Performance Improvement of Nanotechnology in Cathode Materials

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Abstract. The development of battery technology is in full swing. As an important part of battery structure, cathode material is related to a series of electrochemical properties such as battery safety, life, and specific capacity. According to the development of cathode materials, the bottleneck of battery performance caused by various properties of the material itself needs to be broken through. In many research directions of battery modification, the nano crystallization of cathode materials has the advantages of shorter ion transport distance, more active sites, more stable material structure and physical and chemical properties by virtue of its own structural advantages, which realizes more efficient battery electrochemical performance and solves some technical bottlenecks that traditional cathode materials cannot overcome. Therefore, this paper summarizes the improvement of cathode materials and battery performance brought by the multi-dimensional application of nanotechnology, and briefly expounds the prospects and challenges of nano-cathode materials.

Keywords: Nanotechnology; cathode material; electrochemical performance.

1. Introduction

Today, the battery market's requirements for high-performance products continue to increase. Among them, secondary batteries (such as rechargeable Li^+ batteries, Na^+ batteries, etc.) stand out due to their excellent cost control and conversion efficiency. In the structure of the battery, the electrochemical performance of the cathode material is particularly critical. A large number of related studies have improved the structure or composition of cathode materials, which can effectively improve such performance indicators, (such as ionic conductivity, energy transfer power, etc.) [1]. However, the existing battery products reveal that traditional cathode materials cannot explore higher levels of battery performance defects due to the constraints of their own structure and properties [2]. In the traditional non-nano electrode, the random distribution of conductive additive carbon particles is easy to cause the problem of electron aggregation in the related reaction process, which is because the poor contact of electron connection caused by the uneven distribution of large particle materials. The main reason is that the large particle material cannot be effectively fixed by the adhesive at the required site, thus forming a barrier for traditional materials to continue to break through the electrochemical performance of the battery [3].

The traditional method to solve this problem is to increase the amount of adhesive to achieve the purpose of fixing the conductive additive particles. However, the use of a large number of adhesion agents will increase the resistance. Although it can solve the problem of electron aggregation, the increase of resistance will inevitably have a negative impact similar to the butterfly effect on the electrochemical performance of the battery, such as ion transmission rate. Therefore, Ye Shi et al. developed a nanostructure-supported cathode framework by attaching a conductive polymer gel to $LiFePO_4$ particles using a nanostructure-stabilized layered porous network and efficient ionic conductivity, bypassing the traditional method of increasing the binder. Compared with the solution of traditional materials, the high transmission rate of the positive electrode and the charging and discharging times of the battery are greatly improved while reducing the amount of binder. It highlights the promotion of particle transport by the high conductivity of nano frames and layered porous networks, as well as the effective improvement of battery performance, especially specific capacity and energy density, reflecting the unique advantages of nano cathode materials over non-nanomaterials and traditional electrode materials [3].

Not only in the above cases, so far, but the research on battery modification also using nanomaterials has never stopped. Researchers are keen to explore the effects of material nano crystallization in multiple dimensions and the construction of fully nano cathodes. A large number of research results have also confirmed that the addition of nanomaterials has greatly improved the structure of traditional materials. From the modification of zero-dimensional nanomaterials to the construction of three-dimensional nano-stereoscopic networks, the nano crystallization of cathode materials is gradually solving the problems of material modification and performance improvement that are difficult to overcome by large particles of traditional materials. Moreover, compared with traditional cathode materials, nanomaterials have significant advantages in the modification and preparation of battery cathodes. First of all, as mentioned above, nanomaterials can effectively shorten the ion diffusion path due to their small structure, and can build a multi-dimensional conductive network, thereby improving the utilization rate of active materials and achieving more efficient electron conduction and higher specific capacity [4]. For example, the introduction of carbon materials with a 3D grid configuration as the conductive framework matrix could effectively promote ion diffusion due to its porosity. Secondly, the small size structure of nanomaterials can significantly reduce stress concentration. The porous structure or flexible connection network constructed by nanomaterials has better buffering and inhibiting phase transition advantages for traditional materials in the same dimension [5, 6]. Finally, the specific surface area of nanomaterials is relatively high, which can not only support that it is easier to produce a passivation layer in the electrolyte to protect the cathode material, but also support it as a coating shell to achieve the purpose of further releasing the cathode performance without destroying the traditional material. For example, covering the surface of the cathode material (such as NMC) with a nano-protective coating can greatly enhance the safety and stability of the material while ensuring the electrochemical performance [7]. Therefore, the performance improvement of nanomaterials for traditional cathode materials will have obvious advantages in terms of conductivity, stability, cycle times and life extension of the battery. As the above results, the development of nano-cathode materials is gradually stepping onto the center of the stage of battery technology iteration and building a unique R & D architecture for higher performance battery technology.

The essay will continue the research and development boom of nano-cathode materials and devote itself to discussing the impact of nano-cathode materials on battery performance. Through a brief analysis of the performance defects of traditional materials and a challenging list of traditional structures, the characteristics of the dimensional architecture of nanomaterials are briefly described. The mechanism of improving the structural characteristics of nanomaterials and overcoming the bottleneck of battery technology, as well as the necessary comparison between traditional materials and nanomaterials with different dimensions, are expounded. The specific effects of nanostructures with different dimensions on cathode materials are clarified, and the research status and possible future development of nano-cathode materials are stated.

2. The Main Properties and Basic Classification of Cathode

As a main structure of the capacitor, the positive electrode is responsible for the storage and release of energy during charging and discharging, which plays a key role in the potential development of the battery. The cathode is responsible for receiving electrons in the external circuit during the discharge process, experiencing a reduction reaction in the electrochemical reaction, and acting as an oxidation electrode during the charging process [8]. From the above, the author will briefly describe the main performance indicators and classification of cathode materials, so as to more clearly describe the application of nanotechnology in cathode materials.

2.1. Main performance

To protect the good operation of the battery, the cathode should have the following main properties: In terms of material selection, the cathode material should have as low as possible Fermi level and high potential energy, and can achieve ion repetition and stable embedding, stripping and rapid diffusion. At the structural level, a good cathode should have a certain stability to play a buffer capacity to cope with volume changes or a stable operating capacity under a certain high temperature and high pressure. Under the requirements of electrochemical performance, excellent cathodes can achieve higher conductivity, including ionic conductivity and electronic conductivity. Finally, in order to meet the market demand, the preparation of the cathode needs to ensure a certain cost-effectiveness and meet the requirements of environmental friendliness, and as easy as possible to synthesize to achieve a certain degree of scalability [8]. For all the research on cathode materials, such as lithium-ion batteries and sodium ion batteries, there are electrochemical performance defects in one or several directions, which has led to a series of electrode material modification studies.

In this kind of modification research, researchers need to overcome the electrochemical performance defects of traditional cathode materials, so the research must solve the structural limitation of the material itself. For example, at the lattice structure level, the problem that Li can only diffuse along the interlayer structure in $LiCoO_2$ is caused by the layered structure of the material itself, which leads to inevitable low conductivity defects [9]. Similar structural defects are widespread in traditional cathode materials. For example, the olivine structure of $LiFePO_4$ limits Li^+ to have only one-dimensional diffusion channels, cation mixing is easy to occur in the cycle of high-nickel ternary lithium batteries (such as NMC811), and the problem of Ni^{2+} occupying Li^+ sites is a phase change reaction defect caused by its own structural instability [10]. The above problems of traditional materials are mainly due to the fact that their non-nanometer-sized microstructures are not flexible enough or do not meet the needs, and the latest research has effectively solved the key problem of flexible construction of cathode materials by using smaller nanostructures. Therefore, it is certain that the ability of the cathode is closely related to the microscopic state of the material, its non-nanometer size or structure, and even physical and chemical properties. Meanwhile, more subtle structural design of the weak part of the electrode or the development of a protective system that does not affect the performance of the electrode itself has become the future direction of electrode performance research, and nano-material design provides a very high-quality solution for these two aspects of research.

2.2. Basic classification

At present, the research focus of cathode materials is to solve the related bottleneck problems by exploring different material categories, especially in the fields of energy density and stability. For the structure of traditional cathode materials, it mainly includes different structural forms such as polyanion compounds, layered oxides, Prussian blue-like framework materials and tunnel structure oxides. However, these four basic structures all have one-sided advantages and defects [11]. If we want to make a basic breakthrough on this basis, we need to further modify them by means of doping and nano crystallization.

3. Dimension Characteristics of Nano Cathode Materials

Nanomaterials are nanoscale in at least one dimension, that is, (0.10-100.00nm). According to the microscopic dimension characteristics, they are divided into materials from 0-dimensional to 3-dimensional. The development of nanomaterials and the specific effects of some research results on the electrochemical performance of batteries will be described from different dimensions from this paper.

3.1. Zero-dimensional (0D) nanomaterials

0D nanomaterials are materials with three dimensions at the nanoscale and are also the most famous nanostructures. Its structure is an isolated, point-like entity composed of a pure substance, or a nanomaterial composed of the building units of the substance or combined with the building units of other substances, which lacks spatial extension in any direction [12]. Combined with the small size advantage of the nanomaterial itself, the zero-dimensional nano cathode material has a short transmission path and high transmission rate higher than the traditional cathode material, which effectively improves the rate performance of the battery. At the same time, thanks to the high specific surface area and rich active sites of zero-dimensional nanomaterials, nanoparticles can provide more flexible solutions for customizable modification and doping cathode modification research [13].

The transmission speed between the zero-dimensional nanostructure cathode and the electrolyte is faster than that of the traditional cathode particles, so they provide more secondary irreversible Faraday reactions. This is obviously because the inherent characteristics of zero-dimensional nanomaterials can promote the rapid transport of electrolytes, resulting in higher charge storage and support higher energy density. These advantages will inevitably promote the research and application of zero-dimensional nanoparticles in the field of cathode materials [14]. The layered oxide LiV_3O_8 of sodium ion batteries has been studied a lot, but the conductivity is not good, and the structure is not stable. Xie Lingling 's team used carbon quantum dots to modify the LVO/CQDs composite cathode material by nano chemical method. The uniform distribution of carbon quantum dots on the surface not only makes the material structure more stable but also optimizes the nano-size to improve the conductivity and cycle performance. The LVO/10 % CQDs cathode has an initial discharge capacity of 185.4 mAh/g at a current of 30 mA / g and a capacity of 116.5 mAh / g after 250 cycles. The performance improvement is because the integration of carbon quantum dots enhances the conductivity and reduces the internal resistance. For example, the experimental data prove that the increase in capacitance and the increase in Na diffusion coefficient bring about a breakthrough in electrochemical performance. Zero-dimensional nanomaterials do have advantages for cathode modification [15].

3.2. One-dimensional (1D) nanomaterials

One-dimensional nanomaterials refer to nanostructures with nanometer size in two dimensions and non-nanometer size in the third dimension, including nanorods, nanobelts, nanowires and nanotubes. It is characterized by a high degree of anisotropy, that is, there are significant differences in the physical and chemical properties in the longitudinal (axial) and radial (transverse) directions. In the field of cathode preparation, compared with zero-dimensional nanomaterials, the increase in the degree of nano crystallization in one-dimensional nanomaterials can effectively promote ion and electron conduction. The one-dimensional nano-cathode material has better conductivity at the theoretical level, because the structure is stable and the surface area is large, and the resistance is small, so the active material has more contact points with the electrolyte [14].

In addition, compared with the interface engineering of zero-dimensional nanomaterials for electrode doping or modification, the most important improvement is that the large aspect ratio of the material helps to easily assemble into the link network, making it suitable for flexible device applications, and its large specific surface area. The advantage is also used for the modification of cathode materials. Taking the modification of lithium iron phosphate cathode (LFP) with high relative heat as an example, Jin Zhixian's team prepared carbon-coated LFP-CNT-GQD composites by solvothermal method. This material not only utilizes the characteristics of good conductivity and large surface area of carbon nanotubes to improve the electrochemical performance, but also strengthens the connection between materials through graphene quantum dots. It exhibits a specific capacity of 107.1 mA h g^{-1} at a high rate of 20 C, and the capacity retention rate is as high as 99.4 % after 300 cycles at a current density of 1 C. The experimental results show that CNT and GQD work together to optimize the conductive network, so that the structure of LFP particles is stable during charge and discharge. The carbon coating layer effectively prevents the dissolution of the active material and reduces the volume expansion problem [16].

3.3. Two-dimensional (2D) nanomaterials

Two-dimensional nanomaterials refer to layered materials with nanometer size in one dimension and micron or larger in the other two dimensions. Since Novoselov, Geim and colleagues successfully prepared graphene from graphite with transparent tape in 2004, the research of two-dimensional (2D) materials has been hot. Its structure is divided into three categories: nanosheets, nanoplates and films. The thin layer is more widely used than the other two groups, usually synthesized on different substrates [17]. Compared with the first two dimensions of nanomaterials, the unique advantage of the two-dimensional nanomaterials is the nanoscale layered structure of the material, which provides an opportunity for the plane extension development of nanomaterials. Specifically, at the cathode material level, the layered structure of the two-dimensional nanomaterials provides a higher specific surface area, thus broadening the path of electron or ion transmission and improving the transmission rate of the cell. Meanwhile, the application of layered structure makes the cathode material have more advantages in buffering or volume strain capacity and promotes the formation of covalent bond structure of ions to enhance the chemical stability of the cathode material. Thanks to the characteristics of two-dimensional materials, a team has developed two-dimensional cathode nanomaterials and achieved better electrochemical properties such as excellent capacity, higher power and longer cycle life of Li^+ batteries [18].

In this paper, the characteristics of two-dimensional nanomaterials are discussed by taking graphene as an example. At the structural level, the layered structure of graphene contributes to the covalent structure of p_x and p_y orbitals, which brings excellent mechanical flexibility and structural stability, and buffers the volume change of cathode material during charging and discharging. Existing studies have shown that the graphene flexible film cathode is used for foldable batteries, so that the battery charge and discharge cycle 1000 times the capacity is only attenuated by 10 %, which is significantly better than the traditional cathode battery attenuation. At the same time, the remaining pz orbital free electrons of graphene have a potential zero band gap. The graphene-modified cathode material has a layered structure with a large specific surface area, which can not only reduce the internal resistance of the electrode but also improve the conductivity of the battery. Finally, it exhibits excellent anti-aging properties while maintaining a high specific capacity [19]. Taking for example, Wang et al. made a graphene sulfur composite material by putting the sulfur particles wrapped in polyethylene glycol into the graphene oxide sheet coated with carbon black. This material was used in the cathode of lithium-sulfur battery for 100 cycles. Under the condition of 600 mA, the capacity decreased by less than 15 %, which is not only stable but also has practical value [20].

In addition, the relative stability of two-dimensional nanomaterials has also been further confirmed by recent research results. Related research shows that 1173 of the dense data search results for more than 50000 inorganic molecules are weakly connected two-dimensional solids. Ras-mussen et al. used density functional theory (DFT) calculations to determine the formation heat of most two-dimensional TMD materials. The results show the advantages of the synthesis reaction of two-dimensional nanomaterials and the relative stability of the materials [21]. If this research progress can be further applied to the field of cathode materials, the safety factor of battery products will be greatly improved.

In summary, two-dimensional nanomaterials have excellent electrochemical and stability properties, which makes researchers interested in the development of more excellent and miniaturized battery or cathode materials. A typical example is the Janus TMD material, which has two different anisotropic nanostructures or microstructures, and opposite physical and chemical properties. Therefore, combined with the advantages of product miniaturization promoted by material nano crystallization, the 100-layer Janus TMD thickness of this kind of material is about 60-70 nm under the action of applied electric field, which can realize miniaturization, cutting-edge 2D technology, high breakdown current and wide dielectric constant [22]. Such results make the electrochemical development prospect of cathode materials full of expectation and research potential.

3.4. Three-dimensional (3D) nanomaterials

Three-dimensional nanomaterials are composite materials composed of one or more basic units in zero-dimensional, one-dimensional and two-dimensional, which mainly include nanomaterials with transverse size less than 100 nm or surfaces with roughness less than 100 nm, assembly and composites of nanoparticles and other materials. The variability and relatively unstable polymerization of its structure have aroused great research interest, which also includes the development of cathode materials in the field of electrochemistry.

It should be affirmed that the early work of electrode modification focused on the synthesis of homogeneous low-dimensional nanomaterials, which continue to contribute to the modification of cathode materials. Compared with low-dimensional nanomaterials, the cathode materials prepared by three-dimensional nanomaterials have unique and widely distributed porous nanostructures with adjustable morphology. Therefore, it is easy to establish a conductive network, effectively reduce the dead surface area of the cathode materials and promote the rapid transport of electrons and ions at the extended interface between the active site and the electrolyte [23]. After solving a large number of polarization defects, the electronic conduction characteristics of traditional cathode materials are enhanced, and the electrochemical performance and work efficiency of electrodes are improved obviously. This mechanism directly affects the optimization of material structure and breaks through the dilemma of efficiency reduction caused by the obstruction of electronic transmission path. The current research focuses on the construction of three-dimensional conductive network, and the carrier mobility is significantly improved [24].

For example, $Na_3V_2(PO_4)_3$, also known as NVP, has a unique 3D open NASICON framework and is considered to be an attractive electrode material in sodium ion batteries (SIBs) due to its wide range of sodium accommodation. However, Rui Ling 's team found that the NVP material has poor capacity and cycle stability during high-rate charge and discharge, mainly because of insufficient electron and ion conductivity. Therefore, they used precursor infiltration and post-heat treatment to prepare NVP @ C / N-doped graphene aerogel. This material has a three-dimensional porous structure that can accelerate the transmission speed of ions and electrons. It not only combines the carbon layer of nitrogen-doped graphene aerogel to form a long-distance conductive network, but also improves the cycle stability. The experimental results show that the electrode has a specific capacity of 74.1 mAh g-1 at 100 C high rate. After 12000 cycles at 20 C, the capacity retention rate is still 84 %, which is better than most of the data reported in the literature, demonstrating the potential of three-dimensional nanomaterials in the design of high-rate and long-life electrode [25].

4. Future Development Direction and Prospect

In this paper, the dimensional characteristics of nanomaterials and the related electrochemical effects of batteries are briefly summarized. According to the existing research situation and the brief discussion of this paper, the addition of nanotechnology can indeed make an indispensable contribution to the improvement of the electrochemical performance of the battery. Among them, the research direction to solve the technical bottleneck of traditional cathode materials is relatively favored, and its contribution to battery technology accounts for a large proportion.

However, due to the immaturity of nanotechnology and the incompleteness of related process routes, if nanotechnology is to be widely used in the preparation of battery cathode materials, further design is needed to ensure the stability, safety and cost control of nanomaterials as host materials. Combined with the specific characteristics and influence factors of nanomaterials with different dimensions proposed in this paper, it is imperative to develop nano cathode materials for efficient operation of batteries. Therefore, coordinating the existing traditional electrode nano-modification modification, constructing nano-films or nano-networks to promote the further release of cathode material properties, and establishing nano-stereo structures to achieve breakthrough performance progress of cathode materials may become an important research direction in the field of cathode materials and electrochemistry in the future.

5. Summary

Nanomaterials have certain structural advantages, and their combination with cathode materials will inevitably become a research and application trend to improve battery performance. On the basis of the existing research, we will further develop the preparation system of nano-cathode materials, make good use of nanomaterials with different dimensions, actively modify and coat traditional materials, and develop new nano-cathode materials for future high-performance batteries. The defects of existing cathode materials will be solved one by one, the electrochemical performance of the battery will be greatly improved, and the revolutionary technology development in the battery field will be realized.

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