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Turkish Journal of Materials

A Comprehensive Analysis of Material Revolution to Evolution in Lithium-ion Battery Technology

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Received: 17.04.2023; Published: 30.07.2023
Turk. J. Mater. Vol: 8 No: 1 Page: 1-13 (2023) ISSN: 2636-8668
SLOI: http://www.sloi.org/sloi-name-of-this-article

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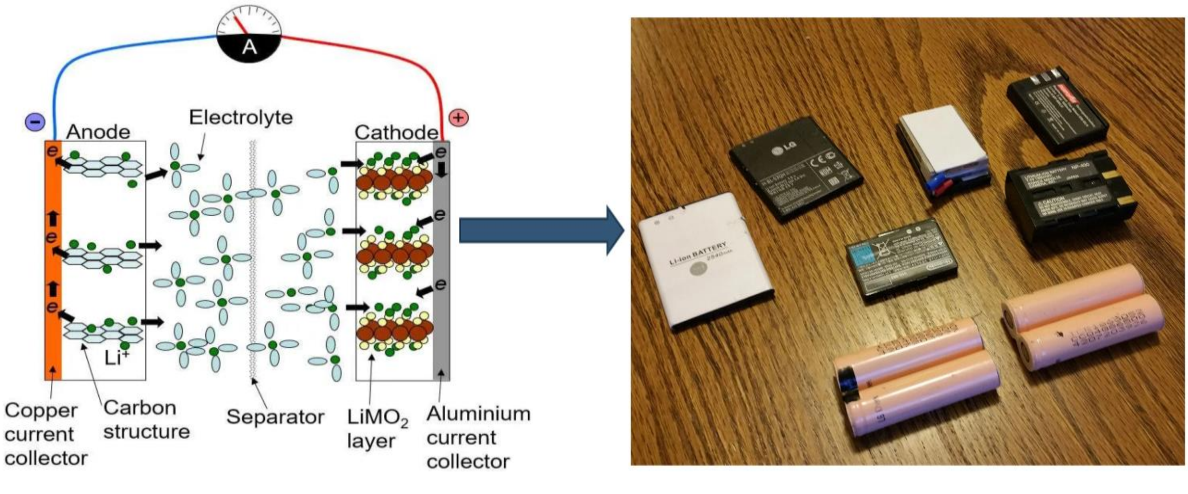
ABSTRACT Lithium-ion batteries (LIBs) have significantly impacted our lives and are now found in various devices such as cell phones, laptops, and electric vehicles. An appropriate electrolyte was produced in LIBs via a twisting route, which relates to the progress of electrode chemistry. Based on recent research and discoveries, LIB has emerged as the technology of choice for storing electrical energy for use in mobile products and electric vehicles. This is due to LIBs' desirable qualities, such as their lightweight, high-energy density, small size, little memory effect, extended lifespan, and low pollution. In this method, a metal oxide is the cathode, and porous carbon is the anode. The electrochemical interaction of lithium with anode materials can generate intercalation products that are the basis for innovative battery systems. At room temperature, structural retention makes this reaction quick and reversible. This concise overview examines the progress of LIB technology and the impact of the materials used in different technologies on cell performance. The section summarizes the evolution of LIB cells and Li^+ ion storage into various materials and intercalation chemistry.

Keywords: Lithium-ion battery, electrolyte, intercalation, graphite, voltage.

Cite this article: T. Azemtsop Manfo, A Comprehensive Analysis of Material Revolution to Evolution in Lithium-ion Battery Technology. Turk. J. Mater. 8(1) (2023) 1-13**.**



Understanding the revolution of lithium-ion battery technology: From Chemistry to Pack

1. INTRODUCTION

As society evolves, energy demands increase in areas such as electronics, renewable energy, and electric cars [1-4]. The energy factor is critical to any society's development [5,6]. Over the previous decades, the world has been altered by the revolution in engineering and technology [7]. LIBs have high energy densities and predictable cycle life, making them ideal for portable electronic gadgets and electric/hybrid cars [8]. LIBs are too anticipated to be basic in empowering the far-reaching substitution of fossil fuel-based control eras with renewable vitality sources like solar and wind, driving to a cleaner, more maintainable world [9]. The quick progression of LIB innovation has drawn much attention from researchers [10]. LIBs have overwhelmed the advertiser for progressed vitality sources in the present day since they are broadly utilized in different ranges, including hardware, electric cars, and vitality capacity frameworks [11]. Battery innovation has progressed in later decades, especially in LIBs [12]. Conventional vitality capacity frameworks like batteries have imperatives such as drowsy charging and a constrained life expectancy. Moreover, whereas the current development of smartphones and tablets has driven client involvement, this development requires electrical gadgets utilizing smaller and lighter LIBs with longer working cycles [13]. Mechanical, electrochemical, and electromagnetic capacity strategies, which store energy in completely different shapes, are more expensive and advanced [14].

Within the 1960s, German researcher R. Schroeder and French Researcher J. Rouxel pioneered the reversible intercalation of Li^+ into transition metal disulfides (MS_2). According to Whittingham's 1976 Science paper, titanium disulfide (TiS_2) is a compelling Li^+ source for vitality capacity via Li+ intercalation (Figure 1). An in-depth study of Li, TiS, and intercalation compounds has been recently published [15-20]. An organic-liquid Li^+ electrolyte is required since alkali metals react strongly with water [21]. As a result of the high degree of order in Li^+ and Co (III) in $LiCoO_2$, LIB has been created [22]. At the same time, various nations studied the reversible intercalation of Li^+ into graphitic carbon. Researchers have demonstrated that Li^+ can be reversibly intercalated into graphitic carbon to produce LiC_6 [23]. The innovative advancement allowed the development of the battery-powered portable phone, which started the remote transformation [24]. The LIB is utilized in crossover and electric road cars, but it has downsides that are propelling endeavors to supplant it [25]. Goodenough recently wrote "A Perspective on Li-Ion Batteries" in Science China Chemical [26], in which he examined the history, current challenges, and fascinating study routes for LIBs, which are widespread energy storage devices in electronics.

From the 1950s to the 1990s, most non-aqueous electrolytes were composed of various lithium salts distributed in a mixture of polycarbonate (PC)-based solvents [27]. After being completely steamed, ethylene carbonate (EC) was recognized as a miraculous solvent that significantly enhanced almost the entire theoretical capacity of LiC_6. In 1990, Fujimoto and his Sanyo colleagues substituted amorphous carbon with graphite, but they faced the challenge of finding an electrolyte that would not destabilize the graphite structure. They also want to minimize EC's high viscosity and melting point by combining it with dimethyl carbonate and diethylene carbonate, which are both linear carbonate esters similar to EC [28].

In LIB, the electrolyte must allow the movement of lithium ions from the anode to the cathode. Unlike other batteries that use aqueous electrolytes, lithium batteries interact violently with water and release hydrogen gas, thus requiring the use of non-aqueous and aprotic solvents [29]. The solvent must have the appropriate polarity to dissolve the lithium salt and produce a solution with high ionic conductivity. The requirements are met by organic solvents such as acetonitrile, dioxane, butyrolactone, methyl formate, and 1,2-dimethoxyethane; propylene carbonate (a heavy metal catalyst that partially breaks the plastic polymers); dimethyl sulfoxide; and tetrahydrofuran. Lithium salts such as $LiClO_4$, $LiPF_6$, LiBr, $LiBF_4$, $LiCF_3SO_3$, and $LiAlCl_4$ with low lattice energies are extremely soluble in these solvents and also exhibit noticeable ionic conductivity.

Lithium primary batteries have been produced in Japan since 1973 as power sources for tiny consumer gadgets. Li/(CF) batteries were the very first lithium batteries made in Japan. Matsushita invented the first $Li/(CF)_n$ battery, which was intended for use in fishing floats. Although the end reaction products are lithium fluoride and carbon, the cell potential of 2.8 to 3.0 V points to a distinct electrochemical process. These compounds are created by a high-temperature chemical reaction between fluorine and carbon [30]. It was assumed that lithium first intercalates the carbon monofluoride lattice and then experiences a dissociation process, $Li + (CF)_n \rightarrow Li_x (CF)_n \rightarrow C + LiF$. Despite significant efforts by others, the response could not be reversed. Sanyo, meanwhile, produced one of the first LIBs using the Li/MnO_2 combination, which was used in solar-powered rechargeable calculators.

Historically, the lithium-ion with the greatest reduction potential and atomic mass was known as an anode. Because the energy created by a battery is a product of the charge provided and its voltage, LIBs are expected to produce extremely high energy per unit mass.

2. HISTORY and DEVELOPMENT of LIB

2.1. Primary rechargeable LIB: Whittingham's technology

The advancement of electrolytes in LIBs was first constrained by cathode chemistry. A LIB cell is particularly attractive because of its low standard reduction potential of -3.05 V. Lithium, however, must be kept away from air and water due to its high reactivity. Researchers had successfully applied non-aqueous electrolyte solutions to lithium electrochemistry work a few years earlier by Whittingham. As compared to lead-acid batteries, Whittingham's LIB has a higher cell potential, 2.5 V instead of 2 V.

An ether-based electrolyte was used in 1972 by Whittingham [31] to increase the potential voltage of TiS_2, which was lower than 3.0V within the stable range of ethers. Ester compounds, however, are unstable above 4.0 V. Whittingham created a high-energy battery in 1976 that used a TiS2 cathode and a lithium metal anode.

Whittingham's LIB cell potential was 2.5V, while the lead-acid battery was 2V. Whittingham's technology, on the other hand, was unstable. Goodenough's discovery of transition-metal oxides (e.g. $LiCoO_2$) as high-potential cathode materials resulted in an unavoidable substitution of ether for esters [32]. John Goodenough and Akira Yoshino improved the technology by replacing the cathode and anode with $LiCoO_2$ and graphite. Figure 1 depicts a schematic representation of LIBs ($LiCoO_2$/Li+ electrolyte/graphite). Stanley Whittingham developed the first practical LIB during its early years, utilizing lithium's immense need to release its external electron.

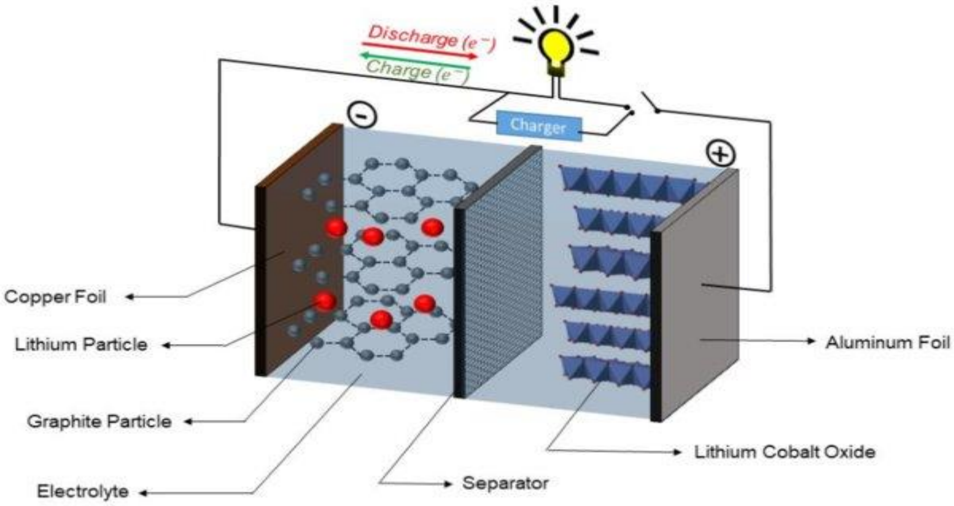


Figure 1. The graphical representation of the first LIB [33].

Rachid Yazami investigated Li intercalation into graphite and discovered that reversible Li insertion into carbon reduces dendritic development [23]. The chemical potential at the anode (μA), μA(Li) − μA(C) = 0.2 eV, prevents a fast charge, which increases the voltage needed to reverse the chemical reaction where Li is placed onto the carbon's surface faster than Li^+ is introduced into the carbon [34]. Although a carbon anode limits the rate of charge, Yoshino [35] constructed the first LIB employing a discharged graphite anode and a discharged $LiCoO_2$, as seen in Figure 2. The electrochemical reaction that occurs from each electrode is given below:

At the anode: $$C + xe^- + xLi^+ \rightarrow Li_xC \quad (1)$$

At the cathode: $$LiCoO_2 + xe^- + xLi^+ \rightarrow Li_{1-x}CoO_2 \quad (2)$$

The presence of a guest Li^+ in layered materials like TiS_2, COO_2, graphite, or any other material was already recognized as intercalation [36].

2.2. Secondary battery

Non-aqueous solvents, specifically carboxylate or carbonate esters, were the two most significant constituents of the ester family during approximately the 1950s [37], primarily EC and PC. The reason for choosing PC was due to its exceptional solubility and voltage stability (> 4.0 V vs. Li+/Li) while EC was viewed as undesirable due to its high melting point (~37°C). Akira Yoshino of Japan was the first to examine the use of organic conductors like polyacetylene as negative electrodes. Akira Yoshino extended the concept of intercalation by investigating a variety of carbonaceous materials. The secondary battery constructed from this unique mix allowed for consistent charging and discharging across many cycles [29]. This 1985 discovery led to the construction of a new secondary battery using a $LiCoO_2$ cathode and petroleum coke-based anode intercalated with lithium. Figure 2 shows the secondary lithium battery designed by Goodenough.

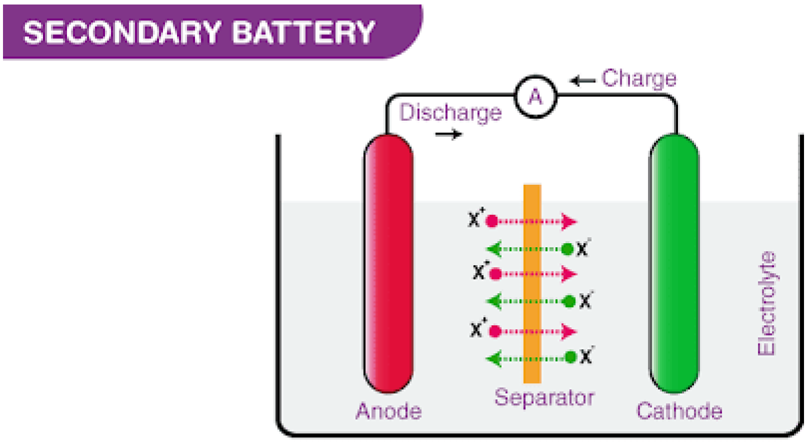
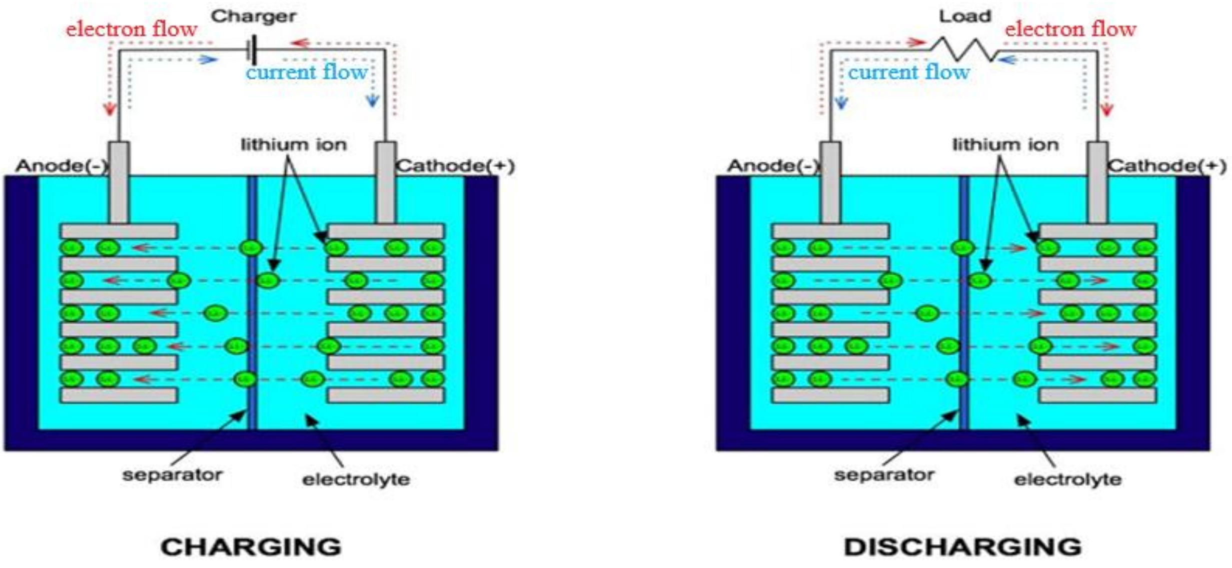


Figure 2. Schematic diagram of a secondary cell

2.3. First commercial LIB

In the first LIB model patent, graphite was excluded using X-ray diffraction to create PC-centric electrolytes [28]. The original LIB was developed as a result of these attempts, which were successfully commercialized by Sony in 1990. Not long after its development in the laboratory, the first commercial LIB was released in 1991, marking the beginning of industrial manufacturing [38]. Asahi Kasei was responsible for inventing and manufacturing the first LIB in response to the need for better batteries. Figure 3 illustrates the design of the first LIB that was commercialized by Asahi Kasei and Sony.



CHARGING

DISCHARGING

Figure 3. The first LIB technology was commercialized by Asahi Kasei and Sony.

Typically, LIB technology uses graphite or carbon as an anode material while the cathode is composed of layered oxide (e.g. $LiCoO_2$, $LiFePO_4$, or $LiMnO_2$). An organic solvent containing complexes of lithium ions, made from organic carbonates such as EC or dimethyl carbonate (DMC), and a lithium salt serves as the electrolyte. The characteristics of a LIB such as voltage, energy density, longevity, and safety might vary depending on the materials employed. While LIBs are more powerful than Ni-Cd batteries, they are also more delicate, have safety risks since they may be held under pressure, and need protective circuits. Nevertheless, they are effective.

In November 1991, Fujimoto and his colleagues [39] filed a patent that described a method for creating modern lithium-ion battery electrolytes. These electrolytes are made by combining $LiPF_6$ with a linear carbonate, which is selected from DMC, diethylene carbonate (DEC), ethyl methyl carbonate (EMC), and EC. Using each of the mixed solvents, they prepared three types of batteries using lithium PF6 electrolyte solutions as shown in Table 1.

Table 1. Summary of the performance results of the three prepared batteries after a discharge at 100mA with different electrolytes [39].

Graphite characteristics	Battery characteristics					
	Capacity per unit weight	Initial charge-discharge efficiency	Capacity	Self-discharge Rate	Cycle life	charge-discharge efficiency
(+) $LiCoO_2$ / (-) graphite Dimethyl carbonate: Ethylene carbonate= 1:1	355	95	610	5	>1,000	100
(+) $LiCoO_2$ / (-) graphite 1,2-Dimethoxyethane: Ethylene carbonate= 1:1	350	95	600	5	>1,000	100
(+) $LiCoO_2$ / (-) graphite Diethyl carbonate: Ethylene carbonate= 1:1	360	95	620	10	>1,000	95

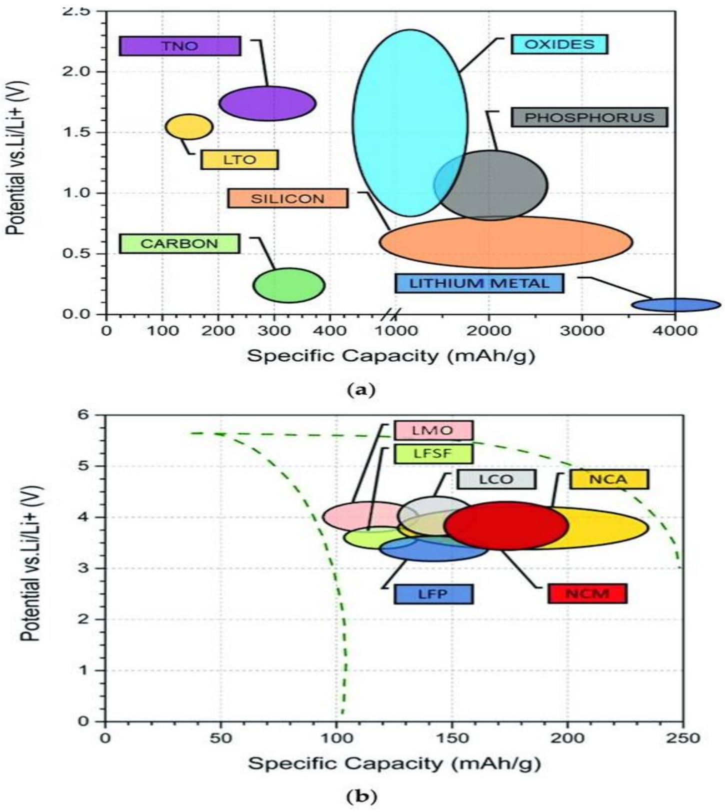
Therefore, graphite-based anode materials posed the next restriction on electrolytes. This electrolyte design (EC/DEC) had been covered in a patent by Okuno et al. [40], but neither graphite nor LiC_6 was supported by the patent.

The LIB has had a tremendous impact on today's world due to its widespread use in electronic devices such as mobile phones and computers. Furthermore, while the present expansion of smartphones and tablets has resulted in greater user experience, this growth continues to require electronic devices with longer working cycles that include skinnier and lighter LIBs.

3. CATHODE MATERIALS for LIBs

For nearly half a century, researchers have worked together to create lithium-ion battery technology. The discovery of new materials, as well as a deeper understanding of their structure-composition-property-performance linkages, have made significant contributions to the field's advancement. A LIB type is named for its cathode composition. Among the different components of a lithium-ion cell, the cathodes (positive electrodes) currently limit energy density and dominate battery costs. It is fascinating to realize that all three major oxide cathode chemistries currently in use originated from John Goodenough's laboratory at the University of Oxford in England and at the University of Texas at Austin (UT Austin) in the United States.

In general, LIBs are recognized by the cathode material chemistry, as the material used as the cathode has a significant impact on both battery performance and cost [36]. However, LCO advantages include a high operating voltage, high mobility of electronic and ionic charge carriers, good cycle performance, and a high energy density [37]. Various lithium metal oxides (LMO), such as lithium cobalt oxide (LCO), nickel cobalt aluminum oxide (NCA), lithium cobalt phosphate (LCP), nickel cobalt manganese oxide (NCM), lithium manganese oxide (LMO), lithium iron phosphate (LFP), lithium iron fluoro-sulfate (LFSF), and lithium titanium sulfide (LTS), are used as cathode materials. These materials have a high capacity for lithium intercalation and appropriate physical and chemical properties for transporting lithium ions. Figure 4 depicts various cathode materials' cell-specific capacity and average discharge potential [35]. LCO, NCA, and NCM are all high-energy materials with layered structures, but they trade off reduced thermal stability for high cobalt prices [43]. LMO has excellent thermal stability, a spinel-like structure, and high voltage despite its modest capacity. Compared to NCM and LCO, LFP offers a good compromise between performance and safety due to its low cost, high average voltage, and reduced sensitivity to thermal runaway [43-46] and offers a good compromise between performance and safety [47-49].



(a)

(b)

Figure 4. The relationship between discharge potential and specific capacity for some common anode and cathode materials [36].

Akira Yoshino patented the first rechargeable Li-ion batteries by combining a $LiCoO_2$ cathode and graphite anode [28]. The original LCO has been modified with additions to stabilize the crystal structure and increase capacity. Figure 5 shows the significant contributions made by Goodenough and others in the chemical tuning of numerous cathode materials, such as $LiCo_{1-x}Ni_xO_2$, $LiMnO_2$, and olivine-based $LiFePO_4$.

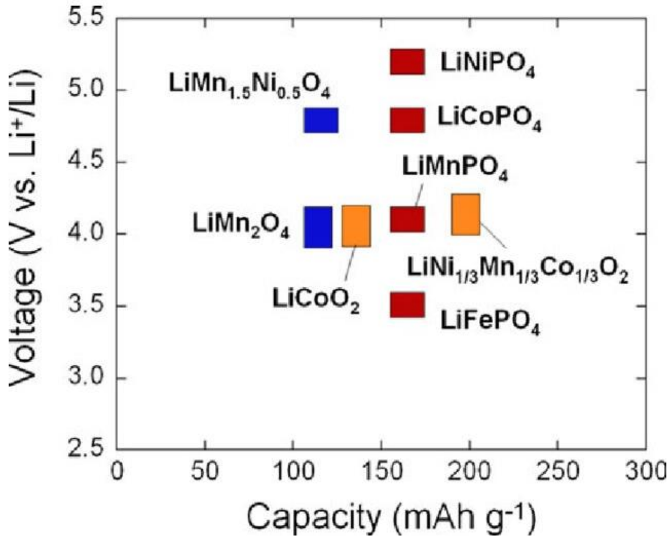


Figure 5. Voltage vs. capacity for the most typical positive electrodes for LIBs [50].

4. ANODE MATERIALS for LIBs

The most commonly used material for LIB anodes is graphite because of its high negative potential. Some materials, such as lithium titanate and silicon, have lower negative voltages, which results in reduced energy and power density. This makes them less practical for most applications, except for fast chargers [51] and solid energy storage devices where energy density is not as important [52]. The electrochemistry of LIBs determines their performance, cost, and safety. High voltage and energy density increase the risk of thermal runaway, which can lead to cell rupture, venting, electrolyte ignition, and fire [53]. In the class of anode materials in which lithium ions are electrochemically intercalated into the gap between the layers of materials, graphite is the substance that best exemplifies this process. A well-designed electrode structure can increase the battery's transmission rate by enhancing the contact area between the electrode and the electrolyte. It is important to consider the distribution of active materials and conductive additives. The distribution of active material and conductive carbon is uniform, enabling it to adjust to volume variations and complete ion exchange effectively. Deformation is caused by the concentration of stress due to active particle aggregation. The shift in volume can cause the electrode materials to detach from the current collector, obstructing the ion channels and leading to a rapid decrease in battery capacity.

Three types of anode materials store lithium ions in distinct ways. The first kind is insertion reaction mechanisms, which comprise a variety of carbon compounds and titanium dioxide. The second category involves alloying reaction mechanisms, which include Si, Ge, Sn, and other alloys. The third group consists of conversion reaction mechanisms, which include transition metal oxides and sulfides. MOFs and their derivatives have lately become popular due to their porous structure and large specific surface area. These materials have recently become the focus of substantial research. Table 2. summarizes the essential properties of current anode materials.

Table 2. Summary of the properties of the typically used anode materials [54-56].

Compound	Acronym	Materials structure	Specifically acquired specific capacity (mAh/g)	Average potential vs. Li/Li+ (V)
Li_xC_6	Graphite	Layered	330-365	0.10
$Li_4Ti_5O_{12}$	LTO	Spinel	130	1.55
$Li_{22}Si_5$ (can be found in several alloy types).	Si	Alloying	4200	0.40

5. INTERCALATION/DE-INTERCALATION in LIB TECHNOLOGY

Liquid and conventional polymer electrolytes conduct both anions and cations. Because cations (Li-ions) are exclusively transferred by electrodes across the electrolyte, this ambipolar conductivity results in a salt concentration gradient, i.e., depletion at the intercalation or coating side and over-concentration at the co-intercalation or dissolving side. This increases electrode polarization and causes dendritic formation in the case of Li-metal plating [57]. Dr. Rachid Yazami presented the world's first successful experiment in 1982 that demonstrated electrochemical intercalation and de-intercalation in graphite [58,59]. Although Dr. Yazami utilized a solid electrolyte, this experimentation laid the technical groundwork for the present-day use of graphite as the anode material in LIBs. A mixture of solvents, such as DMC or DEC, meant to improve battery performance frequently includes lithium salts as the electrolyte in a lithium-ion cell. Graphite undergoes rapid intercalation by lithium, which can occur either chemically or electrochemically. As a result of this widely recognized reaction, the initial stage LiC_6 binary chemical is created. The intercalation principle of LIBs is shown in Figure 6. An electrode is made up of an active material that is attached to a thin metal foil that collects the current. The active material can absorb and release lithium ions, which means that the process of lithium-ion insertion into the material is reversible. In an ideal situation, the active material should act as a host structure without affecting the intercalated lithium-ion. Furthermore, its physical and electrochemical properties should remain unchanged throughout the process.

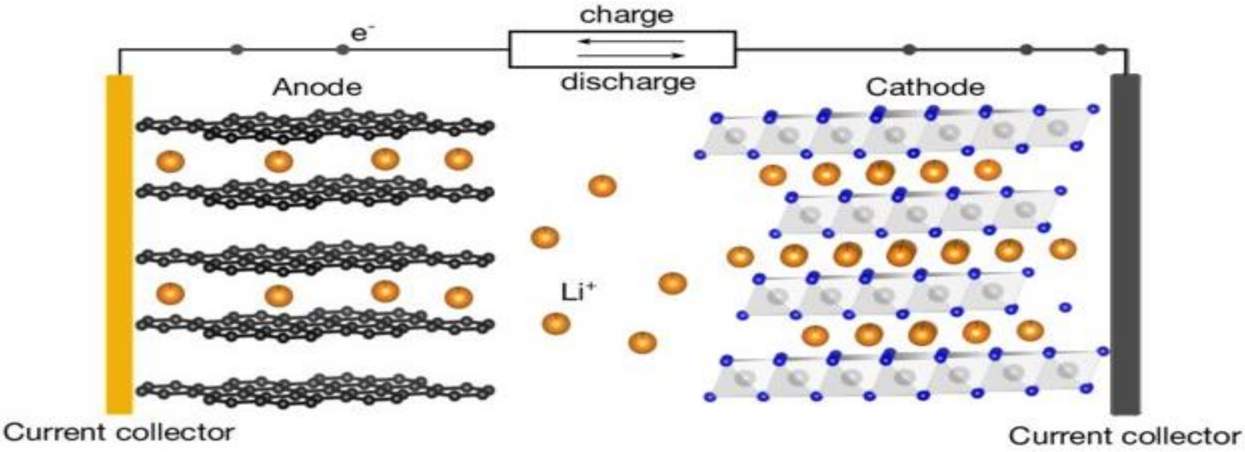


Figure 6. Intercalation principle of LIB [60].

The LIB is a type of rechargeable battery that exhibits a significantly higher voltage than other batteries during the movement of lithium ions between electrodes. This is because lithium ions must be counterbalanced by an equal number of electrons. A single lithium-ion cell is capable of producing a voltage of 3.6 volts or higher, contingent on the cathode materials employed. By comparison, an alkaline battery typically generates a voltage of only 1.5 volts. In the case of a conventional lead-acid automotive battery, six 2-volt cells are required to be stacked together to produce a 12-volt output.

The reactions listed below demonstrate how chemistry works in moles. The chemical reaction of the cathode is given as follows.

$$LiMO_2 \leftrightarrows Li_{1-x}MO_2 + x\,Li^+ + xe^- \tag{3}$$

Where M is the anode material.

During discharge, the cathode reduces as the electrode removes electrons from the circuit and absorbs lithium ions via lithium dioxide.

The anode's chemical reaction is outlined below:

$$C + xLi^+ + xe^- \leftrightarrows Li_xC \tag{4}$$

Charging the battery causes lithium ions to enter the graphitic carbon powder anode, and discharging the battery releases them.

Lithium metal oxide and lithiated graphite constitute the cathode and anode materials of LIBs, which are layer-structured on aluminum and copper current collectors, respectively.

The general reaction of the LIB is stated as follows:

$$LiMO_2 + C \leftrightarrows Li_xC + Li_{1-x}MO_2 \tag{5}$$

Although LIBs have many good characteristics, the fundamental difference between the various LIB types is the substance used as the electrode.

Charging and discharging cycles significantly affect LIB performance and durability. LIBs are charged and discharged in an optimized and high-quality manner to ensure maximum efficiency and a better life cycle. Graphite (C_6) has a stoichiometry of LiC_6, and a reversible specific capacity of 372 mA g^{-1} due to the intercalation of one Li atom per carbon atom. Thus, graphite anodes must be replaced with materials that have better efficiency, power density, and capacity [61].

6. RECENT DISCOVERY on LIB

As of lately 2019, John Goodenough (University of Texas at Austin), M. Stanley Whittingham (Binghamton University in New York) and Akira Yoshino (Asahi Kasei Corp and Meijo University in Japan) were awarded the Nobel Prize in Chemistry for their work on LIBs. Dr. Whittingham invented the first functioning LIB in the early 1970s. Dr. Goodenough doubled the LIB's capability, laying the groundwork for a far more powerful and practical battery. Dr. Yoshino was successful in eliminating pure lithium from the battery and replacing it with lithium ions, which are safer. This allowed the battery to function in practice. The result was a lightweight, long-lasting battery that could be recharged hundreds of times before losing performance. Figure 7 displays the recent LIB technology developed by the three experts.

This method of extracting pure lithium from $LiCoO_2$ effectively doubles the operating voltage and electrical performance compared to the Whittingham method, as the electrolyte's ion transport path is reduced and ion flux remains high. As an anode material, Petroleum Coke presents a heterogeneous, largely autonomous phase with a few linked micro areas. The negative electrode's capacity and cycle efficiency increase as the material's internal structure becomes more orderly and graphite-friendly. The inclusion of $Li+$ in the graphite layer results in bonding between the sheets of graphite and the expansion of their respective layers.

A LIB containing an LCO cathode and graphite, for example, delivers high voltage and energy density but has a higher thermal explosion risk, which can cause cell breakage, venting, electrolyte ignition, and fire [53]. Figure 8 depicts the most recent geometry shape of distinct LIB cells and their components.

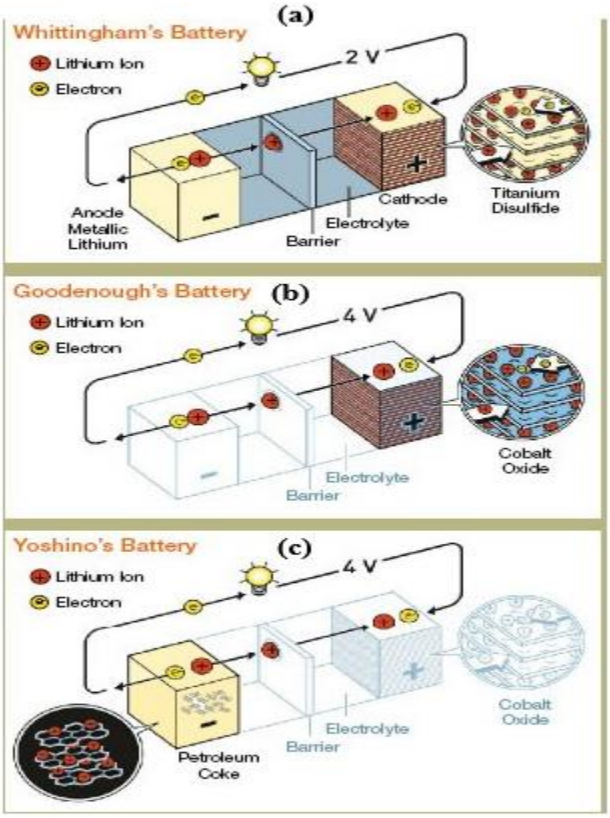


Figure 7. The LIB which was created by Whittingham (a), Goodenough (b), and Yoshino (c) [62].

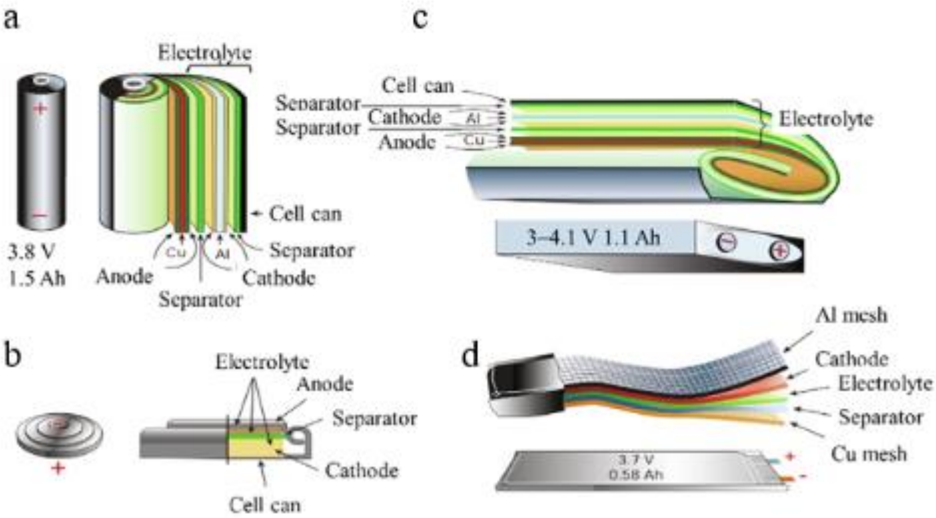


Figure 8. Various LIB cell designs: (a) cylindrical cell, (b) prismatic cell, (c) pouch cell, and (d) coin cell [63].

LIBs have become crucial in decentralized off-grid renewable energy systems, replacing diesel generators in remote areas. LIBs can replace typical fossil fuel-powered devices, offering a cleaner technology [64]. The performance of LIBs depends on electrochemical reactions, battery materials, mobile engineering, and gadget integration [65]. The qualities of substances depend on their chemistry.

Even though the lithium-ion battery market is expanding rapidly, the challenge remains to manufacture it with a higher energy density and longer lifespan. To aid in this research, several scientists are employing various analytical techniques to examine battery components at various phases of their lifecycle.

Scientists employ spectroscopy techniques including Raman, NMR, X-ray diffraction, and mass spectrometry to study the evolution of material structure and composition changes, as well as defect formation. Using these techniques, researchers may examine electrode materials as they charge, yielding previously unavailable information.

7. CONCLUSION

LIBs have transformed modern existence. Whittingham stated at a recent conference, "Lithium batteries have impacted the lives of almost everyone in the world." He's still working on battery development, and we're interested to watch how the Nobel Prize helps propel the sector forward. Rechargeable batteries of smaller size and weight were desired. Nonaqueous electrolytes have poor current density per electrode area, making it challenging to create rechargeable batteries with high current discharges. Metallic lithium in rechargeable batteries has low cycle endurance due to its high chemical reactivity and dendrite development. It also presents a safety risk owing to thermal runaways. Using $LiCoO_2$ as a positive electrode resulted in a cell voltage of at least 4 V. The commercialization and high-volume production of the LIB have led to significant scientific and technological advancements. LIB provides a big scientific challenge. Solid-state batteries made entirely of solid components are under development, with a focus on safety.

Acknowledgment: The author is acknowledged by the Department of Electrical and Electronic Engineering, RTEU.

Competing interests: The author confirms there is no conflict of interest.

Contributions of the authors: This work was conceptualized, written, and edited collaboratively by the author.

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