Proceedings of the 2023 International Conference on Functional Materials and Civil Engineering
DOI: 10.54254/2755-2721/26/20230792

Performance and modification of novel nanomaterials for the anode of lithium-ion batteries

Haoxuan Ji

School of Materials Science and Engineering, China University of Geosciences, Beijing. 100000, China

1003200517@cugb.edu.cn

Abstract. Due to the burning of fossil energy which is a non-renewable nature resource, it has caused many environmental problems, then the world began to face energy shortage and environmental problems. In order to solve these two problems, people have started to develop new energy sources and vigorously research new methods for energy's efficient storage and utilization. The Li-ion battery is a research priority because it has great properties such as high specific energy and environmental friendliness, but they still need further performance improvement before it can be put into use. In this paper, the lithium-ion battery's anode is selected as the research object to investigate the performance of carbon-based nanomaterials, silicon-based nanomaterials, and metal-based nanomaterials, and to study the actual performance and modification methods to analyze the application prospects of the materials. Improving the Li-ion battery cathode material performance can significantly improve the battery's capacity and performance stability, speed up the process of putting lithium-ion batteries into use, and improve people's ability to store and use energy to cope with the energy crisis.

Keywords: lithium ion battery, anode, nanomaterials.

1. Introduction

Resulting from the rapid development of social productivity, human society's demand for energy is also expanding rapidly. In the past, fossil energy sources such as oil and coal, on which human beings depended, could no longer meet human energy needs due to their limited reserves, non-renewability, and various greenhouse gases produced by their combustion. Human society has begun to focus on the development and utilization of new energy sources. At the same time, energy storage and efficient use of energy is also a kind of effective method to alleviate the energy crisis. Lithium-ion batteries have the advantages of light weight, high specific energy, and environmental friendliness, so they will become one of the hot solutions to the energy problem. However, the Li-ion battery's cycle performance varies due to the different materials used in the components of the Li-ion battery, and the stability can change due to the stability of the material properties. When the lithium-ion battery cycles more times, the lithium-ion battery stability will gradually become worse and cause safety hazards. Therefore, lithium-ion batteries need to further improve their performance to meet the application requirements.

The Li-ion battery mainly includes an anode, cathode, separator and electrolyte. When discharging, lithium ions leave the anode, pass through the electrolyte and separator, and become embedded in the cathode. And lithium ion movement path is reversed during the charging process [1].

DOI: 10.54254/2755-2721/26/20230792

The Li-ion battery's negative electrode is one of the vital part, serving as a carrier of lithium ions when the battery is charging and discharging process and determining the entire batteries' capacity and performance. The Li-ion battery's anode needs to allow sufficient reversible de-embedding of lithium ions, have a high specific capacity and a stable structure, and be able to generate a solid electrolyte film with the electrolyte.

However, traditional anode materials have many shortcomings. For example, commonly used graphite suffers from low specific capacity, poor multiplicative performance, and poor safety performance. Alloy materials have the problem of large volume changes. Silicon materials also have the problem of excessive volume change. These can reduce the Li-ion battery's performance and cycle life, and pose a safety hazard.

The application of nanotechnology in lithium-ion battery anode materials can effectively increase the anode materials' specific surface area, thereby increasing the number of lithium storage sites and nanomaterials have a higher rate of lithium ion de-embedding. In addition, nanotechnology can also reduce the volume change of anode materials. This articles selects nano-anode materials to analyze the effect of nanotechnology on the anode materials' performance and evaluates the feasibility and development prospects of nano-technology applications for anode materials by investigating and researching nano-anode materials.

2. Carbon based nanomaterials

2.1. Graphene

Graphene consists of carbon atoms that are sp^2 hybridized, and its carbon atom p orbitals are perpendicular to the plane where the sp^2 hybridized orbitals are located, forming delocalized π bonds, so that the π electrons can move freely [2].

Graphene can be prepared by mechanical exfoliation, redox, oriented epitaxial growth, silicon carbide epitaxy, Hummers method. After measuring graphene-related properties, the researchers found that using graphene can enhance negative electrode conductivity and reduce the energy loss due to battery polarization. Therefore, graphene has the potential to become the key part of the Li-ion battery as an anode material.

However, the industrialization of graphene still has the disadvantages of high cost and imperfect preparation technology. Moreover, graphene has problems such as low Coulomb efficiency and poor rate performance [3]. The preparation of single-layer graphene is prone to stacking, resulting in a reduction of the material's specific surface area and lithium storage space. Therefore, researchers began to study how to improve the graphene's performance, so that graphene can be used in lithium-ion battery negative electrode.

Some researchers have tried to prepare new materials using other materials with excellent properties in combination with graphene, and measured the performance of the new materials to verify the feasibility. Qiang Pang et al. prepared graphene@MoS_2@TiO_2 as the anode material [4]. This new anode material utilized the nano-pores of TiO_2 to reduce the aggregation of MoS_2 and avoid the material's volume changing, and the introduction of graphene improved the conductivity of the material substantially improved. This material's discharge capacity reached 980 mAh per gram at a current density of 0.1 Amps per gram and still maintained 80% capacity after 200 cycles. Because MoS_2 and TiO_2 nanocrystals provide a shorter diffusion pathway for Li^+, graphene facilitates electron transfer. Graphene@MoS_2@TiO_2 materials can achieve discharge capacities of 783 mAh per gram, 680 mAh per gram, and 602 mAh per gram at 1.0 Amps per gram, 1.5 Amps per gram, and 2.0 Amps per gram current densities. Thus, graphene@MoS_2@TiO_2 possesses high rate performance. At the same time, in addition to composite modification, the preparation of materials with a completely new structure can also improve the material, so that the material has more excellent performance. Guoxiu Wang et al. used tin nanoparticles to separate graphene nanosheets and constructed three-dimensional structured tin/graphene nanocomposites [5]. This new negative electrode material had higher reversible properties and the three-dimensional structure of the material allowed the material's electrochemical performance itself to be improved. After the 100th cycle, the material had a capacity of 508 mAh per gram. The three-dimensional structure of the material enables the tin/graphene nanocomposite electrode to have a high reversible lithium storage capacity. In the research to improve the properties of graphene, many researchers are measuring the properties using different materials compounded with graphene, and all of them have achieved results. Xuyang Wang et al. prepared SnO_2/graphene composites, which have excellent rate properties and cycling stability [6]. The new material's capacity reached 590 mAh per gram after 50 cycles at a current density of 400 milliamps per gram. At a current density of 1000 milliamps per gram, the capacity of about 270 mAh per gram could be maintained after 50 cycles.

Graphene, as a nano-carbon-based material, can be modified by compounding with other materials or changing the structure to substantially improve the performance of this material, giving graphene higher Coulomb efficiency and rate performance. Thus, the modified graphene material has a greater possibility to be applied to lithium-ion batteries and demonstrates the potential of nanomaterials in lithium-ion battery anode applications.

2.2. Carbon nanotubes

Carbon nanotubes (CNTs) are one-dimensional materials formed by the hybridization of carbon atoms through a mixture of sp^2 and sp^3. Carbon nanotubes are coaxial hollow circular tubes formed by single or multi-walled graphite sheets curled around the center.

Carbon nanotubes are prepared by arc discharge, laser ablation, solid phase pyrolysis, laser sputtering, and catalytic cracking methods. Carbon nanotubes have good electrical and thermal conductivity, and have high modulus and high strength. However, carbon nanotubes have problems such as high irreversible capacity and voltage hysteresis, as well as structural defects. Therefore, how to improve the carbon nanotubes' performance is also a challenge before using the carbon nanotubes as the anode.

The researchers have used different preparation methods to prepare new composites with new structures, and these new materials also show very good properties. Hui Xia et al. synthesized MnO_2/CNT composites by the facile solution method, and the material's three-dimensional structure was constructed by uniformly coating MnO_2 on carbon nanotubes [7]. This material's large reversible capacity reached 801 mAh per gram. After 20 cycles, the capacity of the material did not decrease, and it had good rate performance. Yanbao Fu et al. prepared the SnO_2/MWCNT composite using the diffusion method. After 40 cycles, the material's reversible discharge capacity still reached 505.9 mAh per gram, and that the reversible capacity of the SnO_2/MWCNT composite was substantially improved contrasted with the single material [8]. Yang He et al. used polyvinyl alcohol (PVA) to modify multi-walled carbon nanotubes, followed by chemical co-precipitation in the presence of Fe^{2+} and Fe^{3+} in an alkaline solution, which resulted in the formation of nanoparticles of iron tetroxide on the sidewalls of carbon nanotubes, and finally the Fe_3O_4/multi-walled carbon nanotubes composites were produced [9]. This composite had excellent electrochemical properties and stability. The discharge capacity still reached 656 mAh per gram after 145 cycles.

Carbon nanotube composites with three-dimensional structure were produced by different preparation methods, demonstrating high reversible capacity as well as good stability, which greatly improves the possibility of carbon nanotube materials used as the anode, and the use of composite modification can also be one of the research focuses to further enhance the performance of carbon nanotubes for practical applications in lithium-ion batteries.

2.3. Fullerene

Fullerene which contains five and six-membered rings, is a spherical zero-dimensional material composed of carbon atoms, usually sixty carbon atoms. They are prepared by arc discharge method, thermal evaporation method and chemical vapor deposition method. Fullerene has good electrochemical and mechanical properties. It can improve the Li-ion battery' capacity, increase the negative electrode's active surface area, and it can be well compounded with other materials. However,

DOI: 10.54254/2755-2721/26/20230792

the actual charging capacity of fullerenes is low and the lithium storage reversibility is poor. Therefore, fullerenes need to be modified to make the fullerenes' properties be better so that they can be applied to the real.

Jaehyun Park et al. formed a novel anode material from fullerenes and contorted hexabenzodiene (CHBC) eutectic, which had a columnar structure providing more lithium ion storage sites [10]. The reversible capacity reached 330 mAh per gram at 0.1 Amps per gram. Moreover, the C_{60} /CHBC material's rate performance far exceeded that of graphite electrodes. In order to improve the reversible lithium the material's capacity, Joseph Anthony Teprovich et al. tested the capacity of the material after hydrogenation of fullerenes, and found that $C_{60}H_x$'s stable capacity reached 588 mAh per gram at a current density of 0.05Amps per gram, which can be cycled more than 600 times [11]. And the hydrogenated fullerene still maintained stable performance after 2000 cycles. Therefore, after modification of fullerene composite, this new material has great potential to be used in the Li-ion battery's anode.

3. Silicon based nanomaterials

As one of the anode materials with development potential, silicon has a higher theoretical capacity about ten times that of graphite, and the structure of silicon allows for rapid embedding and disembedding of lithium ions, which can significantly improve the charging efficiency of the battery.

However, there are many problems with silicon materials that prevent them from being used directly in the Li-ion battery's anode. For example, during the charging and discharging process, the silicon's volume will change, which will cause the silicon particles to break off, and the negative electrode capacity will be significantly reduced, shortening the battery life. Moreover, the volume change will cause the solid electrolyte interface (SEI) film to rupture, and in the process of repairing the SEI film, lithium and electrolyte will be continuously consumed, resulting in a continuous decrease in battery capacity and cycling performance [12]. The conductivity of silicon is also one of the reasons why it cannot be used as a battery cathode. As a semiconductor, silicon has poor conductivity at room temperature, which will lead to blocked diffusion of lithium ions and reduce the battery's multiplier performance.

Therefore, many researchers choose to nanosize silicon and modify the material on silicon nanomaterials, and test the relevant properties of the modified silicon material to check whether the modified silicon material can be applied to lithium-ion battery anode.

3.1. Nanosized silicon

The researchers used a variety of preparation methods to produce silicon nanomaterials, and in tests, silicon nanomaterials with different structures also had different properties. Ning Lin et al. reduced aluminum chloride with magnesium metal at 200 degrees Celsius and then reduced silicon chloride from the obtained aluminum to finally obtain crystalline silicon nanoparticles [13]. The silicon nanoparticles were applied to the lithium-ion batteries' negative electrode to test the performance, and after 50 cycles, the negative electrode still maintained the reversible capacity, which reaches 3083 mAh per gram at a current density of 1.2 Amps per gram. After 500 cycles, the material's reversible capacity still reached 1180 mAh per gram at a current density of 3 Amps per gram. Jianwen Liang et al. used a hydrothermal method to prepare porous silicon nanospheres, and the resulting silicon nanoanode materials possess great reversible capacity and stable performance [14]. The silicon nanoanode's reversible specific capacity reached 2650 mAh per gram at a current density of 0.36 Amps per gram and its stable capacity also reached 950 mAh per gram at a current density of 3.6 Amps per gram after 500 cycles.

Therefore, nanosizing silicon materials can significantly improve the reversible capacity of silicon materials when applied to the lithium-ion batteries' negative electrode, and nanosized silicon can also effectively reduce the losses caused by volume changing during charging and discharging. By studying the performance of silicon nanomaterials made by different preparation methods, it not only demonstrates the feasibility of silicon nanomaterials applied in lithium-ion batteries, but also points out the direction for the next step to improve the performance of silicon nanomaterials, and by comparing the performance of silicon nanomaterials with different structures, finding the best structure for silicon nanomaterials in practical applications will be one of the research focuses.

3.2. silicon nanocomposites

In addition to the preparation of silicon nanomaterials, composite modification on the basis of silicon nanomaterials has also demonstrated great research potential. Heon-Young Lee et al. used a mechanochemical reduction method to produce silicon nanodisperse oxides from SiO, and the material was uniformly coated with carbon to finally obtain carbon-coated silicon nanodisperse oxides [15]. After testing, the uniform distribution of silicon nanoparticles and the buffering effect of graphite, together with the good electrical conductivity provided by the carbon layer, greatly improved the single silicon material's electrochemical performance and stability applied in the lithium-ion batteries' anode. Mingyan Feng et al. used in situ polymerization to prepare Si/polyaniline (PANI) composites and investigated the effect of different levels of PANI on the material properties [16]. It was concluded that the PANI containing 12.3% had the best electrochemical performance and showed good stability, maintaining 72% capacity at 2 Amps per gram current density after 50 cycles.

Silicon nanocomposites with different reinforcement compositions have also shown excellent performance when applied to the lithium-ion batteries' anode. Therefore, after nanosizing and nanocomposite modification, silicon nanomaterials have the potential to become the new lithium-ion batteries' anode materials.

4. Metal-based materials

4.1. Tin-based materials

Metallic tin materials are considered one of the ideal anode materials, which can be used in the Li-ion battery because it has a high theoretical capacity of 993.4 mAh per gram. However, the volume expansion problem that occurs with metallic tin during charging and discharging can lead to a significant reduction in battery functionality and create safety hazards. Moreover, the inability of metallic tin to conduct ions and electrons quickly during cycling can lead to a decrease in battery efficiency. Therefore, the metal tin material also needs to be modified. Nanosizing the metal tin will effectively reduce the effect of volume expansion. Moreover, researchers have continued to add reinforcing base materials to the nano-tin materials to further improve the nano-tin materials' performance.

Tae-Hui Lee et al. used SiC to build grooves on Cu plates to fill the Sn, and then applied polyvinylidene fluoride (PVDF) solution on the Cu plates coated with Sn to immobilize the Sn nanoparticles on the Cu plate surface [17]. The final Cu/Sn/PVDF composite was produced. After 500 and 1000 cycles, the electrodes were tested to still possess high capacities of 274 mAh per gram and 114.5 mAh per gram. PVDF effectively reduced the detachment of Sn, making the electrode performance more stable, while the application of nano-Tin also solved the problem of volume expansion of metallic tin, ensuring the effective operation of the battery for a long time.

By compounding tin-based materials with other materials, the volume change of tin-based materials during lithium-ion battery operation is greatly reduced, and the stability performance of nano-tin-based materials is improved, showing the great potential of nano-tin-based materials applied in the anode of lithium-ion batteries.

4.2. Zinc oxide based materials

ZnO is also considered to be used in lithium-ion battery anode as one of the proper alternative materials since it has high capacity in theory and abundant resources and low fabrication cost. However, the excessive volume change of ZnO during cycling is one of the factors that hinder the further application in the Li-ion battery, and the poor electrical conductivity of ZnO will reduce the efficiency of lithium-ion batteries. To solve the volume expansion problem, nanosizing the material is regarded as an effective way to deal with the problem.

Lei Wang et al. explored one-dimensional, two-dimensional, and three-dimensional ZnO nanomaterials, respectively [18]. It showed that the nanosized ZnO could effectively reduce the volume expansion of ZnO, thus improving the stability of battery performance. By comparing these three structures of ZnO, it was found that the three-dimensional structure of ZnO material had more space and can better cope with the volume expansion of the material, which led to better electrochemical performance and stability of the electrode.

5. Conclusion

Nanotechnology can speed up the transfer rate, and enhance the conductivity of lithium-ion batteries. Moreover, nanotechnology can increase the lithium storage sites of the material and increase the lithium storage capacity.

As a result, carbon, silicon and metallic materials are nanosized and the volume expansion problem is improved and the electrochemical properties are enhanced. The performance of carbon nanomaterials, silicon nanomaterials, and nanometallic materials is further improved by the composite of different reinforced base materials, showing great potential that they can be used in the Li-ion battery as a new generation of anode materials. In this case, researchers will continue their research on the application of nanotechnology to negative electrode materials to find the material with the best performance.

However, the problem of non-industrialization still hinders the practical application of the new materials. The next research focus will continue to be on improving the performance of the new materials, how to reduce production costs and industrialize them.

References

[1] Sheng J, Tong S, He Z, et al. (2017) Recent developments of cellulose materials for lithium-ion battery separators. Cellulose,24: 4103-4122.
[2] Tong Q, Liu Q, Peng W, et al. (2023) Current status of research on optoelectronic properties of graphene and its application technology. Modern Applied Physics,14(2) 1-10.
[3] Zhang B, Wang K, Li J et al. (2022) Research progress on nanocarbon materials for lithium-ion batteries. Materials Guide,36(20):115-127.
[4] Pang Q, Zhao Y, Bian X, et al. (2017) Hybrid graphene@ MoS 2@ TiO 2 microspheres for use as a high performance negative electrode material for lithium ion batteries. Journal of Materials Chemistry A, 5(7): 3667-3674.
[5] Wang G, Wang B, Wang X, et al. (2009) Sn/graphene nanocomposite with 3D architecture for enhanced reversible lithium storage in lithium ion batteries. Journal of Materials Chemistry, 19(44): 8378-8384.
[6] Wang X, Zhou X, Yao K, et al. (2011) A SnO2/graphene composite as a high stability electrode for lithium ion batteries. Carbon, 49(1): 133-139.
[7] Xia H, Lai M O, Lu L. (2011) Nanoflaky MnO 2/carbon nanotube nanocomposites as anode materials for lithium-ion batteries. Journal of Materials Chemistry, 20(33): 6896-6902.
[8] Fu Y, Ma R, Shu Y, et al. (2009) Preparation and characterization of SnO2/carbon nanotube composite for lithium ion battery applications. Materials Letters, 63(22): 1946-1948.
[9] He Y, Huang L, Cai J S, et al. (2010) Structure and electrochemical performance of nanostructured Fe3O4/carbon nanotube composites as anodes for lithium ion batteries. Electrochimica Acta, 55(3): 1140-1144.
[10] Park J, Joo S H, Kim Y J, et al. (2019) Organic semiconductor cocrystal for highly conductive lithium host electrode. Advanced Functional Materials, 29(32): 1902888.
[11] Teprovich Jr J A, Weeks J A, Ward P A, et al. (2019) Hydrogenated C60 as high-capacity stable anode materials for Li ion batteries. ACS Applied Energy Materials, 2(9): 6453-6460.
[12] Jiang S, Cheng J, Fan J, et al. (2023) Research progress of one-dimensional silicon nanowires. Non-ferrous Metal Equipment,37 (01): 16-19.

DOI: 10.54254/2755-2721/26/20230792

[13] Lin N, Han Y, Wang L, et al. (2015) Preparation of Nanocrystalline Silicon from SiCl4 at 200°C in Molten Salt for High-Performance Anodes for Lithium Ion Batteries. Angewandte Chemie International Edition, 54(12): 3822-3825.

[14] Liang J, Li X, Zhu Y, et al. (2015) Hydrothermal synthesis of nano-silicon from a silica sol and its use in lithium ion batteries. Nano Research, 8: 1497-1504.

[15] Lee H Y, Lee S M. (2004) Carbon-coated nano-Si dispersed oxides/graphite composites as anode material for lithium ion batteries. Electrochemistry Communications, 6(5): 465-469.

[16] Feng M, Tian J, Xie H, et al. (2015) Nano-silicon/polyaniline composites with an enhanced reversible capacity as anode materials for lithium ion batteries. Journal of Solid State Electrochemistry, 2015, 19: 1773-1782.

[17] Reddy B S, Lee T H, Reddy N S, et al. (2022) Nano tin encapsulated in copper grooves as an anode for high-performance lithium-ion batteries. Journal of Alloys and Compounds, 918: 165578.

[18] Wang L, Zhang G, Liu Q, et al. (2018) Recent progress in Zn-based anodes for advanced lithium ion batteries. Materials Chemistry Frontiers, 2(8): 1414-1435.