DOI: 10.54254/2755-2721/56/20240637

Application of nanomaterials in lithium-ion batteries

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Abstract. With the rapid development of society, lithium-ion batteries (LIBs) need higher performance to meet its application in different fields. Nanotechnology has been used in the research of high-performance LIBs for many years, due to its improvement of physical, chemical and electrical properties of materials. The application of nanomaterials in LIBs electrodes is the main research direction, mainly focusing on the structural characterization and electrochemical performance analysis of electrode materials. Therefore, in this research, some recent studies on nanoelectrode materials in LIBs are analzyed, focusing on demonstrating the excellent properties brought about by the unique structure of nanoelectrode materials, and their preparation methods are also briefly introduced. The results show that nanoelectrode materials have a great contribution to improving the cycle performance and rate capacity of LIBs. The prospect is expounded through the role of nanotechnology in the application field of LIBs in the future and the changes it may bring.

Keywords: Lithium-Ion Batteries, Nanomaterials, Electrodes.

1. Introduction

Energy storage technology has attracted considerable public attention because of the shortage of power resources caused by social development and the desire for efficient use of electric energy. In addition, the development of sustainable energy requires advanced energy storage technology as a basis to alleviate the non-negligible pollution caused by the excessive exploitation and use of fossil energy. Currently, one of the widely used energy storage technologies is lithium-ion batteries (LIBs), which has a significant impact on industries including electric transportation, medical care and portable electronic devices. Electrodes, separators, and electrolytes are the main components of LIBs. For the charging process of LIBs, lithium ions are removed from the positive electrodes and inserted into the anode, while the electrons flow along the external circuitry in the opposite direction of movement to the lithium ion [1]. During the discharge process, the movement direction of lithium ions and electrons is the embodiment of the inverse of the charging process. The deintercalation and intercalation of lithium ions directly affect the functionality of lithium-ion batteries. Figure 1 depicts the fundamental design of a LIBs.

LIBs have been in commercial use since the 1990s. Excellent characteristics such as high energy density, long cycle life, light weight, and no memory effect make LIBs more practical for applications relative to other types of batteries. Therefore, LIBs occupy a dominant position in the market and have important research value. In particular, the acceleration of social development has led to an increase in the application demand for LIBs. The most obvious example is the continuous expansion of the electric vehicle market in recent years. Referring to the number of electric vehicle sales in China from 2015 to 2019, the annual growth rate is 45.7% [2]. Behind this trend is that the current demand pressure of LIBs to meet market applications is gradually increasing, and further work on developing high-performance LIBs is required.

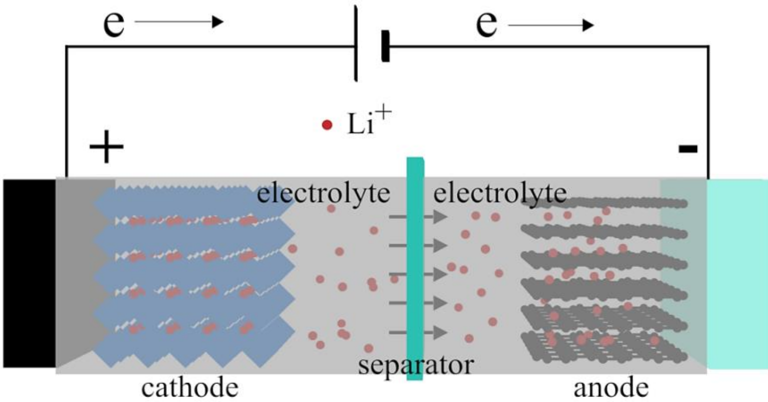

Figure 1. Illustration of the LIBs charging principle (Picture credit: Original).

A potential solution for the creation of high-performance LIBs is nanotechnology, because previous studies have shown that nanomaterials have a good ability to improve the performance of LIBs. A major field of application of nanomaterials in LIBs is electrodes. The nanostructures alter the electrochemical and physical characteristics of the electrodes. Nanostructured electrodes have larger surface area and specific surface area, while surface lithium storage is determined by surface area, so nanoelectrodes have stronger lithium storage capacity, which is conducive to the improvement of the energy density of LIBs, and to improve the current situation that the energy density of LIBs is much lower than that of gasoline [1, 3]. The nanometer size enables electrodes with short diffusion paths, large surface areas, and fast lithium ions diffusion rates, which can enhance the charge-discharge performance of LIBs [3], [4]. In addition, nanomaterials can improve the toughness and mechanical properties of LIBs electrodes, thereby reducing the possibility of electrode fracture during charge and discharge and enhancing the safety of LIBs. The rest of this paper will review the recent research on the application of nanomaterials in LIBs electrodes, and then gives an outlook on the future and impact of nanotechnology. It is hoped that it can give directions for the future development of LIBs.

2. Application of nanomaterials in cathode

Lithium iron phosphate ($LiFePO_4$) battery is a commonly used LIBs at present, the best example is the blade battery used by BYD. $LiFePO_4$ as cathode materials for batteries has the advantages of low cost, long life and good thermal stability, but it also has its own defects, such as low ion diffusion rate and poor conductivity, which hinder the further development of lithium iron phosphate batteries in the future [5]. Pan et al. used Fe powder and a certain quality of carbon black as raw materials to prepare $LiFePO_4$ particles with a secondary cross-linked porous nano-micro structure by a two-step method of co-precipitation-carbothermal reduction, which improved the defects of $LiFeO_4$ as a positive electrode material [6]. The $LiFePO_4$ nanoparticles in this structure do not appear re-agglomerated, but are connected to each other by the residual carbon after calcination and have clear boundaries. Therefore, the material has a large specific surface area and high porosity, which provides a larger area for the contact of the cathode with the electrolyte, so facilitates the diffusion and desorption/embedding reactions of lithium ions. Residual carbon also increases the charge-transfer capability and lithium ion diffusion kinetics. The improvement of these characteristics makes the LiFePO4 cathode show excellent rate capacity and cycle performance, which can achieve a reversible capacity of 124.95 mAh/g at a rate of 20 C, and a retention rate of 87.56% of the specific capacity after 1500 cycles at a rate of 10 C (131.43

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mAh/g initial discharge capacity). In addition, low cost and simple preparation method are obvious advantages, making this material possible for process production. Cao et al. prepared a (010)-manifest $LiFePO_4$/carbon nanofiber electrode material, and the use of poly(vinylpyrrolidone) to promote the formation of N-doped amorphous carbon frameworks and (010)-face-orientated $LiFePO_4$ nano-crystals is noteworthy [7]. $LiFeO_4$ nanoparticles are evenly attached to carbon nanofibers or inserted within carbon nanofibers. This structure provides the material with high porosity, large specific surface area, and certain flexibility. Consequently, the electronic conductivity and the diffusion kinetics of Li ions are enhanced. In addition, highly conductive nitrogen doping enhances the electronic conductivity of the material. Therefore, the performance of $LiFeO_4$ is improved. In addition, the method avoids the use of binders and conductive agents potentially reducing the cost and quality of the cathode, and can also be instructive for other free-standing (010)-oriented $LiMPO_4$/CNF composites.

Nanosized vanadium oxides are another widely studied cathode material for LIBs owing to their larger theoretical capacity based on low procurement cost and abundant abundance in nature. Huang et al prepared V_2O_5 nanocrystals by solution precipitation method [8]. The crystal is annealed at a suitable temperature to generate oxygen vacancies, which leads to an increase in electronic conductivity. In addition, oxygen vacancies can reduce the volume expansion/shrinkage stress caused by lithium ion deintercalation/intercalation during charge and discharge, so the electrode exhibits better cycle performance. Jayalakshmi et al prepared V_2O_5 nanoparticles by combustion method and compared them with micro-sized V_2O_5, which can better demonstrate the advantages of nanotechnology [9]. V_2O_5 nanoparticles have mesoporous properties, making them have greater porosity and specific surface area. This means that V_2O_5 nanoparticles have better cycle performance. Therefore, in the cycle performance test at 0.1 C rate, the initial discharge capacity (290 mAh/g) of V_2O_5 nanoparticles is higher than that of micron-sized V_2O_5 particles (240 mAh/g), and the capacity retention rate is also the same result. It is worth noting that the Coulombic efficiency of V_2O_5 nanoparticles is more stable than that of micron-sized V_2O_5 particles, but the Coulombic efficiency of the two did not show the expected value. In addition, the rate capacity is not satisfactory, the discharge capacity of V_2O_5 nanoparticles at 2 C rate is only 52 mAh/g, but it is still stronger than that of micron-sized V_2O_5. Wu et al. used uniform rotation hydrothermal one-step synthesis to synthesize two-dimensional V_6O_{13} nanosheets [10]. The nanosheet structure improves the electrochemical performance of V_6O_{13}. In addition, the simple and fast manufacturing method is worth promoting. However, low-dimensional nanostructures will cause V_6O_{13} electrodes to suffer structural volume changes and damage. To solve such problems, Liang et al. used V_6O_{13} nanosheets to assemble into three-dimensional micro/nanostructured materials [11]. The material has regular gaps between the nanosheets, which effectively reduces the expansion degree of the electrode caused by deintercalation/intercalation of lithium ions, so improve the stability of the cathode structure.

In general, nanotechnology is very important for lithium iron phosphate and vanadium oxide as excellent LIB cathodes, because it can effectively solve the defects of the materials when they are used as electrodes. Although high theoretical specific capacity is an advantage of vanadium oxide electrodes for next-generation high-performance LIBs, the current cycle performance and rate capacity of vanadium oxide electrodes are not as good as lithium iron phosphate electrodes, which limits its practicability. Therefore, nano-vanadium oxide electrodes still need more research.

3. Application of nanomaterials in anode

Silicon is the ideal material to use for the anode of LIBs, according to its high theoretical specific capacity (4212 mAh/g at high temperature and 3579 mAh/g at room temperature), low redox voltage, high abundance in nature, and environmental friendliness [1, 12]. However, the volume expansion of silicon is as high as 300% during the charge-discharge process of LIBs, resulting in poor cycle performance and limiting the application of silicon anodes [1]. Nanotechnology can provide a feasible solution to the problem of silicon and improve the utilization rate of silicon anodes.

Wang et al. developed a Si/C nanocomposite in which a large number of interconnected silicon nanograins/clusters were encapsulated within a carbon-coated mesoporous silicon shell [13]. This structure efficiently reduces the change in silicon volume during battery charging and discharging, and

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enhance the electrode reaction kinetics, so the rate capability and cycling performance are greatly improved, realizing a reversible capacity of approximately 1040 mAh/g for 500 cycles at a current density of 2 A/g with a retention rate of 90.4%. However, the low initial Coulombic efficiency (55%, at 0.1 A/g) is a non-negligible problem. Xu et al. used plasma-enhanced chemical vapor deposition to prepare Si/SiOx nanofilms with a thickness of 20 nm [14]. The nanofilm can form a rigid artificial solid electrolyte interphase film, reducing the impact of volume changes. In addition, the initial discharge specific capacity is as high as 4000 mAh/g at 0.05 C rate, Outstanding rate capacity (1773.8 mAh/g discharge capacity at 10 C rate), good cycle performance (discharge capacity of 1490.4 mAh/g after 200 cycles at a rate of 0.5 C) are noteworthy. However, there is still the problem of low coulombic efficiency in the initial stage of charging and discharging. Du et al. prepared Si/SiC nano-composites with hierarchical porous structure [15]. The robust heterogeneous structure, porous structure and SiC nanoparticles can inhibit the generation and expansion of cracks and even electrode fracture caused by volume change of silicon during charging and discharging of the electrode. Most notable are the material's relatively high initial Coulombic efficiency (80%) and application potential (assembled coin-type full cells with superrate performance and excellent cyclability). Wang et al. developed a free-standing anode composed of silicon nanoparticles and carbon nanofibers [16]. It is found that the content of the precursor polyethylene oxide-polypropylene oxide-polyethylene oxide triblock copolymer in the preparation process has an impact on the initial Coulombic efficiency of the anode material, up to 85% of the initial Coulombic efficiency.

4. Prospects

Nanotechnology has brought tremendous changes to the field of LIBs, and it is an inevitable trend to further lead LIBs to new heights. In the future, there is a huge possibility that nanotechnology can provide a viable solution to the challenges faced by LIBs. The improvement of electrodes by nanotechnology is expected to greatly increase the energy density of current LIBs several times. In addition, the problems that limit the application of LIBs, such as battery life, safety, and charging and discharging time, will also be resolved.

The overall improvement of the performance of LIBs will make related application products more competitive, and the application market of LIBs will be expanded. For example, the increased endurance, improved safety performance and shortened charging and discharging time will help electric vehicles squeeze most of the market for gasoline vehicles. At the same time, the sustainable green economy will also be affected, and high-performance LIBs will improve the energy storage of renewable energy, and the energy utilization rate will be greatly improved. Finally, high-performance LIBs brought about by nanotechnology will bring about changes in all aspects of daily life.

5. Conclusion

Some recent nanoelectrode materials for LIBs are summarized, their advantages and some problems are presented. In general, the unique structure of nanomaterials has made great contributions to the manufacture of high-performance LIB electrodes, and the preparation methods of some nanoelectrodes are also worth learning. After reasonable improvement, it is expected to enable the production of high-performance LIBs electrodes. However, the low initial Coulombic efficiency of nano-anode materials is a direction that needs to be improved in the future. The Prospects section gives impetus for the further development of nanotechnology for LIBs. For high-performance LIBs, nanoelectrode materials are worth studying.

References

[1] Khan F M N U, Rasul M G, Sayem A S M and Mandal N K 2023 *Journal of Energy Storage* 71 108033.

[2] Liu B, Song C, Liang X, Lai M, Yu Z and Ji J 2023 *Energy Policy* 177 113554.

[3] Jiang C, Hosono E and Zhou H 2006 *Nano Today* 1 28-33.

[4] Riyanto E, Kristiantoro T, Martides E, Dedi, Prawara B, Mulyadi D and Suprapto 2023 *Mater. Today Proc.* 87 164-71.
[5] Sun C, Rajasekhara S, Goodenough J B and Zhou F 2011 *J. Am. Chem. Soc.* 133 2132-35.
[6] Pan X, Sun Y, Zhuang S, Sun G, Jiang S, Ren Y, Wen Y, Li X and Tu F 2023 *Vacuum* 212 112258.
[7] Cao Z, Sang M, Chen S, Jia J, Yang M, Zhang H, Li X and Yang S 2020 *Electrochim Acta.* 333 135538.
[8] Huang X, Li X, Chen Y, Mei J, Xu W, Wang L and Peng D 2021 *J. Alloy. Compd.* 887 161360.
[9] Jayalakshmi T, Harini R and Nagaraju G 2022 *Mater. Today Proc.* 65 200-6.
[10] Wu M, Zhu K, Liang P, Yao Z, Shi F, Zhang J, Yan K, Liu J and Wang J 2021 *J. Alloy. Compd.* 877 160174.
[11] Liang F, Zhong S, Zou Z, Zhang S, Geng J, Wu Q, Ling W, Peng X and Gao Y 2023 *J. Alloy. Compd.* 950 169784.
[12] Li P, Hwang J and Sun Y 2019 *ACS Nano* 13 2624-33.
[13] Wang J, Gao C, Yang Z, Zhang M, Li Z and Zhao H 2022 *Carbon* 192 277-84.
[14] Xu G, Zou Y, Lai Q, Tu C, Xiong L, Jin C, Sun F, Li Y, Zhou L and Yue Z 2023 *Solid State Sciences* 143 107281.
[15] Du J, Zhu R, Chen Q, Xie J, Xian H, Zhang J and Zhu J 2023 *Appl. Surf. Sci.* 617 156566.
[16] Wang H et al 2023 *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 671 131653.