

Improvement of Lithium Battery Anode by Three Kinds of Nanomaterials

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Abstract. In today's world energy structure, the majority of the energy utilized by humans comes from fossil energy including coal, natural gas and oil. According to the current international energy forecast, oil resources will be exhausted in 40 years, natural gas resources will be used up in 60 years, and coal resources can only be used for 220 years. Therefore, people began to vigorously develop electric vehicles, in which battery is the first problem to be solved. In order to improve the performance of lithium battery, nano-materials are used as anode. Including graphene strengthening structure, improving electrochemical characteristics, carbon nanotubes improving silicon lithium batteries, and silicon nanowires improving lithium content of lithium batteries. Studying the improvement of nano-materials on the anode of lithium batteries can improve the current performance of lithium batteries, break through the current theoretical bottleneck, and provide theoretical support for the optimization of the world's energy structure, and provide a feasible direction for improving the cycle stability, safety and other related electrochemical characteristics of lithium batteries.

Keywords: Energy, lithium battery, anode material, nanometer material.

1. Introduction

In the global environment of energy depletion, people began to pay attention to the use of electric energy to replace the inefficient internal combustion engine to provide power for cars. The benefits of pure electric vehicles (EVs) are as follows [1,2]. 1. No emissions. Since only electric energy is used, driving in a pure EV produces no exhaust emissions and no environmental pollution. 2. Compared to vehicles powered by gasoline engines, EVs use energy more efficiently. 3. The structure is simple due to the elimination of the engine, gearbox, oil tank, cooling and exhaust system through the use of a single electric energy source. 4. Low noise. 5. The vehicle can be charged when the power consumption is low, allowing the peak-to-valley difference of the power grid to be stabilized and the power generation equipment to be fully utilized. Lithium battery, as the battery with the widest application scope at present, has become the choice of electric vehicle battery. Graphite carbon anode materials have the advantages of low charge discharge voltage platform, low cost, good safety and low price, and are the main anode materials used in commercial lithium ion batteries at present. However, the layered structure of graphite anode materials is easy to lead to the co embedding of electrolyte solvent ions, resulting in the destruction of the graphite layered structure. The cycle stability and coulomb efficiency of graphite anode materials are affected. At the same time, the anisotropic structure of graphite restricts the free diffusion of lithium ions in the graphite structure, which affects the performance of graphite anode materials. These problems make it difficult for simple carbon anode materials to meet the requirements of high-performance lithium-ion batteries for increasingly developing electronic equipment, electric vehicles, etc. In this case, people began to notice that nanomaterials, graphene, carbon nanotubes, silicon nanowires and other nanomaterials have gradually come into people's view. Nanomaterials can significantly improve the battery storage capacity, improve the range of electric vehicles, light weight, reduce the overall weight, and have low relative cost and long service life. Graphene battery is a honeycomb planar film formed by carbon atoms in the form of sp² hybrid. It is a quasi-dimensional material with only one atomic layer thickness, so it is also called monoatomic layer graphite. A new type of energy battery is developed

by taking advantage of the characteristics of lithium ion's rapid and massive shuttle movement between the graphene surface and the electrode. Due to the characteristics of high conductivity, high strength, ultra-light and thin, graphene is also extremely prominent in the application of aerospace special fields. Carbon nanotubes can be used to improve the conductivity and structural strength of conductive plastics, and show great application value

2. Graphene

There are various preparation methods for graphene [3]. 1 Mechanical stripping method. By reducing the van der Waals interaction between the layers of graphite carbon atoms, mechanical stripping process can generate graphene materials with fewer layers. According to the stripping method, it can be divided into tape method, slight friction method and ultra-thin section method. 2 Direct stripping method in liquid or vapor phase. Due to the van der Waals force between the atomic layers of graphene, the direct stripping method of liquid or vapor phase refers to the preparation of graphene by dispersing graphite in the liquid or gas phase and using this force to destroy the graphite layers. 3 Epitaxial growth method for SiC. Silicon carbide epitaxial growth method, also known as silicon carbide pyrolysis method, uses high temperature (1000~1500 °C) to heat single crystal SiC to sublimate the silicon atoms on its surface. After the silicon atoms on its surface are sublimated and removed, the remaining carbon atoms can rearrange on the surface of single crystal silicon carbide to form graphene with time. 4. Chemical oxidation-reduction method. Chemical oxidation-reduction method refers to the oxidation of graphite to graphene oxide (GO) with strong oxidant, and then the reduction of graphite to graphene with reductant. 5. Chemical vapor deposition (CVD). CVD can be divided into metal substrate chemical vapor deposition and non-metal substrate chemical vapor deposition according to different substrates. This method generally uses a planar substrate as the catalyst and substrate. Under high temperature and low pressure, a certain carrier gas and carbon source are introduced and kept for a certain time, and then graphene products can be generated on the substrate surface. 6. Organic synthesis. The organic synthesis method is generally to synthesize the cycloaddition product through free radical coupling reaction such as Diels Alder reaction or Pd reaction, and then dehydrogenate the cycloaddition product to obtain graphene. 7. N-type doping. Common N-type doped molecules that can form with graphene include metals, organic compounds, N, h-BN, NH₃, H₂, and phosphorous P. N-type doping can be divided into adsorption doping and lattice doping according to different mechanisms, and adsorption doping It refers to the doping reaction between molecules with strong ability to absorb electrons or molecules with strong ability to give electrons and graphene. Usually, some organic compounds with large functional groups are doped with graphene to generate N Type doped graphene. 8. P-type doping. Similar to N-type doping, P-type doping can also be divided into adsorption doping and lattice doping according to different mechanisms. Common molecules that can form doping with graphene mainly include fluorinated (F) polymer, water (H₂O), N₂, N₂O, O₂, oxidizing solution, B, CL, metal, etc

Advantages of graphene as anode material for lithium batteries:

1. The polarization of lithium batteries can be reduced by graphene's large specific surface area (2630m²/g), which also lessens the energy loss brought on polarization. 2. Excellent conductivity and thermal conductivity make graphene a stable and reliable medium for electronic transmission. Graphene shares a mechanism for storing lithium with other carbon-based materials. Lithium ions are removed from the positive electrode during charging and incorporated into the carbon layers to form Li₂C₆. During discharging, lithium ions are taken out and return to the positive electrode. 3. The size of graphene sheets is in the micro nano scale, which is much smaller than that of bulk graphite, shortening the diffusion path of Li⁺ between graphene sheets. The increase of the chip spacing is also helpful for the diffusion and transmission of Li⁺, which helps to improve of the power performance of lithium ion batteries.

Graphene has great potential to replace graphite as a new generation of lithium battery cathode materials due to its unique two-dimensional structure, excellent electron transmission capacity and large specific surface area.

The carrier mobility of graphene at ambient temperature is about $15000\text{cm}^2/(\text{V}\cdot\text{s})$, which is 10 times higher than that of silicon material and more than twice as high as that of InSb, the material with the highest known carrier mobility. Under certain circumstances, such as low temperature, the carrier mobility of graphene can even reach $250000\text{ cm}/(\text{V}\cdot\text{s})$. The electron mobility of graphene is less sensitive to temperature fluctuations than that of many other materials. At any temperature between 50 and 500K, the electron mobility of graphene monolayer is about $15000\text{cm}/(\text{V} \cdot \text{s})$. Additionally, Changing the chemical potential under the electric field allows one to witness the semi-integer quantum Hall effect of electron and hole carriers in graphene. This effect has been seen in graphene at ambient temperature. The explanation of graphene's local super conductivity and high carrier mobility is that its carriers adhere to a special quantum tunneling mechanism that prevents them from back scattering when they encounter impurities, The electrons and photons in graphene have no rest mass, and their velocities are constants unrelated to kinetic energy [4].

More surprisingly, it was found that if C60 and carbon nanotubes were doped into it, its specific capacity could be as high as 784mAh/g. The research shows that although graphene material has a very high lithium ion diffusion rate, it has a high reversible specific capacity for the first time when it is used as the anode material of lithium ion batteries. However, after several cycles, the capacity declines seriously, and the charge discharge curve lags behind seriously, so it is difficult to use it as an electrode material alone. The unique flexible structure of graphene has unique advantages if it is combined with high capacity metal or oxide particles as anode materials. Compared with the traditional anode materials of lithium ion batteries, graphene as the anode materials of lithium ion batteries can effectively improve the specific capacity of the corresponding batteries, enhance the conductive contact between the electrodes and electrolyte, and improve the charge/discharge rate performance. At the same time, the flexible two-dimensional structure of graphene monoatomic layer can also effectively inhibit the material expansion and pulverization caused by the volume change of electrode materials during the charging and discharging process, so as to improve the cycle stability of the battery. The California Lithium Battery Research Group and Argonne National Laboratory of the United States jointly launched the third generation of silicon-graphene composite anode material, which uses advanced cathode materials and electrolyte solvent, with an energy density of 525Wh/kg and a battery negative capacity of 1250mAh/g. Earlier this year, the California Battery Research Group and the Argonne National Laboratory of the United States jointly developed lithium batteries, combined with silicon-graphene cathode materials and other advanced battery materials to produce a square battery with a capacity of more than 400Ah, which will be applied in the field of electric vehicles. The application process of this method in lithium batteries is to embed nano-silicon particles into the graphene layer. This method can greatly increase the energy density of the battery anode without increasing the battery capacity, and solve the problems of the lack of efficiency of the first charge of lithium battery and the reduction of the capacity as the number of charges increases. The laboratory has carried out independent and complete battery unit test, and the test results show that its energy density has increased by nearly three times, and the battery positive capacity has increased by nearly four times. At present, the energy density of lithium battery on the market is 100~180Wh/kg, while the positive capacity is 325mAh/g [5].

3. CNT

Preparation methods of CNTs are as follows [6]. 1. DC arc discharge method. In 1991, Iijima obtained CNTs by arc discharge method for the first time in the process of preparing C60. In 1992, Ebbesen et al. carried out systematic research on the preparation of CNTs by the arc method, and produced grams of CNTs, making this method widely used. 2. The principle of chemical vapor deposition is to decompose the gas containing carbon source through the catalyst surface and generate

CNTs on the side of the catalyst. 3. Laser evaporation method. The laser evaporation method is to use a high energy density laser to irradiate the target in the vacuum cavity under a specific atmosphere to evaporate it, and the excited carbon atoms or atomic groups collide with each other in the carrier gas to generate CNTs.

Carbon nanotubes have excellent electrical conductivity. However, CNT is less effective as a negative electrode material in large rate charging and discharging due to its small depth and short travel path of Li ions, which can enhance the large rate charging and discharging performance of the battery. This is because of its tiny depth and short travel path of Li⁺ when deinterlacing lithium. The p electrons of carbon atoms on CNTs form a variety of delocalized π bonds. Due to the extraordinary conjugation effects, CNTs have some special electrical properties. Carbon nanotubes have good electrical conductivity. There is good electrical conductivity in CNTs. The pipe diameter and the helix angle of the pipe wall effect the theoretical prediction of the conductivity. When the diameter of CNTs is greater than 6 nm, the conductivity declines; When the diameter is less than 6 nm, CNTs can be thought of as 1D quantum wires with good conductivity. It is reported that Huang believes that CNTs with the diameter of 0.7 nm can be superconducting through calculation. Although its superconducting transition temperature is only 1.5×10^{-4} K, it shows potential uses in the superconducting field.

The structure of carbon nanotubes can be seen as a one-dimensional cylindrical tube with graphite sheets wound. Carbon nanotubes have the characteristics of high conductivity (the conductivity of single wall CNTs is up to 10^6 Sm^{-1} , the conductivity of multi wall carbon nanotubes is more than 10^5 Sm^{-1} , low density, high rigidity and high tensile strength (up to 60 GPa) [7].

According to the report, the reversible capacity of single-walled CNTs is up to 300-600 mAh g⁻¹, which is obviously higher than that of graphite (337 mAh g⁻¹). Moreover, the reversible capacity of single-walled CNTs treated by mechanical or chemical methods can reach 1000 mAh g⁻¹. In order to improve the charging capacity of lithium ion batteries and reduce the irreversible capacity, a very practical method is to synthesize carbon nanotube composites as electrode materials [8].

4. Silicon Nanowire

Preparation methods of silicon nanowires will be presented as follows [9]. 1. The main idea of preparing silicon nanowires by chemical vapor deposition is to use gaseous silicon precursors such as SiCl₄ and SiH₄ as raw materials, use Au nanoparticles as catalysts, and control the nucleation and growth process of materials by controlling gas pressure, flow rate and matrix material and other parameters. 2. The technical idea of synthesizing silicon nanowires by laser ablation method is to use the mixture of nano-metal particles such as Au, Fe and nano-silicon powder as the target material. The target material is ablated by laser at high temperature to form high-temperature concentrated steam, and the mixture gas is transformed into alloy droplets under inert atmosphere. When the silicon in the droplet reaches saturation, it will grow into nanowires along the carrier gas flow direction. 3. The technical idea of template method is to use the self-assembly of nanospheres and anodic alumina (AAO) template method to make the noble metal catalysts reach an orderly arrangement, and finally obtain an orderly and regular silicon nanowire array. 4. Electrochemical preparation of silicon nanowires is a new method in recent years. The technical idea of this method is to take SiO₂ as raw material and molten salt as electrolyte. By applying a certain cell voltage, SiO₂ can be reduced by electrolysis to generate simple silicon, which undergoes electrochemical nucleation and growth process under the action of high temperature, and finally obtains linear nano-silicon.

Silicon nanowire technology is to directly grow silicon nanowires on the battery electrode sheet. After absorbing lithium atoms, the silicon nanowires expand to four times the normal volume. However, unlike ordinary silicon structures, silicon materials of this structure can release stress well through axial expansion, without causing cracks or damage to the nanowires, thus preventing the electrode from being powdered. There are four electrons in the outermost layer of silicon, which is easy to form four covalent bonds to achieve an 8-electron stable configuration, so the silicon anode

can absorb more lithium ions, thus improving the battery capacity. NWs grown directly on the current collector do not pulverize or break into smaller particles after cycling. Rather, facile strain relaxation in the NWs allows them to increase in diameter and length without breaking. This NW anode design has each NW connecting with the current collector, allowing for efficient 1D electron transport down the length of every NW [10]. Musk said on Twitter that Tesla will mass produce batteries with a longer service life and a 50% increase in energy density within 3-4 years, that is, 400wh/kg. At present, the energy density of Panasonic 2170 battery cell of Model 3 is 260wh/kg. As Tesla Battery Day approaches, Tesla released the registration page of the Battery Day event on September 19. The background picture of the page is the structural diagram of a new battery material - silicon nanowire. As a known technology, silicon nanowire can reduce the weight and volume of the battery, thus improving the battery efficiency, and helping to manufacture batteries with higher energy density and longer service life, Tesla CEO Musk expressed optimism about the mass production of high energy density (400Wh/kg) power batteries, with multiple clues pointing to the technical route of silicon nanowires (used as lithium battery cathode), the research team of famous scholar Y. Cui of Stanford University and the battery start-up Amprus. The core technology of Amperes is to use silicon nanowire to manufacture battery cathode. The energy density of its 100% silicon nanowire battery products will be 50% higher than the existing lithium ion batteries, while the weight will be reduced and the life will be improved.

5. Conclusion

As people attach importance to the energy structure, public acceptance of EVs has been improved. Energy density of the battery is the most critical part regarding the popularity of EVs. The use of nanomaterials can improve the performance of lithium ion batteries in various aspects. Graphene can improve the cycle stability, carbon nanotubes have a better optimization role in large rate charging and discharging performance, and silicon nanowires can significantly increase the battery capacity. In the near future, lithium battery can achieve high capacity, high electron transmission efficiency, high cycle life and low cost through nanotechnology.

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