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Application of nanomaterials in the negative electrode of lithium-ion batteries

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Abstract. Li-ion batteries (LIBs) widely power modern electronics. However, there are certain limitations in the energy density, cycle life, and safety of traditional lithium-ion batteries, which restrict their further application and development. Therefore, new methods and technologies need to be explored to improve the performance stability of LIB. The emergence of nanomaterials provides new ideas and methods for the improvement of lithium-ion batteries. Nanomaterials have special structures and properties, and can improve the performance of LIB by regulating their morphology, size, and surface chemical properties. An overview of the development in research on using nanomaterials in LIB is given in this article. First, the features and benefits of nanomaterials were described, as well as the basic principles and development history of lithium-ion batteries. The use and performance of nanomaterials in lithium-ion batteries were then elaborated from a variety of angles, including nanosilicon, nanocarbon, and nanoiron oxide. Finally, the future applications of nanomaterials in lithium-ion batteries were prospected, and their development trends and challenges were pointed out. This article aims to provide a reference for the application of nanomaterials in lithium-ion batteries and promote further development in this field.

Keywords: Nano silicon, nano carbon, nano iron oxide, lithium-ion battery.

1. Introduction

With the gradual depletion of non-renewable resources in human society, energy demand is increasing [1]. Fossil fuels such as natural gas, coal, and oil are the basic energy sources of modern social economy. The practical use of these fuels has promoted the progress of human society and improved quality of life. But the large-scale extraction and long-term use of these fossil fuels have brought serious pollution problems to the environment, such as acid rain, greenhouse effect, haze, etc. And due to the non-renewable nature of fossil energy itself, it has also brought us a series of problems such as energy shortage. Therefore, people are gradually shifting their research focus to the development and utilization of new energy. So how to fully utilize the green, pollution-free and renewable new energy in nature to replace the non-environmentally friendly and non-renewable fossil energy has become an urgent problem that humans need to solve [2]. Numerous researchers have been interested in and have explored lithium-ion batteries as a significant new energy storage device. One of the most crucial components of lithium-ion batteries has received extensive research: the anode material.

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Lithium-ion batteries are a type of secondary battery that uses carbon materials as the negative electrode and lithium-containing compounds as the positive electrode. Essentially, they are chemical batteries that move ions. Its working principle is to use lithium ions as carriers to achieve the conversion of chemical and electrical energy. At the same time, people also vividly refer to this working principle of battery as a "rocking chair battery". During charging, Under the action of external potential difference, electrons flow from the external circuit into the negative electrode. In order to maintain electrical neutrality, lithium ions with the same amount of charge are generated at the positive electrode of the battery while being removed from the positive electrode. They are embedded into the carbon layer micropores of the anode through a separator and electrolyte. The negative electrode's lithium-rich condition causes electrical energy to be converted into chemical energy. Lithium ions leave the positive electrode during discharge and travel through the electrolyte to the negative electrode. The positive electrode is in a lithium-rich condition and electrons are also flowing to the negative electrode through the external circuit at the same time, resulting in the conversion of chemical energy into electrical energy.

However, lithium-ion batteries are unable to keep up with the expanding demands of human life because of their low energy density. Because of this, researchers are constantly improving the efficiency of lithium-ion batteries. The negative electrode material of lithium-ion batteries is one of the most important components in batteries, and its physical and chemical properties directly affect the performance of lithium-ion batteries in various aspects [3]. At this point, using nanomaterials as the negative electrode can greatly improve the performance of the battery. The size of nanomaterials is usually between 1-100 nanometers, and compared to traditional micrometer-scale nanomaterials, nanomaterials have a larger surface area. So, using nanomaterials as negative electrode materials can increase the surface area of the active material of the battery, and improve the energy density of the battery [4]. Nanomaterials can increase the transport and diffusion rates of lithium ions in batteries because they have smaller particle sizes and higher surface energies. Therefore, the use of nanomaterials can improve the charging and discharging rate and cycle life of batteries [5]. Based on the advantages of nanomaterials, this article will next introduce the specific applications of nanocarbon, nano silicon, and nano iron oxide in the negative electrode of lithium-ion batteries.

2. Application of nanomaterials in the anode of lithium-ion batteries

2.1. Nanosilicon

During the cycling process of lithium batteries, the negative electrode of metallic lithium usually produces a large number of lithium dendrites, which also poses a significant risk to the safety of the battery [4]. Nanosilicon has a greater specific surface area and smaller particle size than silicon, which has a very high specific capacity of roughly 4200mAh/g. Therefore, nanosilicon of the same weight can give more lithium ion storage capacity. Nanosilicon can reduce stress because of silicon's ability to expand and contract in volume during charging and discharging because its particle size is so small., thereby improving the stability of nanosilicon in batteries. Based on the above advantages, nano silicon negative electrodes will become one of the materials that can replace graphite negative electrodes in the future [6, 7]. Mi-Hee Park et al. reported on the preparation of silicon nanotubes using alumina templates to reduce and decompose silicon precursors, with a wall thickness of 40 nm. After 200 cycles, silicon nanotubes exhibited a reversible capacity of 3247 mAh/g at 1 C magnification, which was 10 times the capacity of graphite electrodes. The silicon nanotubes were not affected by volume changes during the insertion and removal of lithium ions and were not damaged. Compared to granular materials, silicon nanotubes had a larger specific surface area and effective electrochemical reaction contact area, which could increase the participation of more active materials in electrochemical reactions, thereby improving the specific capacity [8].

Bogart et al. also conducted a study that demonstrated enhanced cycling and rate performance of silicon nanowires in lithium storage when coated with carbon skin. In a recent endeavor, Ti@Si core-shell coaxial nanorods were proposed to further enhance the electrochemical properties of Si nanorods (Figure 1). Compared to pristine Si nanorods, the inclusion of a metallic core offers the advantage of significantly reducing the axial resistance observed in solid Si nanorods. The metallic Ti core enables easy transfer of electrons during the electrochemical reactions of dealloying/alloying for LixSi to the Ti foil current collectors, unlike in solid semiconductor Si nanorods. By incorporating a metallic Ti core, the Li diffusion distance is dramatically reduced from the radius of the solid Si nanorod to only the thickness of the shell in the core-shell Ti@Si nanorod. Additionally, the charge transfer in the longitudinal direction, which occurs over the length of a few micrometers in solid Si nanorods, is reduced to the thickness of the shell in the case of Ti@Si core-shell coaxial nanorods. Furthermore, the contact area between Si and Ti is increased, thereby improving the connection between the active materials and the collector. However, despite these improvements, capacity fading still persists, indicating the need for further optimization of the core-shell materials. This concept can also be extended to the preparation of other core-shell materials.

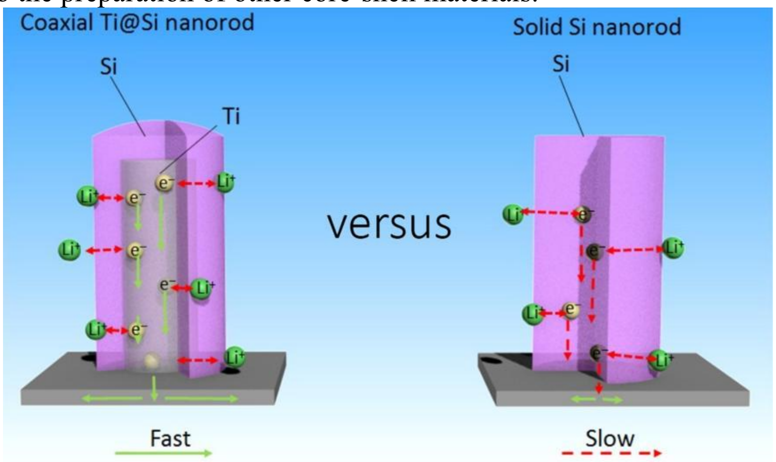

Figure 1. Li ions and electrons transfer of the Ti@Si core-shell coaxial nanorod (left) and the solid Si nanorod (right) [9].

However, there are still several difficulties that humans need to overcome to achieve the commercial application of silicon-based negative electrode materials. For example, traditional silicon materials undergo volume changes during the charging and discharging process, and the volume expansion rate is very high, which can cause damage to the electrode material, thereby affecting the lifespan and performance of the battery. Moreover, due to the large volume variation, low conductivity, and electrode polarization of silicon materials, their cycling performance in lithium-ion batteries is poor, often resulting in performance degradation after only a few dozen cycles. In order to overcome the shortcomings of traditional silicon materials in lithium-ion batteries, new material design and preparation methods need to be adopted. A common method is to use nanosilicon materials as anode materials. By reducing volume changes and polarization phenomena, nanosilicon materials with high specific surface areas and lithium storage capacities can increase the cycle life and energy density of lithium-ion batteries. Moreover, the surface area of nanosilicon is relatively large, making it easy to form oxides and carbonates on the surface, which increases the internal resistance of the battery and reduces its conductivity [10]. However, nanosilicon materials also have problems such as high preparation costs and poor durability, so further research and improvement are needed.

2.2. Nanocarbon

Carbon nanotubes (CNTs) are a type of carbon nanomaterial with unique properties. CNTs have many special properties, such as great mechanical qualities, a very high specific surface area, excellent conductivity, excellent thermal conductivity, etc. Its structural properties are conducive to the embedding of lithium ions, and it also has a high charging capacity (approximately 1000 mAh/g).

Due to their superior conductivity, CNTs can be employed as negative electrode materials for lithium-ion batteries, allowing electrons to quickly transport within them, ensuring low internal resistance and high charging and discharging efficiency of the battery. CNTs can boost electrode capacity and charge-discharge rate while minimizing electrode material volume change, thereby improving the cycling life of batteries. CNTs can serve as carriers for electrode materials, depositing metal nanoparticles on the inner and outer surfaces of carbon nanotubes [11, 12]. Then these particles can form composite materials, enabling the negative electrode to have a high lithium capacity of metal and become less prone to crushing. The reason is that the highly conductive CNT serves as the matrix for the adhesive metal nanoparticles. Overall, CNTs have a wide range of applications in lithium-ion batteries, which can enhance battery safety and performance. However, there are still some technical and economic challenges for their large-scale application. For example, issues such as high production costs and high process difficulty also require further development and improvement by researchers.

2.3. Nanometer iron oxide

The theoretical capacitance of Fe_2O_3 is relatively high (1005 mAh/g), and it has a very high specific surface area, which can improve the reaction activity of the electrode material, thereby improving the performance of the battery. However, Fe_2O_3 is prone to expansion and aggregation during charging and discharging, and its conductivity is average [13]. Nano iron oxide has good conductivity. During the charging and discharging process, Fe_2O_3 can capture 6 electrons and effectively transfer charges, improving the output power of the battery. In addition, compared to other materials, it has advantages such as low price, large storage capacity, and non-toxic properties [14, 15]. It is one of the nanomaterials with great potential to replace graphite electrode materials. Alternatively, Fe_2O_3 can be composited onto a nano matrix to alleviate material volume changes through its unique shape and structure, while also effectively alleviating issues such as easy aggregation and crushing. Bonil Koo's team studied the electrochemical performance of hollow nano iron oxide particles and used them as anode materials for lithium-ion batteries. Such nanoparticles can be effectively employed for reversible Li ion insertion without structural modifications because they have a very high concentration of cationic vacancies. High capacity (132 mAh/g at 2.5 V), 99.7% Coulombic efficiency, outstanding rate performance (133 mAh/g at 3000 mA/g), and excellent stability (without fading at a rapid rate over 500 cycles) may all be produced by cycling in the high voltage range [16].

3. Conclusion

A popular area of study in batteries is the use of nanomaterials in LIBs. This article summarizes research on the application of nano silicon and carbon nanotubes in lithium-ion batteries (LIBs). Firstly, nano silicon materials show promise in the negative electrode of LIBs, improving energy density and cycle life. With their high specific surface area and reversible embedding/de-embedding ability, nano silicon materials achieve higher energy storage density and cycle life while maintaining electrode stability. However, challenges remain, such as volume expansion and capacity degradation, necessitating further research. Secondly, carbon nanotubes as negative electrode materials offer potential applications. They possess excellent conductivity, high specific surface area, and good mechanical properties, increasing electrode surface area, energy storage capacity, power density, and cycle life. Their controllability and scalability in preparation and integration provide wide application space for high-performance LIBs. Lastly, nano iron oxide has garnered attention in LIBs. Compared to traditional iron oxide electrodes, nano iron oxide materials exhibit higher specific surface area and improved energy storage performance. Modifying their morphology, particle size, and structure factors further enhances electrode performance and cycling life. Nonetheless, challenges like capacity decay and volume expansion require further research. In conclusion, nanomaterials hold great potential in the study of lithium-ion battery materials. Despite existing challenges and limitations, continued research and innovation are expected to unlock more solutions and possibilities for higher-performance LIBs.

References

[1] Huang J., Wang W., Lin X., et al. 2018 Journal of Power Sources 378 677-684.
[2] Obama B. 2017 Science, 355 126-129

DOI: 10.54254/2755-2721/24/20230716

[3] Poizot, P., Laruelle, S., Grugeon, S., et al. 2000 Nature 407, 496–499
[4] Qin Y 2018 Oxidative modification and crosslinking of a new type of adhesive for silicon negative electrodes. Harbin Engineering University
[5] Peled, E.; Menachem, C.; Bar-Tow, D., et al. 1996 Journal of the Electrochemical Society. 143 L4-L7.
[6] Li B, Sun Q, Zhang Y, et al. 2017 ACS Appl. Mater. Interfaces 9 12511–12517
[7] Chan, C. K., Peng, H., Twesten, R. D., Jarausch, K., Zhang, X. F., & Cui, Y. 2007 *Nano Letters*, *7* 490-495
[8] Park M H, Kim M G, Jooahn J, et al. 2009 Nano Letters, 9 3844-3847
[9] Deng, D. (2015), Li-ion batteries: basics, progress, and challenges. Energy Sci Eng, 3: 385-418.
[10] Sun S, Yuan D, Xu, Y, et al. 2016 ACS Nano 10 3648–3657
[11] Kim Y, Yoon R, Shin R. 2009 Journal of Analytical & Applied Pyrolysis 85 57-560
[12] Chen W X, Lee J Y, Liu Z. 2003 Carbon 41 959-966
[13] Coey, J. M. D., Berkowitz, A. E., Balcells, L., et al. 1998 Applied Physics Letters 72 734-736
[14] Xiao, W., Wang, Z. X., Guo, H. J., et al. 2013 Applied Surface Science 266 148-154
[15] Liu, H., Wang, G. X., Park, J., et al. 2009 Electrochimica Acta 54 1733-1736
[16] Koo B, Xiong H, Slater M D, et al. 2012 Nano Letters 12 2429-2435