

The Impact of Nanotechnology on Lithium-Ion Battery Used in Electric Vehicles

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Abstract. The global environment has already been polluted by the traditional fuel vehicles and become more and more serious. In this situation, the electric vehicles (EVs) came to the attention of the worldwide people. In recent years, the electric vehicles have developed rapidly. As a result, the components of the electric vehicles were logically achieved great success, particularly the rechargeable lithium-ion battery. Fortunately, the nanotechnology, at the same time, made a great deal of huge achievements and appeared in numerous fields. Nanotechnology obviously plays a critical role in the field of lithium-ion battery and nearly all elements of lithium-ion battery are changed to varying degrees. The performances of lithium-ion are becoming more suitable for commercial production, such as higher power and energy density, lower price, better stability and increased capacity. The recent and advanced developments of different kinds of welcomed anode materials, graphite, nanostructural silicon, lithium titanate and titanium dioxide, and cathode materials, lithium cobalt oxide, LiFePO_4 , lithium manganese oxide, nickel-rich cathode, and solid electrolyte nanomaterials, are discussed and emphasized with the advantages and disadvantages, limitations, methods for improving and future development. The modification caused by nanotechnology truly can improve the performance of the lithium-ion battery. Lots of further researches that is changing the traditional materials into nanoscale or adding nanomaterials will be processed in the purpose of finding the most practical lithium-ion battery used in electric vehicles.

Keywords: Nanotechnology, lithium-ion battery, EVs.

1. Introduction

1.1. Introduction to the lithium-ion battery

Over the past few decades, the rapid development of transportation industry has, at the same time, promoted the economy of entire world. However, it is unfortunate that this prosperity has brought many adverse influences in the meantime. For instance, a great number of non-renewable fossil fuels have depleted and the environment are polluted in a great extent. According to the statistics, nearly twenty-five percent of worldwide greenhouse gases that is related to the energy are emitted by the conventional transportation vehicle. As a result, many efforts are made by humans to alleviate these issues, such as developing electric vehicle to substitute fuel vehicle [1].

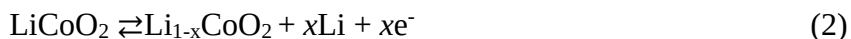
Battery performance is very important for the electric vehicle. A battery is defined as a kind of electrochemical equipment which can utilize its electrode and oxidation-reduction reaction to convert the electric energy to the chemical energy and store when experienced the charging process. And during the discharging process, the energy can be released by battery in the form of electricity [2]. Among all kinds of commercial batteries, lithium-ion battery has shown great potential. That is because the energy density supplied by lithium-ion battery is two to three times higher than nickel-hydrogen battery, nickel-cadmium battery and lead-acid battery. The power density of lithium-ion battery is also five to six times higher than that of batteries mentioned above. What is more, there are lots of other advantages of lithium-ion battery, particularly the long cycling life [3]. The representative lithium-ion battery is mainly composed of an anode part, a cathode part, a electrolyte and a separator. Currently, the transition metal oxides and phosphate active materials are commonly used to build the cathode part. The graphite is mostly chosen to be the anode material. The separator is mainly used to prevent the electric contact between the anode and cathode [4]. The working principle of lithium-ion battery can be described that when the battery is charged, Li can deintercalate

from cathode part and intercalate to anode part. On the contrary, Li can intercalate to cathode part when it is recharged. The diffusion of lithium ions enables the transformation of the electric energy and chemical energy. Following shows one example of chemical reactions happened in the lithium-ion battery where the anode material is graphite and the cathode material is Lithium cobalt oxide [3].

Anode:



Cathode:



The performance of lithium-ion battery can be improved by nanotechnology. Many positive changes of the lithium-ion batteries will show up after experienced the nanostructural processes. Firstly, the flowing time of lithium ions can be shortened because the dimension of nanomaterial is reduced, which is beneficial to accelerate the charging and discharging process. Secondly, due to the fact of the small size, nanomaterial has an aptitude for accommodating the serious volume expansion happened during the intercalation and deintercalation, which can effectively prevent materials to pulverize. Thirdly, the surface area of nanomaterial becomes larger, which leads to intensive capacity. This is owing to the increase of interfacial Faradaic reaction happened inside the battery and the acceleration of diffusion of lithium ions through the separator. More importantly, nearly all nanomaterials have a nicely steerable crystallinity. This property can provide many stable tunnels to facilitate lithium ions to transport and also enhance the nanomaterials' ability of cycle strain resistance. Then the stability of battery is logically increased [5].

1.2. Introduction to the solid electrolyte interphase

When the battery is initially charged, the electrolytes will experience the reduction and decomposition on the anode. After that, the solid electrolyte interphase is formed. The solid electrolyte interphase should be insulated for electrons and conduction for ions, which means it can prevent further decomposition of electrolytes. Therefore, the performance of solid electrolyte interphase plays a critical role in the safety, lifetime, and power of battery [6].

2. Anode Materials for Lithium-Ion Batteries

It is well known that the graphite has always been the primary choice for anode materials since the lithium-ion battery was firstly introduced to the world, which benefits greatly from its cycle over cycle efficiency. The expansion of graphite during the process of intercalation and deintercalation is very low, which means graphite has the ability to keep a high standard of the charge capacity even experienced numerous cycles [7]. The theoretical capacity of graphite is 372 mAhg^{-1} . Although its capacity is relatively low compared to other commercial anode materials, it can satisfy the requirement of most electronic devices on the market. This is the reason why graphite still dominates the market of anode materials today.

Unfortunately, there are still some limitations that hinder its development. For example, the graphite is easily reacted with some common organic electrolytes ($C_3H_4O_3$, $C_5H_{10}O_3$ and $C_4H_6O_3$) which can provide excellent conductivity of lithium ions. These irreversible and harmful reactions mainly include that the graphene sheets exfoliate and other electrolytes are reduced and decomposed. One way to deal with this problem is to utilize the nanocoatings, which is the solid electrolyte interphase during the initial charge. At present, there are three different kinds of nanocoatings that are widely used. First one is the amorphous carbon nanocoating. It is usually created by thermal vapour deposition method together with organic precursors in a high-temperature environment. This process doesn't cost too much which is very suitable for cosmically industry production. Second one

is the metals and metal oxides nanocoating, which is in the size of ten to twenty nanometers. This kind of nanocoating can efficiently decrease the useless reactions of electrolyte and naturally improve the rate characteristic of the battery. There has been a great number of metals or metal oxides chosen to build this nanocoating, such as copper, nickel, tin, zinc, aluminum, titanium dioxide and tin dioxide. The last one is the polymeric nanocoating. All of these methods have opportunities to be used in electric vehicles industry [2].

Silicon is also an extraordinary potential material for lithium-ion battery anode due to the fact that silicon has a relatively low discharging potential of approximately 370 mV, which enables itself to match some high-power appliances very well. And more importantly, silicon has a very high theoretical specific capacity of more than 3500 mAhg^{-1} , which is more than ten times than the capacity of graphite. But in commercial practice, there is an inevitable challenge of the silicon-based anode that has limited its development, which is in the anode of the lithium-ion battery, a severe repetitive volumetric expansion and contraction of approximately 300% occur when the battery experiences the process of lithium insertion. This serious problem will lead to the silicon surface cracking, and ultimately cause the rapid dropping of its energy storage performance and the short life span [8].

In order to solve this problem, many nanostructural silicon materials are chosen to be the anode. This is because when the size of silicon reaches the nanoscale, the electronic connection to the collators and electrolytes becomes better. Therefore, the capacity of batteries that use the silicon nanomaterials can reach 2000 mAhg^{-1} and the cycle ability remains to be good. Another use of silicon nanoparticles is to synthesize a more complex composite together with graphitic carbon, called silicon-carbon nanocomposite. There are many uses of carbon part, such as offering places for electrons movement, accommodating the volumetric expansion caused by silicon and hosting the lithium ions. The capacity of this special structure can reach to 1950 mAhg^{-1} .

Although all of these researches of nanostructural silicon are worth to encourage, the truth is it is very hard to produce a thin enough anode with low-cost to match the thickness of cathode currently used [2].

The lithium titanate (LTO) spinels have already been proved to be the perfect substitute of graphitic anode material because its lithium ions reversibility is excellent at high operating potential. The mechanism of the insertion process is that the lithium ions flow into the lithium titanate lattice and then take up the empty octahedral positions. The volume change caused by this way to insertion and deinsertion can be ignored, which is very attractive. Therefore, the immutable capacity loss of lithium titanate during the cycle process is smaller than that of the graphite. What is more, the electrochemical potential of lithium titanate is high enough to prevent the reactions with organic electrolytes. However, the imperfect crystal structure of lithium titanate and big electronic bandgap bring many limitations to itself. For instance, the theoretical capacity of lithium titanate is so small (175 mAhg^{-1}), as well as its conductivity. As a result, the application of lithium titanate anode is very limited [2].

Therefore, in order to improve the poor electrochemical performances of lithium titanate, nanotechnology has been used in many researches. First method is to use nanostructural lithium titanate, which can visibly shorten the diffusion way of lithium ions and increase the effective area where the electrodes and electrolytes contact with. This can make the operation current become higher. Second method is to coat the surface of lithium titanate. It is beneficial to make ions transport faster between the lithium titanate and the electrolytes. The last method is to mix the nanostructural lithium titanate with some conductive materials, which is useful to mitigate the problem of low conductivity [2].

The titanium dioxide (TiO_2) is obviously a very potential material for anode of lithium-ion battery due to the fact that it cost low and can be easily manufactured. There are lots of attractive advantages of titanium dioxide, such as high electronic ability, stable chemical performance and rich abundant. Therefore, it is very suitable to build the lithium-ion battery, especially for electric vehicle industry. One molecular of titanium dioxide can hold one molecular lithium and the theoretical capacity of titanium dioxide can reach to 330 mAhg^{-1} . The process of intercalation and deintercalation occurred

in the titanium dioxide is typically affected by particle size and structural area. The titanium dioxide microspheres is an advanced production of nanotechnology, which is composed of six to eight nanometers nanocrystals and four to six pore-sized microstructures. It shows many excellent performances, such as large capability of lithium storing and high cycle ability. And the titanium dioxide nanotubes also exhibit the maximum capacity around 300 mAhg^{-1} . More importantly, these titanium dioxide nanotubes can remain the capacity of 250 mAhg^{-1} after one hundred cycles [4].

3. Cathode Materials for Lithium-Ion Batteries

Lithium cobalt oxide (LiCoO_2) has been extensively chosen and commercially accepted in a large amount of fields and logically gained a significant position during the market of the cathode materials. Many excellent performances of lithium cobalt oxide have been explored. LiCoO_2 can be easily processed, which is the main reason why it is widely used in the actual production. The electrochemical property of LiCoO_2 is perfect. This means LiCoO_2 is very stable and hardly react with the environment. Most importantly, the tap density of LiCoO_2 is high enough to enhance the volume-specific capacity and create better performed battery. Many efforts of nanotechnology have been made to the lithium cobalt oxide so as to obtain better performance. Two approaches, solid-state reaction and solution-assisted, are used to create the LiCoO_2 nanoparticles. When the structure of lithium cobalt oxide changes to the nanofiber, the distance that the lithium ions need to diffuse becomes shorter. As a result, the higher charge ability and cycle ability can be obtained [9].

Even though the charge ability and cycle ability of lithium cobalt oxide perform greatly, there are still many disadvantages of it such as high-cost and the pollution to environment. Therefore, it has been abandoned to be the cathode materials for electric vehicles. LiFePO_4 is one of the successful substitutes of lithium cobalt oxide used in building the electric vehicles' battery. Although the energy density of LiFePO_4 is lower than that of lithium cobalt oxide, the power density, life time and safety problem of LiFePO_4 perform better. According to many researches, it has already been proved that the electronic conductivity of LiFePO_4 was the mainly limited by the covalent characteristic of polyanion framework. As a result, LiFePO_4 nanostructure was developed to shorten the way for electron movement [2].

The lithium manganese oxide (LiMnO_2) is another better choice to replace the lithium cobalt oxide because it has lower cost and cause lighter pollution than lithium cobalt oxide. Compare every lithium manganese oxide compound, the layered orthorhombic LiMnO_2 is the top of all, for the theoretical capacity is the highest (285 mAhg^{-1}). However, the development of layered orthorhombic LiMnO_2 is mainly limited by one problem. The layered orthorhombic LiMnO_2 will change to the spinel phase when experienced the electrochemical cycle. In order to solve this problem, nanotechnology is devoted to design a kind of nanocoating which can protect it from the surrounding environment [9].

The nickel-rich cathode ($\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$) is different from the cathode materials mentioned before. The nickel-rich cathode can provide a reversible capacity of 200 mAhg^{-1} and the capacity stability of nickel-rich cathode is also perfect. When the nickel-rich cathode is charged, it can react with the non-aqueous electrolyte, which leads to the loss of reversible capacity and power density and the serious decrease of the safe performance of the batteries. Lots of efforts are made to protect the nickel-rich cathode not to react with the non-aqueous electrolyte. Among them, nanocoating is a very useful way to protect, for it can form a separator between the nickel-rich cathode and the electrolyte. These nanocoating methods can be made by oxide, fluoride and phosphate. These types of protecting coatings mainly consist of nanoparticles, which is ranged from five to twenty nanometers. An interesting phenomenon of these nanoparticles is that the movement tendency of these nanoparticles is aggregation in order to protect some specific surfaces. Therefore, more nanoparticles can be released to create a thick layer (100 nanometers) [2].

4. Electrolyte for Lithium-Ion Batteries

Electrolyte also plays an important role in the lithium-ion battery apart from the anode and cathode. In recent years, the solid electrolytes have become more and more popular and already taken the place of traditional liquid electrolytes. Nanotechnology has shown great potential in the development of the solid electrolytes improvement. It is very useful way to increase the ionic conductivity by adding nanomaterials or changing previous materials into nanoscale. The chemical stability will not change, which is very satisfied. A typical example is nanocrystalline Li_3PS_4 . At the room temperature, the ionic conductivity of bulk crystalline Li_3PS_4 is measured as 3×10^{-7} S/m, which is too low for commercial use. On the contrary, the ionic conductivity of nanocrystalline Li_3PS_4 can reach to 1.6×10^{-4} S/m, which is nearly three orders of the bulk crystalline Li_3PS_4 's [10]. Another example is putting the zirconia powders into the $(\text{PEO})_{20}\text{LiCF}_3\text{SO}_3$ and making them dispersed. The ionic conductivity of plain solid electrolyte is terrible at room temperature. After the addition, the performance of transport is significantly improved [11].

Although it is now shows that the positive nanosize influence can make the performance of ionic conductivity of solid electrolyte become better, their future is not that promising if the practical production is considered about. The limitation is that the current technologies cannot control the structure with high accuracy [10].

5. Conclusion

The development of lithium-ion batteries is still likely to be affected by the innovation of nanotechnology. More and more nanomaterials will make extreme influence to the field of lithium-ion battery. And the electric vehicles will also achieve more success. This review firstly introduced some advanced research of anode nanomaterials for lithium-ion battery, which is mainly about how to solve the volume expansion problem. A silicon nanomaterial with a graphitic carbon has been discussed. As for the cathode materials, the lithium cobalt oxide, LiFePO_4 , lithium manganese oxide and nickel-rich cathode are discussed. Initially, the advantages and disadvantages of lithium cobalt oxide cathode is discussed and the nanomaterials of lithium cobalt oxide are reviewed. Secondly, the advantages and improvement method of LiFePO_4 are discussed. After that, the limitations of lithium manganese oxide are listed. Finally, in the case of lithium manganese oxide cathode, nanocoating is made to improve the performance.

Except the limitations mentioned above, the researches have done recently and the development of nanotechnology are clearly show that the materials in nanoscale and the nanocomposite offer great amount opportunities for lithium-ion batteries.

References

- [1] Ding Y, Cano Z P, Yu A, et al. Automotive Li-ion batteries: current status and future perspectives [J]. *Electrochemical Energy Reviews*, 2019, 2 (1): 1 - 28.
- [2] Lu J, Chen Z, Ma Z, et al. The role of nanotechnology in the development of battery materials for electric vehicles [J]. *Nature nanotechnology*, 2016, 11 (12): 1031 - 1038.
- [3] Ji L, Lin Z, Alcoutlabi M, et al. Recent developments in nanostructured anode materials for rechargeable lithium-ion batteries [J]. *Energy & Environmental Science*, 2011, 4 (8): 2682 - 2699.
- [4] Goriparti S, Miele E, De Angelis F, et al. Review on recent progress of nanostructured anode materials for Li-ion batteries [J]. *Journal of power sources*, 2014, 257: 421 - 443.
- [5] AbdelHamid A A, Mendoza-Garcia A, Ying J Y. Advances in and Prospects of Nanomaterials' Morphological Control for Lithium Rechargeable Batteries [J]. *Nano Energy*, 2021: 106860.
- [6] Takenaka N, Bouibes A, Yamada Y, et al. Frontiers in theoretical analysis of solid electrolyte interphase formation mechanism [J]. *Advanced Materials*, 2021, 33 (37): 2100574.
- [7] De las Casas C, Li W. A review of application of carbon nanotubes for lithium ion battery anode material [J]. *Journal of Power Sources*, 2012, 208: 74 - 85.

- [8] Prosini P P, Cento C, Alessandrini F, et al. Electrochemical characterization of silicon nanowires as an anode for lithium batteries [J]. Solid State Ionics, 2014, 260: 49 - 54.
- [9] Li B, Meng Y, Tang W. The role of nanotechnology in the design of materials for Lithium-ion battery [C]//E3S Web of Conferences. EDP Sciences, 2021, 308.
- [10] Emerging nanotechnologies in rechargeable energy storage systems [M]. William Andrew, 2017.
- [11] Panero S, Scrosati B, Wachtler M, et al. Nanotechnology for the progress of lithium batteries R&D [J]. Journal of power sources, 2004, 129 (1): 90 - 95.