

The Modification of Graphite in Lithium-Ion Batteries and its Applications

Anqi Li *

Robert Louis Stevenson School, CA, USA

* Corresponding author: ali25@stevensonschool.org

Abstract. Lithium-ion batteries (LIB) dominate the battery market because of their excellent performance. However, the potential safety hazard of lithium-ion batteries is still regarded as an important factor hindering their further development. Lithium-ion batteries are highly flammable. In fact, there have been multiple cases of explosions caused by lithium-ion battery which result in severe burns over the past decades. Other concerns including recyclability and low power density produces obstacles to this technology. Graphite is a material with excellent conductivity. It has many outstanding electronic and mechanical properties. The basic and applied research on graphite has become a current frontier and hotspot. Therefore, graphite is also used to modify lithium-ion batteries. Especially using graphite to modify the anode material greatly improves its original performance. This work firstly introduced the physical and chemical properties of graphite. Subsequently, how graphite can enhance the efficiency LIB was introduced. A detailed introduction was given concerning with graphite modified anode materials. This work will promote the application of graphite in lithium-ion batteries.

Keywords: Lithium-ion battery, graphite, anodes.

1. Introduction

Lithium-ion batteries (LIB) are devices which can achieve energy storage. Enhancing energy density and lowering cost is something that scientists have always been committed to. Lithium-ion batteries have become the core energy storage components for many systems due to their outstanding performance in energy density and potential. In addition, it also holds a long cycle life, low self-discharge rate, and no memory effect [1]. In recent decades, there has been a visible rise in energy storage of LIB. However, with the increasing demand for battery capacity, high-performance new materials need to be applied to further improve the performance of LIB. The material graphite is a versatile conductor that is notably compatible for LIB.

Graphite materials have excellent conductivity, abundant reserves, and low prices. It is very suitable for graphite to modify LIB. LIB consists of cathode materials, anode materials, electrolyte, and other components. Researchers have conducted numerous experiments on cathode and anode materials. Interestingly, cathode materials have drastically changed over the years, but graphite anode had remained the same for decades. Although there have been potential substitutions such as silicon, sulfides, oxides, etc., few of them have can replace graphite. Therefore, the modification of LIB anode materials is basically based on graphite anode materials.

While the demand for graphite in the battery world is unquestioned. Recent research had revealed that graphite can further enhance the performance of LIB. Especially after modification based on graphite anode, the original performance has been improved. It is very necessary to summarize the work of using graphite for LIB modification. This paper seeks to give useful insight to its characteristics and functionalities. In addition, the advantages and disadvantages of which graphite brings to the battery technology were also discussed.

2. Lithium Ion Batteries and the Subsequent Modification of Graphite

2.1. Characteristics and Functionalities of Graphite

Many material scientists study the chemical and physical properties of graphite which ensures their crucial function in a battery. The material graphite is the most stable crystalline allotrope of carbon. It comes in three forms: crystalline flake, lump and amorphous. Each of the three forms have different purity levels. The electronics industry separates the graphites into synthetic and natural. Synthetic graphite comes from the amorphous form heated in high temperatures. Though purifying synthetic graphite is very expensive. On the other hand, natural graphite consists of all three forms, lump, amorphous and crystalline. However, most companies use crystalline flake. Of all graphite, flake is the most prominent form of graphite to be used. Purity of graphite is an imperative criterion in electronic production. Contemporarily, the best way to analyze purity is by wavelength dispersive X-ray fluorescence (WDXRF).

Graphite displays good-natured properties such as heat resistance, electric conductive, light and highly malleable. Graphite can hold up to 3600 celsius until it sublimates. In fact, it strengthens at high temperatures like 1000 celsius, making them more durable than most metal materials. Unlike diamonds whom has a 3D tetrahedral shape, graphite has two dimensional layers [2]. Graphite is made of carbons each with three strong covalent bonds, this makes them a trigonal planar. The extra valence electron creates Van der Waal forces with the other layers of graphite. This weak link allows the battery to conduct electricity.

Although it is mentioned earlier that graphites are great electricity conductors, there are certain points where they aren't. The disadvantages of a 2D plane structure are that some regions, notably the basal regions have more conductivity than the edge plane which is perpendicular to it.

The hybridization form of graphite takes in structure of sp^2 , this allows the graphite layers to perform uncomplicated intercalation process [2-5]. Intercalation, in other words, is defined as the injection of certain ionic molecules to enter the prismatic surfaces of the graphite. This is the key procedure used in Lithium batteries. To great design, the lattice structure of graphite will be retained during the integration of Graphite Intercalation Compounds (GICs). There are different stages and different kinds of GICs, the most distinct differences are the acceptor compounds and the donor compounds. In this case, lithium ion is a donor GIC compound to the graphite layers, meaning that it donates an electron to graphite [6]

2.2. The Function of Graphite in Lithium Ion Batteries

Firstly, it is necessary to understand the working principle of LIB. Lithium is the lightest metal among others, it also carries the most energy density and the highest electrochemical potential. Lithium Batteries discharge by moving lithium ions from anodes to the cathodes. Similarly, charge would require moving in the opposite direction. During the primary stage of LIB in the 1990s, companies used coke for anodes but quickly substituted with graphite for it has a slower and milder discharge curve [7]. While lithium alone is highly reactive, it is considerably stable in metal oxide forms. When lithium ions are removed from the structure during discharge lithium becomes unstable again. However, once charged, because of its instability, lithium ions will have a natural tendency to restore itself back to the metal oxide framework [3]. During this process electric current is produced. Following this logic, the anodes are filled with graphite on one side and the cathodes are filled with metal oxides on the other. Two electron receptors will be connected on both sides to run through the electric currents. In between the two sides lies an electrolyte wall and separator made of carbon fibre that prevents valence electron of lithium from traveling with lithium. If they travel together, an electric shortage will break out with the risk of explosion or fire.

Some disadvantages of lithium-ion battery are electrolyte degrading, where electrons attempting to travel pass the electrolyte barrier from the anode to the cathode was damaging the filter. This was a prominent issue in the early development of lithium-ion battery design. This was solved by a mistake. Ostensibly, from the first usage of a battery, meaning when the very first lithium cation s

travel back from anode to cathode, some of the cations will react chemically with graphite to form a barrier called Solid Electrolyte Interphase (SEI). SEI prevents much of degradation [8]. An estimate of roughly 5% of lithium cations will contribute to building the SEI. This barrier also removes organic molecule shells on the lithiums before they are incorporated into the graphite frame.

2.3. Graphite Anodes

Lithium-ion batteries have attracted the attention of many researchers due to their excellent performance, and anode materials are a key factor in improving the performance of lithium-ion batteries. Therefore, it is necessary to study the anode materials of lithium-ion batteries to improve their existing performance. Researchers have conducted extensive work on the modification of graphite as an anode material. There are still remains many questions about graphite as an anode material. Specifically, during its process of Li intercalation. Damaus-Herald mechanism best explains this process [3]. The ultimate goal in the game of LIB is to reduce the amount of thermodynamically predictable lithiums exhausted during constant charging and discharging [4]. This would then amount to greater retention capacity and a longer life cycle [1]. The process of lithiation can be split into different stages. At stage k the lithium atom is intercalated with every k th layer of graphite [9].

Analyzing the drawbacks of using graphite anodes for LIB helps to understand the direction of further research. Though graphite intercalation compound had been heavily researched in the last thirty years, graphite material is still held accountable one of the leading causes for commercial LIB unsatisfactory performance. Especially when it comes to fast charging. Some safety concern that arose during the design and commercialization of LIB is the formation of lithium dendrites [3, 7], [8]. Because graphites store and release lithium cations on a significantly low voltage, lithium dendrites (compounds that destroys electrolytes) form during battery charging. This could lead to electric circuit shortage and potential flames and explosions [7, 10]. The optimization of graphite surface design is imperative to the safety of electric grid vehicles. In order to achieve making electric storing stations a reality like gas stations, engineers also have to improve the cycle stability and coulomb efficiency in graphite. Another concern for graphite in LIB is its weight, by weight, graphite is the biggest component in the battery as it accounts to 30%. This is harmful to a lot of industries where weight matters significantly. A popular example would be the electronic cars, which the weight will affect the safety of people and the functionality of the car, by large. Other concern is about reducing costs, that the purification process of natural graphite (crystalline flake graphite) is expensive and sophisticated. As of now, slightly more industries use natural graphite as opposed to synthetic graphite.

Analyzing the advantages of using graphite anodes for LIB also contributes to further improve the performances. Graphite is relatively low cost, has great abundance, resistant to corrosion, great physical stability and high specific conductivity [2, 6]. Lithium reduction does not happen as frequently as graphite is applied. This makes graphite anodes have a high cycle life and greater volumetric capacities. In addition, Li-ion exchange through the electrolyte and the lithium diffusion in anode is much faster than other carbonaceous materials [6]. Graphite also performs as a dry lubricant, it can minimize friction and excel in high temperatures and oxidizing environments, which many wet lubricants cannot. Recent new discoveries revealed that a single layer of graphite named graphene can be used to transform the industry. Graphene is touted as extraordinarily strong, thin and will become a new “super-material” in applications included but not restrained to membrane technology, electronics, heat transfer, bio-sensing, battery technology.

Based on the above analysis, future prospects for graphitic materials in LIB are highly worthy of research. New research suggests that there are more electrochemical properties to be renewed. By enhancing microstructure and advancing SEI, it is said that fast charging-discharging of graphite is in the foreseeable future [7, 11]. Modifications of graphite materials to maximize function is also the focus for many engineers. Modifications include coating and oxidation. Pyrolytic carbon, coke, and other carbonaceous materials are coated. Metal oxides: aluminum oxide, nickel oxide silver oxide Oxidizing graphite material is prevalent with numerous gases: fluorine gas, carbon dioxide and ozone,

etc. Pyrolytic carbon, coke, and other carbonaceous materials are coated. Metal oxides: aluminum oxide, nickel oxide, silver oxide is used for enhanced electrochemical properties [7, 12], [12]. Safety issue that arose in graphite can also now be compensated with a more appropriate selection in the electrode binder, whom some are able to interact with the active lithiums once they intercalated with the graphite. Some future applications of graphitic may include touch screens, DNA sequencing, spin transport electronics and fiber optic cables.

3. Conclusion

Graphite is an irreplaceable component of lithium-ion battery. Ever since the first arrival of LIB on the world stage, graphite anode has been applied and continues to be enhanced by modern science. Though cathode materials have carried overtime and now new alternatives have been suggested to replace graphite, no materials have achieved nor surpassed graphite in considering life cycle, energy density and power density. Graphite brings efficiency to our lives from electric vehicles, power stations to daily electronics. The electric vehicles are the rising star above all industries in the usage of LIB and further more graphite. Large companies like Tesla seeks to include but is not limited to hybrid vehicles and plug in vehicles. Technology corporate and their ties to raw metal materials are unquestionable. However efficient graphite is, safety issues also arose in the earlier decades, this is now largely improved by enhancing other components like solid electrolyte interphase and elaborate research. Comprehending the big picture there is still a lot of spaces to improve. There are still debates on whether using artificial graphite is better than natural. Both have invisible costs. There are always tradeoffs between abundance and purity, both are qualities important in the battery industry. In contemporary years, due to the rise of electronic cars and other electronics, the price of graphite increased by a quarter percent and the demand for general anodes grew by nearly half. This imbalance is predicted to continue. In 2022 the Lithium-Ion Battery Industry became the largest industry in demand of graphite, overtaking refractory and foundry industries. = As of now, most of graphite supply is provided by only two countries, China and Africa. New mine expansions are expected to increase graphite supply. The supply chain of graphite in LIB is in need of diversification and renewal.

In this work, the characteristics and functionalities of graphite were introduced. Then, the function of graphite in lithium-ion batteries was discussed in detail. Graphite anodes were introduced finally. The advantages and disadvantages of graphite as an anode material have been systematically analyzed. Through this work, the relevant knowledge of lithium-ion batteries has been systematically introduced.

Modifying the structure of graphite anode materials will be a promising research direction in the future. Doping other new materials to improve the performance of graphite materials may also help improve the existing problems of graphite anodes. Combining graphite with other materials to form composite materials as anode materials will also be one of the possible research directions. This work will contribute to further application of graphite materials in LIB.

References

- [1] Peng Chuan, Liao Dong Ming, Lv Lin Xue, et al. Large-scale synthesis of highly structural-connecting carbon nanospheres as an anodes material for lithium-ion batteries with high-rate capacity. *Chemical Engineering Journal Advances*. 2020, 2 (15): 100014.
- [2] Zhang Hao, Yang Yang, Ren Dongsheng, Wang Li, He Xiangming. Graphite as anode material: Fundamental mechanisms, recent progress and advances. Elsevier. 2020, 34: 134 - 170.
- [3] Insinna Teresa, Bassey N. Euan, Marker Katherina, et al. Graphite anode for lithium-ion batteries: An electron paramagnetic resonance investigation. *American Chemical Society*. 2023, 35 (14): 5497 - 5511.
- [4] Rachid Yazami. Surface chemistry and lithium storage capability of the graphite-lithium electrode. Elsevier. 1999, 45 (1-2): 87 - 97.

- [5] Ohzuku Tsutomu, Iwakoshi Yasunobu, Sawai Kejiro. Formation of Lithium-ion graphite intercalation compounds in nonaqueous electrolytes and their application as a negative electrode for a lithium (shuttlecock) ion shell. *The Journal of the Electrochemical Society*. 1993, 140: 2490 - 2498.
- [6] Wu YP., Jiang C., et al. Modified natural graphite as anode material for lithium-ion battery. *Journal of Power Sources*. 2002, 111 (2): 329 - 334.
- [7] Asenbauer Jakob, Eisenmann Tobia, Kuenzel Matthias, et al. The success story of graphite as lithium-ion anode- fundamentals, remaining challenges, recent developments including silicon (oxide) composites. *Royal Society of Chemistry*. 2020, 4: 5387 - 5416.
- [8] Wang Aiping, Kadam Sanket, Li Hong, et al. Review on modeling of the anode solid electrolyte interphase (SEI) for lithium-ion batteries. *Nature NPJ journals*. 2018, 4 (1): 2057 - 3960.
- [9] Xing Baolin, Zhang Chuantao, Cao Yijun, et al. Preparation of synthetic graphite from bituminous coal as anode materials for high performance lithium-ion batteries. *Elsevier Fuel Processing Technology Journal*. 2018, 272: 162 - 171.
- [10] Zhu Xiangdong, Chen Yiwen, Xiao Jin. The strategy for comprehensive recovery and utilization of the graphite anode materials from the end-of-life lithium-ion batteries: Urgent status and policies. *Elsevier Journal of Energy Storage*. 2023, 68: 107798.
- [11] Goodenough John B., Park Kyu-Sung. The Li-Ion Rechargeable Battery: A Perspective. *Journal of the American Chemical Society*. 2013, 135 (4): 1167 - 1176.
- [12] Zhao L, Ding B, Qin XY, et al. Revisiting the Roles of Natural Graphite in Ongoing Lithium-Ion Batteries. *National Library of Medicine*. 2022, 34 (18): e2106704.