Carbon Coating Method

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The carbon coating has the following main mechanisms: (1) Modifying surface chemical stability, (2) Enhancing structural stability, and (3) Improving Li-ion diffusion.

carbon coating specific capacity

1. Carbon Coating Method

The effect of carbon coating is also significantly affected by the coating techniques. Firstly, different coating methods would lead to the diverse microstructure of coating layer, which results in various abilities of Li-ions diffusion through the coating. Furthermore, the coating methods may have impacts on the surface structure of cathode. Therefore, various coating methods have been studied according to different cathode material structures. Meanwhile, the carbon layer prepared by surface coating methods still had problems of inhomogeneity and incomplete cover, the techniques which could fabricate a more uniform and thinner carbon layer are studied. The carbon coating methods can be divided into two categories: wet chemical method and drying coating.

2. Wet Chemical Methods

The wet chemical methods are the traditional techniques for surface coating on electrode material, which are the most widely used methods in the market production, including hydrothermal/solvothermal, sol-gel, chemical polymerization routes, etc.

2.1. Hydrothermal/Solvothermal

In a typical routine, the precursors with solvents are added to an autoclave at a set temperature, and placed the autoclave in an oven for some time. Afterward, the reaction solution is cooled to room temperature followed by drying and annealing. For example, Qi et al. [1] reported that using hydrothermal reaction and followed by heat treatment to prepare $LiFePO_4$ and $LiFePO_4$ microspheres coated with carbon, mixing the sucrose and $LiFePO_4$ then transferring the reaction solution into the autoclave for some time followed by cooling to room temperature and drying. The results showed the increasing electrochemical performance and cycling stability. This simple method can reduce the production cost and improve the host structural stability by surface coating. However, it is still a challenge to form uniform coating layer on the electrode surface and form a complete physical protection layer [2].

2.2. Sol-Gel Method

Sol-gel method is one of the conventional approaches to coating inorganic materials on the surface of electrode, including two main reactions: (1) hydrolysis of the precursor and (2) polycondensation of the hydrolyzed products to form a polymeric network [3]. Using a sol-gel approach to prepare the coating layer on the surface of electrode has the following advantages: (1) the process can be conducted at a lower temperature which prevents the host structure damage caused by carbon reduction due to high temperature when coating certain electrode materials like NCA or NCM, (2) shorter calcination time and efficient control over stoichiometric-ratio, (3) forming compound with good crystallinity and (4) making uniform particle size distribution and smaller size particle size in the nanoscale. It is an available technique for large-scale production with relatively lower production cost and simple operation. However, this method experiences problems involving the low yield, high cost of precursor, heterogeneous and discontinuous carbon coating layer and the generation and change of acidic gases during heat treatment [2].

2.3. The Chemical Polymerization Routes

These routes can be divided into two types including in situ and ex situ. The in situ is a preparation method that the precursors which dissolved in the polymeric solution deposited on the surface of host material particles by the chemical reduction, thermolysis, photolysis, etc. In situ method could remain the homogeneous distribution of the polymer matrix and suppress the agglomeration of the host material particles. In the ex-situ process, the host material was prepared by wet chemical method before dispersing into the polymeric matrices [2]. It was believed that ex situ method was the most common and simple approach in the surface coating methods for cathode material, preparing the host material by a wet chemical approach before dispersing it into the polymer matrix. With the relatively high technical maturity, it effectively provides a protective layer against the corrosion of HF and increases interfacial stability between electrode and electrolyte. Besides, ex situ can be used for the large-scale production of surface coating for cathode material, however, this method is difficult to achieve uniform distribution of the matrix particles during the dispersion process of polymer matrix [2].

3. Dry Coating

Recently, due to the cost-effective and environmentally friendly properties, dry coating technique has attracted widespread attention. The larger size particle can be coated mechanically by nanoparticles through dry coating method which forms a core-shell structure. This method includes chemical vapor deposition, atomic layer deposition, physical vapor deposition, etc.

3.1. High-Temperature Solid-State Method

High-temperature solid-state method is one of relatively simple dry coating techniques. The carbon-coated cathode materials can be obtained by mixing the cathode powder material and carbon source to get uniform powder, then calcinating at high temperature for several hours. For instance, Cao et al. [4] reported the synthesis route of high temperature solid-state to prepare carbon-coated $LiMn_2O_4$. The products of MnO_2 nanowire and glucose were put into a Teflon-lined stainless autoclave in the 180 °C, attaining carbon-coated MnO_2 nanowire. Then, making carbon-coated MnO_2 nanowire and LiOH anneal at high temperature for several hours in air environment can prepare $LiMn_2O_4$ coated with carbon layer. The previous research indicated the uniform and complete carbon layer could be attained by dry coating, and the electrochemical performance of Li-ion battery can be improved. However, due to the distinctive physical and chemical properties of different coating material, the optimal calcination or annealing temperature depends on the different coating material, which still needs further exploration.

3.2. Chemical Vapor Deposition

Chemical vapor deposition (CVD) is one of the most common techniques used to prepare high-quality and high-performance thin film coating on the surface of host materials [5]. The process of CVD mainly involves two steps: (1) exposing the host material to the precursors with volatility, (2) the reaction or decomposition of precursors to form a thin film on the substrate surface. For example, Tian et al. [6] coated carbon on the surface of $LiFePO_4$ by CVD in a quartz tube. The solid glucose as the carbon source decomposed, forming vapor when the quartz tube was heated up to 550 °C and condensing in the form of small carbon clusters on the surface of $LiFePO_4$. It showed that CVD was a novel environmentally friendly and controllable carbon coating method to get more uniform carbon layer, making $LiFePO_4$ possess good rate capacity, long cycling lifetime and high-power densities. However, the lower decomposition rate of CVD caused the longer production time, which is not suitable for large-scale production. In addition, more sophisticated facilities are needed in the CVD process which caused higher production cost. Therefore, this technique still needs to be optimized according to different cathode materials to achieve improvement in electrochemical performance of the electrode.

3.3. Physical Vapor Deposition

Physical vapor deposition (PVD) is an important method to prepare the protective film with the properties of anti-corrosion and wear resistance [7]. The deposition of material on the substrate is a line-of-site impingement type for PVD, while it is a multi-directional type for CVD [8]. The process of PVD which conducts at the vacuum includes that solid or liquid material transfer to a vapor phase, then the metal vapor congeals and forms a solid and dense film on the surface of the substrate material [7]. Nevertheless, PVD technique generally operates at high temperature and vacuum, which needs a skilled operator. In addition, the process of PVD requires a cooling water system for heat dissipation.

3.4. Atomic Layer Deposition

Atomic layer deposition (ALD) is an emerging technique applied for surface modification of cathode material by forming a thin and homogeneous film to prevent the reaction of electrode and electrolyte to improve the electrochemical performance [9]. In general, two or more precursors containing different elements are needed in the ALD process, which is provided one at a time in sequence to proceed with surface coating. The precursors are injected into the reaction chamber to synthesize the desired material by chemical surface reaction, which is separated by inert gas purging to prevent gas phase reactions before injecting the next precursor. Its unique selfterminating growth mechanism is in favor of getting conformality and thickness uniformity of the film. The advantages of ALD are as follows: (1) the thickness of coating layer could be controlled by the number of ALD process cycles and the coating deposited has conformality with the substrate surface, which means the shape of coating layer conforms to the substrate surface so that the thickness of coating is uniform, (2) ALD can be applied to deposit a wide range of materials, both conductive and insulating materials surface, (3) the operation temperature is relatively low and (4) the surface coating can effectively reduce the rate of surface reaction and enhance the ionic conductivity of electrode [2]. However, ALD technique involves the complicated chemical reaction procedures, as well as the high cost of requested facilities. In addition, the excess precursors need to be removed when the coating is finished, which makes the coating preparation process more complicated.

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