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Synthesis and application of electrode materials for lithium-ion batteries

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Abstract. Lithium-ion battery has been widely used in various portable electronic products due to its benefits of high energy density, power density and average output voltage, longer cycle life and so on. However, the traditional LiCoO₂ cathode material has many problems, such as resource scarcity, high price, toxicity and small actual specific capacity, which cannot meet the current development needs of lithium-ion batteries. Therefore, the development of new high capacity and low price electrode materials is one of the focuses of lithium-ion battery research. This paper summarizes the development and pros/cons of organic and inorganic hybrid materials, conductive polymers and transition metal chalcogenides as new electrode materials, covering the design, synthesis and electrochemical properties of each material. Meanwhile, the structure and morphology of the new electrode material can be characterized by means of transmission electron microscope, scanning electron microscope, X-ray diffraction, Raman spectrum, infrared spectrum and other characterization methods, which could explain the performance of lithium storage.

1. Introduction

The energy crisis in the second half of the 20th century has aroused people's attention to new energy. After entering the 21st century, various environmental protection organizations have sprung up like mushrooms, and various countries have enacted more stringent environmental protection laws, which has promoted the development of new energy [1-3]. It should be noted that, like hydrogen energy, electric energy must be stored and released by some devices, such as batteries, capacitors and so on. Since Sony successfully introduced lithium-ion batteries to the market in 1991, lithium-ion batteries have been widely used in portable electronic devices (such as mobile phones, laptops, digital cameras, etc.). [4-7]

Batteries are composed of a variety of electrochemical cells that are connected in parallel or in series to provide the required voltage and capacity, respectively. Each electrochemical cell contains an anode and a cathode, and both two electrodes are separated by an electrolyte solution containing salts, thus making it possible for charge to transfer between the electrodes. After the two electrodes are connected externally, chemical reactions take place at the electrode and obtaining/releasing electrons, providing current for the user [1]. Rechargeable lithium battery does not contain lithium metal. It is lithium-ion equipment, composed of graphite anode, non-aqueous electrolyte and layered LiCoO₂ cathode material (shown in fig. 1) [4, 8-10]. The current large-scale commercial production of memory-free secondary lithium battery in which Li⁺ robs back and forth between the two stages of the interface like a rocking chair, was first launched by Sony in the 1990s. The charging and discharging process is based on the reversible insertion and release of Li⁺ in carbon-containing materials (specific electrolytes are required). During the discharge process, Li⁺ migrated from the graphite layer across



the electrolyte to the cathode material LiCoO_2 , and the charging process was completely opposite to the discharge process.

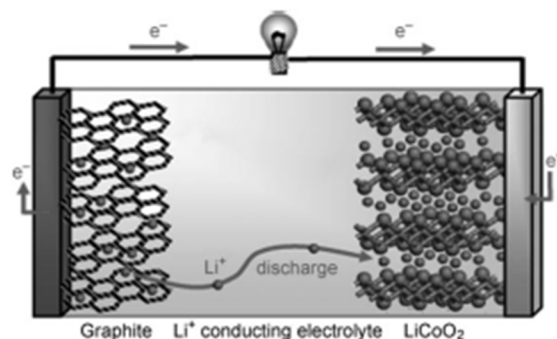


Figure 1. schematic diagram of lithium battery, the cathode material LiCoO_2 and anode graphite are separated by non-aqueous liquid electrolyte [4]

There have been continuous attempts to replace graphite with nanometer graphite particles, which can accelerate the Li^+ deintercalation and intercalation speed and thus improve the rate capability. However, it is also faced with a critical problem: Li^+ insertion usually occurs at 1V, and within this voltage range, the electrolyte will undergo a reduction reaction to generate a solid electrolyte film (SEI). Intense film forming reactions can lead to excessive charging, which, on the one hand, cause the battery consumption. On the other hand, considering the fact that most Li^+ is inserted into graphite under 100mV, lithium will deposit on the electrode surface if the charging process cannot be controlled precisely. Those depositions will lead to safety problems for nanoparticles [4]. Silicon nanowires can also be applied to lithium cathode, with a theoretical capacity of $4200\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ at a low electric potential. However, when lithium ions are inserted and disembedded silicon usually performs a drastic change in volume (400%), which lead to material crushing and a sharp decrease in capacity. After making it linear, however, the ability to withstand pressure is greatly improved, and the conductivity is also increased. Therefore, this negative electrode material has reached the theoretical capacity, with recycling charge and discharge capacity reaching 75% of the theoretical capacity. However, the process of manufacturing electrodes is too complicated and expensive to have practical application value [11].

In recent years, new materials represented by organic-inorganic composite materials have become a research hotspot and have been continuously applied to lithium-ion battery electrode materials.

2. Organic-inorganic composite material

With the development of material research towards limit, the focus of material researches has shifted from single component to multi-components. The composition of multiple components will not only retain the properties of the original single component, but also produce some new properties when the two components interact and enhance each other. For example, common organic and inorganic hybrid materials, whose organic and inorganic components are compounded together at the nanoscale by various physical and chemical actions, such as hydrogen bond, electrostatic action, hydrophilic and hydrophobic action, van der Waals force, etc. At present, the understanding of reaction mechanism is not complete, and the properties, capacity and morphology of products may be affected by small organic molecules. In addition, inorganic crystal framework also affects the formation of products. Therefore, many physical and chemical factors can affect the morphology of hybrid materials' growth. Compared with single component, composite materials are more difficult to prepare and synthesize. Due to the instability of organic components at high temperature, it is necessary to abandon some of the traditional methods of synthesizing inorganic nanomaterials. At present, common methods are laser method, chemical vapor deposition method, water/solvent hot method, self-assembly method, embedding method, coprecipitation method, template method, non-aqueous sol gel method and electrochemical methods such as electroplating, plating, electricity, etc. [12].

For example, by electrochemical polymerization, conductive polymers are deposited on the surface of metal oxides with nano-structure, which can be used to synthesize nano-lattice with excellent performance of metal oxides/conductive polymers hybrid structure, which has excellent electrochemical energy storage and optical characteristics. By controlling the current and deposition time, it is possible to obtain branched and coaxial conductive polymers on different skeletons (nanorods, nanosheets, and nanowires). For example, coaxial TiO₂/PANI shows excellent optical properties, rapid adjustment of optical properties and excellent cycling stability. In addition, Co₃O₄/PANI core-shell nanowires can be used as the anode electrode of lithium battery and have a higher capacity than a single Co₃O₄ nanowire [13].

For some specific material, synthetic method is very simple. For example, mixing Co(NO₃)₂ and benzoic acid sodium together and then the mixture go through a simple heat mixing processing at 95 °C for 48 h. A pink organic inorganic layered benzoic acid cation intercalating Co(OH)₂ nano fiber can be obtained. By adjusting the concentration of the reactants, the diameter and length of the fiber can be changed. This substance with uniform crystal and particle size distribution turns blue after losing water and pink after water absorption, and can be applied in catalytic, gas storage and gas sensitivity technologies in the future [14].

And through the process of power spinning, for example, with sodium molybdate, polypropylene as raw material, N-doped carbon fiber type of defect mode, superconducting MoS₂ rich sulphur nano layer can be produced. It can be used as a hydrogen response of catalyst which has an over-potential of 135mV in 10mA. Under voltage of 200 mV, cathode current density of 65.6 mA·cm⁻² is detected, and maintain a superior cycle stability [15].

Self-assembly is a common and simple method of preparing organic-inorganic hybrid materials. Dissolving the aniline in CCl₄ solution and dissolving the potassium permanganate in deionized water, on the interface of organic and inorganic, aniline polymerize. At the same time, MnO₄⁻ is reduced into manganese oxide precipitation, aniline constantly spread from organic phase to inorganic phase and eventually form aniline intercalating layered manganese oxide nanometer compound which can be used in lithium-ion battery storage [16].

3. Conductive polymer/chalcogenide composites

3.1 Conductive polymer

In the organic and inorganic hybrid materials described above, the composite conductive polymer of inorganic components has obvious advantages as the electrode material of lithium-ion battery. Although some inorganic components have a high capacity, they usually have poor conductivity and are prone to collapse after several cycles. Conductive polymers, however, have better conductivity and higher elasticity compared with inorganic ones. The impact of Li⁺ on the electrode material during charging and discharging can be reduced, thus improving the life of the electrode. Conductive polymers and inorganic materials make up for each other by synergistic action, thus greatly improving the electrode life, multiplier rate capability and voltage of lithium-ion batteries. Nowadays, conductive polymers are mainly applied in the following categories: polyaniline(PANI), polypyrrole, polythiophene and their derivatives, since the above substances all have a deep research foundation, commercial feasibility and low complexity of the synthesis process [17].

There are various preparation methods available to obtain conductive polymer-inorganic hybrid materials, including in-situ synthesis, non-in-situ synthesis, mechanical synthesis, polymer matrix and inorganic nanoparticle mixing method, sol-gel method, layer self-assembly, ion exchange method, template method, etc.

3.2 Transition Metal Dichalcogenides

Transition metal dichalcogenides (TMD), with sandwich structure (graphite like). MX₂ can generally represent the chemical formula, where M can be any IV, V group elements such as IV B (Ti, Zr, Hf), VB (V, Nb, Ta), VI B (Mo, W), VII B (Tc, Re); X can be sulfur group elements (S, Se, Te). The

structure of this compound is similar to that of a sandwich, with two layers of X on both sides and a hexagonal transition metal layer sandwiched in the middle [18] (shown in fig. 2). These substances are widely used in both scientific research and industrial fields. Crystal structure includes hexagonal crystal system P63/mmc including MoS₂ and WS₂, and MoTe₂ and WTe₂ in rhombic structure Pmn21 WS₂[19]. Because of the anisotropy of these crystal structures, MoS₂ and WS₂ can be used as solid lubricants and are superior to graphite in withstanding high temperatures.

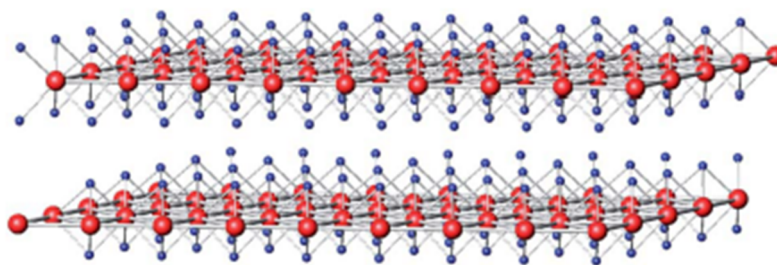


Figure 2. schematic diagram of structure of layered transition metal dichalcogenides, layered hexagonal structure (P63/mmc symmetric group, red represents Mo and W, blue represents S and Se) [19]

This unique structure is often considered as an ideal host material: compared with the strong interaction between atoms within layer, van der Waals force in interlayer is weaker along the c axis. This reduces hindrance of insertion of the foreign molecules or ions, such as Li and Mg. The advantages are obvious in the field of reversible energy storage. Besides TMD has relatively low working voltage and higher theoretical capacity, making it a potential material as the electrode. Due to the weak interaction between atomic layers, it is possible to peel off sheet layers by mechanical or chemical processes, so as to form a single layer or layers of graphene-like structure. TMD of this structure can solve the disadvantage of low bulk phase conductivity and enhance energy storage effect [20].

4. Conclusion

Lithium-ion battery is currently the most widely used secondary battery in portable electronic equipment market. With the rapid development of some emerging fields such as electric vehicles and smart grid, new requirements such as large scale, high energy density and low cost have been put forward for lithium-ion battery. This paper summarizes the preparation, development and performance of new lithium-ion electrode materials, mainly introducing the synthesis and properties of organic-inorganic composites, conductive polymers and chalcogenide composites, and describing the synergistic effects of several materials on electrode materials. Hopefully this paper can provide a powerful reference and guidance for researchers who dedicate in preparation of energy storage battery materials with high capacitance and charging and discharging speed.

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