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Research progress of nano-modified materials for positive electrode of lithium-ion battery

Sirong Ren

School of Metallurgy and Environment, Central South University, Changsha, 410083, China

8204201328@csu.edu.cn

Abstract. Energy is an essential element in human production and life. In the context of today's energy shortage and increasingly serious environmental problems, electric vehicles have gradually begun to occupy the mainstream market, and improving the performance of electric vehicle batteries has become a hot topic for researchers. Today's electric cars generally use lithium-ion batteries. In this paper, the research progress of nano-scale material modification of lithium-ion battery cathode materials was explored, especially the modification of LiFePO4 and NCM ternary materials. For LiFePO4, the preparation process of nanoscale LiFePO4 was explored. Carbon nano-modified materials, such as nano-graphite, CNCs, and modified LiFePO4 cathode materials are also mentioned. For NCM ternary materials, the oxide nanomaterials, lithium salt nanomaterials, and carbon nanomaterials modified ternary cathode materials were explored. Among them, the oxide nanomaterials include Al2O3 and SiO2, the lithium salt nanomaterials include LiAlO2, LiNbO3, Li2TiO3, and Li2ZrO3, and the carbon nanomaterials include CNTs, graphene and graphene-oxide SnO2. After investigation, it was found that these nano-scale modified materials can improve the electrochemical performance of lithium-ion battery cathode materials.

Keywords: nanomaterials, lithium-ion battery, cathode, modification.

1. Introduction

Energy plays an important role in the production and life of human beings. In the course of previous historical development, the energy used by human beings is divided into three stages. The first stage is the raw biomass fuel energy, such as wood, straw, and so on. The second stage is the coal period, and the steam trains and steamships in the Industrial Revolution used coal as energy. The third stage is the oil and natural gas period, when the invention of the internal combustion engine in the post-industrial era, and the rise of fuel vehicles also make the widespread use of oil energy [1]. In the context of the shortage of fossil energy, people have to seek cleaner and sustainable new energy. At the same time, environmental problems are becoming more and more serious, and greenhouse gas emissions have become the focus of attention [2]. Vehicle exhaust emissions are also a key part of the environmental problem, and replacing traditional fuel vehicles with electric vehicles is also one of the ways to alleviate the emission problem. Many governments, such as Germany, France, the United Kingdom, etc., have introduced relevant policies [3]. Lithium-ion batteries are widely used in electric vehicles, and how to

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improve battery performance has become a key issue in the development of electric vehicle batteries.

Modification of the positive and negative electrodes of the battery is an effective way to increase the performance of the battery. For the positive electrode of the battery, in addition to investigating novel materials to provide higher performance and change the positive electrode structure of the battery, modifying the positive electrode of the battery is also an effective way to improve its electrochemical performance. There are many kinds of modified materials, such as elemental, oxide, salt, etc., and the different structures and particle sizes of the modified materials will also affect the modification effect. Nowadays, researchers are also focusing on the modification of lithium-ion battery cathode materials by nano-scale modified materials. Lithium iron phosphate and NCM ternary materials are the commonly used cathode materials for lithium-ion batteries, which have a large application market and a good application prospect. The use of nano-modified materials to modify lithium iron phosphate and NCM ternary materials can provide ideas for improving their electrochemical properties so that these two materials have a better use.

In this paper, the research progress of the modification of lithium iron phosphate and NCM ternary materials will be explored, and the electrochemical properties of nano-modified materials before and after modification of these two materials, especially the charge-discharge capacity and cycle performance will be compared. Through these comparisons, the authors understand the common types of nano-modified materials and their role in material modification.

2. Modified lithium iron phosphate cathode material

As a lithium ion battery cathode material, LiFePO4 has been applied to the market, but its low conductivity and Li+ diffusion performance have become the main factors hindering its development. Nanomaterials have the characteristics of surface effect, small size effect, and quantum size effect. Therefore, it has a large specific surface area, high surface activity, and short ion diffusion path, which can improve the lithium ion removal and embedding ability of lithium ion anode materials and extend the cycle life of batteries [4]. At present, there are many nanomaterials that can modify LiFePO4 cathode materials, the most important of which is carbon nanomaterials. The preparation of nano LiFePO4, modification based on carbon nanomaterials, and modification based on other materials will be introduced.

2.1. Preparation of nano $LiFePO_4$

Researchers have used a number of methods to prepare nanostructured LiFePO4, such as solid phase, microwave synthesis, hydrothermal, coprecipitation and sol-gel, spray drying, etc.

Among all the solid phase methods, the self-propagating high-temperature synthesis process has solved the problems of high energy consumption and impure product of the ordinary solid phase method. Compared with the ordinary solid-phase synthesis method, the self-propagating high-temperature synthesis method has lower energy consumption, a short production cycle, and high product purity [5,6], so it is a relatively successful synthesis process at present. LI et al. prepared nano-LiFePO4 materials by self-propagating high-temperature synthesis process and conducted morphology analysis and electrochemical performance research on them [7]. The results of morphology analysis showed that the synthesized LiFePO4 was spherically distributed, with an olivine structure, and the particle size distribution between 50 and 100 nm, which met the requirements of nanomaterials. The electrochemical performance test shows that the first specific discharge capacity of the synthesized nano-LiFePO4 material was 109.3 mAh/g at 0.1 C, and the capacity retention rate is 88.7% after 50 cycles, which reflects the characteristics more conducive to Li+ removal and embedding and better cycling performance.

In the preparation of nano-scale materials for lithium-ion batteries, the dispersion problem is often encountered in the slurry, which greatly reduces the processability of the battery and makes the battery performance not effectively improved. Therefore, additives are often used in the preparation process. LIU et al. used polyvinylidene fluoride (PVDF) and terpene resin (TX) as binary binders to improve the dispersibility and cycling stability of nanoscale LiFePO4 cathode materials [8]. The morphology and electrochemical properties of the prepared materials were analyzed. The capacity retention rates of

PVDF, PVDF/3%TX, and PVDF/10%TX after 60 cycles at C/2 and 55 °C were 85.9%, 93.4%, and 70.1%, respectively. This study proves that the right proportion of binary adhesives can improve material properties.

2.2. Modification based on carbon nanomaterials

At present, most of the modifications of nano-LiFePO4 materials use carbon nanomaterials, and carbon nanomaterials with different structures have different effects on material modification. At present, the modified materials studied are nano-graphite, carbon nanocages, nano-hollow carbon and so on.

HU et al. synthesized spherical LiFePO4 materials coated with nano graphite by using wet ball lapping and spray drying methods [9]. The results of this study show that the composite material with 0.75% nano graphite mass fraction has the best electrochemical performance, the specific capacity was 160.9 mAh/g at 0.1 C, and the specific capacity is 120.5 mAh/g under high magnification at 5 C, showing a good specific capacity maintenance rate.

FENG et al. prepared LiFePO4/CNCs composite cathode materials with particle sizes ranging from 10 nm to 25 nm using carbon nanocages (CNCs) as the carrier [10]. The electrochemical test results show that the initial specific discharge capacity reaches 163 mAh/g at 0.1 C. The specific discharge capacities at 15 C and 30 C magnifications are 96 and 75 mAh/g, respectively. After 200 cycles at 15 C, the specific discharge capacity remained at 92 mAh/g. These results show that LiFePO4/CNCs composite anode material has excellent magnification performance and cycle stability.

Using lithium phosphate (Li3PO4) nanospheres as a template and precursor, LU et al. successfully synthesized carbon-coated LiFePO4 nanospheres (LFP@C HSs) [11]. At the highest magnification 5 C, the capacity of LFP@C HSs remains at 101.4 mA·h−1·g−1. At a current density of 1C, LFP@C HSs retained 92.5% of its initial capacity after 500 cycles. Overall, the material exhibits excellent cyclic properties.

3. Modified NCM ternary cathode material

NCM terpolymer is an oxide layer material that integrates the advantages of lithium cobaltate, lithium nickelate, and lithium manganate, and its composition is $LiNi_xCo_yMn_zO_2$(x+y+z=1). Among them, Ni is the main component and is considered to be the main electrochemically active substance, and the appropriate use can improve the capacity of the positive electrode material. Co in the material can improve the rate performance of the battery, inhibit the disorder of the ion arrangement of the transition metal (cation arrangement), reduce the ohmic impedance, and improve the conductivity. As a non-electrochemically active substance, Mn plays a supportive role in the structure, maintaining the layered crystal structure of the material when lithium ions are embedded and removed, improving the cycling and thermal stability [12]. According to the difference in the proportion of the three transition metal elements, the NCM ternary material is divided into nickel-manganese equivalent type and nickel-manganese unequal type. For example, NCM424 and NCM111 are nickel-manganese equivalent materials, while NCM811, NCM721, and NCM622 are nickel-manganese unequal materials [13]. In recent years, the modification of NCM ternary materials by nanomaterials has become an effective method to improve their properties. The researchers coated or doped NCM ternary materials, among which the main oxide nanomaterials, lithium salt nanomaterials, and carbon nanomaterials doping and coating modification. Next, the author will introduce the current NCM ternary material modification from three aspects: oxide nanomaterials, lithium salt nanomaterials, and carbon nanomaterials.

3.1. Modification based on oxide nanomaterials

As far as the current research results are concerned, the modification of NCM ternary materials by nano-oxide is indeed an effective modification method. At present, the oxides used in the modification are mainly Al_2O_3, SiO_2, etc., and most of them belong to the coating modification. Through the coating, the side reaction degree between the electrolyte and the cathode material is reduced, so as to improve the material performance.

WANG et al. prepared nano-Al_2O_3 coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ ternary cathode material by a solid phase coating method [14]. The electrochemical test confirmed that compared with the uncoated material, the initial discharge capacity of the battery was increased from 159 mAh/g to 162.57 mAh/g at 0.1 C after the mass fraction of 0.1% nano-Al_2O_3 coating. After 35 cycles, the capacity retention rate of the battery increased from 74.38% to 94.89%. Nano-Al_2O_3 coated materials showed stronger conductivity, higher specific discharge capacity, better cycle stability and rate performance. TIAN et al. explored a simpler and more efficient way to modify NCM materials with nano-Al_2O_3 [15]. Nano-Al_2O_3 slurry was prepared with high-purity Al_2O_3 as raw material and ammonium polyacrylate as a dispersant, and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ was coated. During the study, a relatively stable nano-Al_2O_3 slurry was obtained, and the morphology and electrochemical properties of the material before and after coating were studied. The electrochemical test confirmed that the initial discharge capacity of the battery increased from 163.41 mAh/g to 172.26 mAh/g at 1 C after being coated with 0.1% nano-Al_2O_3. After 100 cycles, the battery capacity retention rate increased from 75.61% to 82.95%. The modified nano-Al_2O_3 coating material showed better cycle stability and better rate performance. At the same time, compared with the common solid phase coating method, the coating layer with uneven thickness can be obtained by using nano-Al_2O_3 slurry. The thinner Al_2O_3 coating layer cannot effectively inhibit the side reaction between the organic electrolyte and the positive electrode material in the lithium-ion battery, and the thicker coating layer is easy to hinder the removal and embedding of lithium ions, and will also reduce the conductivity of the positive electrode material. Therefore, the uneven thickness of the coating layer can achieve a certain balance between the two to a certain extent and can improve the electrochemical performance of the material.

CHEN's et al. used nanoscale SiO_2 with a mass fraction of 0.5% to coat and modify $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523), and analyzed its morphology and electrochemical properties [16]. Although the structure and morphology of NCM523 were not significantly changed after nano SiO_2 coating, the rate performance, cycle performance, and thermal stability of NCM523 after coating were significantly improved. After 100 cycles at 0.1 C, the capacity retention rate increased from 68.0% to 82.5% after 0.5% nano-SiO_2 coating.

3.2. Modification based on lithium salt nanomaterials

Lithium salt nanomaterials are also common materials for the modification of NCM ternary materials. The research proves that lithium salt nanomaterials can also improve the electrochemical performance of NCM ternary cathode materials. Currently used lithium salt nanomaterials are $LiAlO_2$, $LiNbO_3$, Li_2TiO_3, and Li_2ZrO_3.

WANG et al. prepared the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM111) cathode material covered by nano-$LiAlO_2$ with a mass fraction of 3% by solid phase coating method [14]. The electrochemical test shows that the specific capacity of primary discharge increased from 159 mAh/g to 164.85 mAh/g before and after coating. Nano-$LiAlO_2$ coated materials showed higher specific discharge capacity and rate performance. However, compared with the nano-$LiAlO_2$, the coating of nano-Al_2O_3 made the material exhibit better electrochemical properties.

ZUO et al. explored the surface coating modification of $LiNi_{0.9}0Co_{0.05}Mn_{0.05}O_2$ (NCM90) cathode material using nano-sized $LiNbO_3$ at a high potential interval (3.0-4.5 V) and low potential interval (3.0-4.3 V) and carried out morphology analysis and electrochemical performance analysis [17]. The results of morphology analysis show that the chemical bond between the $LiNbO_3$ coating layer and NCM ternary material was stable. The electrochemical performance analysis showed that the material capacity retention rate of $LiNbO_3$ coated with 1% mass fraction increased from 63.04% to 75.61% after 200 cycles under the test conditions of 3.0-4.5 V and 250 mA/g. Under 3.0-4.3 V and 50 mA/g test conditions, after 200 cycles, the material capacity retention rate before and after coating of $LiNbO_3$ with a mass fraction of 1% increased from 51.12% to 69.38%. The results show that due to the low intrinsic electron conductance of the coating layer, the effect of the coating layer on the magnification performance and the diffusion coefficient of lithium ions was different in different potential intervals. However, in general, the nano-$LiNbO_3$ coating modification inhibited the fragmentation of the material and thus improved the electrochemical properties of the material.

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LI et al. synthesized nano-Li_2TiO_3 (LTO), nano-Li_2Zro_3 (LZO), and nano-Li_2TiO_3-Li_2ZrO_3 composite (LTZO) coating surface coated with modified $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) material by wet chemical method and heat treatment process [18]. The morphology and electrochemical properties were analyzed. According to the electrochemical test, among the three-surface modified and unmodified materials, the NCM811 material modified by nano LTZO showed the best electrochemical performance. At 1 C, after 150 cycles, the capacity retention rate of LTO@NCM811 increased 75.64% from 68.86% compared to unmodified NCM811, LZO@NCM811 increased to 80.94%, and LTZO@NCM811 increased to 83.04%. Among the three modified materials, it has the highest reversible capacity and the best cycle performance.

3.3. Modification based on carbon nanomaterials

In addition to nano-oxide and nano-lithium salt materials, nano-carbon materials are also one of the materials commonly used for NCM ternary positive electrode modification of lithium-ion batteries. When nanocarbon materials are combined with NCM, they often exhibit excellent electrochemical properties.

PAN et al. prepared NCM622/CNTs composites by evenly mixing single-wall CNTs slurry with $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622) powder without adding adhesive and conducted morphology analysis and electrochemical tests. [19] It was found that the mass fraction of CNTs had a significant effect on the electrochemical properties of NCM622/CNTs composites, such as specific discharge capacity, cycle stability and rate performance. The experiments showed that NCM622/CNTs composites with a mass fraction of 2% showed high specific discharge capacity (168.9 mAh/g), good magnification performance, and strong cyclic stability (capacity retention rate of 85.6% after 100 cycles) at a magnification rate of 0.5 C.

ZHANG et al. prepared CNTs/NCM811 composites and graphene/CNTs/NCM811 composites by coating graphene and carbon nanotubes on $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) using ultrasonic technology and liquid phase aggregation method and analyzed and compared the morphology and electrochemical properties of the three composites [20]. At 1 C, after 100 cycles, the capacity retention rate of uncoated NCM811 was 77.6%, that of 0.5%-CNTs/NCM811 was 93.2%, and that of graphene/CNTs/NCM811 was 93.9%. It is concluded that under the same conditions, graphene/CNTs/NCM811 composites have the best cycling performance.

MA et al. prepared the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material (GO-SnO_2-NCM111) coated with graphene oxide and SnO_2 by wet chemical method. According to the morphology analysis, the GO-SnO_2 double-coated structure did not destroy the crystal structure of NCM ternary material [21]. According to the electrochemical test results, at 1 C, after 100 cycles, the capacity retention rate of the material after GO coating increased from 74.3% to 90.7%, which had better cyclic performance.

4. Conclusion

In this paper, the research on the modification of $LiFePO_4$ cathode materials and NCM ternary cathode materials using nanomaterials is studied and explored, the types and modification effects of nano-modified materials are analyzed, and the following conclusions are drawn.

Nano-scale modified materials used for the modification of LFP and NCM include oxide nanomaterials, lithium salt nanomaterials, and carbon nanomaterials. The oxide nanomaterials mentioned in the paper include Al_2O_3, SiO_2, and SnO_2; the lithium nanomaterials include $LiAlO_2$, $LiNbO_3$, Li_2TiO_3, and Li_2ZrO_3; and the carbon nanomaterials include CNTs, CNCs, nano-graphite, graphene and graphene oxide. For the preparation of nanoscale $LiFePO_4$, the use of adhesives can improve its electrochemical performance. In this paper, PVDF and TX binders are mentioned, and the two binders combined with the right proportion can improve the electrochemical properties of the materials significantly better than the mono binders. The nano-scale modified materials mentioned in the paper can improve the electrochemical properties of the materials. At the same time, the double-layer nanomaterials have better modification effects than the single-layer nanomaterials, which can better improve the electrochemical properties of the materials.

This paper only summarizes the modification of lithium-ion battery cathode materials by nano-structured modified materials and does not give a detailed description and example of nano-structured cathode materials. Only two cathode materials LFP and NCM are summarized, and other types of cathode materials, such as lithium cobaltate and lithium manganate, are not considered. In the summary of the modification of lithium iron phosphate, only carbon nanomaterials are specifically introduced. Most of the modified materials mentioned in this paper are in the laboratory stage and cannot be used in large-scale production at present.

In the future, it is expected that more types of nanostructured modified materials will be applied to different types of positive and negative battery materials. It can also start with changing the structure of materials, especially carbon nanomaterials, which still have a lot of room for development. The modified material of multi-material composite is also a broad research direction, which makes the modified material more diversified. Exploring solutions that can further integrate nanomaterials into production will benefit society as a result of the experiment.

References

[1] Smil V. 2018 Energy and Civilization [M]. United States of America: Penguin Random House.
[2] Mohammadzadeh N. et al. 2021 Applied Energy 288 116471.
[3] Rezvani Z, Jansson J, Bodin J. 2015 Transport Res Part D: Transp Environ; 34:122–36.
[4] Tang K. M. et al. 2009 Micronanoelectronic Technology. 46(2): 84-90.
[5] Sun B. X. et al. 2015. Powder metallurgy industry, 25(6): 40.
[6] Zhong H. H. et al. 2017 Powder metallurgy industry, 27(1): 1.
[7] Li H. et al. 2018 Metallic Functional Materials, 25(5): 1-6.
[8] Liu S, Zhong H, Zhang C, et al. 2019 Composite Interfaces, 26:11, 1013-1024.
[9] Hu J. J. et al. (2016) Contemporary chemical industry, 45(2): 244-246.
[10] Feng R. et al. (2014) Chinese Academy of Sciences, 72, 653-657.
[11] Liu J. J. et al. (2019) Ionics 25:4075–4082.
[12] Wang P. et al. (2022) Journal of Southwest University (Natural Science Edition), 44(03):29-43.
[13] Zhang Y. et al. (2022 Energy Storage Science and Technology,11(06):1693-1705.
[14] Wang Z. et al. Journal of Liaocheng University (Natural Science Edition). 1-10.
[15] Tian P. et al. Inorganic Chemicals Industry. 1-12.
[16] Chen C. et al. 2017 Journal of Alloys and Compounds 709 708-716.
[17] ZUO J. X. 2022 Study on surface modification of Ni-rich cathode material LiNi0.90Co0.05Mn0.05O2 by LiNbO3. Xi'an, Shanxi, P. R. China. Xi'an University of Technology.
[18] Li J. et al. 2020. Solid State Ionics 349 115292.
[19] Pan Y. B. 2021 Interface modification of NCM/CNTs composite cathode and its application in lithium metal batteries. Wuhan, Hubei, P. R. China. Huazhong University of Science and Technology.
[20] Zhang S. X. 2021 Synthesis and properties of high nickel ternary cathode material LiNi0.8Co0.1Mn0.1O2 coated with graphene/CNTs. Changsha, Hunan, P. R. China. Central South University of Forestry and Technology.
[21] Ma Y. X. et al. 2019 Journal of Nanomaterials 2019, 7586790.