Improvement and Development Prospects of Carbon Anode Materials for Lithium-ion Batteries

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Abstract. With the research progress in the field of electrochemistry and the introduction of new materials, lithium-ion batteries (LIB) have begun to achieve breakthrough progress. In contrast with traditional lead-acid batteries and nickel-cadmium batteries, LIB do not have memory effect, they will not be affected because of incomplete charge or long idle time and they are more convenient to use. The self-discharge rate of LIB is low, and it is easy to maintain a higher charge state when the storage time is longer than that of lead-acid batteries and nickel-cadmium batteries. LIB do not contain heavy metals such as lead and cadmium, and the manufacturing and recycling process of LIB has less impact on the environment than lead-acid batteries and nickel-cadmium batteries. Although the battery field has changed a lot and many problems have been solved, LIB still face some challenges, in the lithium-ion battery materials, there are still battery capacity attenuation during the battery cycle charge and discharge process, cycle life is insufficient, and charge and discharge speed is limited. In this context, several commonly used carbon anode materials for lithium-ion batteries are briefly introduced in this paper, mainly introducing the improvement methods of silicon carbon anode materials and metal oxide and carbon matrix composites. Compared with the traditional manufacturing method, the electrode material prepared by the new technology has better electrode performance and stability. In terms of silicon carbon anode materials, electrostatic electrospinning and carbon silicon nanotubes are the most promising large-scale development, and in terms of metal/metal oxide composites, the use of sodium chloride particle surface as a template to manufacture Fe_3O_4/C composites has great advantages. By improving the electrochemical performance of LIB by improving the carbon anode material, batteries with better performance, wider use and higher safety.

Keywords: Lithium-ion battery, anode material, cathode materials, composite materials.

1. Introduction

With the research progress in the field of electrochemistry and the introduction of new materials, LIB have begun to achieve breakthrough progress. In contrast with traditional lead-acid batteries and nickel-cadmium batteries, LIB is not affected by the memory effect, they do not need to be completely emptied before charging, nor do they need to be fully filled, and they are more convenient to use. The discharge rate of LIB is minimal, allowing for a higher charge retention during extended storage compared to lead-acid and nickel-cadmium batteries. Additionally, LIBs are free from heavy metals like lead and cadmium, resulting in a manufacturing and recycling process that has less environmental impact than their counterparts. These benefits position LIB as the favored energy provider in the realm of portable electronic gadgets, including smartphones, tablets, and laptops [1].

With the continuous development of LIB, there has been a persistent endeavor to improve their performance and ensure safety through continual innovative measures. For example, several new anode and cathode materials such as lithium manganate, lithium cobaltate and lithium iron phosphate were introduced, as well as new electrolyte and diaphragm materials were developed. These innovations have driven a growing range of applications for LIB, such as electric vehicles, solar energy storage systems and drones [2].

Although countless problems have been solved in the field of LIB, LIB still face some challenges, and there are still large limitations in lithium-ion battery electrode materials. For example, capacity attenuation, in the lithium-ion battery cycle charging and discharging process, the electrode material will appear capacity attenuation phenomenon, resulting in a decline in battery energy storage performance. This may be due to the change of electrode material structure, the side reaction produced in the process of lithium-ion migration and other reasons. Limited cycle life is also a big problem, and the service life of LIB is limited by the cycle life of the electrode material. Problems such as loss, particle precipitation and structural change may occur during the process of electrode material cycling, leading to electrode performance attenuation and ultimately affecting battery life. The stability of the interface between the electrode material and electrolyte plays very important role in determining the performance of LIB. Upon contact with the electrolyte, chemical reactions may take place within the electrode material, resulting in decomposition of the electrolyte and alterations in the structure of the electrode material. These changes have a direct impact on battery capacity, cycle life, and safety performance. Additionally, high-power applications are hindered by limited charge and discharge rates in LIB. The rate at which these processes occur is affected by various factors such as electrode material conductivity, ionic diffusion properties, and interactions between electrodes and electrolytes [2, 3].

Since the emergence of lithium, a lot of negative electrode materials have been born, there are conversion negative electrode materials, transition metal oxides, etc., but so far, only carbon-based electrode materials can be commercialized, and other materials will have their shortcomings more or less. Therefore, combined with previous studies, this paper analyzed and summarized the carbon anode materials for LIB to solve problems such as insufficient capacity, short cycle life and poor stability [4, 5]. In this paper, the improved method of carbon silicon anode material and Fe_3O_4/C composite material are used to solve the electrode problem.

2. Carbon Anode Material

As the negative electrode of LIB, carbon anode material has many advantages. First of all, it has a high safety, compared with metal oxide anode materials, it is more stable and safer, reducing the risk of fire and explosion. Secondly, carbon materials have good electrical conductivity, which can support high power output and fast charging and discharging of batteries. In addition, carbon materials have a long cycle life and a low-capacity decay rate, which can maintain a high battery life. Moreover, carbon materials are environmentally friendly, can be recycled, and do not contain toxic and harmful substances. However, the low specific capacity of carbon materials, capacity attenuation, low energy density and limited charge and discharge rate are some of its shortcomings. In future development, these problems need to be solved to further improve the performance and application range of carbon anode materials in LIB. Therefore, the following improvements are available to address the shortcomings of traditional carbon electrodes.

3. Silicon Carbon Anode Material

As the negative electrode of LIB, carbon anode material has many advantages. First of all, it has a high safety, compared with metal oxide anode materials, it is more stable and safer, reducing the risk of fire and explosion. Secondly, carbon materials have good electrical conductivity, which can support high power output and fast charging and discharging of batteries. In addition, carbon materials have a long cycle life and a low-capacity decay rate, which can maintain a high battery life. Moreover, carbon materials are environmentally friendly, can be recycled, and do not contain toxic and harmful substances.

However, compared with other anode materials, carbon anode materials have lower specific capacity. This means that batteries cannot store the same amount of energy per unit volume as other materials. The electrode reaction rate of carbon negative materials is relatively slow, so it may be limited in high power applications. This may affect the battery's charging speed and power output.

Compared with carbon anode materials, other materials such as silicon and tin also have their specific advantages and disadvantages. For example, silicon anode materials have higher specific capacity, but there are problems such as fast capacity decay and mechanical brittleness. On the other hand, the tin anode material has high specific capacity and good cyclic stability, but it faces problems such as violent reaction with lithium and volume expansion.

In summary, although carbon anode materials have some limitations, the reason why they are widely used in LIB is their good cycle stability, appropriate specific energy and low cost. As technology advances, researchers are always looking for alternative materials to further improve battery performance.

After analysis, the silicon-based material of lithium-ion battery is just complementary to the carbon-based material because of its high specific capacity and higher conductivity, and it is selected as a part of the carbon-based electrode material in this paper. Metals and metal oxides are also part of this paper because of the reasons such as low cost and excellent conductive efficiency. In this paper, the improvement direction of carbon anode materials for LIB will be analyzed from these two discharge surfaces.

3.1. Chemical Vapor Deposition (CVD)

Chemical vapor deposition is a method used to prepare thin film materials. It involves the chemical reaction of the gas raw material under the gas phase condition to convert it into a solid or liquid film deposited on the substrate. The chemical vapor deposition method has many advantages, such as the preparation of high-quality and uniform films, the control of material composition and structure, and the preparation of large-area films [6, 7]. Therefore, a class of composite materials of porous silicon and graphite-carbon has been developed, and they are usually selected carbon coatings or carbon nanotubes, using a CVD process to form uniform nanoparticle silicon particles on the carbon surface.

Fig. 1 shows the fabrication of a silicon/carbon nanotube hybrid nanostructure consisting of vertically aligned multi-walled carbon nanotube (VACNT) and nanoscale Si droplets through a two-step liquid injection CVD process [7]. However, in practical applications, the silicon precursor SiH_4 is highly toxic and explosive. Moreover, this technology requires higher temperatures and has a high demand for reaction conditions. The deposition rate of this technology is limited, and it can also produce many by-products, so it cannot be applied on a large scale. Despite these drawbacks, CVD is still an important thin film preparation technology and widely used in many fields. By improving equipment and process parameters, these shortcomings can be partially overcome and the efficiency and feasibility of CVD technology can be improved.

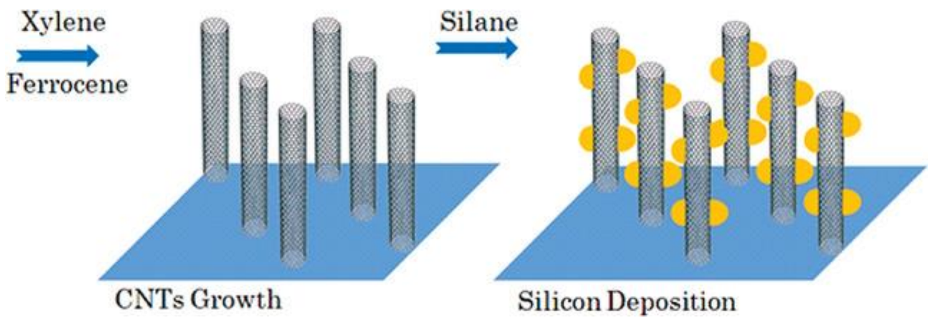

Figure 1. The process of CVD. https: //chemistry-europe.onlinelibrary.wiley.com/doi/full/10.1002/celc.202001060? saml_referrer

3.2. Electrostatic Spinning

Electrospinning by spraying a polymer solution or molten polymer from the tip under a high electric field, the polymer molecules in the solution gradually solidify and form fibers. This process can prepare nanofibers with specific properties, which does not require high temperatures or complex operations, so it is expected to achieve large-scale applications [6, 7]. In a study conducted by Wang et al., the researchers dissolved polyacrylonitrile (PAN) in N-N-dimethylformamide (DMF) to create a polymer precursor. They discovered that when the carbon-to-silicon mass ratio was 77: 23, the yield of carbon precursor reached approximately 50%. Furthermore, they observed that reducing the silicon concentration resulted in smoother fiber formation. As a result, the team conducted experiments under these optimized conditions to fabricate and analyze a new type of electrospun nanofiber composite consisting of carbon and silicon. The study revealed that compared to conventional anodes where carbon and silicon are mechanically mixed together, the composite nanofibers showed improved electrochemical performance due to the even distribution of silicon particles within the carbon matrix. These fibers showcased a significant reversible capacity of 1240mAh g^{-1} and maintained stable capacity retention even after undergoing more than 40 cycles. This finding holds great promise for advancing high energy density LIB [8].

3.3. Carbon-silicon Nanotubes

Carbon nanotubes, being a type of conductive carbon material, possess a unique one-dimensional structure consisting of hollow tubes. These tubes are composed of curled graphene sheets and have an end cap featuring a hemispherical fullerene structure. It is a homologous of graphite, and its lithium storage capacity is greatly improved compared with graphite due to its unique structure and properties. However, its own lithium reaction capacity is low, which limits the overall capacity of the battery. Therefore, silicon carbon nanotubes have become a new solution to increase battery capacity [6]. A composite material consisting of a silicon core and a shell made of amorphous carbon nanotubes (ACNTs) has the potential to serve as an anode electrode substance in LIB.

Fig. 2 illustrates the preparation process of Si/ACNT composites [6, 9]. This composite of Si/ACNT exhibits a remarkable specific capacity of 1496 mAh/g when subjected to a current density of 100 mA/g, demonstrating exceptional cycle stability with an impressive retention rate of 80% even after undergoing 300 cycles.

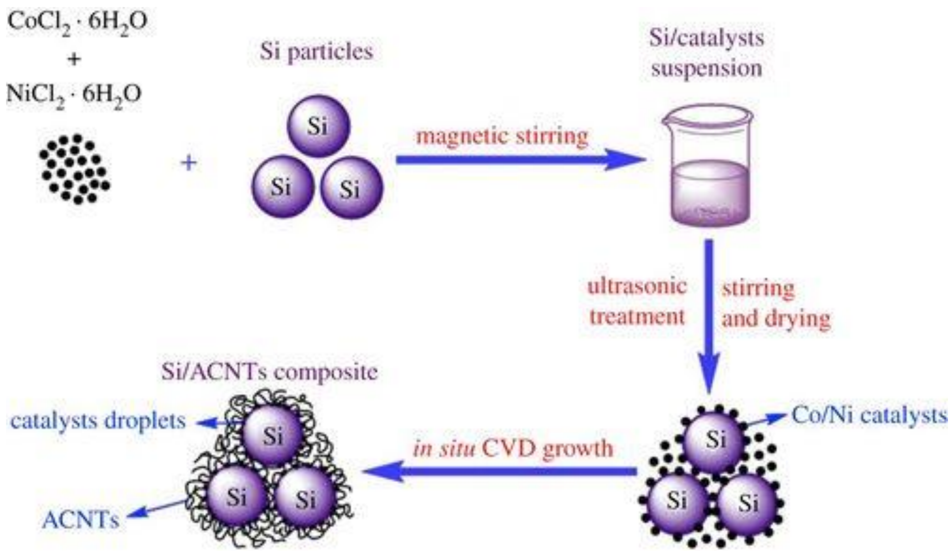

Figure 2. Manufacturing Si/ACNT composite materials using impregnation and in-situ CVD methods, and growing coiled ACNT on silicon particles. https: //royalsocietypublishing.org/doi/full/10.1098/rsos.172370#d3e336

4. Forming Composite Materials with Metals and Metal Oxides

For example, carbon encapsulated Fe_3O_4 nanoparticles used as anode materials for LIB [6, 10]. In the improvement of anode materials for lithium-ion batteries, the composite materials of metal and metal oxides have become an important research direction. One of the promising materials is carbon-encapsulated Fe_3O_4 nanoparticles, which are used as the negative material part of LIB.

The preparation method of carbon encapsulated Fe_3O_4 nanoparticles has undergone a series of optimization and improvement. By controlling the temperature and reaction conditions in the carbon coating process, composites with excellent electrochemical properties can be successfully prepared. Carbon encapsulation effectively solves the problems of Fe_3O_4 capacity attenuation and electrode structure destruction in LIB. In addition, carbon provides enough conductivity and stability to support high-performance battery cycles.

The utilization of carbon encapsulated Fe_3O_4 composites presents a range of benefits when used as negative electrode materials in LIB. Firstly, the high theoretical capacity of Fe_3O_4 enables the design of batteries with high energy density. Secondly, the incorporation of carbon packaging enhances the resistance of Fe_3O_4 against issues such as volume expansion and dissolution, thereby prolonging the battery's cycle life. Moreover, carbon packaging also facilitates improved electronic conductivity between Fe_3O_4 particles, thereby enhancing the overall conductivity of the composite material. Nevertheless, due to several limitations associated with traditional Fe_3O_4 composites, a novel production method has been developed. Two-dimensional nanosheets composed of Fe_3O_4@C@PGC were synthesized by utilizing sodium chloride particles' surface as a template for fabrication purposes (Fig. 3) [10].

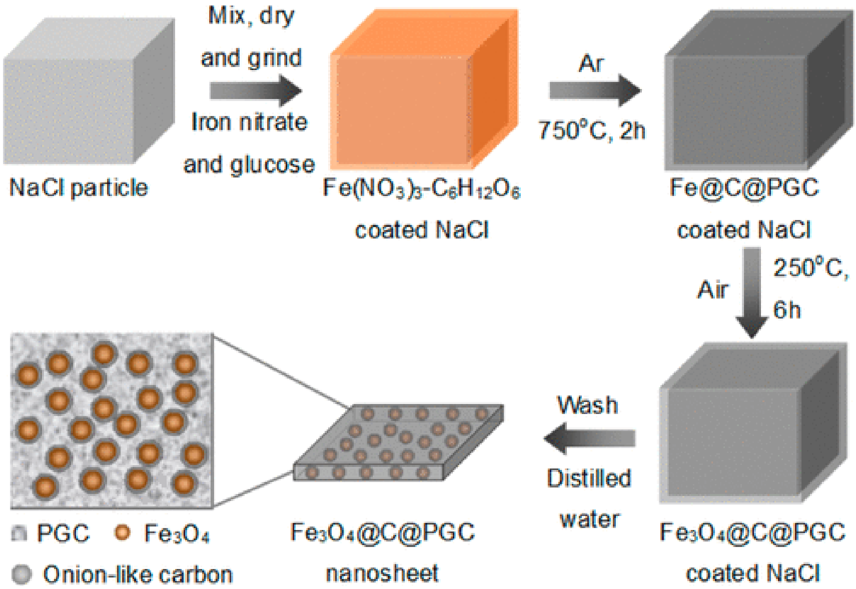

Figure 3. Using the surface of sodium chloride particles as a template to manufacture two-dimensional materials Fe_3O_4@C@PGC nanosheets. https: //pubs.acs.org/doi/abs/10.1021/nn401059h

The improved fabrication method of 2D Fe_3O_4@C@PGC nanosheets offers several advantages compared to traditional 3D Fe_3O_4/C composites. In terms of cycle life, the composite electrode made from 2D Fe_3O_4@C@PGC demonstrates superior cycle retention rate when compared to commercial Fe_3O_4 nanoparticles. Additionally, it exhibits a significantly higher reversible capacity than the 3D Fe_3O_4/C composite material. After undergoing 50 cycles, the reversible capacity reaches an impressive value of 1003 mA/g and remains at a commendable level of 998 mA/g even after completing 100 cycles. These values correspond to approximately 98.2% and 97.7% of the initial capacity. The reason for the performance improvement may be that in traditional 3D Fe_3O_4/C composites, exposed Fe_3O_4 particles tend to impede ion transport due to their higher resistance and are prone to forming clusters that negatively impact lithium-ion retention rate. However, by utilizing the innovative structure of the nanosheets in the form of 2D Fe_3O_4@C@PGC, stable reversible capacity is maintained even under high charge-discharge rates.

However, carbon encapsulation of Fe_3O_4 nanoparticles as the anode material part of LIB still faces some challenges. These problems include the complexity of the preparation method, the thickness control of the carbon encapsulation layer, cycle stability and capacity maintenance. Therefore, the future research direction will be to further improve the preparation method, optimize the structure of the carbon encapsulation layer, improve the performance of the composite material, and solve its practical application challenges.

These investigations have recognized the possibility and outlook of Fe_3O_4 nanoparticles enclosed in carbon as materials for the anode electrode in LIB. Through diverse enhancements and additional exploration, this amalgamated substance is anticipated to have a significant impact on the advancement of LIB by enhancing their performance and longevity.

5. Conclusion

This paper analyzes how to improve the carbon anode materials, silicon carbon anode materials and metal and metal oxides and carbon composite materials have the most application prospects. The use of CVD, electrostatic electrospinning and carbon-silicon nanotubes can solve the problem of volume expansion of silicon-based materials and small specific capacity of carbon-based materials, and further improve the cycle stability of carbon anode materials. Compared with traditional Fe_3O_4/C composites, 2D Fe_3O_4/C composites fabricated by the new method have many advantages in high power discharge stability and other fields. In short, through the combination of carbon and silicon, changing the structure of carbon and metal oxides can increase the electrochemical performance, including the coulomb efficiency and reversible capacity of the first cycle are improved. These are currently the most promising ways to implement applications. However, in practical applications, they will have some limitations and shortcomings, still need to find more and better electrode preparation methods. In summary, carbon anode materials have important application value in LIB, and there is still a lot of potential in improvement and development. With more in-depth research and breakthrough innovation, carbon anode materials will make important contributions to the performance improvement of LIB and the development of sustainable energy.

References

[1] Rodolfo D.L., Ghassan Z., et al., The lithium-ion battery: State of the art and future perspectives, Renewable and Sustainable Energy Reviews, 2018, 89: 292 - 308.

[2] Kim T., Song W., Son D.Y., Ono L.K., Qi Y., LIB: Outlook on present, future, and hybridized technologies, Journal of Materials Chemistry A, 2019, 7: 2942 - 2964.

[3] George E.B., The Development and Future of Lithium-Ion Batteries, Journal of The Electrochemical Society, 2016, 164: 1.

[4] Nzereogu P.U., Omah A.D., Ezema F.I., Iwuoha E.I., Nwanya A.C., Anode materials for LIB: A review, Applied Surface Science Advances, 2022, 9: 100233.

[5] Arumugam M., An Outlook on Lithium-Ion Battery Technology, ACS Cent. Sci. 2017, 3 (10): 1063 – 1069.

[6] Liu X.Y., Zhu X.J., Pan D., Solutions for the problems of silicon–carbon anode materials for LIB, Royal Society Open Science, 2018, 5 (6).

[7] Li X.Z., Zhang M., Yuan S.X., Lu C. X., Research Progress of Silicon/Carbon Anode Materials for LIB: Structure Design and Synthesis Method, ChemElectroChem, 2020, 7: 21.

[8] Wang L., Ding C.X., Zhang L.C., Xu H.W., Zhang D.W., Cheng T., Chen C.H., A novel carbon–silicon composite nanofiber prepared via electrospinning as anode material for high energy-density lithium-ion batteries, Journal of Power Sources, 2010, 195 (15): 5052 - 5056.

[9] Wu Y.P., Rahm E., Holze R., Carbon anode materials for lithium-ion batteries, Journal of Power Sources, 2003, 114 (2): 228 - 236.

[10] He C.N., Wu S., Zhao N.Q., Shi C.S., Liu E.Z., Li J.J., Carbon-Encapsulated Fe3O4 Nanoparticles as a High-Rate Lithium-Ion Battery Anode Material, ACS Nano, 2013, 7 (5): 4459 - 4469.