SCIENTIFIC REVIEWS

Nobel Prize of Chemistry 2019 for Lithium-ion Batteries that Revolutionised Lives of Humankind.

Power source for portable electronics, electric vehicles, and storage of energy from renewable sources

Athanasios Valavanidis
Department of Chemistry, National and Kapodistrian University of Athens, University Campus, 15784, Athens, Greece

E-mail : valavanidis@chem.uoa.gr

Abstract

Undoubtedly, Lithium-ion batteries have revolutionised the lives of humankind in the last decades. They have laid the foundation of a wireless civilisation, forming the powerhouse for the personal digital electronic revolution. They are currently the dominant mobile power sources for portable electronic devices, exclusively used in cell phones and laptop computers. Another expanding market for Li-ion batteries is electric and hybrid vehicles, which require next-generation Li-ion batteries with high power, high capacity and high charging rate. Also, Li-ion batteries can be employed to buffer the intermittent and fluctuating green energy supply from renewable resources (solar, wind) leading the effort for a fossil fuel-free society. The Nobel Prize of Chemistry 2019 recognised three scientists who contributed to research and discovery of Li-ion batteries and their beneficial applications for the whole of humankind. Professors Michael Stanley Whittingham, John Bannister Goodenough and Yoshino Akira, were the recipients of the prize for their valuable contribution to the discovery of lithium-ion batteries. In 1991 Sony, dominant maker of personal electronic devices (Walkman) commercialized Li-ion batteries. It was a tremendous success and supported the revolution of personal mobile electronics. Also Professor Rachid Yazami, Moroccan scientist and engineer, played an important role in the applications of Li-ion batteries. When Li-ion battery is compared with other commercial rechargeable batteries for energy densities clearly shows its superiority. It is expected that for the next decade the advantages of Li-ion batteries will still be dominant in the rechargeable battery market. The basic design of Li-ion cells today is still the same as those cells Sony commercialized two decades ago, although various kinds of electrode materials, electrolyte, and separators have been explored and applied to superior performance batteries. More research has been devoted worldwide investigating for new materials for cathode and anode electrodes, separators and electrolytes of Lithium-ion batteries. This review collected the most relevant and important research papers, books and reports on Lithium-ion batteries and the promising future of new materials to be used for electric vehicles and storage of fluctuating grid energy produced by renewable energy sources (solar, wind power).

Introduction: Lithium-ion baterries as dominant mobile power sources

Lithium-ion batteries (Li-ion) have been established as the most advanced rechargeable batteries. They are currently the dominant mobile power sources for portable electronic devices, exclusively used in cell phones and laptop computers.[1,2] In the last decade applications and uses of Li-ion batteries have increased substanially for the benefit of humankind. In particular, as long-range power source of electric vehicles, portable devices, and for storage of fluctuating grid energy produced by renewable energy sources (solar, wind power). Li-ion batteries have advanced rapidly because of their high specific energy densities, rechargeability and stable cycling performance in most applications.[3-5]

Li-ion batteries are considered the powerhouse for the personal digital electronic revolution starting from about two decades ago. Another important expanding market for Li-ion batteries is electric and hybrid vehicles, which require next-generation Li-ion batteries with high power, high capacity, high charging rate, long life and easily rechargeable. Research on Li-ion batteries has also dramatically improved safety performance and low cost.[6,7]

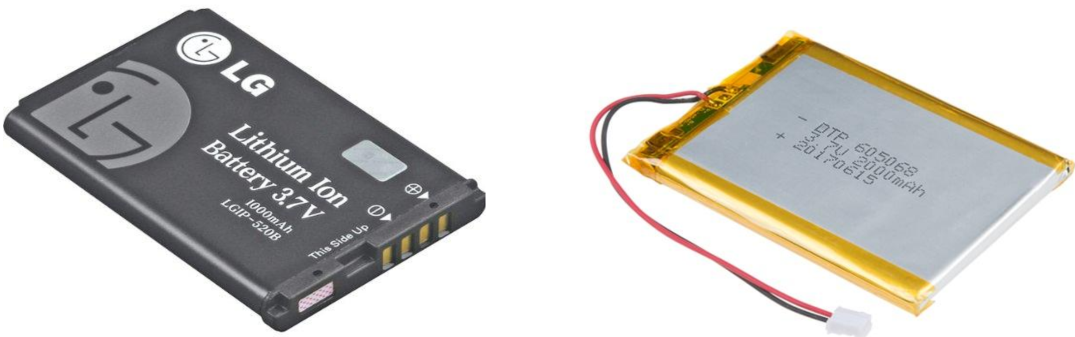


Figure 1. Lithium-ion batteries are very slim, extremely light and based on Lithium (Li) Ion chemistry. Each cell outputs a nominal 3.7V at 2000mAh!

In the last decade the demand for Li-ion batteries increased rapidly, because of the high demand from electric-powered vehicles. In addition, scientists established that Li-ion batteries can be employed to buffer the intermittent and fluctuating green energy supply from renewable resources, such as solar and wind power facilities. This buffeting is very important to smooth the difference between energy supply and demand in an electricity supply grid. For example, extra solar energy generated during the day time can be stored in Li-ion batteries that will supply energy at night when sun light is not available. Large-scale Li-ion batteries for grid application will require next-generation batteries to be produced at low cost.[8-10]

Another important aspect of Li-ion batteries is related to battery safety. It is inevitable that safety is a crucial issue and will trigger another wave of extensive research and development to enhance safety of Li-ion batteries, beyond pursuing high-energy density. The Li-ion system is safe, providing certain precautions are met when charging and discharging. Today, lithium-ion is one of the most successful and safe battery available withh low self-discharge and environmentally friendly. The safety of Li-ion batteries is a serious scientific issue. Some accidents related to fires and explosions of Li-ion batteries occurred in the past, especially involving cell phones, laptops, electric vehicles, and airplanes. Some accidents have caused serious threats to human life and health and have led to numerous product recalls by manufacturers.[11-13]

For example, the Tesla electric car battery fire (November 2013), the Boeing 787 Dreamliner battery problems (2013, 4 aircraft suffered from electrical system problems stemming from Lithium-ion batteries), Samsung Note 7 fires and explosions, etc. have attracted mass media attention. On 2 September 2016, Samsung suspended sales of the Galaxy Note 7 and announced an informal recall, after it was found that a manufacturing defect in the phones' batteries had caused some of them to generate excessive heat, resulting in fires. In July 2017, 9 months after the Note7 recall, Samsung released a refurbished version of the Galaxy Note 7 called Galaxy Note Edition (marketed as Samsung Galaxy Note FE). The initial phopne contained a design flaw that made electrodes on the top-right of the battery susceptible to bending. This weakened separation between positive and negative tabs of the battery, thus resulting in thermal runaway and short circuits. [c/net 2016 https://www.cnet.com/news/samsung-confirms-global-recall-replacement-galaxy-note-7-faulty-battery/].

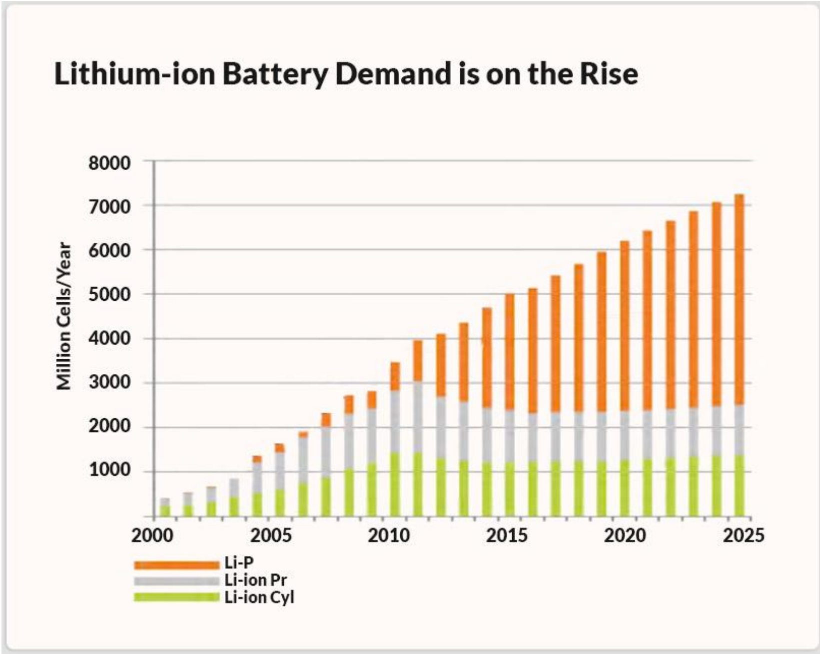


Figure 1. The global lithium-ion battery market size is estimated to touch nearly U.S. Dollars 105.0 billion by 2025, owing to the increasing demand from consumer electronics and electric vehicles. Lithium-cobalt oxide battery (such as $LiCoO_2$) dominated the market with a revenue share of more than 30% in the year 2018.

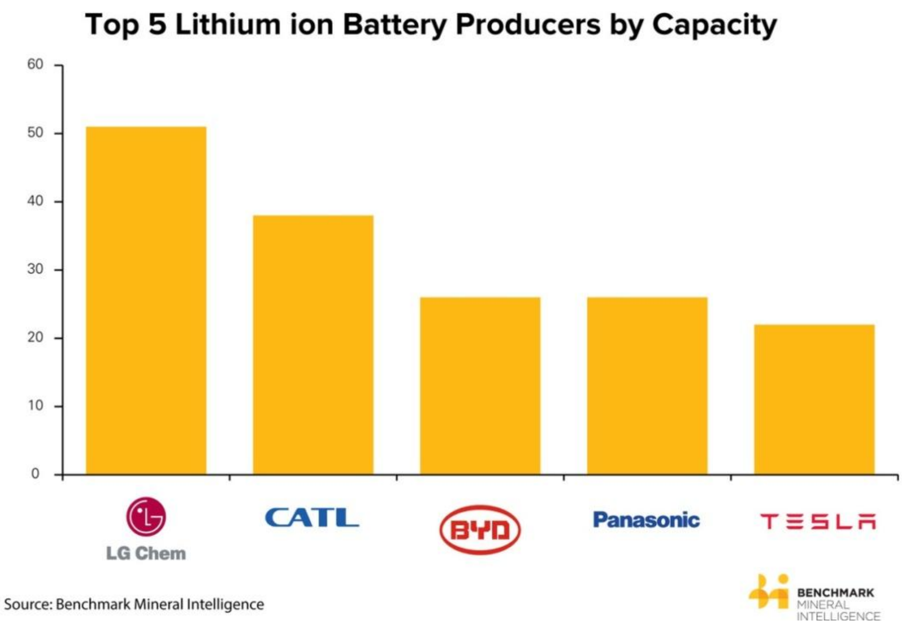


Figure 2. **LG Chem** saw the South Korean lithium-ion battery producer rise to the number one. But in 2019, Panasonic (Sony) from Japan is the largest producer of Lithium-ion batteries for electric mobility at 23GWh, followed by Contemporary Amperex Technology (CATL, Chinese), BYD (Chinese) and Tesla (USA). Source: Benchmark Mineral Intelligence**.**

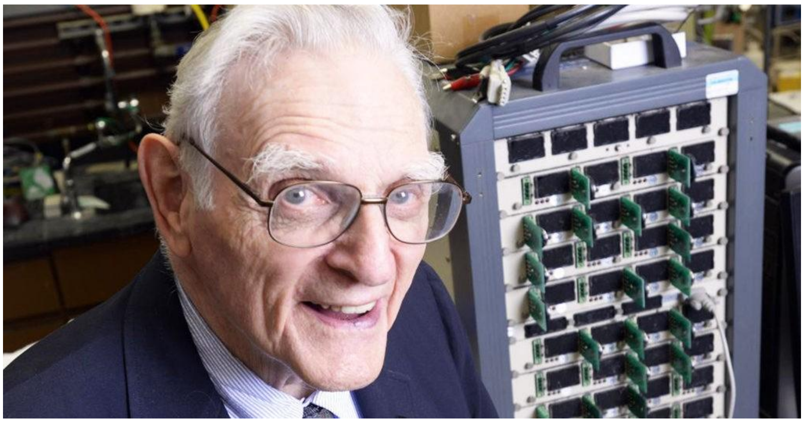
History of the discovery and development of Li-ion batteries

The first rechargeable Li-ion batteries with cathode of layered TiS_2 and anode of metallic Li was reported by **Whittingham** while working at Exxon in 1976.[14] Michael Stanley Whittingham (born 1941 in Nottingham, England, studied Chemistry at Oxford University). Whittingham M.S. is currently, professor of chemistry and director of both the Institute for Materials Research and Materials Science and Engineering program, Binghamton University (State University of New York). [https://www.binghamton.edu/chemistry/people/whittingham/whittingham.html].

Prof. Whittingham discovered the intercalation electrodes (late 1970s).

Prof. Whittingham is a key figure in the history of the development of lithium batteries. He described for the first time the concept of intercalation reaction for rechargeable batteries. He holds the original patents on the concept of the use of intercalation chemistry in high-power density, highly reversible lithium batteries. Therefore, he is called Founding Father of rechargeable lithium batteries. Exxon subsequently tried to commercialize the Li-ion batteries, but was not successful due to the problems of Li dendrite formation and short circuit upon extensive cycling and safety concern.

In 1981, material science scientist John Bannister **Goodenough** first proposed to use layered $LiCoO_2$ as high energy and high voltage cathode materials in batteries. John Bannister Goodenough (born 1922, Jena, Germany, to American parents). Graduated from Yale University, and obtained his Ph.D in physics from Chicago University. He is a materials scientist and solid-state physicist and professor of Mechanical Engineering and Materials Science at the University of Texas at Austin (USA). He is widely credited with the identification and development of the Lithium-ion battery. Goodenough in the 1980s expanded and used Li_xCoO_2 as a lightweight, high energy density cathode material. His research proved that this material could double the capacity of lithium-ion batteries. Interestingly, layered $LiCoO_2$ did not attract much attention initially.[15]



John Bannister Goodenough (born 1922, Jena, Germany) is an American materials scientist and solid-state physicist.

In 1983, Goodenough also identified manganese spinel as a low-cost cathode material. However, the lack of safe anode materials limited the application of layered oxide cathode of $LiMO_2$ (M = Ni, Co) of Nickel and Cobalt, in Li-ion batteries.[16]

Dr. Yoshino Akira, (born in Japan, 1948) filed a patent (with Sanechika K, and Nakajima T, USP4,668,595 and JP1989293) and built a prototype cell using carbonaceous anode and discharged $LiCoO_2$ as cathode which are stable in air, a property that is highly beneficial from the engineering and manufacturing of batteries. This battery design enabled the large-scale manufacturing of Li-ion batteries in the early 1990s.[17]

Dr. Akira Yoshino, Visiting Professor Kyiushu University, Japan.

Dr. Yoshino focused his research on the creation of a practical new nonaqueous electrolyte secondary battery to meet the emerging need for a small and lightweight power source for portable electronics. He conceived the lithium-ion battery (LIB) in the early 1980s, and completed a practical prototype in 1986. Priority patent application was filed in 1985 and prototype cells were fabricated on consignment by a US company in 1986, with application to the United States Department of Transportation.[17]

Also, Dr. Akira Yohsino carried out the first safety test on Li-ion batteries to demonstrate their enhanced safety features without ignition by dropping iron lump on the battery cells, in contrast to that of metallic lithium batteries which caused fire. Yohsino's success is widely considered the beginning of modern commercial rechargeable Li-ion batteries.[18]

Eventually Sony, dominant maker of personal electronic devices such as Walkman at that time, commercialized Li-ion batteries in 1991. It was a tremendous success and supported the revolution of personal mobile electronics.

Figure 3. Compact Type G InfoLithium rechargeable battery pack for the Sony DSC-N1 Digital Camera, Maximum Output Voltage- DC4.2V, Quick Charging, Battery Capacity: 3.4Wh. After some accidents Sony recalled Lithium-Ion Batteries used in Hewlett-Packard, Toshiba and Dell laptop computers because they posed a fire hazard. According to the company, the batteries can overheat and cause a fire. The Sony recalled 35,000 lithium-ion batteries in the USA and, and additional 65,000 batteries worldwide.

Also Professor **Rachid Yazami** (Moroccan scientist and engineer, born 1953) played an important role in the applications of Li-ion batteries. Yazami's research project included a study of graphite intercalation compounds for lithium battery applications. In 1985 he joined the French National Centre for Scientific Research (CNRS) as Research Associate. He was later promoted to Research Director (Professor) position in 1998. In 1980 Yazami was the first scientist to establish the reversible intercalation of lithium into graphite in an electrochemical cell using a polymer electrolyte. Eventually, his critical discovery led to the lithium-graphite anode now used in commercial lithium ion batteries. In 1979–1980 Yazami invented the lithium graphite anode, now used in commercial Li-ion batteries, a $15 billion/year business. He is listed as inventor on more than 70 patents related to battery technology, including nano-Si- and nano-Ge-based anodes for ultra-high rate charge lithium batteries, the lithium-carbon fluoride battery for space and medical applications, and more recently liquid anodes. He is a founder of CFX battery, Inc. (now Contour Energy Systems), a primary and rechargeable lithium and fluoride battery start-up in Azusa, California; director of energy storage programs at the Energy Research Institute [National Academy of Engineering, USA, https://www.nae.edu/105813/Rachid-Yazami].

To acknowledge their pioneering contribution to the development of Li-ion battery, Goodenough, Yazami, and Yoshino were awarded the 2012 the famous Institute of Electrical and Electronics Engineers (IEEE) Medal for Environmental and Safety Technologies

Professor Rachid Yazami, contributed to critical stages that led to the lithium-graphite anode now used in commercial lithium ion batteries.

According to data for the year 2016, 4 countries dominated lithium-ion battery manufacturing, having 97% of the total production capacity: China, the United States, Japan, and South Korea. The top player was, of course, China with 63% share of total applications 44% was for electric vehicle applications. In the past two decades, there is some notable progress in the development of Li-ion batteries, particularly the introduction of low-cost cathode of $LiFePO_4$ by Goodenough in 1996 and high capacity anode of C–Sn–Co by Sony in 2005.

Another innovative discovery was the Lithium Polymer Battery (abbreviated as **LiPo** or **LIP**) using a polymer electrolyte (a gelled polymer) instead of a liquid electrolyte. Lithium-ion polymer battery is used to make ultra-thin lithium batteries. These ultra-thin lithium polymer batteries can be used for smart cards, smart labels, micro speakers, medical equipment, tracking devices, portable sensors power cards, wearables devices and other applications that require battery storage in a very thin battery. LiPo works on the principle of intercalation and de-intercalation of lithium ions from a positive electrode material and a negative electrode material, with the liquid electrolyte providing a conductive medium. To prevent the electrodes from touching each other directly, a microporous separator is in between which allows only the ions and not the electrode particles to migrate from one side to the other.[19-21]

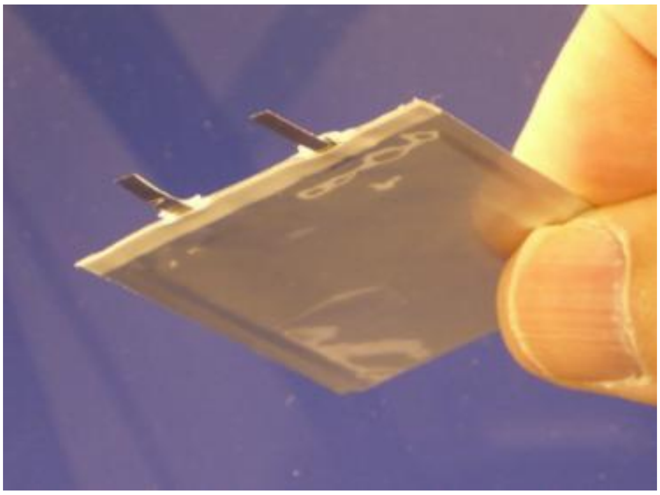


Figure 4. Sony started research on lithium-ion cells with gelled polymer electrolytes in 1988, before the commercialisation of the liquid-electrolyte lithium-ion cell in 1991. At that time polymer batteries were promising and it seemed polymer electrolytes would become indispensable. LiPo batteries are pervasive in mobile devices, power banks, very thin laptop computers, portable media players, wireless controllers for video game consoles, wireless PC peripherals, electronic cigarettes, and other applications where small form factors are sought and the high energy density outweighs cost considerations.

Advantages and superiority of Li-ion batteries compared to other commercial rechargeable batteries

For many years, nickel-cadmium (Ni-Cd) had been the only suitable battery for portable equipment from wireless communications to mobile computing. Nickel-metal-hydride and lithium-ion emerged in the early 1990s, fighting nose-to-nose to gain customer's acceptance. Today, lithium-ion is the fastest growing and most promising battery chemistry.22

Figure 5. There are two types of batteries. Primary batteries in different forms ranging from coin cells to AA batteries that cannot be recharged once depleted. Secondary batteries with electrochemical cells whose chemical reactions can be reversed by applying a certain voltage to the battery in the reversed direction. Also referred to as rechargeable batteries, secondary cells unlike primary cells can be recharged after the energy on the battery has been used up. There are basically four major chemistries for rechargeable batteries; Lithium-ion (Li-ion), Nickel Cadmium(Ni-Cd), Nickel-Metal Hydride(Ni-MH), and Lead-Acid batteries ($Pb-H_2SO4$).

When Li-ion battery is compared with other commercial rechargeable batteries for energy densities clearly shows the superiority of the Li-ion battery. It is expected that for the next decade the advantages of Li-ion batteries will still be dominant in rechargeable battery market. Also, Li-ion batteries have other advantages such as design flexibility allowing to be formed into a wide variety of shapes and sizes, so as to efficiently fit the available space in the devices they power. Li-ion batteries do not suffer from the problem of memory effect, in contrast to Ni-Cd batteries. Li-ion batteries have voltages nearly three times the values of typical Ni-based batteries. The high single-cell voltage would reduce the number of cells required in a battery module or pack with a set output voltage and reduce the need for associated hardware, which can enhance reliability and weight savings of the battery module or pack due to parts reduction. The self-discharge rate is very low in Li-ion batteries – a typical figure is <5% per month which compares very favorably to 20–30% of Ni-based batteries. [https://www.electronics-notes.com/articles/electronic_components/battery-technology/li-ion-lithium-ion-advantages-disadvantages.php].

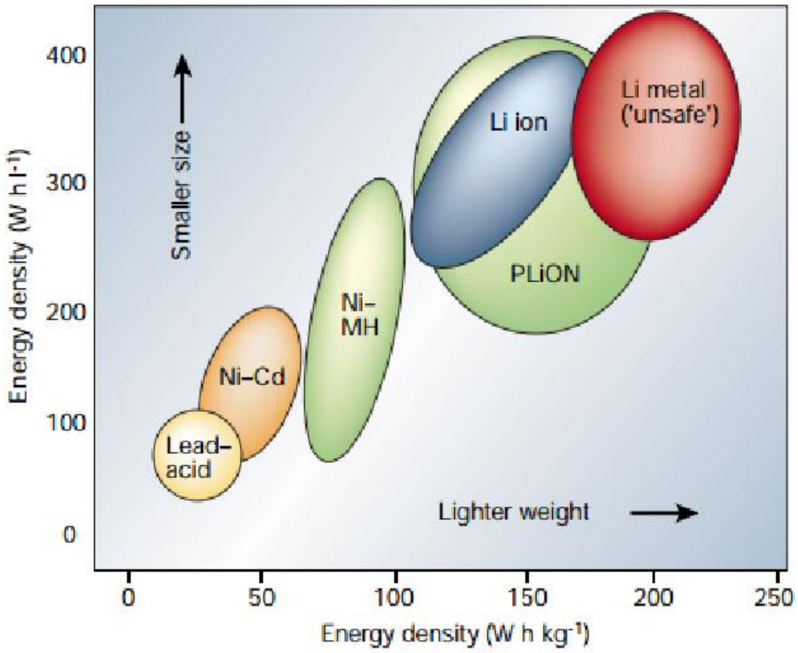


Figure 3. Comparison of energy densities and specific energy of different rechargeable batteries. Reproduced with permission. Tarascon JM, Armand M. Issues and challebges facing rechargeable lithium batteries. *Nature* 414:359-367, 2001.

More research is goimng on in the last decade to new materials and characteristics of rechargeable Lithium-ion batteries but there are limitations. Modern Li-ion batteries hold more than twice as much energy by weight as the first commercial versions sold by Sony in 1991 and 10 times cheaper. But their capacity is nearing their limit. Most researchers think that improvements to Li-ion cells can squeeze in at most 30% more energy by weight. In practical terms, Li-ion cells will never give electric cars the 800-kilometre range of a petrol tank, or supply power-hungry smartphones with many days of power.[23]

The basic characteristics of Lithium-ion batteries

A Li-ion battery is constructed by connected basic Li-ion cells in parallel (to increase current), in series (to increase voltage) or in combined configurations. Multiple battery cells can be integrated into a module and can be intergrade into a battery pack. The Basic Li-ion cell consists of a cathode (positive electrode) and an anode (negative electrode) which are contacted by an electrolyte containing lithium ions. The electrodes are isolated from each other by a separator, typically microporous polymer membrane, which allows the exchange of lithium ions between the two electrodes but not electrons. Typically graphite © is the negative electrode. In addition to liquid electrolyte, polymer, gel, and ceramic electrolyte have also been explored for applications in Li-ion batteries. The basic design of Li-ion cells today is still the same as those cells Sony commercialized two decades ago, although various kinds of electrode materials, electrolyte, and separators have been explored.[24,25]

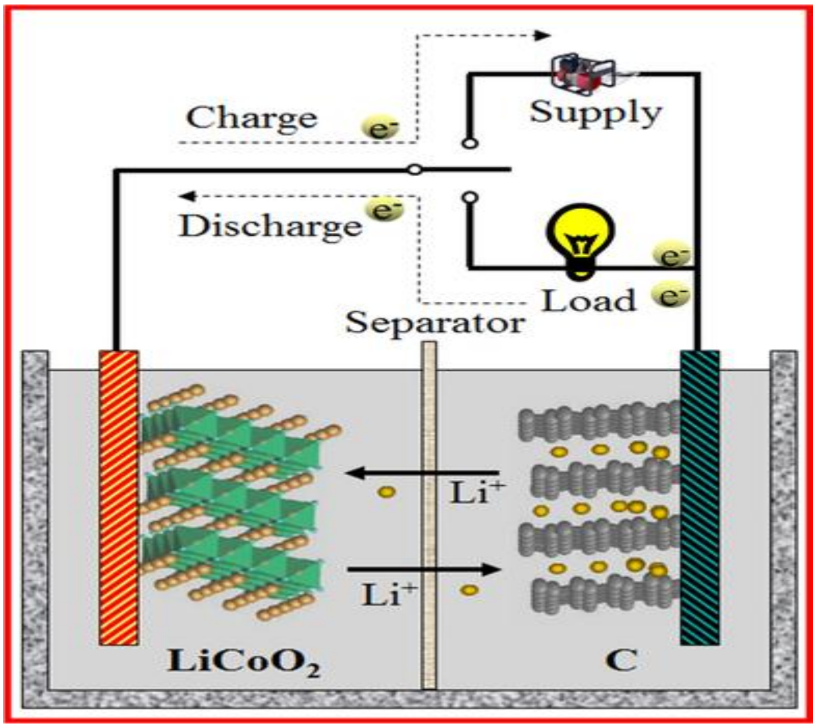


Figure 4. Illustration of the basic components and operation principle of a Li-ion cell. The metal oxide Lithium-cobalt oxide (such as $LiCoO_2$) dominates the market of the Li-ion batteries as a typical cathode material most widely used. The practical capacity of $LiCoO_2$ is about 130-150 mAh g-1 and the experimental charge/discharge potential plateau is around 4.0 V when it's half-delithiated. Graphite is the negative electrode in Li-ion batteries.

The commercial cells are typically assembled in discharged state. The discharged cathode materials (e.g., $LiCoO_2$, $LiFePO_4$) and anode materials (e.g., carbon) are stable in atmosphere and can be easily handled in industrial practices. During charging process, the two electrodes are connected externally to an external electrical supply. The electrons are forced to be released at the cathode and move externally to the anode. Simultaneously the lithium ions move in the same direction, but internally, from cathode to anode via the electrolyte. The opposite occurs during discharging process: electrons move from anode to the cathode through the external load to do the work and Li ions move from anode to the cathode in the electrolyte. This is also known as "shuttle chair" mechanism, where the Li ions shuttle between the anode and cathode during charge and discharge cycles.[26]

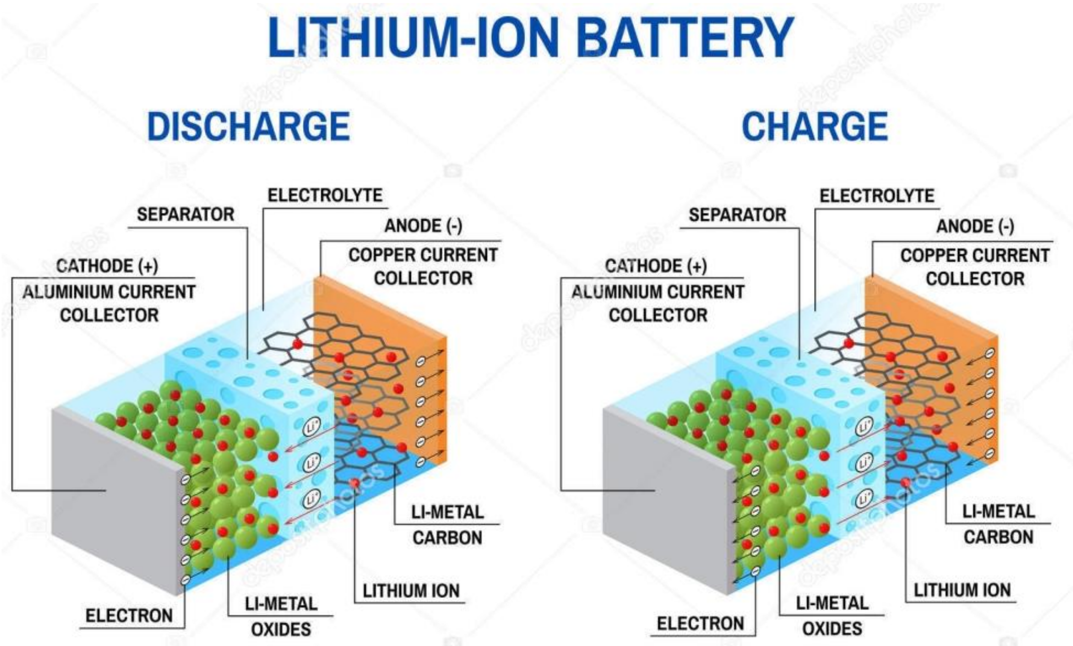


Figure 5. During the discharging process: electrons move from anode to the cathode through the external load to do the work and Li ions move from anode (graphite, C) to the cathode ($LiCoO_2$, $LiFePO_4$) in the electrolyte. During charging process, the two electrodes are connected externally to an external electrical supply. The electrons are forced to be released at the cathode and move externally to the anode. Simultaneously the lithium ions move in the same direction, but internally, from cathode to anode via the electrolyte. A separator, typically microporous polymer membrane, allows the exchange of lithium ions between the two electrodes but not electrons.

Cyclability of Li-ion batteries is very high. The cycle life of Li-ion batteries is affected by depth of discharge and state of charge, as well as operating temperature, in addition to the battery chemistry. Cycle life is enhanced with shallow depth of dicharge cycles and less state of discharge swing, and avoiding elevated temperature. Li dendrite formation on graphite anode can occur at low-temperature charge which should be avoided. Abuse tolerance is a critical requirement for practical application of Li-ion batteries, especially in electric vehicles.[27]

After commercialization what progress in Li-ion batteries

In 1991, Sony Corporation announced a new product called a lithium ion battery. The commercialization of Li-ion batteries and its increasing global production (mobile phones, personal comuters, electric vehicles) has attracted much attention for development research in many university and industrial laboratories for discovering better electrode materials, safer working and rechargeable conditions and lower cost per unit of energy stored.[28]

The Li-ion battery packs for electric vehicles could cost about $600/kWh, and it is anticipated that the cost could be reduced to about $200/kWh by 2020. Some disandvantages of Li-ion can be avoided with new materials. The performances of Li-ion batteries degrade at high temperature. At the same time, it may not be safe for Li-ion battery if rapidly charged at low temperature. Therefore, protective circuits are typically used to avoid overcharge and thermal runaway. Research for better properties is continuing in all aspects of batteries, from anode, cathode, separator, electrolyte, safety, thermal control, packaging, to cell construction and battery management. [29,30]

The electrode materials for Li-ion batteries are critical to the performances because they determine cell voltage capacity, and cyclability. There are a number of potential alternative electrode materials to replace carbon-based anodes and $LiCoO_2$-based cathodes. Composite alloys, Si, Sn-based materials and 3d-metal oxides (Ti, Va, Cr, Mn, Fe, Co, Ni, Cu, Zn) materials have relatively higher specific capacities than graphite. However, they suffer from severe volume expansion during the process of lithiation, which causes the fracture of original structure upon lithium extraction, leading to bad electrical contact between particles and current collectors and poor cycling performance. Li metal has the issue of dendrite formation and is not safe as anode. Given the high capacity of Li metal as anode, it should still be worthy for further exploration and research should focus on depressing the dendrite formation issues. In terms of cathode materials, a number of Co, Mn, Ni-based layered and spinel materials (members of the spinel group include: Aluminium spinels: Spinel: $MgAl_2O_4$, after which this class of minerals is named, Iron spinels: Cuprospinel: $CuFe_2O$, etc) have been explored. Recently, much effort is shifted to polyanionic components, such as $LiFePO_4$ and $LiMnPO_4$. Currently $LiCoO_2$ and $LiFePO_4$ are most widely used in commercial Li-ion batteries because of their good cycle life. $LiCoO_2$ can be easily manufactured in large scale and is stable in air. On the other hand, $LiFePO_4$-based cathode materials are attracting much attention in the past decade due to its low cost and low environmental impact.[31-33]

Cathode materials. The main requirements for cathode materials are high free energy of reaction with lithium, incorporating large quantities of lithium and insoluble in electrolytes. Despite various promising electrode materials that have been proposed, the slow lithium ion diffusivity, poor electronic conductivity and high cost are limiting their practical applications. Recent efforts to improve this aspect forced scientists to turn into nanostructured materials for Li-ion batteries. Researchers suggested that size and shape tunable properties of those lithium-active materials at nanoscale can offer additional parameters for further optimization of their electrochemical performances. Nanostructured electrode materials can offer various advantages not available in conventional bulk materials, and can be material-of-choice for the next-generation Li-ion batteries.[34-36]

Anode materials for Lithium-ion batteries have been extensively investigated in the last decade and there are many candidates and materials for better performance. The better electrochemical performances in Li-ion batteries, include cyclability, charging rate, and energy density. Since the first commercialization of carbonaceous anodes, carbon is still dominant in commercial Li-ion batteries today. Graphitic carbon (C) with layered structure can facilitate the movement of lithium ions in and out of its lattice space with minimum irreversibly, resulting in an excellent cyclability. However, the carbon anodes are soon approaching their theoretical maximum capacity of 372 mAh/g over the past two decades of development. Carbon alternatives with high-energy density and enhanced safety are required to meet the demands for increases in energy and power densities, especially to meet the demands from electric vehicles.[37,38]

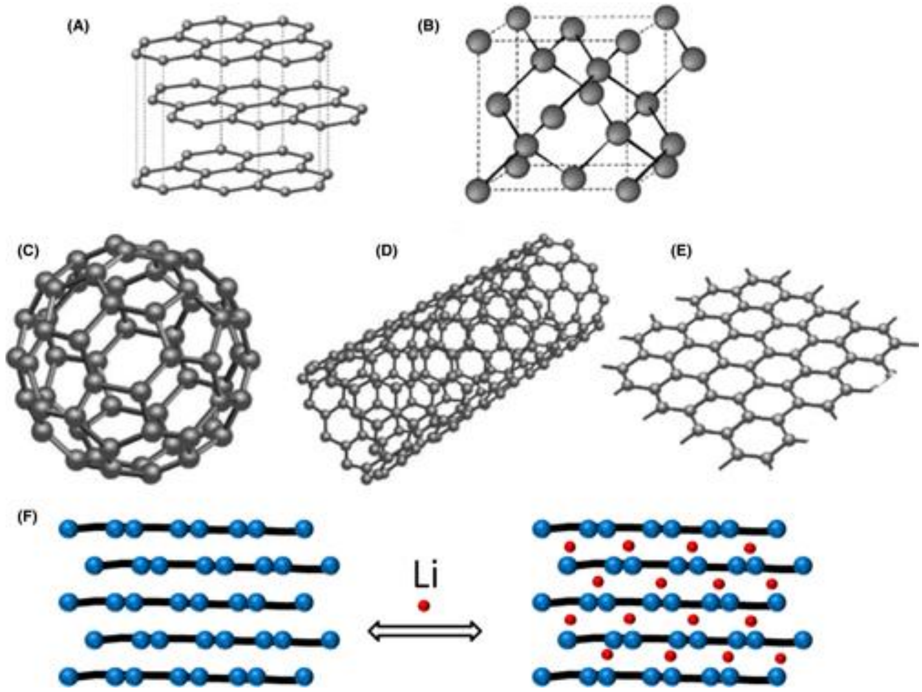


Figure 5. Thre are many different carbon-based materials with different structures. A. graphite, B. diamond, C. buckminsterfullerene,(C_{60}), D. carbon nanotube, E. grapheme of a single layer carbon, F. schematic of lithium intercalation and deintercalation between grapheme layers in graphite. [Scarselli M, Castrucci P, Crescenzi MD. Electronic and optoelectronic nano-devices based on carbon nanotubes. *J Phys* 24:313202, 2012.

Electrolytes for Lithium-ion batteries. Electrolytes for Lithium-ion batteries must be carefully chosen to withstand the redox environment at both cathode and anode sides and the voltage range involved without decomposition or degradation. Additionally, electrolyte should be inert and stable in an acceptable temperature range. In commercial Li-ion batteries, typically a liquid electrolyte is a solution of lithium salts in organic solvents. However, the existing organic liquid electrolyte can potentially catch fires under conditions of thermal runaway or short circuit due to volatile and flammable nature of the solvents which are highly toxic. Ideally, the electrolyte should be non-flammable but also environmentally benign and can be produced at low cost.

Polar aprotic organic solvents, such as carbonate solvents with high dialectic constant, are selected to solvate lithium salts at a high concentration (1 M typically).[39,40]

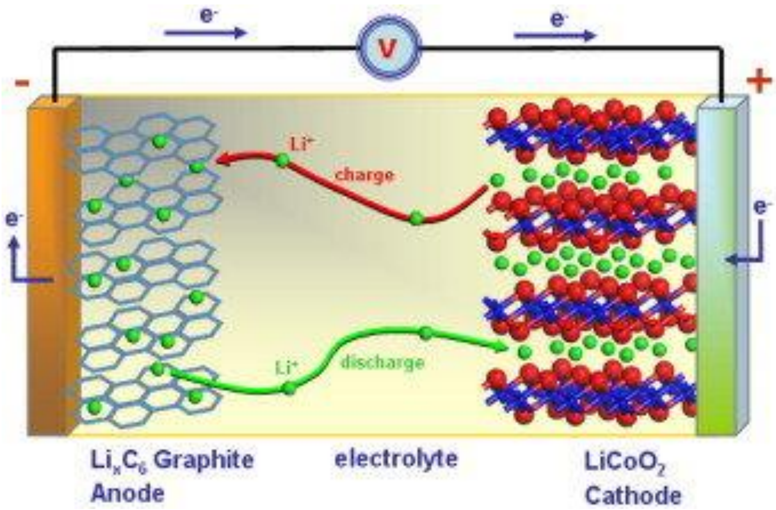


Figure 6. Schematic illustration of a lithium-ion battery. The anode (graphite) and the cathode ($LiCoO_2$) are separated by a non-aqueous liquid electrolyte. The separator in a Li-ion battery plays critical role to avoid direct physical contact between the cathode and anode, and prevents short circuit to occur.

On the other hand, solvents with low viscosity and low melting point are required to meet the requirement for high ionic mobility in the operating temperature range. Various organic solvents have been explored, including dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, propylene carbonate, ethylene carbonate, diethoxyethane, dioxolane, *γ*-butyrolactone, and tetrahydrofuran. Heteroatom-containing organic solvents have also been explored. Various lithium salts have been explored, including $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiClO_4$, and $LiCF_3SO_3$. $LiPF_6$ is a particular outstanding lithium salt from the perspective of safety, conductivity and the balance between ionic mobility and dissociation constant. However, $LiPF_6$ can react with water to form highly corrosive HF. Therefore, moisture must be minimized in handling of $LiPF_6$ electrolyte. In fact, the success of first commercial Li-ion batteries could be ascribed to the industrial scale availability of high-purity $LiPF_6$ with minimal amount of water. Scientists believe that there are many research challenges for the future Li-ion batteries due to high demand for many energy storage and production facilities. [41,42]

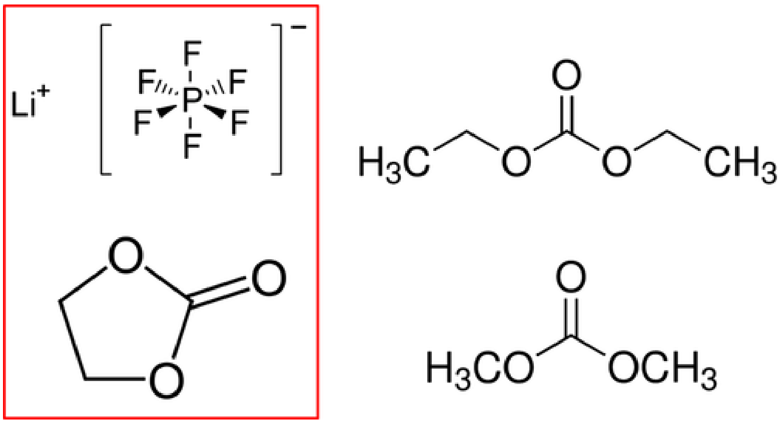


Figure 6. Electrolytes for Li-ion batteries. Chemcial structures of commercial electrolyte: $LiPF_6$ as the lithium salt and ethylene carbonate as the solvent are present in almost all commercial electrolyte; whereas diethyl carbonate or dimethyl carbonate are also present to reduce viscosity to promote ion transfer.

In the last decade other types of electrolyte for Lithium-ion batteries have also been developed and proposed for advance Li-ion batteries, such as polymer, gel and ceramic electrolyte. Polymer electrolytes are solvent-free using high molecular weight-based polymers with dissolved lithium salts.[43,44]

Recently, researchers have investigated and applied c**eramic electrolytes** in lithium-ion batteries. The obvious advantage to use ceramic electrolyte in batteries is safety because flammable organic solvents are needed. Those batteries with ceramic electrolyte can find applications in high-temperature environment, including handheld orthopedic tools and other batteries powered medical devices that need to be sterilized in autoclaves under high temperature and high pressure conditions. Another interesting advantage to use ceramic electrolyte for high-temperature applications is that the ionic conductivity of ceramic electrolyte increases with increasing temperature.[45]

Separators of Lithium-ion batteries. Separators are essential components of Li-ion batteries. In fact, separators are commonly used in most electrochemical systems with liquid electrolyte, including fuel cells, capacitors and various kinds of batteries based on different chemistry. The separator in a Li-ion battery plays the critical roles to avoid direct physical contact between the cathode and anode, and prevents short circuit to occur. At the same time, the separator allows lithium ions in the electrolyte to pass through it. The separators must be chemically stable and inert in contact with both electrolyte and electrodes. At the same time, it is required to be mechanically robust to withstand the tension and puncture by electrode materials and the pore size should be less than 1 μm. Although various separators, including microporous polymer membranes, nonwoven fabric mats and inorganic membranes have been explored, the microporous polyolefin materials based polymer membranes are dominantly used in commercial Li-ion batteries with liquid electrolyte. For the development of future Li-ion batteries for high-temperature applications, inorganic membranes as separators are highly attractive.[46,47]

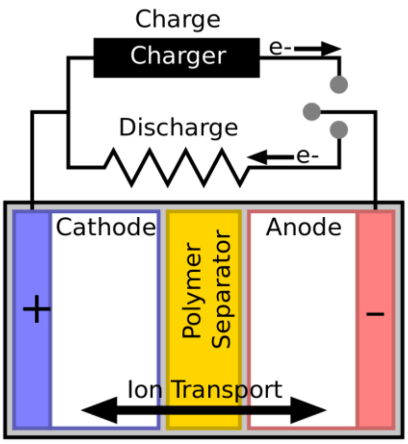


Figure 7. Lithium-ion battery separators are critical components. Separator is a polymeric membrane forming a microporous layer, chemically and electrochemically stable with regard to the electrolyte and electrode materials and mechanically strong enough to withstand the high tension during battery construction.

Future technological challenges of Lithium-ion baterries

After 20 years of commercial Lithium-ion batteries there are now new technological challenges for the requirements of new generation Lithium-ion batteries in modern electric vehicles and for sustainable energy grids to store green energy generated from renewable sources (Photovoltaic solar panels, wind energy through wind turbines). The increasing demand for energy storage requires further improvements in the existing Li-ion batteries and the development of next-generation Li-ion batteries, in particularly, to reduce the cost of Li-ion batteries. It is still very challenging to develop new battery chemistry to replace the existing Li-ion battery technology. Increasing energy density of Li-ion batteries is very desirable. Also, new electrode couples with both high-specific capacities and high operating cell voltage is another challenge in research. In the last decade many research groups investigate new anode electrode candidates that could dramatically increase the specific capacities, particularly with highly attractive Si- and Sn-based anodes.[48]

In contrast research for new anode candidates face many difficulties and challenges. The existing cathode material of $LiCoO_2$ is very expensive and highly toxic. The increasingly popular $LiFePO_4$ has a low cell capacity. Highly attractive cathodes of Ni-Co-Mn-based materials have been developed by Argonne National Laboratory. However, the specific capacity is still considered moderate, and both Co and Ni are expensive and toxic. LNMO (Lithium Nickel Manganese Oxide) cathode material is a novel and promissing candidate with a cobalt-free high-voltage (5V) spinel for use in next-generation lithium-ion rechargeable batteries.[49.]

Green energy storage and Lithium-ion batteries

All countries in the last decade take into account the rising demand for electrical energy and the fact that fossil-fuel resources are depleted slowly and they contribute inevitably to climate change and CO_2 to the Earth's atmosphere. There is high demand worldwide for sustainable energy alternatives, including both renewable energy sources and sustainable storage technologies for the fluctuating energy produced by solar panel and wind turbines. The surge of interest in energy storage has propelled Lithium-ion Batteries (LiBs) to a prominent place in the transformation of the power grid into a more flexible, responsive resource of electricity.[50]

Although energy storage worldwide is still dominated by pumped storage (comprising 96% of all storage capacity,) Li-ion is the fastest growing, estimated to reach 15 GW by 2025. Emerging energy storage have been favorably predisposed to Lithium-ion baterriess, due to their ability to deploy quickly and participate in smaller-scale development schemes on the "gridedge" (closer to end-use customers). For example, in 2016, AES Energy Storage deployed the largest of these farms for San Diego Gas & Electric, connecting 400,000 individual batteries into 24 containers to store 120 MWh of electricity for up to four hours. These deployments essentially consist of massive banks of batteries, stacked and interconnected, in temperature controlled tanks.

Figure 8. In 2016, AES Energy Storage deployed the largest of these farms for San Diego Gas & Electric, connecting 400,000 individual batteries into 24 containers to store 120 MWh of electricity for up to four hours. From Power Engineering, 2019. Implications of lithium-ion storage transformation [https://www.power-eng.com/2017/11/15/implications-of-a-lithium-ion-storage-transformation/#gref].

In 2019, the company Contemporary Amperex Technology Co., Limited (CATL), a China-based manufacturer of lithium-ion batteries (LiBs), has delivered world's first and China's largest battery energy storage system (BESS) multi-mixed energy power station as part of the Luneng Haixi Multi-mixed Energy Demonstration Project (Golmud, China), which is the first of its kind in China to integrate wind (400MW), photovoltaic (200MW), concentrated solar power (50MW), and an energy storage system (ESS) (100MWh) into one unified system on the grid. The Station coordinates three different renewable, with fluctuating and particularly unstable, sources of energy and is required to respond consistently to fluctuating demand, making its batteries and battery management system crucial to the reliability of the system. CATL, the exclusive battery supplier for the Project, managed succesfully the requirements during product design and development stage. The first priority when building an energy storage station was safety. By selecting reliable materials, CATL minimize the possibility of failure incident and second damage explosion. CATL identified risks and risk mitigation plans in early stages of product development, manufacturing and management to ensure safe operation of the battery system. Utilizing a three-layer relay protection system, CATL further assured performance of the battery system from damages caused by over-charging/discharging, over-current, mitigate over and under temperature working conditions. One of the key challenges of safety was thermal management. The Station, installed at Golmud where temperature varies from -33.6 to 35.5 degrees Celsius. To ensure 15 years of battery performance, CATL has deployed a special cooling system.

Figure 9. Golmud, China, 2019. CATL the China-based manufacturer of lithium-ion batteries (LiBs), has delivered world's first and China's largest battery energy storage system (BESS) multi-mixed energy power station as part of the Luneng Haixi Multi-mixed Energy Demonstration Project, CISION PR Newswire. CATL connects world's first and China;s largest BESS multi-mixed energy power station to the grid. 30.1.2019, [https://www.prnewswire.com/news-releases/catl-connects-worlds-first-and-chinas-largest-bess-multi-mixed-energy-power-station-100mwh-to-the-grid].

Energy storage in the lasrt decades relied to well-known technologies such as pumped-hydro systems and lithium-ion batteries. But these methods have their limitations. The Hydro power has natural limitations with power plants gobbling up enormous amounts of land, whereas lithium-ion batteries have steadily assumed a growing role with falling battery prices and larger battery sizes. Li-ion batteries have numerous advantages. They can store large amounts of energy and release it again to the grid within seconds. Furthermore, they are efficient, meaning they return most of the energy that you store in them. But until now Li-ion battery energy storage systems have not had the sufficient scale to play a significant role in handling peak electricity demand.[51,52]

The European Union Commission recognised the importance of effective research and innovation in accelerating the transformation of the EU's energy system and bringing promising new low-carbon technologies to the market. Between 2014 and October 2018, Horizon 2020, the principal research programme of the Commission, had granted €1.34 billion to projects for grid energy storage or for low carbon mobility. The EU understands that there are numerous energy storage technologies are available or under development, such as pumped-hydro storage, different types of batteries, hydrogen storage, compressed air storage, thermal storage systems and different types of gas storage.The EU policy framework for energy storage is based on strategic initiatives such as the European Battery Alliance, support for research and innovation in energy storage technologies, and legislation covering the electricity markets and low-carbon transport. The EU agres that there is fundamental role of energy storage in achieving a low-carbon, mainly renewables based energy system, but there are challenges to the development and deployment of energy storage in the EU.[53]

Electric vehicles and Li-ion batteries

Global market indicators and statistical evidence show that electric vehicles (Evs) and their battery systems are set to grow globally with automobile manufactures set to introduce these cars in full stream in the year 2020. The onboard battery used in electric vehicles can be classified under one of the following three types: nickel metal hydride, lead-acid, and lithium-ion batteries. China, South Korea and others in Asia countries are the front-runners in sales of electric vehicles. The key vendors of EVs batteries include Samsung LG, Toshiba, BYD, and Panasonic.

Despite the growth of the battery systems in electric vehicles market, it is curtailed by some serious challenges too. The range and performance of the battery in the electric vehicles are the significant restraints for the market. The batteries are typically less powerful and have limited range (60-100 miles per charge) and are considered suitable only for short distance travel

Figure 10. The top key players for Lithium-ion batteries for electric vehicles:: LG, BYD, Toshiba, SDI, Hitachi, Panasonic, AESC, Lithium Energy Japan (LEJ), Li-Tec, Valence and Johnson Matthey Battery Systems

The Lithium-ion battery is one of the most common batteries used in Electric Vehicles (EVs) due to the specific features of high energy density, power density, long life span and environment friendly. Due to the concerns of climate change and environmental, electrification of the transport sector has been advanced as the national strategy by many countries. The promotion of Electric Vehicles (EVs) been supported by financial incentive, lower taxes, free charging facilities, free parking, etc. Sales of new petrol and diesel vehicles will be banned for the coming decades and inevitable electric vehicles will be promoted.[54]

The Li-ion baqtteries have some inherent benefits, such as high energy density, high capacity, long cycle life, reliable charge performance and low maintenance. Inevitably Li-ion batteries make it the preferred choice for applications spanning from portable consumer devices to stationary energy storage and backup systems to motive equipment and vehicles. As this growth demand continues, further improvements and advancements in materials, system design, technology and safety will also need to take place.[55]

Conclusions

Lithium-ion batteries have revolutionised the lives of humankind in the last decades and formed the powerhouse for the present personal digital electronic revolution. The commercial application from the 1990s of high-energy-density lithium-ion batteries for portable electronic radios, laptops, tablets and mobile phones became finally the batteries of choice in countless consumer electronics and the latest electric vehicles. The Nobel Prize of Chemistry 2019 to three scientists who contributed substantially to the discovery of Li-ion batteries is a rewarding prize for these research pioneers.

Although the cost of Li-ion batteries decreased and their safety improved substantially, there are several shortcomings and challenges for the future. Some of the advantages of the lithium-ion batteries are their high energy density, self-discharge, rechargeability, low maintenance and their flexible design. But new research is going on in many laboratories to improve most of the basic metals and materials used in the batteries.

In recent years, Li-ion batteries have also become a staple solution in efforts to solve the interlinked conundrums of climate change and renewable energy. Increasingly, Li-ion batteries are being used to power electric vehicles and applied as the principal components for storage of fluctuating energy generated from renewable sources (solar panels, wind turbines), helping to balance an increasingly diverse and smart electrical grid. Research and new technological advances have improved the quality and safety of Li-ion batteries. Experts have succeeded in making Li-ion batteries 5–10% more efficient each year, just by further optimizing the existing architecture.

But as our society if moving very fast for a carbon-free economy there is high demand for better-performing batteries. For example, in electric vehicles, scientists demand high density batteries, small in size and lightweight and of lower cost as possible. Achieving that goal calls for energy densities that are much higher than the 300 Wh/kg and 800 Wh/L which are seen as the practical limits for today's Li-ion technology. Another issue holding back the adoption of electric vehicles is cost, which is currently still around 300–200 $/kWh, although that is widely projected to go below 100 $/kWh by 2025 or even earlier. The time required to recharge a battery pack – still in the range of a few hours – will also have to come down, and as batteries move into economically critical applications such as grid storage and grid balancing, very long lifetimes (a decade or more) will become a key consideration too.

Scientists believe that there is still some room left to improve existing Li-ion technology, but not enough to meet future requirements. Instead, the process of battery innovation needs a step change: materials-science breakthroughs, new electrode chemistries and architectures that have much higher energy densities, new electrolytes that can deliver the necessary high conductivity. These characteristics in a battery are very important. In addition Li-ion batteries must be more safe, long-lasting, low cost, easily and fast recharged and sustainable to produce.

Figure 11. Today's electric vehicles are almost exclusively powered by lithium-ion batteries (LiBs), but there is a long way to go before electric vehicles become dominant in the global automotive market. In addition to policy support, widespread deployment of electric vehicles requires high-performance and low-cost energy storage technologies, including not only batteries but also alternative electrochemical devices.

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