery. It is pin shaped. It has a diameter of 3.5mm and a weight of 0.6g.^[110] A coin cell form factor resembling that of ordinary lithium batteries is available since as early as 2006 for LiCoO₂ cells, usually designated with a "LiR" prefix.^{[111][112]}

Electrochemistry

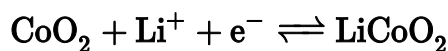
The reactants in the electrochemical reactions in a lithium-ion cell are materials of anode and cathode, both of which are compounds containing lithium atoms. During discharge, an oxidation half-reaction at the anode produces positively charged lithium ions and negatively charged electrons. The oxidation half-reaction may also produce uncharged material that remains at the anode. Lithium ions move through the electrolyte, electrons move through the external circuit, and then they recombine at the cathode (together with the cathode material) in a reduction half-reaction. The electrolyte and external circuit provide conductive media for lithium ions and electrons, respectively, but do not partake in the electrochemical reaction. During discharge, electrons flow from the negative electrode (anode) towards the positive electrode (cathode) through the external circuit. The reactions during discharge lower the chemical potential of the cell, so discharging transfers energy from the cell to wherever the electric current dissipates its energy, mostly in the external circuit. During charging these reactions and transports go in the opposite direction: electrons move from the positive electrode to the negative electrode through the external circuit.^[a] To charge the cell the external circuit has to provide electric energy. This energy is then stored as chemical energy in the cell (with some loss, e. g. due to coulombic efficiency lower than 1).

Both electrodes allow lithium ions to move in and out of their structures with a process called *insertion* (intercalation) or *extraction* (deintercalation), respectively.

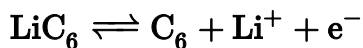
As the lithium ions "rock" back and forth between the two electrodes, these batteries are also known as "rocking-chair batteries" or "swing batteries" (a term given by some European industries).^{[113][114]}

The following equations exemplify the chemistry.

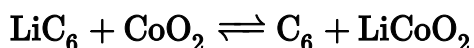
The positive electrode (cathode) half-reaction in the lithium-doped cobalt oxide substrate is^{[115][116]}



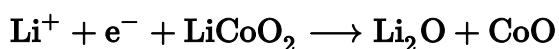
The negative electrode (anode) half-reaction for the graphite is



The full reaction (left to right: discharging, right to left: charging) being



The overall reaction has its limits. Overdischarging saturates lithium cobalt oxide, leading to the production of lithium oxide,^[117] possibly by the following irreversible reaction:



Overcharging up to 5.2 volts leads to the synthesis of cobalt(IV) oxide, as evidenced by x-ray diffraction:^[118]



In a lithium-ion battery, the lithium ions are transported to and from the positive or negative electrodes by oxidizing the transition metal, cobalt (Co), in $\text{Li}_{1-x}\text{CoO}_2$ from Co^{3+} to Co^{4+} during charge, and reducing from Co^{4+} to Co^{3+} during discharge. The cobalt electrode reaction is *only* reversible for $x < 0.5$ (x in mole units), limiting the depth of discharge allowable. This chemistry was used in the Li-ion cells developed by Sony in 1990.^[119]

The cell's energy is equal to the voltage times the charge. Each gram of lithium represents Faraday's constant/6.941, or 13,901 coulombs. At 3 V, this gives 41.7 kJ per gram of lithium, or 11.6 kWh per kilogram of lithium. This is a bit more than the heat of combustion of gasoline, but does not consider the other materials that go into a lithium battery and that make lithium batteries many times heavier per unit of energy.

Electrolytes

The cell voltages given in the Electrochemistry section are larger than the potential at which aqueous solutions will electrolyze.

Liquid electrolytes

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.^[120] A liquid electrolyte acts as a conductive pathway for the movement of cations passing from the negative to the positive electrodes during discharge. Typical conductivities of liquid electrolyte at room temperature (20 °C (68 °F)) are in the range of 10 mS/cm, increasing by approximately 30–40% at 40 °C (104 °F) and decreasing slightly at 0 °C (32 °F).^[121]

The combination of linear and cyclic carbonates (e.g., ethylene carbonate (EC) and dimethyl carbonate (DMC)) offers high conductivity and solid electrolyte interphase (SEI)-forming ability.

Organic solvents easily decompose on the negative electrodes during charge. 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,^[122] which is electrically insulating, yet provides significant ionic conductivity. The interphase prevents further 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.^[123]

Composite electrolytes based on POE (poly(oxyethylene)) provide a relatively stable interface.^{[124][125]} 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.

Room-temperature ionic liquids (RTILs) are another approach to limiting the flammability and volatility of organic electrolytes.^[126]

Solid electrolytes

Recent advances in battery technology involve using a solid as the electrolyte material. The most promising of these are ceramics.^[127]

Solid ceramic electrolytes are mostly lithium metal oxides, which allow lithium ion transport through the solid more readily due to the intrinsic lithium. The main benefit of solid electrolytes is that there is no risk of leaks, which is a serious safety issue for batteries with liquid electrolytes.^[128]

Solid ceramic electrolytes can be further broken down into two main categories: ceramic and glassy. Ceramic solid electrolytes are highly ordered compounds with crystal structures that usually have ion transport channels.^[129] Common ceramic electrolytes are lithium super ion conductors (LISICON) and perovskites. Glassy solid electrolytes are amorphous atomic structures made up of similar elements to ceramic solid electrolytes, but have higher conductivities overall due to higher conductivity at grain boundaries.^[130]

Both glassy and ceramic electrolytes can be made more ionically conductive by substituting sulfur for oxygen. The larger radius of sulfur and its higher ability to be polarized allow higher conductivity of lithium. This contributes to conductivities of solid electrolytes are nearing parity with their liquid counterparts, with most on the order of 0.1 mS/cm and the best at 10 mS/cm.^[131]

Functional electrolytes

An efficient and economic way to tune targeted electrolytes properties is by adding a third component in small concentrations, known as an additive.^[132] By adding the additive in small amounts, the bulk properties of the electrolyte system will not be affected whilst the targeted property can be significantly improved. The numerous additives that have been tested can be divided into the following three distinct categories: (1) those used for SEI chemistry modifications; (2) those used for enhancing the ion conduction properties; (3) those used for improving the safety of the cell (e.g. prevent overcharging).

Charge and discharge

During discharge, lithium ions (Li^+) carry the current within the battery from the negative to the positive electrode, through the non-aqueous electrolyte and separator diaphragm.^[133]

During charging, an external electrical power source (the charging circuit) applies an over-voltage (a higher voltage than the battery produces, of the same polarity), forcing a charging current to flow **within the battery** from the positive to the negative electrode, i.e. in the reverse direction of a discharge current under normal

conditions. 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.

Energy losses arising from electrical contact resistance at interfaces between electrode layers and at contacts with current-collectors can be as high as 20% of the entire energy flow of batteries under typical operating conditions.^[134]

Procedure

The charging procedures for single Li-ion cells, and complete Li-ion batteries, are slightly different.

- A single Li-ion cell is charged in two stages:^[135]
 1. Constant current (CC).
 2. Constant voltage (CV).
- A Li-ion battery (a set of Li-ion cells in series) is charged in three stages:
 1. Constant current.
 2. Balance (not required once a battery is balanced).
 3. Constant voltage.

During the *constant current* phase, the charger applies a constant current to the battery at a steadily increasing voltage, until the voltage limit per cell is reached.

During the *balance* phase, the charger reduces the charging current (or cycles the charging on and off to reduce the average current) while the state of charge of individual cells is brought to the same level by a balancing circuit, until the battery is balanced. Some fast chargers skip this stage. Some chargers accomplish the balance by charging each cell independently.

During the *constant voltage* phase, the charger applies a voltage equal to the maximum cell voltage times the number of cells in series to the battery, as the current gradually declines towards 0, until the current is below a set threshold of about 3% of initial constant charge current.

Periodic topping charge about once per 500 hours. Top charging is recommended to be initiated when voltage goes below 4.05 V/cell.

Failure to follow current and voltage limitations can result in an explosion.^{[136][137]}

Extreme temperatures

Charging temperature limits for Li-ion are stricter than the operating limits. Lithium-ion chemistry performs well at elevated temperatures but prolonged exposure to heat reduces battery life.

Li-ion batteries offer good charging performance at cooler temperatures and may even allow 'fast-charging' within a temperature range of 5 to 45 °C (41 to 113 °F).^[138] Charging should be performed within this temperature range. At temperatures from 0 to 5 °C charging is possible, but the charge current should be reduced. During a low-temperature charge, the slight temperature rise above ambient due to the internal cell resistance is beneficial. High temperatures during charging may lead to battery degradation and charging at temperatures above 45 °C will degrade battery performance, whereas at lower temperatures the internal resistance of the battery may increase, resulting in slower charging and thus longer charging times.^[138]

Consumer-grade lithium-ion batteries should not be charged at temperatures below 0 °C (32 °F). Although a battery pack^[139] may appear to be charging normally, electroplating of metallic lithium can occur at the negative electrode during a subfreezing charge, and may not be removable even by repeated cycling. Most devices equipped with Li-ion batteries do not allow charging outside of 0–45 °C for safety reasons, except for mobile phones that may allow some degree of charging when they detect an emergency call in progress.^[140]

Performance

- Specific energy density: 100 to 250 W·h/kg (360 to 900 kJ/kg)^[141]
- Volumetric energy density: 250 to 680 W·h/L (900 to 2230 J/cm³)^{[2][142]}
- Specific power density: 300 to 1500 W/kg (at 20 seconds and 285 W·h/L)^[1]

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

The open circuit voltage is higher than aqueous batteries (such as lead acid, nickel-metal hydride and nickel-cadmium).^[143] Internal resistance increases with both cycling and age.^{[143][144]} Rising internal resistance causes the voltage at the terminals to drop under load, which reduces the maximum current draw. Eventually, increasing resistance will leave the battery in a state such that it can no longer support the normal discharge currents requested of it without unacceptable voltage drop or overheating.

Batteries with a lithium iron phosphate positive and graphite negative electrodes 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 positives with graphite negatives have a 3.7 V nominal voltage with a 4.2 V maximum while charging. 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. In 2015 researchers demonstrated a small 600 mAh capacity battery charged to 68 percent capacity in two minutes and a 3,000 mAh battery charged to 48 percent capacity in five minutes. The latter battery has an energy density of 620 W·h/L. The device employed heteroatoms bonded to graphite molecules in the anode.^[145]

Performance of manufactured batteries has improved over time. For example, from 1991 to 2005 the energy capacity per price of lithium ion batteries improved more than ten-fold, from 0.3 W·h per dollar to over 3 W·h per dollar.^[146] In the period from 2011–2017, progress has averaged 7.5% annually.^[147] Differently sized cells with similar chemistry also have the same energy density. The 21700 cell has 50% more energy than the 18650 cell, and the bigger size reduces heat transfer to its surroundings.^[142]

Materials

The increasing demand for batteries has led vendors and academics to focus on improving the energy density operating temperature, safety, durability, charging time, output power, elimination of cobalt requirements,^{[148][149]} and cost of lithium ion battery technology. The following materials have been used in commercially available cells. Research into other materials continues.

Cathode materials are generally constructed from LiCoO₂ or LiMn₂O₄. The cobalt-based material develops a pseudo tetrahedral structure that allows for two-dimensional lithium ion diffusion.^[150] The cobalt-based cathodes are ideal due to their high theoretical specific heat capacity, high volumetric capacity, low self-discharge, high discharge voltage, and good cycling performance. Limitations include the high cost of the material, and low thermal stability.^[151] The manganese-based materials adopt a cubic crystal lattice system,

which allows for three-dimensional lithium ion diffusion.^[150] Manganese cathodes are attractive because manganese is cheaper and because it could theoretically be used to make a more efficient, longer-lasting battery if its limitations could be overcome. Limitations include the tendency for manganese to dissolve into the electrolyte during cycling leading to poor cycling stability for the cathode.^[151] Cobalt-based cathodes are the most common, however other materials are being researched with the goal of lowering costs and improving battery life.^[152]

As of 2017, LiFePO_4 is a candidate for large-scale production of lithium-ion batteries such as electric vehicle applications due to its low cost, excellent safety, and high cycle durability. For example, Sony Fortelion batteries have retained 74% of their capacity after 8000 cycles with 100% discharge.^[153] A carbon conductive agent is required to overcome its low electrical conductivity.^[154]

Electrolyte alternatives have also played a significant role, for example the lithium polymer battery.

Positive electrode

Positive electrode

Technology	Company	Target application	Date	Benefit
<u>Lithium nickel manganese cobalt oxide</u> ("NMC", $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$)	Imara Corporation, <u>Nissan Motor</u> , ^{[155][156]} <u>Microvast Inc.</u> , <u>LG Chem</u> , ^[157] <u>Northvolt</u> ^[158]	<u>Electric vehicles</u> , <u>power tools</u> , <u>grid energy storage</u>	2008	good specific energy and specific power density
<u>Lithium Nickel Cobalt Aluminium Oxide</u> ("NCA", LiNiCoAlO_2)	<u>Panasonic</u> , ^[157] <u>Saft Groupe S.A.</u> , ^[159] <u>Samsung</u> ^[160]	<u>Electric vehicles</u>	1999	High specific energy, good life span
<u>Lithium Manganese Oxide</u> ("LMO", LiMn_2O_4)	<u>LG Chem</u> , ^[161] <u>NEC</u> , <u>Samsung</u> , ^[162] <u>Hitachi</u> , ^[163] <u>Nissan/AESC</u> , ^[164] <u>EnerDel</u> ^[165]	<u>Hybrid electric vehicle</u> , <u>cell phone</u> , <u>laptop</u>	1996	
<u>Lithium Iron Phosphate</u> ("LFP", LiFePO_4)	<u>University of Texas/Hydro-Québec</u> , ^[166] <u>Phostech Lithium Inc.</u> , <u>Valence Technology</u> , <u>A123Systems/MIT</u> ^{[167][168]}	<u>Segway Personal Transporter</u> , <u>power tools</u> , <u>aviation products</u> , <u>automotive hybrid systems</u> , <u>PHEV conversions</u>	1996	moderate density (2 A·h outputs 70 amperes) High safety compared to Cobalt / Manganese systems. Operating temperature >60 °C (140 °F)
<u>Lithium Cobalt Oxide</u> (LiCoO_2 , "LCO")	<u>Sony</u> first commercial production ^{[61][119]}	broad use, <u>laptop</u>	1991	High specific energy

Negative electrode

Negative electrode materials are traditionally constructed from graphite and other carbon materials, although newer silicon based materials are being increasingly used (see Nanowire battery). These materials are used because they are abundant and are electrically conducting and can intercalate lithium ions to store electrical charge with modest volume expansion (ca. 10%).^[169] The reason that graphite is the dominant material is because of its low voltage and excellent performance. Various materials have been introduced but their voltage is high leading to a low energy density.^[170] Low voltage of material is the key requirement; otherwise, the excess capacity is useless in terms of energy density.

Negative electrode

Technology	Density	Durability	Company	Target application	Date	Comments
Graphite			<u>Targray</u>	The dominant negative electrode material used in lithium ion batteries, limited to a capacity of 372 mAh/g. ^[98]	1991	Low cost and good energy density. Graphite anodes can accommodate one lithium atom for every six carbon atoms. Charging rate is governed by the shape of the long, thin graphene sheets. While charging, the lithium ions must travel to the outer edges of the graphene sheet before coming to rest (intercalating) between the sheets. The circuitous route takes so long that they encounter congestion around those edges. ^[171]
Lithium Titanate ("LTO", $\text{Li}_4\text{Ti}_5\text{O}_{12}$)			<u>Toshiba, Altairnano</u>	Automotive (Phoenix Motorcars), electrical grid (PJM Interconnection Regional Transmission Organization control area, ^[172] United States Department of Defense ^[173]), bus (Proterra)	2008	Improved output, charging time, durability (safety, operating temperature -50 – 70 °C (-58 – 158 °F)). ^[174]
Hard Carbon			Energ2 ^[175]	Home electronics	2013	Greater storage capacity.
Tin/Cobalt Alloy			Sony	Consumer electronics (Sony Nexelion battery)	2005	Larger capacity than a cell with graphite (3.5Ah 18650-type battery).
Silicon/Carbon	Volumetric: 580 W·h/l		Ampricus ^[176]	Smartphones, providing 5000 mA·h capacity	2013	Uses < 10wt% Silicon nanowires combined with graphite and binders. Energy density: ~74 mAh/g. Another approach used carbon-coated 15 nm thick crystal silicon flakes. The tested half-cell achieved 1.2 Ah/g over 800 cycles. ^[177]

Anode research

As graphite is limited to a maximum capacity of 372 mAh/g ^[98] much research has been dedicated to the development of materials that exhibit higher theoretical capacities, and overcoming the technical challenges that presently encumber their implementation. The extensive 2007 Review Article by Kasavajjula et al. ^[178] summarizes early research on silicon-based anodes for lithium-ion secondary cells. In particular, Hong Li et al. ^[179] showed in 2000 that the electrochemical insertion of lithium ions in silicon nanoparticles and silicon nanowires leads to the formation of an amorphous Li-Si alloy. The same year, Bo Gao and his doctoral advisor, Professor Otto Zhou described the cycling of electrochemical cells with anodes comprising silicon nanowires, with a reversible capacity ranging from at least approximately 900 to 1500 mAh/g. ^[180]

To improve stability of the lithium anode, several approaches of installing a protective layer have been suggested. ^[181] Silicon is beginning to be looked at as an anode material because it can accommodate significantly more lithium ions, storing up to 10 times the electric charge, however this alloying between lithium and silicon results in significant volume expansion (ca. 400%), ^[169] which causes catastrophic failure for the battery. ^[182] Silicon has been used as an anode material but the insertion and extraction of Li^+ can create cracks in the material. These cracks expose the Si surface to an electrolyte, causing decomposition and the formation of a solid electrolyte interphase (SEI) on the new Si surface (crumpled graphene encapsulated Si nanoparticles). This SEI will continue to grow thicker, deplete the available Li^+ , and degrade the capacity and cycling stability of the anode.

There have been attempts using various Si nanostructures that include nanowires, nanotubes, hollow spheres, nanoparticles, and nanoporous with the goal of them withstanding the (Li^+)-insertion/removal without significant cracking. Yet the formation of SEI on Si still occurs. So a coating would be logical, in order to account for any increase in the volume of the Si, a tight surface coating is not viable. In 2012, researchers from Northwestern University created an approach to encapsulate Si nanoparticles using crumpled r-GO, graphene oxide. This method allows for protection of the Si nanoparticles from the electrolyte as well as allow for the expansion of Si without expansion due to the wrinkles and creases in the graphene balls. ^[183]

These capsules began as an aqueous dispersion of GO and Si particles, and are then nebulized into a mist of droplets that pass through a tube furnace. As they pass through the liquid evaporates, the GO sheets are pulled into a crumpled ball by capillary forces and encapsulate Si particles with them. There is a galvanostatic charge/discharge profile of 0.05 mA/cm² to 1 mA/cm² for current densities 0.2 to 4 A/g, delivering 1200 mAh/g at 0.2 A/g. ^[183]

Polymer electrolytes are promising for minimizing the dendrite formation of lithium. Polymers are supposed to prevent short circuits and maintain conductivity. ^[181]

Diffusion

The ions in the electrolyte diffuse because there are small changes in the electrolyte concentration. Linear diffusion is only considered here. The change in concentration c , as a function of time t and distance x , is

$$\frac{\partial c}{\partial t} = -\frac{D}{\varepsilon} \frac{\partial^2 c}{\partial x^2}.$$

The negative sign indicates that the ions are flowing from high concentration to low concentration. In this equation, D is the diffusion coefficient for the lithium ion. It has a value of $7.5 \times 10^{-10} \text{ m}^2/\text{s}$ in the LiPF_6 electrolyte. The value for ε , the porosity of the electrolyte, is 0.724. ^[184]

Use

Li-ion batteries provide lightweight, high energy density power sources for a variety of devices. To power larger devices, such as electric cars, connecting many small batteries in a parallel circuit is more effective^[185] and more efficient than connecting a single large battery.^[186] Such devices include:

- *Portable devices*: these include mobile phones and smartphones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights).
- *Power tools*: Li-ion batteries are used in tools such as cordless drills, sanders, saws, and a variety of garden equipment including whipper-snippers and hedge trimmers.^[187]
- *Electric vehicles*: electric vehicle batteries are used in electric cars,^[188] hybrid vehicles, electric motorcycles and scooters, electric bicycles, personal transporters and advanced electric wheelchairs. Also radio-controlled models, model aircraft, aircraft,^{[189][190][191]} and the Mars Curiosity rover.

Li-ion batteries are used in telecommunications applications. Secondary non-aqueous lithium batteries provide reliable backup power to load equipment located in a network environment of a typical telecommunications service provider. Li-ion batteries compliant with specific technical criteria are recommended for deployment in the Outside Plant (OSP) at locations such as Controlled Environmental Vaults (CEVs), Electronic Equipment Enclosures (EEEs), and huts, and in uncontrolled structures such as cabinets. In such applications, li-ion battery users require detailed, battery-specific hazardous material information, plus appropriate fire-fighting procedures, to meet regulatory requirements and to protect employees and surrounding equipment.^[192]

Self-discharge

Batteries gradually self-discharge even if not connected and delivering current. Li-ion rechargeable batteries have a self-discharge rate typically stated by manufacturers to be 1.5–2% per month.^{[193][194]}

The rate increases with temperature and state of charge. A 2004 study found that for most cycling conditions self-discharge was primarily time-dependent; however, after several months of stand on open circuit or float charge, state-of-charge dependent losses became significant. The self-discharge rate did not increase monotonically with state-of-charge, but dropped somewhat at intermediate states of charge.^[195] Self-discharge rates may increase as batteries age.^[196] In

1999, self-discharge per month was measured at 8% at 21 °C, 15% at 40 °C, 31% at 60 °C.^[197] By 2007, monthly self-discharge rate was estimated at 2% to 3%,^[198] and 2^[7]–3% by 2016.^[199]

By comparison, the self-discharge rate for NiMH batteries dropped, as of 2017, from up to 30% per month for previously common cells^[200] to about 0.08–0.33% per month for low self-discharge NiMH batteries,^[201] and is about 10% per month in NiCd batteries.



A lithium-ion battery from a laptop computer (176 kJ)

Battery life

Life of a lithium-ion battery is typically defined as the number of full charge-discharge cycles to reach a failure threshold in terms of capacity loss or impedance rise. Manufacturers' datasheet typically uses the word "cycle life" to specify lifespan in terms of the number of cycles to reach 80% of the rated battery capacity.^[202] Inactive storage of these batteries also reduces their capacity. Calendar life is used to represent the whole life cycle of battery involving both the cycle and inactive storage operations.

Battery cycle life is affected by many different stress factors including temperature, discharge current, charge current, and state of charge ranges (depth of discharge).^{[203][204]} Batteries are not fully charged and discharged in real applications such as smartphones, laptops and electric cars and hence defining battery life via full discharge cycles can be misleading. To avoid this confusion, researchers sometimes use cumulative discharge^[203] defined as the total amount of charge (Ah) delivered by the battery during its entire life or equivalent full cycles,^[205] which represents the summation of the partial cycles as fractions of a full charge-discharge cycle. Battery degradation during the storage is affected by temperature and battery state of charge (SOC) and a combination of full charge (100% SOC) and high temperature (usually > 50 °C) can result in sharp capacity drop and gas generation.^[206]

Multiplying the battery cumulative discharge (in Ah) by the rated nominal Voltage gives the total energy delivered over the life of the battery. From this one can calculate the cost per kWh of the energy (including the cost of charging).

Degradation

Over their lifespan batteries degrade gradually leading to reduced capacity due to the chemical and mechanical changes to the electrodes.^[207] Batteries are multiphysics electrochemical systems and degrade through a variety of concurrent chemical, mechanical, electrical and thermal failure mechanisms. Some of the prominent mechanisms include solid electrolyte interphase layer (SEI) growth, lithium plating, mechanical cracking of SEI layer and electrode particles, and thermal decomposition of electrolyte.^[207]

Degradation is strongly temperature-dependent, with a minimal degradation around 25 °C, i.e., increasing if stored or used at above or below 25 °C.^[208] High charge levels and elevated temperatures (whether from charging or ambient air) hasten capacity loss.^[209] Carbon anodes generate heat when in use. Batteries may be refrigerated to reduce temperature effects.^[210]

Pouch and cylindrical cell temperatures depend linearly on the discharge current.^[211] Poor internal ventilation may increase temperatures. 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). In contrast, the calendar life of LiFePO_4 cells is not affected by high charge states.^{[212][213]}

The advent of the SEI layer improved performance, but increased vulnerability to thermal degradation. The layer is composed of electrolyte – carbonate reduction products that serve both as an ionic conductor and electronic insulator. It forms on both the anode and cathode and determines many performance parameters. Under typical conditions, such as room temperature and the absence of charge effects and contaminants, the layer reaches a fixed thickness after the first charge, allowing the device to operate for years. However, operation outside such parameters can degrade the device via several reactions.^[214]

Lithium-ion batteries are prone to capacity fading over hundreds^[215] to thousands of cycles. It is by slow electrochemical processes, the formation of a solid-electrolyte inter phase (SEI) in the negative electrode. SEI forms in between the first charge and discharge and results in the consumption of lithium ions. The consumption of lithium ions reduces the charge and discharge efficiency of the electrode material.^[216] However, SEI film is organic solvent insoluble and hence it can be stable in organic electrolyte solutions. If proper additives are added to the electrolyte to promote SEI formation, the co-embedding of solvent molecules can be effectively prevented and the damage to electrode materials can be avoided. On the other hand, SEI is selective and allows lithium ions to pass through and forbids electrons to pass through. This guarantees the continuity of charging and discharging cycle.^[217] SEI hinders the further consumption of lithium ions and thus greatly improves the electrode, as well as the cycle performance and service life. New data has shown that

exposure to heat and the use of fast charging promote the degradation of Li-ion batteries more than age and actual use.^[218] Charging Li-ion batteries beyond 80% can drastically accelerate battery degradation.^{[219][220][221][222][223]}

Reactions

Five common exothermic degradation reactions can occur:^[214]

- Chemical reduction of the electrolyte by the anode.
- Thermal decomposition of the electrolyte.
- Chemical oxidation of the electrolyte by the cathode.
- Thermal decomposition by the cathode and anode.
- Internal short circuit by charge effects.

Anode

The SEI layer that forms on the anode is a mixture of lithium oxide, lithium fluoride and semicarbonates (e.g., lithium alkyl carbonates).

At elevated temperatures, alkyl carbonates in the electrolyte decompose into insoluble Li_2CO_3 that increases film thickness, limiting anode efficiency. This increases cell impedance and reduces capacity.^[208] Gases formed by electrolyte decomposition can increase the cell's internal pressure and are a potential safety issue in demanding environments such as mobile devices.^[214]

Below 25 °C, plating of metallic Lithium on the anodes and subsequent reaction with the electrolyte is leading to loss of cyclable Lithium.^[208]

Extended storage can trigger an incremental increase in film thickness and capacity loss.^[214]

Charging at greater than 4.2 V can initiate Li^+ plating on the anode, producing irreversible capacity loss. The randomness of the metallic lithium embedded in the anode during intercalation results in dendrites formation. Over time the dendrites can accumulate and pierce the separator, causing a short circuit leading to heat, fire or explosion. This process is referred to as thermal runaway.^[214]

Discharging beyond 2 V can also result in capacity loss. The (copper) anode current collector can dissolve into the electrolyte. When charged, copper ions can reduce on the anode as metallic copper. Over time, copper dendrites can form and cause a short in the same manner as lithium.^[214]

High cycling rates and state of charge induces mechanical strain on the anode's graphite lattice. Mechanical strain caused by intercalation and de-intercalation creates fissures and splits of the graphite particles, changing their orientation. This orientation change results in capacity loss.^[214]

Electrolytes

Electrolyte degradation mechanisms include hydrolysis and thermal decomposition.^[214]

At concentrations as low as 10 ppm, water begins catalyzing a host of degradation products that can affect the electrolyte, anode and cathode.^[214] LiPF_6 participates in an equilibrium reaction with LiF and PF_5 . Under typical conditions, the equilibrium lies far to the left. However the presence of water generates substantial LiF , an insoluble, electrically insulating product. LiF binds to the anode surface, increasing film thickness.^[214]

LiPF₆ hydrolysis yields PF₅, a strong Lewis acid that reacts with electron-rich species, such as water. PF₅ reacts with water to form hydrofluoric acid (HF) and phosphorus oxyfluoride. Phosphorus oxyfluoride in turn reacts to form additional HF and difluorohydroxy phosphoric acid. HF converts the rigid SEI film into a fragile one. On the cathode, the carbonate solvent can then diffuse onto the cathode oxide over time, releasing heat and thermal runaway.^[214]

Decomposition of electrolyte salts and interactions between the salts and solvent start at as low as 70 °C. Significant decomposition occurs at higher temperatures. At 85 °C transesterification products, such as dimethyl-2,5-dioxahexane carboxylate (DMDOHC) are formed from EC reacting with DMC.^[214]

Cathode

Cathode degradation mechanisms include manganese dissolution, electrolyte oxidation and structural disorder.^[214]

In LiMnO₄ hydrofluoric acid catalyzes the loss of metallic manganese through disproportionation of trivalent manganese.^[214]



Material loss of the spinel results in capacity fade. Temperatures as low as 50 °C initiate Mn²⁺ deposition on the anode as metallic manganese with the same effects as lithium and copper plating.^[208] Cycling over the theoretical max and min voltage plateaus destroys the crystal lattice via Jahn-Teller distortion, which occurs when Mn⁴⁺ is reduced to Mn³⁺ during discharge.^[214]

Storage of a battery charged to greater than 3.6 V initiates electrolyte oxidation by the cathode and induces SEI layer formation on the cathode. As with the anode, excessive SEI formation forms an insulator resulting in capacity fade and uneven current distribution.^[214]

Storage at less than 2 V results in the slow degradation of LiCoO₂ and LiMn₂O₄ cathodes, the release of oxygen and irreversible capacity loss.^[214]

Conditioning

The need to "condition" NiCd and NiMH batteries has leaked into folklore surrounding Li-ion batteries, but is unfounded. The recommendation for the older technologies is to leave the device plugged in for seven or eight hours, even if fully charged.^[224] This may be a confusion of battery *software* calibration instructions with the "conditioning" instructions for NiCd and NiMH batteries.^[225]

Multicell devices

Li-ion batteries require a battery management system to prevent operation outside each cell's safe operating area (max-charge, min-charge, safe temperature range) and to balance cells to eliminate state of charge mismatches. This significantly improves battery efficiency and increases capacity. As the number of cells and load currents increase, the potential for mismatch increases. The two kinds of mismatch are state-of-charge (SOC) and capacity/energy ("C/E"). Though SOC is more common, each problem limits pack charge capacity (mA·h) to that of the weakest cell.

Safety

Fire hazard

Lithium-ion batteries can be a safety hazard since they contain a flammable electrolyte and may become pressurized if they become damaged. A battery cell charged too quickly could cause a short circuit, leading to explosions and fires.^[226] Because of these risks, testing standards are more stringent than those for acid-electrolyte batteries, requiring both a broader range of test conditions and additional battery-specific tests, and there are shipping limitations imposed by safety regulators.^{[136][227][23]} There have been battery-related recalls by some companies, including the 2016 Samsung Galaxy Note 7 recall for battery fires.^{[15][228]}

Lithium-ion batteries, unlike rechargeable batteries with water-based electrolytes, have a potentially hazardous pressurised flammable liquid electrolyte, and require strict quality control during manufacture.^[229] A faulty battery can cause a serious fire.^[226] Faulty chargers can affect the safety of the battery because they can destroy the battery's protection circuit. While charging at temperatures below 0 °C, the negative electrode of the cells gets plated with pure lithium, which can compromise the safety of the whole pack.

Short-circuiting a battery will cause the cell to overheat and possibly to catch fire. Adjacent cells may then overheat and fail, possibly causing the entire battery to ignite or rupture. In the event of a fire, the device may emit dense irritating smoke.^[230] The fire energy content (electrical + chemical) of cobalt-oxide cells is about 100 to 150 kJ/(A·h), most of it chemical.^{[135][231]}

While fire is often serious, it may be catastrophically so. Around 2010, large lithium-ion batteries were introduced in place of other chemistries to power systems on some aircraft; as of January 2014, there had been at least four serious lithium-ion battery fires, or smoke, on the Boeing 787 passenger aircraft, introduced in 2011, which did not cause crashes but had the potential to do so.^{[232][233]}

In addition, several aircraft crashes have been attributed to burning Li-Ion batteries. UPS Airlines Flight 6 crashed in Dubai after its payload of batteries spontaneously ignited, progressively destroying critical systems inside the aircraft which eventually rendered it uncontrollable.

To reduce fire hazards and increase battery safety, research interest has grown to develop non-flammable electrolytes. Researchers are making efforts to formulate safe (non-flammable) electrolytes with enhanced battery performances. Promising options are:

- Solid state electrolytes ^[234]
- Gel polymer electrolytes ^[235]
- Non-flammable liquid electrolytes
 - Based on flame-retardant solvent ^[236]
 - Using flame-retardant additives ^[237]
 - Based on fluor or phosphonates ^[238]
 - Organosilicon-containing electrolytes ^[239]
 - Ionic liquids (with or without solvents) ^[240]

Damaging and overloading

If a lithium-ion battery is damaged, crushed, or is subjected to a higher electrical load without having overcharge protection, then problems may arise. External short circuit can trigger the battery explosion.^[241]

If overheated or overcharged, Li-ion batteries may suffer thermal runaway and cell rupture.^{[242][243]} In extreme cases this can lead to leakage, explosion or fire. To reduce these risks, many lithium-ion cells (and battery packs) contain fail-safe circuitry that disconnects the battery when its voltage is outside the safe range of 3–4.2 V per cell.^{[119][200]} or when overcharged or discharged. Lithium battery packs, whether constructed by a vendor or the end-user, without effective battery management circuits are susceptible to these issues. Poorly designed or implemented battery management circuits also may cause problems; it is difficult to be certain that any particular battery management circuitry is properly implemented.

Voltage limits

Lithium-ion cells are susceptible to stress by voltage ranges outside of safe ones between 2.5 and 3.65/4.1/4.2 or 4.35V (depending on the components of the cell). Exceeding this voltage range results in premature aging and in safety risks due to the reactive components in the cells.^[244] When stored for long periods the small current draw of the protection circuitry may drain the battery below its shutoff voltage; normal chargers may then be useless since the battery management system (BMS) may retain a record of this battery (or charger) 'failure'. Many types of lithium-ion cells cannot be charged safely below 0 °C,^[245] as this can result in plating of lithium on the anode of the cell, which may cause complications such as internal short-circuit paths.

Other safety features are required in each cell:^[119]

- Shut-down separator (for overheating)
- Tear-away tab (for internal pressure relief)
- Vent (pressure relief in case of severe outgassing)
- Thermal interrupt (overcurrent/overcharging/environmental exposure)

These features are required because the negative electrode produces heat during use, while the positive electrode may produce oxygen. However, these additional devices occupy space inside the cells, add points of failure, and may irreversibly disable the cell when activated. Further, these features increase costs compared to nickel metal hydride batteries, which require only a hydrogen/oxygen recombination device and a back-up pressure valve.^[200] Contaminants inside the cells can defeat these safety devices. Also, these features can not be applied to all kinds of cells, e.g. prismatic high current cells cannot be equipped with a vent or thermal interrupt. High current cells must not produce excessive heat or oxygen, lest there be a failure, possibly violent. Instead, they must be equipped with internal thermal fuses which act before the anode and cathode reach their thermal limits.

Replacing the lithium cobalt oxide positive electrode material in lithium-ion batteries with a lithium metal phosphate such as lithium iron phosphate (LFP) improves cycle counts, shelf life and safety, but lowers capacity. As of 2006, these 'safer' lithium-ion batteries were mainly used in electric cars and other large-capacity battery applications, where safety is critical.^[246]

Recalls

- In October 2004, Kyocera Wireless recalled approximately 1 million mobile phone batteries to identify counterfeits.^[247]
- In December 2005, Dell recalled approximately 22,000 laptop computer batteries, and 4.1 million in August 2006.^[248]
- In 2006, approximately 10 million Sony batteries used in Dell, Sony, Apple, Lenovo, Panasonic, Toshiba, Hitachi, Fujitsu and Sharp laptops were recalled. The batteries were found to be susceptible to internal contamination by metal particles during manufacture. Under

some circumstances, these particles could pierce the separator, causing a dangerous short circuit.^[249]

- In March 2007, computer manufacturer Lenovo recalled approximately 205,000 batteries at risk of explosion.
- In August 2007, mobile phone manufacturer Nokia recalled over 46 million batteries at risk of overheating and exploding.^[250] One such incident occurred in the Philippines involving a Nokia N91, which used the BL-5C battery.^[251]
- In September 2016, Samsung recalled approximately 2.5 million Galaxy Note 7 phones after 35 confirmed fires.^[228] The recall was due to a manufacturing design fault in Samsung's batteries which caused internal positive and negative poles to touch.^[252]

Transport restrictions

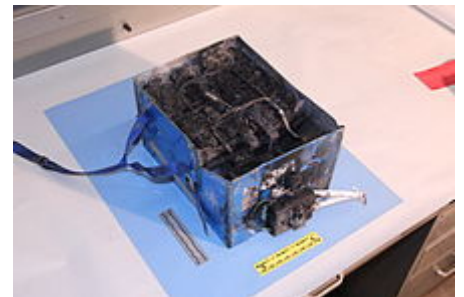
IATA estimates that over a billion lithium and lithium-ion cells are flown each year.^[231]

Carriage and shipment of some kinds of lithium batteries may be prohibited aboard certain types of transportation (particularly aircraft) because of the ability of most types of lithium batteries to fully discharge very rapidly when short-circuited, leading to overheating and possible explosion in a process called thermal runaway. Most consumer lithium batteries have built-in thermal overload protection to prevent this type of incident, or are otherwise designed to limit short-circuit currents. Internal shorts from manufacturing defect or physical damage can lead to spontaneous thermal runaway.^{[253][254]}

The maximum size of each battery (whether installed in a device or as spare batteries) that can be carried is one that has an equivalent lithium content (ELC) not exceeding 8 grams per battery. *Except*, that if only one or two batteries are carried, each may have an ELC of up to 25 g.^[255] The ELC for any battery is found by multiplying the ampere-hour capacity of each cell by 0.3 and then multiplying the result by the number of cells in the battery.^[255] The resultant calculated lithium content is not the actual lithium content but a theoretical figure solely for transportation purposes. When shipping lithium ion batteries however, if the total lithium content in the cell exceeds 1.5 g, the package must be marked as "Class 9 miscellaneous hazardous material".

Although devices containing lithium-ion batteries may be transported in checked baggage, spare batteries may be only transported in carry-on baggage.^[255] They must be protected against short circuiting, and example tips are provided in the transport regulations on safe packaging and carriage; e.g., such batteries should be in their original protective packaging or, "by taping over the exposed terminals or placing each battery in a separate plastic bag or protective pouch".^{[255][256]} These restrictions do not apply to a lithium-ion battery that is a part of a wheelchair or mobility aid (including any spare batteries) to which a separate set of rules and regulations apply.^[255]

Some postal administrations restrict air shipping (including EMS) of lithium and lithium-ion batteries, either separately or installed in equipment. Such restrictions apply in Hong Kong,^[257] Australia and Japan.^[258] Other postal administrations, such as the United Kingdom's Royal Mail may permit limited carriage of batteries or cells that are operative but totally prohibit handling of known defective ones, which is likely to prove of significance to those discovering faulty such items bought through mail-order channels.^[259] IATA provides details in its Lithium Battery Guidance document.



Japan Airlines Boeing 787 lithium cobalt oxide battery that caught fire in 2013



Transport Class 9A:Lithium batteries

On 16 May 2012, the United States Postal Service (USPS) banned shipping anything containing a lithium battery to an overseas address, after fires from transport of batteries.^[260] This restriction made it difficult to send anything containing lithium batteries to military personnel overseas, as the USPS was the only method of shipment to these addresses; the ban was lifted on 15 November 2012.^[261] United Airlines and Delta Air Lines excluded lithium-ion batteries in 2015 after an FAA report on chain reactions.^{[262][263][264]}

The Boeing 787 Dreamliner uses large lithium cobalt oxide^[265] batteries, which are more reactive than newer types of batteries such as LiFePO_4 .^{[266][136]}

Starting on 15 January 2018, several major U.S. airlines banned smart luggage with non-removable batteries from being checked in to travel in the cargo hold due to the risk of fire.^[267] Some airlines continued to mistakenly prevent passengers from bringing smart luggage as a carry on after the ban went into effect.^[268]

Several smart luggage companies have been forced to shut down as a result of the ban.^[269]

Environmental impact and recycling

Since Li-ion batteries contain less toxic metals than other types of batteries which may contain lead or cadmium,^[119] they are generally categorized as non-hazardous waste. Li-ion battery elements including iron, copper, nickel and cobalt are considered safe for incinerators and landfills. These metals can be recycled,^{[270][271]} usually by burning away the other materials,^[272] but mining generally remains cheaper than recycling.^[273] Recycling may cost \$3/kg.^[274] In the past, not much was invested into recycling Li-ion batteries due to cost, complexity and low yield. Since 2018, the recycling yield was increased significantly, and the recovering of lithium, manganese, aluminum, the organic solvents of the electrolyte and graphite is possible at industrial scales.^[275] The most expensive metal involved in the construction of the cell is cobalt, much of which is mined in Congo (see also Mining industry of the Democratic Republic of the Congo). Lithium iron phosphate is cheaper, but has other drawbacks. Lithium is less expensive than other metals used and is rarely recycled,^[272] but recycling could prevent a future shortage.^[270]

The manufacturing processes of lithium, nickel and cobalt, the solvent, and mining byproducts present significant environmental and health hazards.^{[276] [277][278]} Lithium extraction can be fatal to aquatic life due to water pollution.^[279] It is known to cause surface water contamination, drinking water contamination, respiratory problems, ecosystem degradation and landscape damage.^[276] It also leads to unsustainable water consumption in arid regions (1.9 million liters per ton of lithium).^[276] Massive byproduct generation of lithium extraction also presents unsolved problems, such as large amounts of magnesium and lime waste.^[280]

Lithium mining takes place in selected mines in North and South America, Asia, South Africa, Central Andes and China.^[281] China requires car manufacturers to be responsible for the battery's end of life, and Europe requires half of batteries to be recycled.^[272]

Manufacturing a kg of Li-ion battery takes about 67 megajoule (MJ) of energy.^{[282][283]} The global warming potential of lithium-ion batteries manufacturing strongly depends on the energy source used in mining and manufacturing operations. Various estimates range from 62^[284] to 140 kg CO₂-equivalents per kWh.^[285] Effective recycling can reduce the carbon footprint of the production significantly.^[286]

Recycling lithium-ion batteries from electric vehicles

In 2017, sales of electric vehicles exceeded one million cars per year for the first time, resulting in at least 250,000 tons of unprocessed battery waste.^[287] Although current recycling efforts can keep some batteries from the landfill, accumulation of battery waste remains a serious problem. Since the environmental impact of

electric cars is heavily affected by the production of these lithium-ion batteries, the development of efficient ways to repurpose waste is crucial.

Recycling is a multi-step process, starting with the storage of batteries before disposal, followed by manual testing, disassembling, and finally the chemical separation of battery components. Re-use of the battery is preferred over complete recycling as there is less embedded energy in the process. As these batteries are a lot more reactive than classical vehicle waste like tire rubber, there are significant risks to stockpiling used batteries. ^[288]

Recycling methods

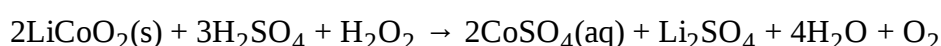
Pyrometallurgical recovery

The pyrometallurgical method uses a high-temperature furnace to reduce the components of the metal oxides in the battery to an alloy of Co, Cu, Fe, and Ni. This is the most common and commercially established method of recycling and can be combined with other similar batteries to increase smelting efficiency and improve thermodynamics. The metal current collectors aid the smelting process, allowing whole cells or modules to be melted at once. ^[289]

The product of this method is a collection of metallic alloy, slag, and gas. At high temperatures, the polymers used to hold the battery cells together burn off and the metal alloy can be separated through a hydrometallurgical process into its separate components. The slag can be further refined or used in the cement industry. The process is relatively risk-free and the exothermic reaction from polymer combustion reduces the required input energy. However, in the process, the plastics, electrolytes, and lithium salts will be lost. ^[290]

Hydrometallurgical metals reclamation

This method involves the use of aqueous solutions to remove the desired metals from the cathode. The most common reagent is sulfuric acid.^[291] Factors that affect the leaching rate include the concentration of the acid, time, temperature, solid-to-liquid-ratio, and reducing agent.^[292] It is experimentally proven that H_2O_2 acts as a reducing agent to speed up the rate of leaching through the reaction:



Once leached, the metals can be extracted through precipitation reactions controlled by changing the pH level of the solution. Cobalt, the most expensive metal, can then be recovered in the form of sulfate, oxalate, hydroxide, or carbonate. [75] More recently recycling methods experiment with the direct reproduction of the cathode from the leached metals. In these procedures, concentrations of the various leached metals are premeasured to match the target cathode and then the cathodes are directly synthesized.^[293]

The main issues with this method, however, is that a large volume of solvent is required and the high cost of neutralization. Although it's easy to shred up the battery, mixing the cathode and anode at the beginning complicates the process, so they will also need to be separated. Unfortunately, the current design of batteries makes the process extremely complex and it is difficult to separate the metals in a closed-loop battery system. Shredding and dissolving may occur at different locations.^[294]

Direct recycling

Direct recycling is the removal of the cathode or anode from the electrode, reconditioned, and then reused in a new battery. Mixed metal-oxides can be added to the new electrode with very little change to the crystal morphology. The process generally involves the addition of new lithium to replenish the loss of lithium in the cathode due to degradation from cycling. Cathode strips are obtained from the dismantled batteries, then soaked in NMP, and undergo sonication to remove excess deposits. It is treated hydrothermally with a solution containing $\text{LiOH/Li}_2\text{SO}_4$ before annealing. ^[295]

This method is extremely cost-effective for noncobalt-based batteries as the raw materials do not make up the bulk of the cost. Direct recycling avoids the time consuming and expensive purification steps, which is great for low-cost cathodes such as LiMn_2O_4 and LiFePO_4 . For these cheaper cathodes, most of the cost, embedded energy, and carbon footprint is associated with the manufacturing rather than the raw material. ^[296] It is experimentally shown that direct recycling can reproduce similar properties to pristine graphite.

The drawback of the method lies in the condition of the retired battery. In the case where the battery is relatively healthy, direct recycling can cheaply restore its properties. However, for batteries where the state of charge is low, direct recycling may not be worth the investment. The process must also be tailored to the specific cathode composition, and therefore the process must be configured to one type of battery at a time. ^[297] Lastly, in a time with rapidly developing battery technology, the design of a battery today may no longer be desirable a decade from now, rendering direct recycling ineffective.

Research

Researchers are actively working to improve the power density, safety, cycle durability (battery life), recharge time, cost, flexibility, and other characteristics, as well as research methods and uses, of these batteries.

See also

- Aluminium-ion battery
- Comparison of commercial battery types
- European Battery Alliance
- Gigafactory 1
- Glass battery
- List of battery sizes – Wikipedia list article
- List of battery types – Wikipedia list article
- List of energy densities
- Lithium as an investment
- Lithium battery
- Lithium-ion capacitor (LIC)
- Lithium ion manganese oxide battery
- Lithium iron phosphate battery – Type of Li-ion cell using LiFePO_4
- Lithium polymer battery – Lithium-ion battery using a polymer electrolyte
- Lithium–sulfur battery
- Lithium-titanate battery – Fast rechargeable lithium ion battery
- Lithium vanadium phosphate battery
- Lithium-ion flow battery
- Lithium–air battery
- Lithium–silicon battery

- Nanotechnology – Field of applied science whose theme is the control of matter on atomic and (supra)molecular scale
- Nanowire battery
- Plug-in electric vehicle fire incidents – Type of vehicle incident
- Solid-state battery
- Thin film lithium-ion battery
- Sodium-ion battery
- Potassium-ion battery

Notes

- a. According to the definitions of anode and cathode, technically this means that the positive electrode should be called anode and the negative electrode should be called cathode during charging (opposite from how they are called during discharging), but in practice, for rechargeable Li-ion cells, the negative electrode is usually called anode and the positive electrode is usually called cathode regardless of whether the cell is discharging, resting, or charging.

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Further reading

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External links

- Energy Storage Safety at National Renewable Energy Laboratory (<https://web.archive.org/web/20170207004939/http://www.nrel.gov/transportation/energystorage/safety.html>)
- NREL Innovation Improves Safety of Electric Vehicle Batteries (<https://web.archive.org/web/20160301144207/http://www.nrel.gov/news/features/2015/21589>), National Renewable Energy Laboratory, October 2015

- Degradation Mechanisms and Lifetime Prediction for Lithium-Ion Batteries – A Control Perspective (<http://www.nrel.gov/docs/fy15osti/64171.pdf>), National Renewable Energy Laboratory, July 2015.
 - Addressing the Impact of Temperature Extremes on Large Format Li-ion Batteries for Vehicle Applications (<https://purl.fdlp.gov/GPO/gpo41672>), National Renewable Energy Laboratory, March 2013.
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