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Influences of Carbon Nanotubes as Electrode Materials on the Energy Storage for Lithium-Ion Batteries

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Abstract: Due to inherent theoretical capacity limitations and safety issues associated with commonly used anode materials in lithium-ion batteries, carbon nanotubes (CNTs), with their unique one-dimensional tubular structure and superior mechanical, electrical, and thermal properties, can partially address these deficiencies and enhance lithium storage capacity. Therefore, this paper concentrates on the impacts of carbon nanotubes as electrode materials on energy storage for lithium-ion batteries. It discusses three aspects in detail: the use of CNTs as direct anode materials, as composite anode materials, and as flexible electrode materials. Each application will be examined in terms of its specific advantages, existing challenges, and corresponding solutions to improve battery performance. The paper also evaluates the role of CNTs in enhancing the electrochemical stability, improving cycle life, and achieving higher power densities, which makes them highly promising for next-generation energy storage solutions, particularly for portable and flexible electronic devices. Additionally, the unique ability of CNTs to form a highly conductive network facilitates efficient charge transport and reduces internal resistance, further contributing to the overall performance of the battery. Future research directions may focus on optimizing the synthesis methods and improving the interface interactions between CNTs and other active materials, to fully leverage their properties for enhanced safety, higher efficiency, and lower costs. As such, carbon nanotubes are seen as key materials that could play an important role in meeting the growing demand for advanced energy storage systems.

Keywords: Carbon nanotubes, energy storage, electrode materials.

1. Introduction

The overuse of fossil fuels has been giving rise to several grave problems such as environmental pollution and energy crisis worldwide[1]. Hence, it is strongly necessary to find a new green renewable energy source to replace fossil fuels. However, restricted by geographical distribution differences and potential safety hazards, currently developed green energy sources, concluding solar, nuclear, etc, are still facing certain challenges in their advances and applications. With the in-depth study of energy storage technology, electrochemical energy storage has been gaining widespread attention owing to its high energy storage efficiency and excellent environmental performance[2]. Since Sony's first commercial lithium-ion battery was introduced in 1991[3], lithium-ion batteries which are famous for their higher energy density were gradually becoming the focus in this territory.

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Lithium-ion batteries' charging and discharging processes are mainly completed by the repeated embedding/disembedding behavior of lithium ions between anodes and cathodes. Therefore, the strength of lithium storage capacity has become one of the criteria of measuring electrode materials. Since carbon materials can store large amounts of lithium ions, so, they are often served as anode materials. But, currently common anode materials have inherent theoretical capacity limitations, as well as frequent battery explosions and other problems. Consequently, for the sake of the further developments of a new type of high-performance electrode materials, the researches of new anode materials of lithium batteries are necessary.

Carbon nanotubes (named as CNTs) are seamless one-dimensional tubular structures formed by carbon atoms bonded by sp^2 hybridization, with high aspect ratios and outstanding electrical, mechanical and thermal properties[4]. In terms of the quantity of graphite layers contained in them, CNTs can be categorized into single-walled carbon nanotubes (SMCNTs) and multi-walled carbon nanotubes (MMCNTs). And in terms of the curling methods of graphite layer, CNTs can be divided into three types of structures: armchair type, zigzag type and spiral type. The layer spacing of CNTs is about 3.4-3.5 nm, which is beneficial for lithium ions' diffusion and deep embedding. When lithium ions are embedded, the volume of CNTs expands and the layer spacing will be increased by 10%[5], further enhancing their lithium storage performance. In addition, the high specific surface area of CNTs offers numerous active sites helping to increase battery capacity and shorten charging time. In particular, the modified materials compounded with metals have more excellent energy storage performance. Liu[6], by compositing MMCNTs and LiMNO4 manufactured composite electrode materials and assembled them as lithium-ion batteries' cathodes. The evaluations of these batteries' capacity at high cycles revealed that after 20 weeks of charge/discharge cycling, the capacity may reach 99% of its maximum capacity. While comparing to those batteries which only use LiMNO4 as cathodes, their capacity can only be maintained at about 90% under the same experimental conditions.

To sum up, in this paper, the effects of using CNTs as electrode materials on the energy storage for lithium-ion batteries will be elaborated in detail from three aspects:CNTs directly as electrode materials, as composite electrode materials and as flexible electrode materials, respectively.

2. Carbon nanotubes in lithium ion batteries

On account of CNTs' high conductivity (up to 10^5 S/m), excellent resistance to electromigration, prefect flexibility and unique chemical structure, they can be utilized directly for electrode material for lithium-ion batteries, or composited with other materials to form composite electrode materials, as well as served as flexible electrode materials.

2.1. Carbon nanotubes directly as electrode materials

CNTs, as a carbon material with a graphitized layered structure with good electron and ion conductivity, can provide a host of embedding sites, enabling lithium ions to complete the embedding behavior in a short period of time. In particular, when CNTs are directly used as anode materials, their rich pore structure facilitates the improvement of lithium-ion battery charging and discharging capacities and current densities, which ultimately leads to the improvement of their energy storage capacity. Consequently, the abundant nanostructures of CNTs can make lithium-ion batteries have ultra-high theoretical specific capacity and excellent multiplicity performance. If lithium ions can be stored as tightly as possible on the inside and outside of surfaces, as well as between the interstices of the CNTs, the theoretical lithium storage capacity can be as high as 1116 mAh/g[7], which is much higher than those of batteries whose anodes are made from common graphite.

Although the first charging capacity of CNTs can reach more than 1000 mAh/g when they are directly used as anode materials, the first charging and discharging efficiencies of these batteries are

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often lower than 50% due to the very large capacity loss caused by their first irreversible capacity[8], which greatly restricts the applications of pure CNTs as anodes. Ng[9], synthesized irregularly arranged SMCNTs as anodes of lithium-ion batteriesunder positive pressure via a simple filtration method. The electrochemical tests show that the first discharge capacity was found to achieve 1700 mAh/g and the reversible capacity was only 400 mAh/g. Some similar conclusions were came to by Welna[10], who synthesized multi-walled carbon nanotube arrays by pyrolyzing iron phthalocyanine, adopted them as lithium-ion batteries' anodes. The electrochemical estimation reveals that the first discharge capacity was up to 1800 mAh/g and the reversible capacity was only 782 mAh/g. This is thanks to the fact that when the voltage is higher, the substances in the electrolyte and lithium ions will get electrons from anodes and then decompose and react, generating insoluble lithium salts, which will gradually deposit on the electrodes, eventually forming solid electrolyte interface films (defined as SEI film), leading to a loss of batteries' capacity. On the other hand, the presences of SEI films make it difficult for lithium ions to diffuse in carbon material and polarize easily during charging and discharging, so that once embedded, ions are difficult to de-embed thoroughly and quickly in a short period of time. These ultimately result in lithium-ion batteries exhibiting high first-time irreversible capacity. Apart of those above problems, when CNTs are directly applied as anodes, they cannot maintain a stable charging and discharging platform during the whole process, which makes the batteries unable to satisfy practical applications by failing to provide a stable power supply voltage for electronic devices[11].

Therefore, in order to solve the defective problems of CNTs, which are directly used as anodes of lithium-ion batteries, Wang[12], found that these problems could be mitigated by increasing the amount of cathodes used. And they tested the performance of these lithium-ion batteries after copper plating the CNTs. The results show that the first charge/discharge efficiency after copper plating is 55.9%, which is a significant improvement over that before copper plating. This is attributed to the fact that copper plating of CNTs significantly increases the content of cathodes, and since the increased metal ions could compensate for the loss of lithium ions due to the generation of insoluble deposited salts or blockage by SEI films, which ultimately leads to the demonstration of a high capacity during the first charge/discharge. Besides, those problems can also be solved by optimizing various structural parameters of CNTs. Wang[13], used cobalt oxide embedded in the wall of acid-purified multi-walled carbon nanotubes to obtain porous carbon nanotubes, with multiple holes of 4 nm in diameter distributed on the wall, and found that their reversible capacity was 625 mAh/g under a current of 25 mA/g for 20 weeks of cycling, whereas the reversible capacity of the untreated carbon nanotubes was only 421 mAh/g. This is attributed to the fact that the pore structure facilitates the embedding/de-embedding behavior of lithium ions, which can improve the reversible capacity of the battery to some extent.

In summary, although the critical issue of irreversible capacity loss when CNTs are directly used as anodes of lithium-ion batteries can have significant impacts on batteries, this phenomenon can be significantly improved by either modifying them with metal oxides or optimizing their structures.

2.2. Carbon nanotubes as composite electrode materials

Because of their outstanding mechanical and electrical properties, CNTs can be combined with other active electrode materials to form composite electrode materials to obtain electrode materials with higher electrochemical properties. Typically, CNTs are useful in composite electrode materials in two main ways: on the one hand, they are used as carriers to optimize the comprehensive performances of the composite electrode materials by using their excellent properties, so as to make one-dimensional nanocomposites with new structures with more perfect performances[14]. Feng[15], coated $MnSiO_3$ on the surface of CNTs by hydrothermal method to obtain CNT@$MnSiO_3$ composites, and these new coaxial composites were examinated to have a charge/discharge specific capacity of

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920 mAh/g under a 0.5 A/g current density for 650 cycles. This is owing to the fact that CNTs have a unique one-dimensional nanostructure that not only improves the electrical conductivity of $MnSiO_3$, but also inhibits the volume change of $MnSiO_3$ during charging and discharging process, which makes the composite electrode material have more excellent electrochemical performance than CNTs. On the other hand, synergizing the advantageous properties of CNTs and other active materials to improve the conductivity and stability of composite electrode materials comprehensively[14]. Wang[16], coated CoS nanoparticles on CNTs' surface by hydrothermal methods to manufacture CoS/CNTs composite electrode materials, which were discovered, under the synergistic effect of both CoS and CNTs, could reach 780 mAh/g specific charge/discharge capacity under a 0.1 A/g current density for 50 cycles. This is on account of the fact that the high capacity of CoS and high conductivity of CNTs can compensate for the poorer cycling stability and multiplicity performance of CoS to a certain extent, and composite electrode materials can perform higher electrochemical properties under the synergistic effects of both.

However, CNTs still have certain flaws when served as composite electrode materials. Currently common CNTs composite electrode materials, such as CNTs/transition metal oxides, CNTs/tin-based composites and CNTs/silicon-based composites, have a high specific capacity when used as anodes, but the first-time irreversible capacity is still high and relevant cycling stability is still poor too. This is attributed to the potential poor binding, difficulty in uniform dispersion, and susceptibility to agglomeration during the complexation of CNTs with other active materials[17]. Consequently, the problems, that may occur during the preparation of CNTs composite electrode materials, can be avoided from adjusting the structural parameters of CNTs and modifying the CNTs[18].

To be concluded, CNTs are able to be combined with substantial active electrode materials producing composite electrodes, thereby substantially enhancing the electrochemical performances of electrodes. On the other hand, these materials are still disadvantageous in terms of first irreversible capacity and cyclic stability. Hence, future researches should focus on optimizing CNTs' structural parameters and surface decorations to prompt overall performances and the applications of composite electrode materials.

2.3. Carbon nanotubes as flexible electrode materials

The high specific surface area and excellent chemical stability of CNTs can ensure the completeness of electrode structures during working periods; the ultra-high electrical conductivity can prompt the electrochemical properties of electrodes; the wonderful flexibility can, to a certain extent, inhibit the inevitable volume changes of electrode materials during charging and discharging processes. As a consequence, CNTs are optimal materials making flexible electrode materials. The current approaches to the applications of CNTs in this field fall into two main categories. Most commonly, CNTs are composited with flexible substrates to prepare flexible electrode materials. Among them, CNTs with ultra-high conductivity can provide excellent electron/ion transport channels and abundant lithium-ion reactive sites, while flexible substrates can ensure good mechanical supports. Zhang[19], conduct CNTs@SnO_2/SnO/Sn flexible composite anodes by depositing CNTs and SnO_2/SnO/Sn composite layers on a nickel foam skeleton that are able to provide better mechanical support using electrodeposition and anodic oxidation. Tests demonstrated that lithium-ion batteries' capacity fitting with this anode can achieve up to 1,260 mAh/g, as well as a 99% Coulombic efficiency. This is attributed to the fact that CNTs with ultra-high conductivity can not only provide excellent transport channels targeting at electrons or ions, but also mitigate SnO_2/SnO/Sn systems' volume change during repeated embedding/de-embedding of lithium ions, thus enabling lithium-ion batteries to exhibit more excellent electrochemical performances. Another method is to prepare CNTs directly into flexible electrode materials. Since those produced flexible electrode materials have excellent mechanical and electrical properties, this method is of high value for application in the field of flexible

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energy storage. Zhang[20], oriented and assembled TiO_2 nanofibers with functionalized CNTs to form CNTs/TiO_2 flexible composites, and the composite electrodes were tested to have a reversible capacity of 150 mAh/g under a current density of 16.7 mA/g for 100 cycles. This is due to the fact that TiO_2 nanofibers and functionalized CNTs are structurally interwoven with each other, which not only inhibits the agglomeration of TiO_2 nanofibers, but also promotes electrons/ions' diffusion, thereby enabling these flexible electrodes to still be in a position to ensure a high cycling performance and reversible capacity. Due to the late start of researches on flexible electrode materials, there is still much room for improvement, like developing high-performance CNTs/flexible composite electrodes, functionalized modifying CNTs for surface controllability and establishing a standardized evaluation system for flexible batteries to evaluate their performances.

All in all, CNTs are ideal for flexible electrode materials because of their high specific surface area, brilliant electrical conductivity and remarkable flexibility. According to the applications of flexible electrodes, CNTs can be compounded with flexible substrates to provide positive electron/ion transport channels and mechanical support, thereby significantly enhancing the electrochemical performances and cycling stability of electrodes. Meanwhile, CNTs can further improve the electrochemical performances of electrodes by combining with other active materials. Moreover, since the researches on flexible electrode materials are carried out lately, there is still a need of in-depth studies on prompting the performances of composite electrodes, functionalized modifying CNTs, and establishing performance evaluation criteria of flexible batteries, in order to push the developments and practical applications in this field.

3. Conclusion

CNTs have become an optimal material for enhancing the energy storage performances of lithium-ion batteries thanks to their peculiar structural features and excellent physicochemical behaviors. Hence, not only can CNTs be used directly as an electrode material, but it can also be compounded with other active electrode materials or developed as flexible electrode materials. However, CNTs still face the problems of large irreversible capacity loss during the first time, poor cycling stability and high preparation cost in practical applications. As a result, future researches need to further optimize the structural designs and surface modifications of CNTs and develop efficient and low-cost preparation processes to prompt their comprehensive performances in lithium-ion batteries, which are important directions to push these fields forward. These studies will bring new opportunities for lithium-ion batteries and even the entire field of energy storage, expecting to lay the foundation for the realization of more efficient and stable energy storage technology.

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