Advanced Design of Electrode Nanomaterials of Lithium-Ion Batteries for Electric Vehicles

Donggen Li*

School of Water Conservancy and Hydropower Engineering, The University of Sichuan Agricultural, Sichuan,625099, China

* Corresponding Author Email: 201902450@stu.sicau.edu.cn

Abstract. In the era of increasing global pollution and energy consumption, pollution-free new energy electric vehicles have become the future development direction. In recent years, researchers have used lithium-ion batteries (LIBs) as the main energy source for the electrically-operated car. With the development of new electronic equipment and the increasing demand for new pollution-free electric vehicles, new material science and technology, especially nanomaterial technology, have been widely concerned by researchers. Nanomaterials can improve the electrochemical function of LIBs, such as energy and power density. This paper summarizes the help of nanomaterials to improve the performance of lithium-ion batteries and the application of nanomaterials in the electrode materials of LIBs. It introduces how to improve the electrochemical performance of LIBs via special treatment on the anode and cathode materials.

Keywords: LIBs, Electric vehicle, Electrode material, Electrochemical performance

1. Introduction

Modern electric vehicles do not produce harmful gases that pollute the environment. For them, the most important energy is batteries. It is a device that stores electrical energy. To find electrodes with high cycle stability for new pollution-free electric vehicles, researchers have studied lithium-ion batteries (LIBs) for many years. Because of its excellent performance: high energy density, no pollution, small size, lightweight, high cycle stability, high power density, and no memory effect. With the development of microelectronic technology at the end of the 20th century, lithium battery application in electric vehicles and other relevant fields has grown rapidly. Its application has penetrated many fields of civil and military applications, including mobile phones, tablet computers, laptops, digital cameras and other multi-functional portable electronic products.

The biggest single component cost of electric vehicles is batteries, which is also the focus of research and development of major electric vehicle manufacturers, and this is where nanotechnology can help. Manufacturing the nanoparticles of some chemical components used in the battery can not only improve the battery's efficiency but also increase the current and reduce the long-term degradation of the battery capacity. Electric vehicle batteries, like smartphones, will lose some capacity over time during charging and use.

Although the research and application of the batteries get more popular, LIBs still need to be improved and further optimized in some performance respects. In modern times, researchers believe that nanotechnology is the most effective way to develop the function of LIBs. Through nanotechnology, nanomaterials can be applied in many fields. The main problem that researchers have to solve ought to be developing LIBs to satisfy the needs of electric automobiles and other fields.

2. Distinctive Merits of Nanomaterials

Compared with traditional materials, nanomaterials are much smaller in size, which means that the transmission distance of lithium ions in nanomaterials is much shorter. The following formula determines the average transport time.

$$T_{eq}=L^2/2D \quad (1)$$

Where L represents the transmission distance, and D represents the diffusion coefficient. From the formula, it can be inferred that there are two methods to shorten the transmission time. One method is to increase the diffusion coefficient D, which can be improved by doping impurity atoms. Another method is to reduce the transmission distance L of lithium ions in the material, which can be achieved by applying nano-sized electrode materials [1]. The first method of doping impurity atoms is not of great significance because this method can only improve the cell rate performance limited, and introducing impurity atoms may bring other problems, such as bulk stability. Another method to reduce the transmission distance can effectively develop the function of LIBs. The use of nano-sized electrode materials will not harm lithium-ion batteries. Some materials cannot store lithium ions in micron size, but they can store them in nanometer size.

Nanomaterials provide a larger contact area between electrode materials and electrolytes, reducing the specific current density of active materials and improving the batteries' high-rate performance. There are many pores between the particles of nanomaterials. Their role is to relieve the stress caused by the change of material volume to maintain the structural stability of electrode materials [2].

3. Fabrication methods of electrode materials

3.1. One-Dimensional Electrode Materials

There are many one-dimensional nanostructure materials. For example, nanotubes, nanowires, nanorods, and so on. The radial direction of one-dimensional nanostructured materials is also nano-scale, which shows that it can reduce the transmission distance of lithium ions. Because it is a one-dimensional structure, it can generate an electron transmission channel, improve the electron transmission rate, and generally shorten the transmission time. This kind of one-dimensional nanostructure material can shorten the transmission time and quickly complete the charge and discharge when applied to LIBs, which is of great substantive significance for the battery application of electric vehicles.

The material synthesis method of one-dimensional nanostructure:

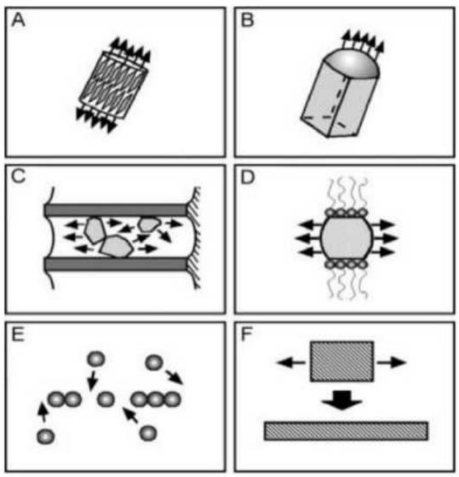


Figure 1 Different synthesis methods [3].

3.2. Two-Dimensional Electrode Materials

There are generally two methods for the synthesis of two-dimensional electrode materials: one is the top-down synthesis method, and the other is the bottom-up synthesis method.

The first method can be seen as synthesizing graphene material from large, layered graphite, and the top-down method peels two-dimensional nanostructures from raw materials through physical and chemical methods. This method does not need complex instruments and can be easily completed. So, it is easy to apply to other fields. However, the problem with this method is that it has high

requirements for the material itself, and the two-dimensional material made by this method has a wide range of thickness distribution and uneven thickness. Another method is the bottom-up synthesis method, which controls the growth of two-dimensional nano electrode materials by assembling molecules, atoms or proteins [4]. The problem with this approach is also obvious. The use of this method requires complex synthesis steps. Another preparation method is nanomaterials compounded with graphene. Graphene has good conductivity, mechanical stability, thermal stability, and a large specific surface area. The composite two-dimensional materials of electrode materials and graphene can provide a fast lithium-ion transmission rate and excellent conductivity. The following are some two-dimensional nanomaterials used in LIBs.

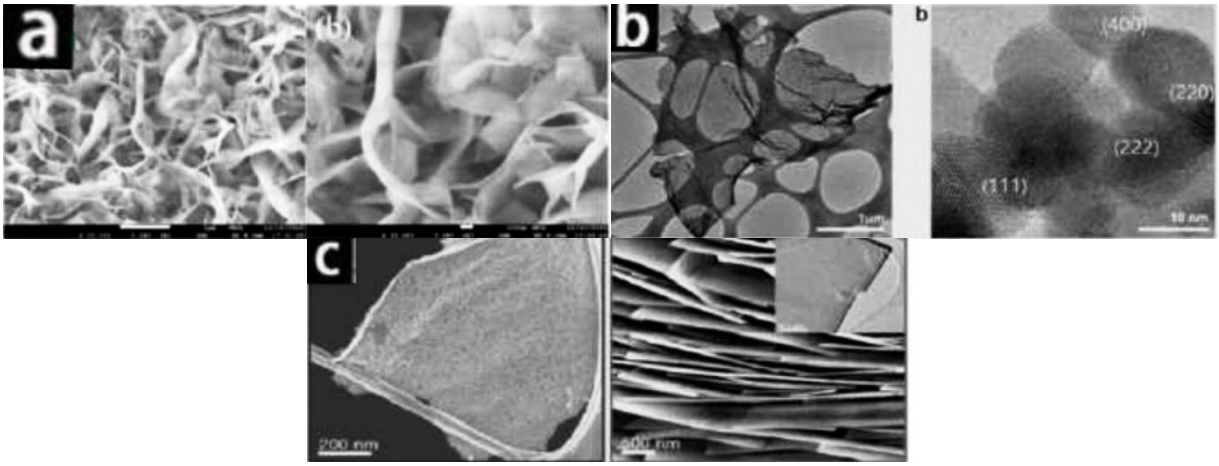


Figure 2 (a) Ni-Co-Mn ternary cathode material with 2D nanostructure, (b) Cobalt trioxide 2D nanostructure and (c) Lithium iron phosphate nanosheet as the positive electrode [5-7].

3.3. Multi-Level Structure Electrode Materials

The thermodynamic stability of nanoelectrode materials in LIBs is very poor, which leads to easy agglomeration. Moreover, the tap density of these nanomaterials is very low, which leads to the decline of battery volume energy density. These factors limit the commercial application of nanomaterials. For these shortcomings, an effective solution is nano multi-level structure materials. The following is the schematic diagram of multi-level structural materials.

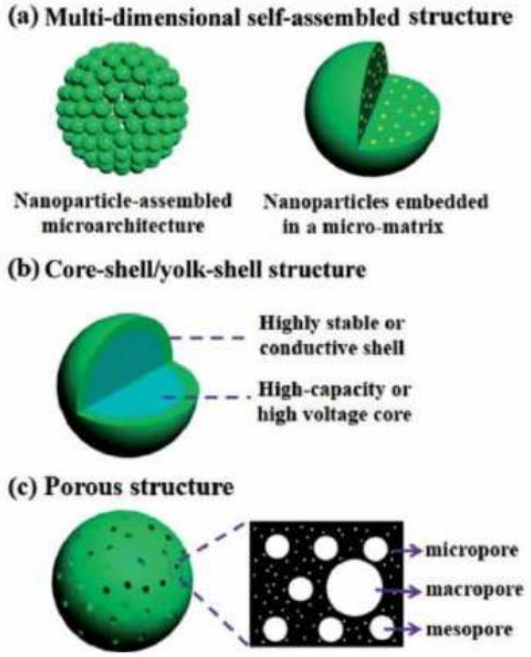


Figure 3 Multi-level structural materials [8].

The multi-level structure can be divided into three composition modes. The first one is a nano micron multi-level structure. This structure can be divided into two types, namely micron-sized materials assembled by nanoparticles and nanoparticles embedded in micron-sized host materials. The second is a core-shell structure composed of two different functional materials. For example, the material with better stability is used as the shell, and the material with higher capacity is used as the protected core. The third is porous structure, which can be divided into micropore, mesopore and macropore according to the pore size. Micropores can provide additional lithium-ion storage capacity, mesopores can provide a shorter lithium-ion transmission path, and macropores can effectively alleviate the volume change of materials during lithium-ion deinterlacing [8].

4. Cathode materialS

As the core component of LIBs, cathode materials occupy a dominant position in LIBs. Currently, the market's mainstream for LIBs mainly falls into three categories. $LiCoO_2$ and $LiNi_{1-x-y}Co_xMn_yO_2$ have achieved the earliest commercialization represented by $LiCoO_2$. At the same time, the mainstream ternary material lithium nickel cobalt manganate ($LiNi_{1-x-y}Co_xMn_yO_2$) as a power battery has been widely studied and applied in new energy vehicles. The second type is the anode material with spinel structure. Typical representatives are $LiMn_2O_4$ and$LiNi_{0.5}Mn_{1.5}O_4$. The third type is polyanionic anode materials, and the typical representative is $LiFePO_4$ with an olivine structure.

4.1. Layered Transition Metal Oxides

$LiCoO_2$ is representative of transition oxide materials with a layered structure. The structure of $LiCoO_2$ is two-dimensional α- $Nafeo_2$ is layered, belonging to a hexagonal crystal system, and the theoretical specific capacity can reach 274 mAh g^{-1}. The material's structure is easily damaged or even collapsed, so the battery resistance increases and the discharge-specific capacity decreases. The actual discharge capacity is only 140mAhg^{-1}. At the same time, the material also performs poorly in capacity attenuation and thermal stability. Therefore, to solve these problems, researchers usually carry out a series of modifications to the material to improve its performance, which the modification generally starts from the two aspects of doping and coating.

Needham et al. prepared the layered compound $LiM_{0.02}Co_{0.98}O_2$ through an easy method of synthesis and reported the effect of the doping of these three elements on the electrochemical properties of $LiCoO_2$ materials; Doping these three elements has confirmed that some secondary phases will be generated in varying degrees, which will destroy the structure of $LiCoO_2$. At the same time, the increased concentration of Co^{4+} ions will affect the electronic structure of the material [9].

It forms a solid solution on the surface of the active substance and plays a role in protecting the active substance. Gu et al. Coated the spinel interface coating formed in situ through the reaction in the surface area of $LiCoO_2$ to obtain the composite $LiCo_xMn_{2-x}O_4$, which has face-centered cubic stacking close to $LiCoO_2$; The spinel coating also has good electrochemical stability. The results show that the composite $LiCo_xMn_{2-x}O_4$ has better cycle stability at high temperatures [10].

4.2. NiCoMn Ternary Materials

Another representative of transition metal oxide materials with the layered structure are nickel diamond manganese ternary materials ($LiNi_{1-x-y}Co_xMn_yO_2$), which are also the research hotspot of many scientists. Ternary transition metal oxide cathode materials have the characteristics of good structural stability, good thermal stability and high specific capacity, which meet the needs of most markets. Each metal element in ternary materials plays a different role. Nickel mainly provides high lithium intercalation capacity for ternary materials, but too much nickel will lead to dislocation with lithium, which will affect the electrochemical performance of the materials.

Xu et al. Prepared CE doped transition metal oxide material $LiNi_{0.497}Ce_{0.003}Co_{0.2}Mn_{0.3}O_2$ by combustion method and then coated graphene on the surface of $LiNi_{0.497}Ce_{0.003}Co_{0.2}Mn_{0.3}O_2$. The results showed that the $LiNi_{0.497}Ce_{0.003}Co_{0.2}Mn_{0.3}O_2$ composite coated with 3 wt.% graphene showed

better cycle stability. After 50 cycles at 2 C current density, the capacity retention rate was 77.47%, while the capacity retention rate of uncoated samples was 72.02%[11].

4.3. Spinel Structured Materials

$LiMn_2O_4$ represents Spinel Cathode materials. Spinel lithium manganate $LiMn_2O_4$ as a cathode material with a three-dimensional lithium-ion channel was first prepared by Hunter in the 1980s. In modern times, many researchers tried to improve its performance by various means.

One method is doping metal cations, and the other is the surface modification of $LiMn_2O_4$. Cai et al. Studied the aluminum (Al) mixture changes the performance of $LiMn_2O_4$. Al-doped $LiMn_{2-x}AL_2O_4$ composites were prepared by combustion synthesis using absorbent cotton fiber as the carrier; The experimental results show that the lattice parameters and particle size of $LiMn_{2-x}AL_2O_4$ composites decrease with the increase of Al doping ratio, and Al doping shortens the path of lithium-ion diffusion, increasing contact between surface and electrolytes [12].

Lai et al. Coated spinel $NiFe_2O_4$ on the surface of cathode material $LiMn_2O_4$. $NiFe_2O_4$ coating has good crystallinity. After $NiFe_2O_4$ coating is applied on $LiMn_2O_4$ material, a continuous and uniform film is formed. This operation changes its rate performance; The constant current charge-discharge test verifies the excellent energy density and stability. In comparison, the capacity retention rate of surface-modified $LiMn_2O_4$ after 500 cycles is 89.1% under the same conditions. [13].

4.4. Polyanion Material

Polyanion cathode materials show good cycle stability and high safety in the process of charge and discharge due to their characteristics, which are suitable for the needs of the public.

Common polyanionic materials include $LiMnPO_4$, $LiFePO_4$ and $Li_3V_2(PO_4)_3$. However, this kind of material also has a common disadvantage. That is, the material's conductivity is very low, and the discharge-specific capacity is usually very low in high current discharge, which also limits the application and development of this material in the market. At present, metal cation doping is often used to solve these problems.

Yang et al. Synthesized Fe doped $LiMnPO_4$ by one-step electrospinning technology. The electrochemical test showed a high lithium-ion diffusion coefficient and excellent battery performance. The ability to discharge electricity was 150 $mAhg^{-1}$ at 0.2 C current density, and the capacity retention rate for 500 cycles was 119%; Under the current density of 5 C for 2000 cycles, the specific discharge capacity can reach 102 $mAhg^{-1}$, which is attributed to the more uniform morphology of the material due to the appropriate proportion of Fe. It can be seen that the doping of metal cations has achieved good results in improving the electrochemical properties of $LiMnPO_4$ cathode materials.

4.5. Graphene-Based Materials

Graphene is widely used in electric vehicles, electronics, information, new energy, aerospace and other fields because of its excellent electrical, thermal and optical properties. Among the graphene-based cathode materials, there are three main technical issues to be focused on: i) long cycle life and good high current cycle performance; ii) Improving the specific capacity of LIBs; iii) Improvement of problems such as easy falling off, short circuit, product deterioration and looseness of the cathode.

To develop the conductivity of LIBs, the proportion of conductive agents can be increased, but the proportion of binder needs to be increased to maintain electrode forming, which will lead to low capacity. Doping a specific proportion of modified graphene into the positive material slurry to form graphene positive composite can improve the conductivity of doped positive material, shorten the transmission distance of Li^+ in the intercalation process, and improve the diffusion speed of Li^+. In addition, the specific capacitance can be further improved by doping one or more nitrogen, phosphorus, sulfur and boron. The lithium iron phosphate cathode material based on graphene and Co-doped with nitrogen, phosphorus and sulfur developed in reference [14] has a first discharge

specific capacity of more than 161mAh/g and a charge-discharge efficiency of more than 98% at 0.1 C; At 8.0 C rate, the specific discharge capacity is still higher than 146 mAh g^{-1}.

To improve the problem that the anode material is easy to fall off, short circuit, product deterioration and looseness, The proportion and structure of positive active material, binder and conductive agent can be optimized so that graphene, as a coating layer with good uniformity and few layers, can be uniformly and closely combined with the electrode material matrix, so that the positive material is not easy to fall off, not easy to agglomerate and wrinkle, reduce the side reaction. The nano lithium manganate inlaid with graphene-coated nickel cobalt aluminum ternary material developed in reference [15] has a nanolayered structure with a size of 0.1~10.0 nm. The loading amount of nanolayered lithium manganate is 20%~90%, and the coating material is uniform and completely covered。

5. Anode materials

Tin oxide (SnO_2) is a direct band gap semiconductor material with a high theoretical specific capacity, abundant reserves and low cost.

The volume of the negative electrode material will change significantly in the multiple charges and discharges process of Sn and Li alloying and dealloying. This is a difficult problem in the large-scale application of SnO_2-based materials as anode materials [16].

5.1. Tin Oxide-Based Materials

Wang et al. synthesized homogeneous polycrystalline SnO_2 nanotubes by the alumina template (AAO) method. The results show that its initial capacity reaches 940 mAh/g with 525 mAh/g after 80 cycles [17]. Paek et al. assembled graphene nanosheets and SnO_2 nanosheets into three-dimensional layered nanoporous electrodes in glycol solution [18]. That is, the capacity remains about 70%. This may be since graphene nanosheets are uniformly filled between loose SnO_2 nanosheets, improving electrode materials' electrochemical performance.

5.2. Si-Graphite Materials

To obtain the high-capacity performance of silicon and realize long-term stable cycle life, nano Si and graphite are surfaces modified to bring the required functional groups [19]. Then they are mixed and ground in a certain proportion to replace the weak van der Waals force between molecules so that nano silicon and graphite have a more solid interaction through chemical bonds; ensure that nano silicon can always keep good combination with graphite in the cycle process, ensure good conductivity of electrode in the cycle process, and buffer the volume effect of nano Si in the cycle process, to obtain stable cycle performance. After heat treatment with a pan as a binder, the impedance of the electrode sheet decreased greatly, and then the conductivity of the composite was improved. Nano silicon-carbon composites have stable charge-discharge cycle performance.

6. Conclusions and Outlook

There are many shortcomings in using nanomaterials as LIBs. The main disadvantage is its density. Due to nanomaterials' porous structure, the nanomaterials' density is lower than that of micromaterials. Accordingly, the filling density of electrodes prepared with nanomaterials is also very low, which greatly limits the volumetric energy density. The large specific surface area of nanomaterials will accelerate many adverse side reactions on the surface of materials. The template and hydrothermal methods are usually used in synthesizing nanomaterials. These methods are more complex than the solid-phase method, with much higher cost and lower output.

Nano lithium batteries in the future, emphasizing high-energy and high-energy quantification, also pay close attention to high power. LIBs will continue to rely on the innovation of nanotechnologies. It is expected that the rational design of nanomaterials will play a crucial role in future research.

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