Advanced Materials for Lithium-ion Batteries and Modification Strategies in Elimination of Lithium Dendrite

Xiaobo Wang*

Department of materials science and engineering, Michigan State University, East Lansing, United States

*Corresponding author: wangx232@msu.edu

Abstract. With the development of the world, energy issues have also been paid more and more attention. In order to further reduce reliance on non-renewable energy sources and protect the environment, reliance on electricity has also increased. The energy storage problem is inevitable in electricity use. With the development of new materials, the concept of lithium batteries was proposed and further explored. This article will introduce lithium batteries' principles, materials, advantages, and disadvantages. And the advanced cathode and anode materials and electrolyte materials of lithium-ion batteries (LIBS) are summarized in this paper to provide a state-of-art understanding of designing high-performance LIBs. Lithium dendrites are the culprit in reducing the cycle life of lithium batteries, and the accumulation of dead lithium produces them. In the face of lithium dendrites, one of the most difficult problems in lithium batteries, two typical solutions for eliminating lithium dendrites is discussed: the electrochemical polishing strategy and the self-heating-induced strategy. In general, several certain solutions have been proposed for lithium dendrites. However, to further improve the performance of lithium batteries and reduce the harm, new lithium dendrite solutions and material selection will become new problems.

Keywords: Lithium-ion Battery, Lithium Dendrites, Lithium-ion Battery Cathode Material, Lithium-ion Battery Anode Material.

1. Introduction

As technology improves, the world faces the energy revolution again. In the 18th century, the steam machine was innovative when coal was the main fuel for power. However, as more and more fuel has been recovered, oil replaced the place of coal because of its clean and high quality. The unit mass of oil could produce nearly twice the energy of coal. In the 21st century, the oil reserve will be exhausted in 50 years. The human race is finding a new generation of energy. At the end of the 20th century, some scientists suppose that take electricity is the next energy revolution. The battery has become a hot topic in the scientific world. In the field of batteries, lithium batteries have gained the favor of society with their high energy density. This rechargeable lithium battery can provide enough energy for electronic products worldwide in a limited space [1].

LIBs are also called rocking chair batteries by some scientists. When a lithium battery works, lithium ions swing back and forth between the anode and cathode to generate a potential difference in electricity. Of course, it also has its strengths and weaknesses. In order to make it clear to most people that lithium batteries are not a perfect solution, the following will discuss the performance and environmental impact of the advantages and disadvantages of lithium batteries. Through analyzing the advantages of lithium batteries, a further understanding of the working principle of lithium batteries is provided and clarifies the further research direction. Clear advantages can be more clear about the difference between materials when choosing a product energy source.

On the other hand, environmental issues are also the focus of today's society. Environmental issues arising from the use of non-renewable energy sources are also the driving force behind social development based on electricity. Lithium batteries, as a leader in power batteries, their impact on the environment, and their hazards are things that people and scientists need to be clear about. This comparison will list examples of the current social lithium battery materials used in anode, cathode, and electrolyte. Their performance differences and development potential will help people needing this information [2].

A problem that cannot be ignored in LIB is the generation of lithium dendrites. It can cause internal short circuits and fires in lithium batteries. In order to solve this problem that cannot be ignored in the current development of lithium batteries, this article will discuss lithium dendrites in lithium batteries. First, readers can obtain the reasons and harms caused by lithium dendrites in lithium batteries from the following. Secondly, regarding timely observation of the lithium dendrites, this article will introduce the latest characterization technology – the operando imaging techniques, and will also describe the differences at common temperatures of lithium dendrites. Finally, this paper will propose electropolishing treatment and self-heating solutions to the lithium dendrite problem. Given the current major problem of lithium batteries, this article points out the development bottlenecks of lithium batteries and the currently available solutions.

2. Advantages of LIBs

2.1. Performance of LIBs

The purpose of how a LIB works are two tabs. In an ordinary battery, the electrolyte melts the metal electrode and divides it into ions and electrons. The electrons move from the negative electrode to the positive electrode to generate an electric current, and then electricity is generated. LIBs use a lithium-containing metal compound in the positive electrode in advance and use carbon (graphite) that can absorb and store lithium in the negative electrode. With such a structure, charging and discharging can be achieved without melting the electrodes with an electrolyte. This not only slows down the aging of the battery itself, can store more electricity, and increases the number of charging and discharging, but also, because lithium is small and light, it has lightweight characteristics in industrial applications.

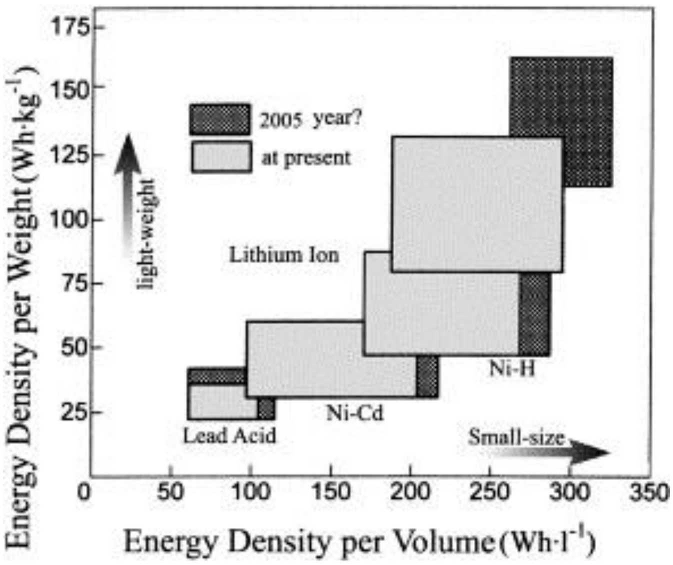

Figure 1. The energy density of secondary batteries [2].

Lead-acid and nickel-cadmium batteries traditionally used, or nickel-metal hydride batteries (NMHB) under development, cannot be reduced in size and are not dominant in weight. Lithium batteries have much-advanced energy density compared with the other kinds of batteries. As shown in Figure 1, the NMHB and LIBs are both excellent in terms of their energy density in volume. Although nickel-cadmium batteries are more dominant in energy per unit volume, LIBs can hold more energy in a limited mass. The LIB is superior in energy density in weight as it provides 1.5 times as much energy as the NMHB. LIBs account for two excellent characteristics and have become the first choice for new batteries [1, 2].

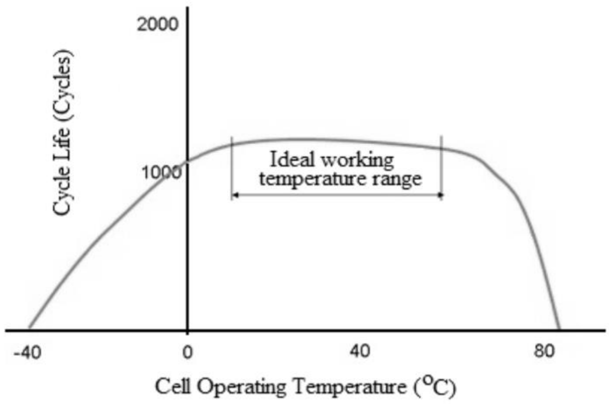

Figure 2. Lifecycle and temperature [3]

Compared with other batteries, lithium batteries have a higher life cycle. Figure 2 shows that the battery performance will greatly degrade at extreme operating temperatures. This loss is irreversible and can have a dramatic impact on the life of a battery. The formation of lithium dendrites is inevitable during lithium batteries, which will also have an irreversible impact on the service life. Although these problems still exist in LIBs, their overall cycle life is also longer than other types of batteries.

2.2. Environmental friendliness of LIBs

LIBs have less environmental pollution. Carbon dioxide and greenhouse gases are generated during the production and preparation of lithium batteries and the disposal of used lithium batteries. Although this generation is much smaller than the consumption during the use of fuel vehicles, it is a problem that needs to be considered. With nickel-based and cobalt-based anodes and cathodes, there are substantial ring effects in the production process. The hazards of nickel and cobalt compounds to personnel in production cannot be ignored. So to reduce this hazard, one option is to use other anode and cathode materials such as carbon. Another option is a technological upgrade of the recycling process. Reducing the preparation and production of raw materials can reduce the harm to the environment, among which feasible recovery methods are hydro-metallurgical recovery, pyrometallurgical recovery, and direct recovery [4].

In order to further reduce the pollution of LIBs to the environment, reuse has become a necessary issue. The utilization of precious and rare metals can be reduced by remanufacturing old parts and designing new batteries. As the world's demand for lithium batteries continues to increase, recycling valuable and harmful substances in lithium batteries has also become a top priority. Valuable substances include Co and Li. Some scholars have adopted the reduction, reuse, and recycling methods for the follow-up treatment of lithium batteries. The plan is to reduce the proportion of rare metals used in future lithium battery production. While maintaining a certain performance, the more accessible materials are selected to replace part of the rare metals to realize the concerns about future mineral resources. New anode and cathode materials will be used under this scheme. Another focus will be the redesign of lithium batteries. Some valuable parts are designed to be removable. In this way, after the lithium battery is used up, these precious parts can be removed and continue to be used to reduce the use of some rare materials. The focus of reuse can be to re-integrate old batteries into the grid system after using lithium batteries. A redesigned battery management system will also be added to the lithium battery to achieve extended service life. The recycling of aluminum and copper can be applied to lithium batteries' anode and cathode materials. These valuable metals can be re-refined and used [5].

To solve the problem of recycling, it is possible to use organic acid leaching as an environmentally friendly attempt. When trying to protect the environment, using organic acids to recycle the positive and negative materials of lithium batteries was proposed. Because the positive and negative electrodes of waste lithium batteries contain many harmful substances, it will cause much trouble to the environment and the human body. Scientists have proposed using organic acids such as ascorbic acid as reducing agents. Compared with the secondary pollution of inorganic acids, organic acids can achieve less harm and lower use costs. In the preparation process, certain physical disassembly steps are required to dispose of the spent lithium batteries, and metal ions are leached through chemical solvents [6].

3. Disadvantages of LIBs

Whether in lithium metal or LIBs, the formation of lithium dendrites is a problem that cannot be ignored. Lithium dendrites will reduce battery life and have a certain impact on the safety purpose of producing Lithium dendrites. The reason for this impact is that the cations in the electrolyte may move very fast during the charging and discharging process. Therefore, the metal does not have a preferred growth direction caused by the shallower concentration gradient near the electrode. When mass transport is not considered, relatively large particles are usually formed without sharp protrusions. Once the plated metal particle becomes a new current collector by reaching a large size, the dendrites will be grown on the surface.

Furthermore, decomposition products form a solid electrolyte interface (SEI) layer due to the reaction of lithium metal with the organic solvent of the electrolyte. If the surface area of dendritic lithium is higher, there will be more reactive in forming. The insulating SEI layer would worsen the non-uniform electric field distribution on the anode side, leading to more dendrite growth [7].

4. Materials choices on LIBs

4.1. Materials used on anode

Sony developed Lithium cobalt oxide ($LiCoO_2$) in 1991. This material is widely used in personal electronics. It has the characteristics of high energy density, long service life, and low manufacturing difficulty. But it also has the characteristics of high manufacturing cost and low thermal stability. Lithium nickel oxide ($LiNiO_2$) is a material with great potential. It has a theoretical capacity of 250 Ah in a kilogram. It is also cheap to manufacture and has a large theoretical capacity. But its chemical reaction will form a self-passivation layer, which is also dangerous. Using suffering becomes a problem. In exchange for more stable thermal stability, lithium manganese oxide ($LiMn_2O_4$) has 33% less capacity and certain service life than lithium cobalt oxide. Because of its low internal resistance, it realizes the functions of fast charging and large-scale discharge. Three-dimensional spinel junctions bring this about. It can also be combined with lithium manganese cobalt oxide to increase capacity and service life. Lithium iron phosphate ($LiFePO_4$) has relatively good electrochemical properties, low resistance, high rated current, and long cycle life. Among them, phosphate brings better thermal stability and heat resistance. Hence better temperature differentiation. It can work between -30 and 60 ºC. Its high self-discharge characteristics bring certain service life problems. However, its good power-to-weight ratio and high safety features still have broad application prospects [3, 8].

4.2. Materials used on cathode

Carbon used in carbon-based electrodes is a material that is abundant in yield, low in cost, and non-hazardous. It features high specific capacity, low average voltage, and voltage flatness. However, there is a fire risk because he can react with oxygen in the air. It is undeniable that it is a common and easy-to-use negative electrode material. Lithium titanate ($Li_4Ti_5O_{12}$) is a spinel structure that replaces the carbon-based electrodes in some typical lithium batteries. Having a relatively flat voltage change brings a very high level of safety. And because there are not many volume changes during the lithiation process, it brings enough service life. Unfortunately, the low conductivity of this material results in low performance under high power usage conditions. Metal lithium has a very large capacity, which leads to a smaller mass under the same capacity. Brings a nice curb quality to the production product. In addition, it has the lowest negative electrochemical potential. A disadvantage that cannot be ignored is that a large number of lithium dendrites will bring about many safety hazards. Eliminating the risk of explosion and fire is an important consideration. The lithium-silicon alloy in the silicon-based electrode can bring the theoretical capacity beyond that of metal lithium, reaching 4200Ah kg^{-1}. Unfortunately, it will cause 280% deformation during use. Such volume changes can cause the entire battery to crack or break. Capacity may drop as a result. It also suffers from a low Li^+ diffusion coefficient and high resistivity. These issues are still in the process of being resolved [2, 8].

4.3. Materials used on electrolyte

The main purpose of the electrolyte to provide ionic conductivity is to shuttle Li^+ between the two electrodes in a lithium battery. Mainly divided into liquid and solid. Water electrolyte is a safe and less harmful option for the environment. But its limited electrochemical voltage window cannot enable Li^+ in lithium batteries. Future research may further increase the voltage to achieve the desired goal. Organic liquid electrolytes usually add propylene carbonate or ethyl carbonate. Adding some salt can bring good electrochemical stability and high Li-ion conductivity. It brings a better working environment for lithium batteries and reduces the possibility of flammability and explosion. Undeniably, if the organic liquid leaks, the environmental harm is still great, and the flammability is also a problem that cannot be ignored after the reduction. Polymer electrolytes contribute to the improvement of electrolyte and battery safety performance. The polyoxymethylene-based material has been further developed, and its gel-like solid electrolyte properties bring users a reassuring experience. Ceramic electrolytes, especially those using superior lithium conductors, bring strong electrical conductivity to solid electrolytes. Such performance is already comparable to the characteristics of liquid electrolytes [2, 8, 9].

5. Methods to Improve Li-ion Battery Performance based on Lithium dendrites

5.1. The principle of lithium dendrites

In the process of using lithium batteries, people discovered LIBs and lithium metal batteries. Scientists have debated whether the two types of batteries are good or bad because of their different dangers and performance. Regardless of the type of battery, the problems related to lithium dendrites are major ones affecting battery performance. Many researchers have also proposed different methods to compensate for their shortcomings. Many methods have been proposed for the formation of lithium dendrites, the phenomenon of dead lithium, and the unstable solid-electrolyte interface common in lithium batteries. The following will sort out and analyze the generation and solutions of lithium dendrites.

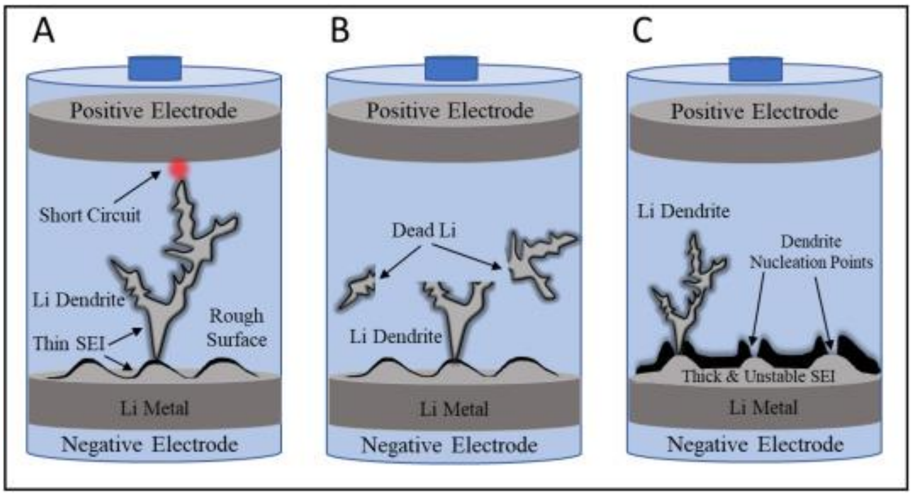

Figure 3. Schematic diagram of short circuit, dead Li, and unstable solid electrolyte interface [10]

Lithium dendrites are an important indicator that affects the life of lithium batteries. Figure 3 shows a schematic diagram of the short circuit, dead Li, and unstable solid electrolyte interface (SEI). The charging and discharging process is the separation of Li^+ from the positive electrode compound to reach the negative electrode, and the negative electrode will release the same amount of e- into the positive electrode. This is because the positive electrode is in a high-potential lithium-poor state, and the negative electrode is in a low-potential lithium-rich state. This spontaneous charge balance completes a charge-discharge process. However, during this process, lithium dendrites are generated. As the name suggests, this is a crystal with a multi-branched structure. The dead lithium brought about by this situation can cause many Li^+ to lose its original role. The negative effect of this is that the activity of the battery is reduced, and the charging and discharging process becomes slower and less. The massive deposition of Li dendrites also risks puncturing the solid electrolyte interface (SEI). The solid electrolyte interface is formed by the decomposition products of the electrolyte, responsible for passing to Li^+ and organizing the further decomposition of the electrolyte. As a result, the explosion and fire are hazards when the solid electrolyte interface (SEI) has been broken. This situation will bring unpredictable risks to users.

5.2. Methods to Optimize the lithium dendrites

Observing from in situ techniques is a visualized way to study the mechanism of lithium dendrite formation. What needs to be introduced here are in situ and manipulation imaging techniques. Previous studies on lithium dendrites have been calculated through many mathematical theories, such as density functional theories (DFT), and such models will ignore some influential parameters. In addition, these models also cover all the phenomena and mechanisms of Li dendrite generation. The research and development of a new generation of observation methods have been mentioned as a top priority.

In addition, unlike ex situ characterization techniques, in situ experiments periodically image lithium deposition by pausing the current/voltage and restarting. In this way, the high reactivity of lithium and its sensitivity to moisture/air brings many challenges and artifacts to the isotopic study of lithium dendrites that can be ignored to a certain extent. Because this technique is not information obtained using invasive operational monitoring techniques, this valuable information is free from potential artifacts caused by the exposure of lithium metal to the environment and moisture after battery disassembly. These imaging techniques include optical, electron, X-ray, scanning probe, neutron, and resonance-based microscopy [10].

In different usage scenarios, different temperatures will also affect the formation of lithium dendrites. Between the normal temperature of -10 to 20 ºC, the higher the temperature, the slower the formation of lithium dendrites. At lower temperatures, Li^+ moves from cathode to anode and coats the anode surface, resulting in the charge-balancing action of e- from anode to cathode. Such coating behavior causes lithium dendrites to grow faster [11].

5.3. Strategies to suppress the formation of lithium dendrites

5.4.1 Electrochemical Polishing Strategy for Eliminating Li Dendrites

Electrochemical polishing optimizes the inhibition of lithium dendrites with the protection and corrosion properties of halide ions against solid electrolyte interphase (SEI). This ion can etch the protruding part of the SEI surface to complete the dynamic balance of the SEI. In this way, the generation and accumulation of lithium dendrites can be more uniformly distributed in the negative electrode, thereby reducing the impact of lithium dendrites on lithium batteries. This dynamically smooth SEI film can be accomplished with simple processing. The polished SEI film can bring more than 700 hours of service life to the battery with carbonate electrolyte. The redistribution of lithium dendrites brings more active elements and less risk of puncture and fire in lithium batteries. The act of simply manipulating an existing battery to increase performance is also an extremely impressive way of contemporary technology [12].

5.4.2 Healing of lithium dendrites from a self-heating–induced strategy

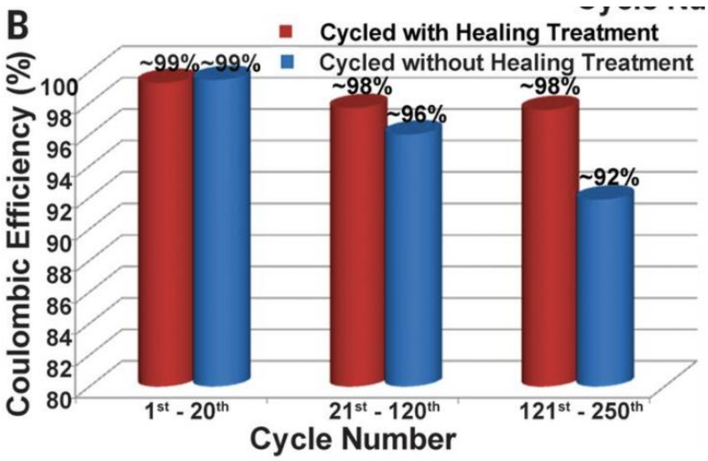

Figure 4. Coulombic efficiency in Li-S battery [13]

Some scientific studies have shown that heating lithium dendrites and annealing can help lithium batteries eliminate part of lithium dendrites and improve battery life. Figure 4 shows the coulombic efficiency difference between the battery with and without healing treatment. This conclusion conflicts with the traditional perception that healing will accelerate the formation of lithium dendrites. The experimenters used a current of 9 milliamps per square centimeter to bring the lithium dendrites to a target temperature. Such currents generate sufficient temperature and spread over all lithium dendrites. At the same time, this temperature will not exceed the limit temperature of the thermal insulation layer. After using a current of 15 mA per unit area, the service life of the lithium battery has been increased from the original 500 hours to 2000 hours. This nearly 4 times improvement reduces the cost of using lithium batteries [13].

6. Conclusions

In conclusion, lithium batteries have better energy density to perform better than the same type of batteries. Lithium batteries can also use organic acids to further recycle some materials to lower pollution with less environmental pollution. On the road to further improving lithium batteries' performance, there is already a solution to the problem of lithium dendrites. The generation of lithium dendrites can be better observed and analyzed by a new generation of in situ/operational imaging technology. Under the electropolished solution, lithium dendrites can be more uniformly distributed to achieve a later piercing of the solid electrolyte interphase. Under the self-heating solution, part of the lithium dendrites can be eliminated by the high temperature at a safe temperature. Both solutions can be achieved by targeting lithium dendrites to prolong the service life of lithium batteries.

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