Current State of Lithium Ion Battery Components and Their Development

Maria Kayra Saksia, Evvy Kartini
1 BINUS Serpong graduate, Science Stream, South Tangerang, Indonesia
2 Science and Technology Center for Advanced Materials, National Nuclear energy
Agency (BATAN), Indonesia, Puspiptek Area, Serpong, South Tangerang 15314,
Indonesia

skyegenet@gmail.com

Abstract. LIB is a secondary (rechargeable) battery and have been in the spotlight of battery
development due to its advantageous qualities in our era of mobile electronics. To improve the
LIB for its application in day-to-day life and beyond, development of its separate components,
namely the cathode, anode and electrolyte, is essential. Hence, this paper compiles past
developments of Lithium Ion Battery (LIB) components, focusing on a general overall view of
cathode, anode and electrolytes materials, and including the recent development of LIB in
Indonesia.

Keywords: Lithium-ion battery (LIB), cathode, anode, electrolyte, solid electrolyte, neutron
diffraction

1. Introduction

Batteries are so ubiquitous today that they're almost invisible to us. Yet they are a remarkable invention
with a long and storied history, and an equally exciting future. The first electric battery was built by
Volta in 1800, which before was called the voltaic pile. Since then numerous scientists have been
undergoing research on improving and developing better materials for electric batteries, using a variety
of combinations of elements. Batteries are very important in our current daily lives due to the
omnipresence of electrical gadgets. From mobile phones to electric cars, everything seems to run on
batteries these days. Not only are lighter and better batteries needed as technology develops, for example
the invention of smartphones that has long replaced old mobile phones, we also expect batteries to
become safer and less hazardous in their applications. It is even more so with the advent of Electric
Vehicles (EVs) coming much closer than ever. With manufacturers aiming to sell EVs commercially, it
is important to find longer-lasting batteries that are reliable and light [1]. Consumers would not invest
in EVs if replacing its batteries cost the same or even more than a fossil fuel-using car.

This is why it is very important for research on batteries to proceed and bring new solutions to
improve our everyday electrical needs. This review will highlight the development of batteries, more
specifically Lithium Ion Batteries (LIBs), through the development of its separate components.

2. Development of Batteries

Batteries work by converting chemical potential energy into electric energy, or vice versa when it is
recharged, through electrochemical, otherwise known as redox, reactions. These reactions occur
between the anode and the cathode, which has a potential difference, when in contact with an electrolyte,
which acts as a medium in which ions migrate from one end to the other. So the cathode and the anode determines the voltage of the battery. A separator between the anode and the cathode allows movement of protons but not of electrons. The mechanism can be seen as shown in Figure 1. The potential difference between the 2 electrodes acts as an electromotive force that forces the electrons to move through the circuit, hence forming electricity.

Batteries can be divided mainly into 2 categories: primary batteries and secondary batteries. Primary batteries are also known as non-rechargeable batteries, and actually plays an important role as they have relatively high specific energy, long storage times and instant readiness. They have been used in military combat, pacemakers, smart meters, animal-tracking, light beacons, watches, and other uses. A few examples of primary batteries are as follows: Carbon Zinc, Alkaline, Silver Oxide, Zinc Air and Lithium Cells. The lithium is not to be mistaken with Lithium Ion Batteries, Lithium Batteries are not rechargeable [2].

Secondary batteries, meanwhile, are batteries that can be recharged and used over and over again. This is not just due to its recharge ability, but also because they have low internal resistance, therefore able to form high current that is required by most electrical devices in the current industry. The following are a few examples of secondary batteries, excluding LIBs: Rechargeable Alkaline, Nickel-Cadmium, Nickel-Metal Hydride and Lead-Acid. The later was the most popular rechargeable battery worldwide due to lower cost and high reliability. Not used in consumer applications due to its heavy weight, and contains lead, which is toxic and carcinogenic.

This paper focuses on Lithium Ion Battery, which is a secondary battery. They are a relatively recent breakthrough and one of the most researched types of batteries due to their potential in consumer applications [3].

3. Current State of Lithium Ion Battery
One of the best batteries of today that are commercially available, due to its lightness and high energy density, among other advantages, are Lithium Ion Batteries (LIB). The first LIB was first formulated by Armand in the late 1970s, using intercalation materials of different potentials for the two electrodes, and is often called a rocking chair battery because of the flow of lithium ions back and forward between the two electrodes. The idea was then quickly taken up by other laboratories, which soon figured out that mixing Lithium with other elements (ex. transition metal oxides) [4]. A typical LIB works through the
reversible transfer of lithium ions between the cathode and the anode. The general mechanism of an LIB is shown in Figure 2.

![Figure 2. General mechanism of discharging (left) and charging (right) Lithium-ion Battery.](image)

It had been debated that LIB cathodes may develop a layer called the interfacial protective film (IPF) during storage, which increases internal resistance and may lead to lithium plating. However the nature of this layer is still not fully understood. Solid electrolyte interphase (SEI) layer is formed on the electrode surface when the solvent and electrolytic salt in the electrolyte are reduced. However, the layer can show positive and/or negative effects. Good SEI formation can improve the LIB. Composition of electrolyte and electrode micro- and nanostructure may affect the type of SEI formation. SEI insulates the anode but does not block ionic diffusion, though it does lower the capacity. Furthermore, it protects the battery and increases longevity. Bad SEI layer may affect battery performance, rate capability, cycle life, safety, and cause irreversible charge loss. A good SEI layer is porous and allow ionic diffusion. SEI formation may also get destabilized. High temperatures (75-90°C) may cause the breakdown of SEI layer of most commercial batteries.

Coulombic Efficiency (CE) of a battery defines the degree of transfer of electrons during its charge and discharge. It is able to measure the lithium lost due to SEI growth on the anode and the EO at the cathode. However, it varies with temperature and charge rate. CE decreases as cycle life increases due to self-discharge, but large CE causes large cycle life as well.

4. Development of Cathode
A cathode is also known as the positive electrode, where reduction takes place, of an electrochemical cell. Hence they have a more positive electrode potential than the anode. LIB cathodes, however, usually work by storing guest ions, in this case Li\(^+\) ions, which move reversibly from the cathode to the anode. They do this through one of 2 mechanisms: either they are made of a material with a structure that allows insertion and separation of the ions, in other words a ‘host network’, or, the cathode itself undergoes a reversible redox reaction. LIBs are dual intercalation systems, in which both the cathode and the anode have structures that allow reversible insertion and extraction of lithium cations. Originally, LIB cathodes use cobalt as its main active component, however, nowadays there had been many different synthesis of cathode materials so as to be researched and optimized [5-8]. LIB has been named due to Lithium Ion (Li\(^+\)) being its active material, then shortened to form the LIB acronym. Similarly, LIB have been known to be named after the other active Li\(^+\)-containing material used, shortened to form easier names when discussing them, instead of using their chemical formula. Table 1 summarizes the averaged abilities of LIBs with the 5 currently most common cathodes.
Table 1. Summary of Abilities of LIBs with Commonly Found Cathodes [9].

| Name                        | Lithium Cobalt Oxide (LCO) | Lithium Manganese Oxide (LMO) | Lithium Nickel Manganese Cobalt Oxide (NMC) | Lithium Iron Phosphate (LFP) | Lithium Nickel Cobalt Aluminum Oxide (NCA) |
|-----------------------------|-----------------------------|-------------------------------|---------------------------------------------|-----------------------------|--------------------------------------------|
| **Formula**                 | LiCoO$_2$                   | LiMn$_2$O$_4$                 | LiNiCoAlO$_2$                               | LiFePO$_4$                  | LiNiCoAlO$_2$                               |
| **Voltage (V)**             | 3.0 – 4.2                   | 3.0 – 4.2                     | 3.0 – 4.2                                   | 2.5 – 3.65                  | 3.0 – 4.2                                   |
| **Energy Density (Wh/kg)**  | 150 – 240                   | 100 – 150                     | 150 – 220                                   | 90 – 120                    | 200 – 260                                   |
| **Charge rate (C)**         | 0.7 – 1.0                   | 0.7 – 3.0                     | 0.7 – 1.0                                   | 1.0                         | 0.7; faster charge for some                 |
| **Discharge rate (C)**      | 1.0                         | 1.0; 10 for some; 30 if pulse (5s) | 1.0; 2.0 for some; 40 if pulse (2s)        | 1.0                         | 1.0                                         |
| **Cycle Life**              | 500 – 1000                  | 300 – 700                     | 1000 – 2000                                 | 1000 – 2000                 | 500                                         |
| **Thermal Runaway (°C)**    | 150                         | 250                           | 210                                         | 270                         | 150                                         |
| **Applications**            | Small portable electronics  | Power tools, medical devices, electric vehicles | Portable electronics, electric vehicles, industrial use | Portable and stationary appliances requiring high load current and endurance | Medical devices, industrial uses, electric vehicles |
| **Disadvantages**           | Short life span, low thermal stability, low specific power, high cost | Low energy density | Lower voltage, patent issues | Low energy density, high self-discharge, lower shelf life, sensitive to moisture, require special preparation | Low thermal stability, Sensitive to moisture, higher cost |

All the cathode materials in the table have ‘host networks’, and the material itself does not undergo redox reactions. Cathode materials which do can go through one of 2 reactions, both reversible. In first type reaction, metal halides react with lithium to form metal nanoparticles and lithium halides, which contains lithium ions. Second type reactions are undergone by lithium and one of the following elements: sulfur, selenium, tellurium, iodine and oxygen. However, only a few of these type of cathode material is suitable for commercial use. Design of electrodes may also affect its capabilities. For example, their placement, thickness, carbon content of cathode, their porosities, and the type of carbon used as the anode. Carbon-coated LiFePO$_4$ cathode in battery prepared by hydrothermal route also improve the electronic conductivity [10, 11].

5. Development of Anode
The anode can be said to be almost completely opposite of the cathode, in both mechanism and placement within the LIB. Whereas reduction occurs in the cathode during discharging, oxidation occurs at the anode. The anode have also been called as the negative electrode. Anode material for current LIBs require high porosity, conductivity, durability, light weight, low cost, and suitable voltage when matched with the cathode. Hence, for the most common cathodes as shown above, carbon-based anodes are used. Usually this consists of processed graphite that is baked onto copper anodes, and meet the requirements of the cathodes. However, due to safety, cost and environmental concerns of future batteries, graphite may no longer satisfy these requirements. Increasing energy demand also plays a part in possible commercial anode material change.

Silicon has been tested as an anode material due to its large capacity; over ten times that of graphite. However, it experiences drastic volume change during charging and forms an unstable SEI layer. Furthermore, it has poor mechanical stability and is chemically passive. Lithium metal has also been used as an anode material for both Lithium Battery and LIBs. It has a similar capacity to silicon, which is why it had been researched extensively in the past. However lithium metal is highly reactive and may cause safety issues. Its usage as an anode also cause bad SEI formation and dendrite growth. Alloy anodes seem to have a distinct advantage compared to purely carbon anodes, due to their potential for higher capacity and decreased corrosion. For example, addition of silicon particles in small amounts on carbon-based anodes have been shown to improve cycle life and capacity with little difference in cost. Corrosion of the anode may lead to SEI growth and degradation. This can be prevented by improving anode coating, modifying surface structure of anode, or changing the composition of the electrolyte.

Another popular choice for LIB anodes is lithium titanate (Li$_4$Ti$_5$O$_{12}$, battery name LTO), which has been known since the 1980s and has shown potential due it being structurally stable, environmentally friendly, and having lower cost. However, it has relatively lower charge/discharge capability. The material have faced significant improvement when combined with carbon nanotubes to form a composite. Its use have been shown to improve rate capability, cycle life, as well as safety of LIBs. Usage of lithium titanate material as the anode minimizes SEI formation and volume change [12, 13]. It has a wide temperature range and long life, and have been applied in electric trains and street lighting. Lithium Titanate seems to be open to further improvement through different synthesis methods, as shown by various researches in recent years, such as Li$_4$Ti$_5$O$_{12}$ anode material prepared by hydrothermal process [11, 14].

6. Development of Electrolytes
Cathode and anode materials are not the only components that are being improved in order to create better LIBs. Qualities such as energy density, power density, lower resistance and safety need to be reflected in the electrolytes used as well. Furthermore, electrolytes must have good ionic conduction while preventing electron transfer, is stable and tolerant to possible environmental changes, and especially for commercial batteries, must be non-toxic, environmentally friendly and costs cheaper. Most current commercially available batteries use liquid electrolytes due to its high conductivity, relatively wide temperature range and the added potential for additives. The first electrolyte used commercially in LIBs is liquid organic electrolyte, which is non-aquatic and consists of a lithium salt dissolved in an organic solvent. They are widely used in handheld electronics and energy storage due to its stability, good voltage, and high energy density. These solvents include carbonates, esters, and ethers, while the salts may be LiBF$_4$, LiPF$_6$, Li Triflate, Li Imide, LiFAP, Li imidazolidie or various others. Moreover, they are highly flammable, which has raised concerns of the safety of its application. Inappropriate insulation and heat management of the battery have caused electronics to short-circuit and catch on fire.

Aqueous electrolytes solves this problem as they are non-flammable, while also being low cost. Research on these electrolytes, which replaces organic solvents with water, has shown promising findings. However, it is not as stable as other electrolytes as water may evaporate or be electrolyzed to form gases. Water also limits the electrochemical reactions that can occur within the electrolyte, so that its voltage may be lower than other types of electrolytes. Ionic liquids (ILs), in comparison, consists of
a liquid with a cation and an anion, as well as a lithium-containing salt. Its properties are largely dependable on the cation and anion selection. They are non-flammable, have high chemical stability, ion conductivity, and solubility of both organic and inorganic compounds. However, their viscous nature may reduce ionic conductivity, and they costs more than other organic solvents [15]. Another type of electrolyte is the solid polymer electrolyte. They have advantages over liquid electrolytes as they have better structural properties, better safety, and may prevent formation of dendrites. Unfortunately, they only work at elevated temperatures, and are no longer commercially available. Gel polymer electrolytes (GPEs) have similar properties as solid polymer electrolytes, but they are more commercially suitable as they also have some similarities with liquid organic electrolytes. They are composed of a salt, a liquid organic solvent, and a polymer.

The development of solid electrolytes is one of the most significant advancements in LIB research [16-18]. It solves the problem of flammability of LIBs that operate using other types of electrolytes, will not cause leakage, mitigates dendrite formation, and have higher energy, voltage and power density than previously expected. Solid Electrolytes may replace commercially used organic electrolytes due to its better safety and toxicity. However, it does have room for improvement as it experiences several disadvantages.

7. Development of Solid Electrolyte

There are two kinds of solid electrolytes (SEs). The first is ceramics solid electrolytes, otherwise known as crystalline electrolytes, which in turn also have several sub-types. Both of these types of electrolytes must allow diffusion of lithium ions, which would require a different mechanism when compared to liquid electrolytes. The difference between liquid and solid electrolytes is shown in Figure 3.

![Figure 3. Simple battery mechanism with liquid electrolyte (left) and solid electrolyte (right).](image)

Both types of solid electrolytes are single ion conductors, which means that they allow the conduction of only one ion, while other cations and anions form the framework or structure of the electrolyte. This may also prevent side reactions and decomposition of the electrolyte. Most other electrolytes cannot replicate this kind of property, and usually have downsides when they do. Furthermore, they do not cause leakage and have relatively stable temperatures.

LISICON-type SEs have low conductivity during room temperature which improves at 300°C. But improvements on the material, for example by replacing oxide by sulfur in its framework, can highly improve its ionic conductivity. Garnet-type electrolytes have high conductivity and chemical stability.
Li$_3$La$_{2.5}$Zr$_{0.25}$O$_{12}$ (LLZO) is one example, which exhibits very good safety and electrochemical stability, able to perform excellently when applied properly in an LIB. Perovskite-type electrolytes have high bulk conductivity. Li$_{0.25}$La$_{0.57}$TiO$_3$ (LLTO) is an example of it. It has high ionic conductivity when amorphous and is used as a thin film, thus reducing resistance as ions diffuse through a shorter distance. It is also stable even at high voltages. The above SEs are highly researched upon as a commercial electrolyte for day-to-day applications, especially for EVs. The second type of SEs, namely glass-based electrolytes, also have potential in commercial use.

Glassy electrolytes do not suffer from any grain boundary resistance, are easy to form into a thin film, which is especially useful in cylindrical battery applications, and have relatively high ionic conductivity [19]. They can also prevent dendrite formation. Glassy electrolytes are typically composed of a lithium salt and modifier, the glass which forms the structure, and if applicable, additives to improve its properties [18, 20, 21]. The glass must allow ion diffusion in order to behave as an electrolyte. Usually, the glassy electrolyte is ground into a fine powder or milled so as to produce amorphous materials, which can allow ion diffusion. Another subtype of glass-based electrolytes are glass-ceramic electrolytes, which involved crystallization of the precursor glass. They have grain boundaries filled with amorphous phases, therefore causing lower resistance.

Indonesia has a lab specifically for battery research in BATAN, Serpong, and has various research on developing materials for battery components, also for contributing battery production and testing at laboratory scale. Recent development at our laboratory on glassy electrolytes based on phosphate glasses, such as LiPO$_4$, Li$_3$PO$_4$, Li$_3$O-P$_2$O$_5$ and its corresponding glasses with variation of doping salts to increase the ionic conductivity [16, 18, 22]. Several methods have been developed such as Li$_3$PO$_4$ powder as solid electrolyte material prepared by wet chemical reaction and solid-state reaction Li$_3$PO$_4$-MMT-PVDF composites as solid electrolyte material is also being developed in this laboratory [18, 19].

8. Conclusion

It is concluded that the research and development of on LIB moving forward. This paper has summarized the early development of batteries and the current state of LIB. Most specific, development of materials cathode, anode and electrolyte as battery components. The research on solid electrolyte is growing due to safety reason. The future of solid state battery will be replacing the current commercial lithium ion battery which based on liquid electrolyte. Until now, both private companies and the Indonesian government has further developed LIB research for various reasons. Profit and an improved economy seems to be their main driving force, as well as the pride of being able to keep up and overcome other, more developed countries in battery research. However, much more time is needed before Indonesia’s citizens would be able to take the lead in battery research, as their attitude is unfortunately currently more apathetic than not towards these kinds of developments within their own country. But with the help of researchers, the push of the government, and financial aid of interested sponsors, battery research in Indonesia has made leaps and bounds from its starting point as almost negligible, until now.

Acknowledgment

The author would like to thank Battery team at BATAN, for their guidance and expertise throughout the writing of this paper, and K parents for their support and understanding. Materials Research Society Indonesia (MRS-INA) for giving opportunity to join the International Conference in Asia of the International Union of Materials Research Society (ICA-IUMRS), Bali, October 30-November 2, 2018.

References

[1] B. Scrosati and J. Garche, “Lithium batteries: Status, prospects and future,” J. Power Sources, vol. 195, pp. 2419–2430, 2010.
[2] J. Hwang, S. Myung, and Y. Sun, “Chem Soc Rev Sodium-ion batteries : present and future,” Chem. Soc. Rev., 2017.
[3] E. Kartini, “Emerging battery research in Indonesia: The role of nuclear applications,” in AIP
Proceeding “5th International Conference on Women in Physics, Waterloo, Canada, 5-8 August 2015”, 2015, vol. 1697, pp. 100001–2.

[4] L. Zhao, D. Zhou, W. Huang, X. Kang, Q. Shi, Z. Deng, and X. Yan, “Electrochemical Performances of Maricite NaFePO 4 / C as cathode material for Sodium-Ion and Lithium-Ion Batteries,” vol. 12, pp. 3153–3165, 2017.

[5] S. Oh, S. Myung, J. Hassoun, B. Serosati, and Y. Sun, “Electrochemistry Communications Reversible NaFePO 4 electrode for sodium secondary batteries,” Electrochim. commun., vol. 22, pp. 149–152, 2012.

[6] Y. Long, Y. Shu, X. Ma, and M. Ye, “In-situ synthesizing superior high-rate LiFePO4/C nanorods embedded in graphene matrix,” Electrochim. Acta, vol. 117, pp. 105–112, 2014.

[7] W. Honggowiran and E. Kartini, “Characterization of LiFePO4 4 Cathode by Addition of Graphene for Lithium Ion Batteries,” in 6th Nanoscience and Nanotechnology Symposium (NNS2015), 2016, vol. 030045.

[8] W. Honggowiranto, Sudaryanto, E. Kartini, and A. Purwanto, “Electrochemical Performance of LiFePO 4 Cylinder Cell Battery,” in AIP Proceeding “6th Nanoscience and Nanotechnology Symposium (NNS2015),” 2016, pp. 030042–1–7.

[9] M. M. Doeff, "Batteries: Overview of Battery Cathodes," in Springer Encyclopedia of Sustainability Science and Technology, pp. 709-739, 2012.

[10] X. Li, T. Li, Y. Zhang, X. Zhang, H. Li, and J. Huang, “Graphene nanoribbon-wrapping LiFePO4 by electrostatic absorbing with improved electrochemical performance for rechargeable lithium batteries,” Electrochim. Acta, vol. 139, pp. 69–75, 2014.

[11] W. Honggowiranto and E. Kartini, “Characterization of LiFePO4 4 Cathode by Addition of Graphene for Lithium Ion Batteries,” in AIP Proceeding, 2016, vol. 030045.

[12] B. Priyono, A. Z. Syahrial, A. H. Yuwono, E. Kartini, M. Marfelly, and W. R. F. Muhamad, “Synthesis of Lithium Titanate (Li4Ti5O12) through Hydrothermal Process by using Lithium Hydroxide (LiOH) and Titanium Dioxide (TiO2) Xerogel,” Int. J. Technol., vol. 4, pp. 555–564, 2015.

[13] A. Z. Syahrial, B. Priyono, A. H. Yuwono, E. Kartini, H. Jodi, and Johansyah, “Synthesis of Lithium Titanate (Li4Ti5O12) through Hydrothermal Process by using Lithium Hydroxide (LiOH) and Titanium Dioxide (TiO2) Xerogel,” Int. J. Technol., vol. 3, pp. 392–400, 2016.

[14] N. Sofyan, G. T. Setiadianu, A. Zulfia, and E. Kartini, “Effect of Different Calcination Temperatures and Carbon Coating on the Characteristics of LiFePO4 Prepared by Hydrothermal Route,” IJET, vol. 9, no. 4, pp. 3310–3317, 2017.

[15] A. Reni, S. Evvy, K. Wagiyo, H. Sudaryanto, and R. Hidayat, “Perfomance of Lithium Ion Battery Based on LiTFSI Lithium Salt as Electrolyte Compared to LiPF 6,” vol. 1, no. 1, pp. 1–5.

[16] N. I. P. Ayu, E. Kartini, L. D. Prayogi, M. Faisal, and Supardi, “Crystal structure analysis of Li3PO4 powder prepared by wet chemical reaction and solid-state reaction by using X-ray diffraction (XRD),” Ionics (Kiel), vol. 353, pp. 1–7, 2016.

[17] E. Kartini and M. Manawan, “Solid Electrolyte For Solid-State Batteries: Have lithium-ion batteries reached their technical limit?,” in AIP Proceeding (in press), 2015.

[18] E. Kartini, M. Nakamura, M. Arai, Y. Inamura, K. Nakajima, T. Maksum, W. Honggowiranto, and T. Y. S. P. Putra, “Structure and dynamics of solid electrolyte (LiI)0.3(LiPO3)0.7,” Solid State Ionics, vol. 262, pp. 833–836, 2014.

[19] E. Kartini, M. Manawan, M. F. Collins, and M. Avdeev, “Physica B : Condensed Matter Neutron diffraction study on Li 3 PO 4 solid electrolyte for lithium ion battery,” Phys. B Phys. Condens. Matter, vol. 551, no. August 2017, pp. 320–326, 2018.

[20] E. Kartini, T. Sakuma, K. Basar, and M. Ihsan, “Mixed Cation Effect on Silver-Lithium Solid Electrolyte (AgI) 0.5(LiPO3)0.5,” Solid State Ionics, vol. 179, pp. 706–711, 2008.

[21] H. Jodi, A. Z. Syahrial, Sudaryanto, and E. Kartini, “Synthesis and Electrochemical Characterization of New Li2O-P2O5 Compounds For Solid Electrolytes,” IJTech 2017, vol. 6,
E. Kartini, T. Y. S. P. Putra, I. Kuntoro, and T. Sakuma, “Recent Studies on Lithium Solid Electrolytes (LixLi1-xPO3) for Secondary Battery,” *J. Phys. Soc. Jpn*, vol. 79, no. Suppl.A, pp. 54–58, 2010.