

Guest Editorial

A Breakthrough in Battery Research: Lithium Ion Batteries

Nadeesha Rathuwadu

Sri Lanka Institute of Nanotechnology

As the energy crisis is growing, the need of having a sustainable energy economy has become crucial more than ever to cope with the high energy dependence and demand of the modern day-to-day work.

Development of cost effective and efficient advanced electrical energy storage systems plays a critical role in ensuring the clean, sustainable, and secure energy supply. At present, lithium ion batteries (LIBs) power most of the portable electronic devices. LIBs have higher specific energy, energy density, and specific power compared to the other energy storage technologies and therefore preferred for energy storage applications. Figure 1 is a Ragone plot of specific power vs specific energy variation and it demonstrates that LIBs have greater specific power and specific energy compared to the other battery technologies [1]. It is anticipated that LIBs will also dominate in applications like transportation and stationary electricity storage in the future. Even currently, LIBs dominate and own 37% revenue share, which is the highest percentage compared to other battery technologies. In 2018, annual worldwide LIB production was estimated to be USD 29.27 billion. By 2026, the market value is expected to reach USD 95.89 billion, growing at a CAGR of 16.4% during the forecast period [2].

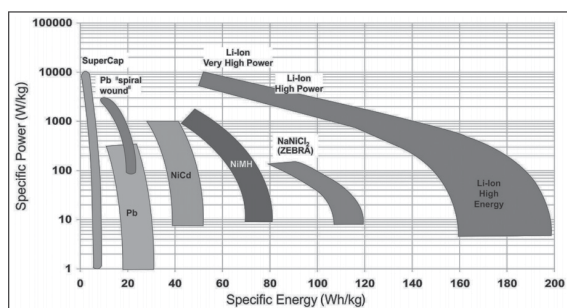


Figure 1. Ragone plot of different battery technologies. SuperCap: supercapacitor; Pb: lead; Li-ion: lithium-ion; NiCd: nickel-cadmium; NiMH: nickel-metal hydride; NaNiCl₂: sodium-nickel chloride; ZEBRA: Zero Emission Battery Research Activities.[1]

Lithium:

Prior to invention of LIBs, the existing battery technologies suffered from limited energy density, low capacity, and low voltage. Researchers were trying to develop better battery materials and lithium was considered due to its favorable properties to serve as an excellent battery element. Lithium is the lightest metal, with an atomic mass of 6.941 g mol⁻¹ and a density of only 0.53 g cm⁻³. Theoretical capacity of lithium is 3861 Ah kg⁻¹. Lithium also has a significantly low standard reduction potential (-3.05 V vs SHE for Li⁺/Li). These properties makes lithium an excellent candidate for high energy dense, high capacity, and high voltage battery chemistry.

Basic structure:

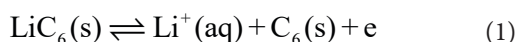
As in any electrochemical system, LIB comprises of a negative electrode (referred as anode) and a positive electrode (referred as cathode) which are connected through an electrical circuit. In a conventional LIB, a graphite anode and a lithiated transition metal oxide (LTMO) cathode are used. There are five main types of commercialized LTMOs used in LIBs. Lithium cobalt oxide (LiCoO₂, LCO), lithium manganese oxide (LiMn₂O₄, LMO), lithium nickel manganese cobalt oxide (LiNiMnCoO₂, NMC), lithium iron phosphate (LiFePO₄, LFP), and lithium nickel cobalt aluminum oxide (LiNiCoAlO₂, NCA) are the five main types of LTMOs used to date in LIBs [3]. Figure 2 is a diagram of the LIB. Anode and cathode are placed in an electrolyte medium. Typically, electrolyte is a mixture of organic carbonates (eg: ethylene carbonate, diethyl carbonate) containing a salt of lithium (eg: lithium hexafluorophosphate, lithium perchlorate, lithium triflate). Battery separators provide a barrier between the anode and the cathode while enabling the exchange of lithium ions from one side to the other. Usually, polyethylene or polypropylene separators are used in LIBs.

Function:

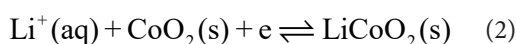
The half reactions take place at the anode and the cathode during discharge are given in Equation (1) and (2) respectively. The cathode discharge half reaction in Equation (2) is given considering LCO as the electrode material. The overall discharge reaction is given in Equation (3), and the reverse reaction takes place during the charging process. During the discharge process, intercalated Li in graphite anode are oxidized to Li^+ , and deintercalated to the electrolyte medium. At the cathode, Li^+ are reduced to Li and intercalated in CoO_2 . Oxidation and reduction reactions drive the intercalation and deintercalation processes. Figure 2 illustrates the discharge process.

During discharge:

Anode half reaction anode:



Cathode half reaction cathode:



Overall reaction:

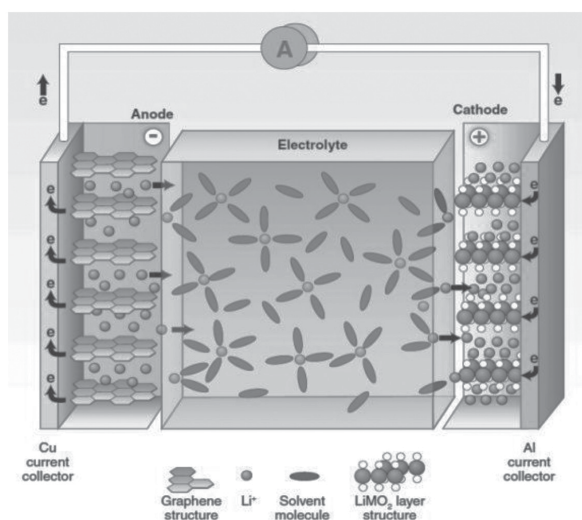
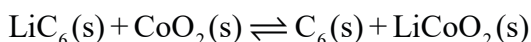


Figure 2. Diagram of the lithium ion battery. Process during the discharge is indicated in the diagram.[4]

Intercalation Chemistry

Intercalation/deintercalation is one of the major mechanisms takes place in LIBs to store energy. Intercalation means incorporation of guest species such as atoms, ions, or molecules, into a host crystal lattice,

without destroying host lattice structure. Two main conditions must be satisfied to achieve successful lithium intercalation/deintercalation with a host structure [5]. (1) The host compound must be crystalline. Also, there must be empty sites in the form of isolated vacancies or 1D channels, 2D layers, or 3D network channels. (2) The host compound must contain a transition metal or rare earth metal which can exhibit one or more stable valency states.

Compounds with vacancies are needed to accommodate lithium. Compounds with isolated vacancies or 1D channels may intercalated easily but they are hard to deintercalate. Therefore, in compounds with 2D or 3D vacancies lithium intercalation/deintercalation is more feasible. When lithium is intercalated, lithium ion is intercalated along with the electron. Intercalation reduces the valency state of the host compound by one unit and the compound should be able to accept the electron. Compounds without one or more stable valency states are not suitable for intercalation.

Lithium metal anode

Initial cell configuration used lithium metal as the anode material. When using lithium metal as the anode, dendrite formation was a huge problem. Upon repeated charge-discharge cycles, lithium metal was plated on anode. These dendrites could be large enough to go through the separator and reach the cathode. When lithium metal dendrites reach and contact with cathode, it causes short circuiting and start a thermal run-away reaction on the cathode. This causes the battery to catch fire. Li metal also suffers from poor cycle life. Due to these reasons, lithium metal anode was avoided during the LIB development. As an alternative, carbonaceous anode material were considered.

Anode material

A material should exhibit following properties to be used as an ideal anode material in rechargeable LIBs [5]. (1) Material should have elements/compounds with low atomic/formula weights and it should have low density. (2) Material should possess the ability to accommodate significantly large amount of Li per formula weight. (3) Material should be cyclable to result large, stable, and reversible gravimetric and volumetric capacities. (4)

The potential of the material should be low with respect to Li, i.e. potential should be close to that of Li. Also, upon lithiation-delithiation, the material should not show significant variations in the potential. (5) Material should be insoluble in the solvents and behave inert with solvents and electrolytes. (6) Material should have excellent electronic and Li ionic conductivity. (7) The material should be inexpensive. (8) The material should be environmentally friendly.

Most common anode material used in LIBs is graphite. Graphite can intercalate Li atoms to form LiC_6 , a stage 1 intercalation product, resulting a theoretical gravimetric capacity of 372 mAh g^{-1} . Graphite has a low potential of $0.15 - 0.25 \text{ V vs Li}$. Due to a chemical reaction takes place between Li and solvent, a protective layer called solid electrolyte interphase (SEI) is formed on the external surface of the graphite particles during the first few charge-discharge cycles. SEI has several advantages. SEI prevents cointercalation of solvent, acts as a good Li ion conductor, enables facile cycling, and protects reducing agent, charged graphite (LiC_6), from unwanted side reactions. Graphite is a semiconductor and has a conductivity ($\sigma_{300\text{K}}$) of $10^{-2} - 10^{-3} \text{ S cm}^{-1}$. Charged graphite (LiC_6) has a metallic-type conductivity ($\sigma_{300\text{K}}$) of $10^2 - 10^3 \text{ S cm}^{-1}$ and a high Li ion diffusion coefficient (DLi^+ at 300 K) of $10^{-8} - 10^{-10} \text{ cm}^2 \text{ s}^{-1}$.

In addition to graphite, lithium titanate oxide (LTO), conversion anode Type A, and conversion anode Type B (eg. Si) are studied as potential anode material for LIBs.

Cathode Material

There are key requirements a material should fulfill to be used as a suitable cathode material in a rechargeable battery [6]. (1) The material should have a readily reducible and oxidizable ion. (2) Material should react with lithium in a reversible way preferably

via intercalation-deintercalation. There should not be co-intercalation of the electrolyte ions. (3) The reaction between material and lithium should have a high free energy, i.e. high capacity and high voltage, which lead to a high energy density. (4) The reaction between material and lithium should be very fast which leads to a high power density. (5) The material should be a good electrical conductor which leads to easy oxidation and reduction during the electrochemical reaction. (6) The material should be stable, i.e. should not degrade or should not change the structure upon intercalation-deintercalation. (7) The material should be inexpensive. (8) The material should be environmentally friendly.

There are mainly two types of cathode materials [6]. The first category is the layered compounds with an anion close-packed lattice. The alternate layers between anions sheets are occupied with a redox active transition metal cation. Lithium can insert into the remaining empty layers. Examples for the first structure type are LCO, NMC, and NCA. Spinel are a special group of material, where the transition metal cations are arranged in all the layers. LMO has a spinel structure. The second category have more open structures. LFP is an example for the second structure type. Due to the compact structures, the main advantage of the first type is having a high energy density. The main advantage of the second structure type is the lower cost. A comparison of the basic properties of the five main commercialized cathode materials are listed in Table 1 [7].

In addition to above mentioned intercalation cathode materials, conversion cathode materials like metal fluorides, metal chlorides, selenium, and tellurium are studied as potential candidates.

Future of lithium battery

Improving LIBs further for high power high and

Table 1. A comparison of the basic properties of the five main commercialized cathode materials [7].

Compound	Specific capacity (mA h g^{-1})		Volumetric capacity (mA h cm^{-3})		Average voltage (V)
	Theoretical	Practical	Theoretical	Practical	
LCO	274	148/145	1363	550	3.8
NMC	280	160/170	1333	600	3.7
NCA	279	199/200	1284	700	3.7
LMO	148	120	596	--	4.1
LFP	170	165	589	--	3.4

energy density applications is the main objective of the current research. To achieve the objective, four critical criteria should be fulfilled [5]. (1) Cost reduction. For the cost reduction, cheaper electrode and electrolyte material needed to be found as these account for about 40% of the cost. (2) Improvements in the energy density. The energy density depends on the capacity and operating voltage of the electrode material. Currently, the practical capacities are less than the theoretical capacities. Electrode materials with higher capacities, as well as electrode materials that can utilize most of the theoretical capacity should be developed. Also, cathode materials with high operating potentials and anode materials with low operating potentials are preferred. Energy densities are expected to improve from about 120 W h kg⁻¹ to 250 W h kg⁻¹. (3) Safety in operation. Safety issues occur due to overcharging or over discharging. The devices can catch fire or evolve smoke. This can be due to charged anode/cathode which are thermally unstable and powerful reducing/oxidizing agents coming into contact with electrolyte or dendrite formation. Presence of a sophisticated safety electronic circuit will prevent overcharging and discharging problems. The other most crucial aspect is the heat management. Like other electrical energy systems, about 15% of the energy is lost as heat. In larger systems with LIBs, explosions can take place if the precautions are not taken. (4) Improvements in the low and high temperature operations. At low and high temperature operation capacity fades. It is anticipated to improve the temperature limits to 0-10 °C from low end and 60-80 °C from high end.

Making history: Nobel Prize in Chemistry 2019

Invention of the LIB is a breakthrough in battery research. Currently, LIBs are the most widely used rechargeable battery type. John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino were jointly awarded the Nobel Prize in Chemistry 2019 “for the development of lithium ion batteries”. Figure 3 shows the graphic of the three Nobel laureates from the official website of the Nobel Prize. Individual work carried out by these researchers became collectively critical to develop the LIB technology. In 1970s, Whittingham developed a battery with a titanium disulfide cathode and a lithium metal anode. Titanium disulfide functioned via intercalation-deintercalation chemistry. Voltage of the battery was around 2 V, but, the use of metal lithium

caused safety issues. In 1980s, Goodenough developed a battery with a remarkable cathode material, lithium cobalt oxide (LCO). This material could double the battery voltage. However, still lithium metal was used as the anode. In 1990s, Yoshino was investigating alternative anode material for lithium metal. He replaced lithium metal with petroleum coke, a by-product from oil industry. LCO was used as the cathode. He was able to develop a safe battery chemistry based on intercalation and deintercalation while not compromising the battery voltage. This led to the commercialization of safe, high energy dense, high voltage lithium ion batteries in 1991.



Figure 3. John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino were jointly awarded the Nobel Prize in Chemistry 2019 “for the development of lithium ion batteries”.[8]

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Themed Collection : Advances in Electrochemical Technology

Themed Collection

Electrochemical Energy Storage: Supercapacitors

Samitha D Panangala

The University of Texas at Dallas, USA

Various technologies are operated to supply the energy demands such as fossil fuels, nuclear energy, and renewable energy sources. Fossil fuels are depleting at an alarming rate emphasizing the need of alternative greener energy sources like solar and wind. The discrepancy between peak supply and demand from energy sources like solar and wind intensifies the necessity of high-performance energy storage systems.

Batteries possess high energy density with low power density whereas conventional capacitors exhibit high power with lower energy density. Supercapacitors also known as ultracapacitors possess a balance of energy and power densities which bridge the gap between conventional capacitors and batteries. Supercapacitors are capable of delivering more power than batteries and store higher energy density than conventional capacitors. This nature of electrochemical performance of supercapacitors makes them for many useful application like alternative energy industries, transportation, electronics, and communication.

Increasing the energy density of supercapacitors while maintaining the other fascinating properties has become an emerging field of research on energy storage. Depending on the energy storage mechanism they possess, supercapacitors can be classified in to two major categories, as pseudocapacitors and electrochemical double layer capacitors (EDLCs). Pseudocapacitors store energy by fast oxidation reduction reactions between electrode material and electrolyte ions.¹ Although this mechanism yields higher energy density it suffers from poor cycling stability and low conductivity, which hinder it the usability of pseudocapacitors in real world applications. On the other hand EDLCs store energy

through pure electrostatic charges accumulated at the electrode/electrolyte interface. Since the EDLCs have electrostatic mechanism it can rapidly release charges, while maintaining exceptional cycle life. Electrochemical performance of supercapacitors depends upon the specific surface area, pore size distribution, and conductivity of the electrode material.

Capacitance (C) is the charge (Q) per unit voltage (V) which is shown in equation 1.1.

$$Q = CV \quad 1.1$$

$$C = \epsilon_o \epsilon_r \frac{A}{d} \quad 1.2$$

Capacitance related to the geometry of electrode which can be expressed as equation 1.2, where ϵ_r , dielectric constant of the electrolyte, ϵ_o , dielectric constant of vacuum, d is the thickness of the double layer.¹ EDLCs, as the name imply two electrodes make two double layers upon charging, which represents a combination of two capacitors in series and the capacitance can be shown by equation 1.3.

$$\frac{1}{C_T} = \frac{1}{C_1} + \frac{1}{C_2} \quad 1.3$$

The energy density and power density of a supercapacitor expressed in equation 1.4 and 1.5.

$$E = \frac{1}{2} CV^2 \quad 1.4$$

$$P = \frac{V^2}{R_s} \quad 1.5$$

Capacitance is directly proportional to surface area and inversely proportional to the thickness of the double layer. Increasing the capacitance enhances the overall electrochemical performance of supercapacitor. The