

Modification of Structural Materials in Lithium Batteries for Energy Density Enhancement

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Abstract:

The intensification of global warming led to finding clean energy a top priority. Lithium batteries have attracted much attention in the energy field due to their environmentally friendly characteristics. However, the current lithium-ion battery system is limited by material properties and faces technical bottlenecks such as low capacity, unstable voltage, and safety hazards, making it difficult to satisfy the high energy density requirements for large vehicles. Based on the research on the modification of lithium battery structural materials, this paper integrates methods that can improve energy density, including modification of anode, cathode, electrolytes, and separators, and provides a review of the overall structural modification of lithium batteries. It is shown by analysis that replacing the existing graphite anode with silicon-based materials and using hollow nano-silicon structures that can reduced volume expansion rates, adding cation doping or adding metal coatings to the cathode material, adding stabilizing additives to the liquid electrolyte or approaching solid electrolytes, and introducing polar groups and ceramic nanomaterials into the separator are all the ways to improve.

Keywords: Energy density; cathode material; anode material; separator; electrolyte.

1. Introduction

Today, global warming is increasingly harmful to the world, and the possibility of extreme weather events around the world has increased dozens of times over the past 100 years. The ice caps are melting and the sea level is rising, seriously disrupting the life patterns of the Earth's creatures. 70% of global warming is due to carbon dioxide emissions, and humans are

aware of these problems and are therefore researching cleaner and safer energy sources. Battery energy is such an environmentally friendly energy source, and the transition to electrified transportation, renewable energy integration has also driven the urgent need for ultra-high energy density batteries.

The internal structure of the current mainstream battery, the lithium battery, is mainly composed of four parts: cathode, anode, separator, and electrolyte. Its

operating principle is that during the charging process, the external electric field drives the cathode to deintercalate lithium ions, which then pass through the electrolyte and separator to the anode. At the same time, the electrons in the external circuit also flow to the anode. Therefore, lithium ions and electrons react and intercalate in the anode, resulting in a lithium-rich anode. The process is just reversed during discharge. Lithium ions are deintercalated from the anode and flow back to the cathode, releasing electrons to supply external circuit devices, similar to the “rocking chair” mechanism.

Lithium-ion battery systems have entered a technical bottleneck period, with their maximum energy density only around 265W/kg-280W/kg, while the energy density of commonly used transportation fuel gasoline is as high as 46500W/kg. Batteries cannot meet the energy density required by medium and large electric vehicles, which need at least 350 W/kg energy density [1]. The energy density of batteries is limited by materials’ strength, stability, capacity, and so on. To improve the energy density of lithium batteries, it is necessary to modify the materials of each part. In 2023, Francis Amalraj Susai, Amreen Bano and others synthesized NC90 cathode material, and by doping Mo and Bo dopants to form strong bonds with oxygen, the oxygen released by the cathode was reduced, so that NC90 improved the thermal stability during high voltage operation compared with ordinary nickel-rich layered cathode materials, and reduced the charge transfer resistance, significantly increasing the cathode voltage from 3.7V to 4.3V, and increasing the specific capacity from 190mAh/g to about 210mAh/g [2]. Although the research on cathode element doping and electrolyte additives is relatively mature, there are few studies that can truly optimize the overall design of the cathode, anode, electrolyte, and separator at the same time.

2. Structural modification

2.1 Anode Material

The most commonly used anode material today is graphite since it has high conductivity, high stability, and low cost, but its theoretical limit specific capacity is low, only 372mAh/g. Since specific capacity is proportional to energy density, graphite cannot be used as an anode material in the future. Scientists are also studying alternatives to the graphite anode. Silicon-based materials are one of them. It has almost 10 times higher specific capacity than that of graphite, up to 4200mAh/g. Because each atom can combine with multiple lithium ions, and silicon resources are abundant, the production cost is low and non-toxic, which meets the needs of sustainable development. In addition,

its delithiation potential is about 0.4V, which is significantly higher than the lithium deposition potential of 0V, indicating that it is less prone to lithium plating (lithium dendrite growth) and exhibits good safety [3].

However, the main problem with silicon-based materials is that upon lithium is embedded, they will undergo a phase change to form the $\text{Li}_{15}\text{Si}_4$ phase. The silicon atomic bonds break, and the lithium atoms are embedded and expanded, resulting in an increase in the distance between atoms, forming a loose and disordered structure, and a significant drop in the tap density to 0.3g/cm^3 . Since volume energy density is proportional to the tap density, the total energy density will also decrease [4]. The continuous and drastic changes in volume will cause a large amount of stress to occur inside the silicon particles, causing them to break. After repeated changes, the silicon particles will gradually pulverize and detach from the conductive network, causing the specific capacity to drop sharply to $<500\text{mAh/g}$ [5].

As for the problems of silicon-based materials, the future improvement direction is to improve the structure of silicon-based materials: nano/porous/hollow structure, so as to release stress faster, and their energy density and tap density are closer to the theoretical value. However, these structures also face different problems: Nano silicon: causes SEI film instability and leads to insufficient energy density; porous silicon: reduces conductivity, etc.; hollow silicon: requires precise design and high manufacturing complexity, etc.

2.2 Cathode

2.2.1 Layered Oxide

Representative materials include lithium cobalt oxide (LCO), ternary materials (NCM/NCA), and LRM. These materials usually exhibit a high theoretical specific capacity ($\geq 280\text{mAh/g}$) and a high working potential (3.7V). The product of specific capacity and the working potential is equal to the energy density, so layered oxide also has a very high theoretical energy density. Among them, lithium-rich manganese-based materials can reach more than 900 Wh/kg [6, 7]. In addition, the migration path of lithium ions between layers (Li layers) is a two-dimensional plane diffusion, which gives it excellent rate performance. Its structure also makes the compaction density reach 3.4-4.2 g/cm, so the volume energy density can be increased to more than 800 Wh/L. However, its main problem is that cracking or irreversible phase change is easy to occur during the reaction process, and oxygen is released at the same time, resulting in a decrease in voltage and energy density [8]. By doping a small amount of low-cost, highly controllable elements such as Zr, Mg, Ti, etc. to replace transition metal elements or lithium ions in the lattice, or

adding metal oxide coatings (Al_2O_3 , ZrO_2) or metal fluoride coatings, the chemical stability of the interface can be effectively improved, the decrease in specific capacity caused by irreversible phase changes can be alleviated, and its cycle times and stability can be increased [9].

2.2.2 Spinel oxide

Representative materials include lithium manganese oxide (LMO), etc., which have medium theoretical specific capacity (above 140mAh/g) and theoretical energy density above 410Wh/kg. It also possesses a 3D diffusion network, excellent performance, and abundant raw material resources with low production cost [7]. However, compared with layered oxides, their compaction density is only about 3.0 g/cm³. In addition, strong two-phase reactions during the reaction process are easily to occur, generating huge stress, which leads to a decrease in energy density [10]. Dopants such as Al^{3+} and Ti^{4+} can be added to increase the oxidation state of Mn, limit Mn^{3+} , and structural distortion, stabilize the lattice structure, drive two-phase segregation, and reduce stress accumulation, thereby improving energy density and cycle stability [11].

2.2.3 Polyanion oxide

Representative materials include lithium iron phosphate (LFP), lithium iron manganese phosphate (LMFP), sulfate ($\text{Li}_2\text{Fe}(\text{SO}_4)_2$), etc. These materials have high thermal stability: the olivine structure has excellent thermal stability >500°C without oxygen release; long cycle life, most of which are greater than 2500 times; iron and manganese resources are abundant and environmentally friendly, so the production cost will be lower. However, compared with the first two materials, the theoretical specific capacity and energy density of polyanion oxides are relatively low, at only about 120Wh/kg and 170mAh/g respectively, and their conductivity is poor, requiring conductive coatings or nano-particles, which also reduces the volume energy density [7, 10]. The redox potential of Mn can be improved from 4.0 V to 4.2 V and the specific capacity can be increased by 20% by Mg^{2+} doping, or anion doping can be added to replace O^{2-} with F^- , thereby enhancing the strength of chemical bonds, broadening the Li^+ diffusion channel, and improving the working voltage and volume energy density [9].

2.3 Electrolytes

Nowadays, the mainstream electrolyte, liquid electrolyte, often uses mixed solvents, because the electrolyte needs to meet a variety of conditions, including high dielectric constant, wide electrochemical stability, and compatibility, to effectively enhance the energy density and safety of the electrode materials. Among them, carbonate liquid electrolyte is more common, and its components include

lithium salt LiPF_6 , organic solvent cyclic carbonate and chain carbonate, additives (mostly VC, FEC) [12, 13]. As an ion conduction pathway between electrodes, the ion conductivity at room temperature is 10mS/cm, and SEI can be formed on the anode, which increases the number of battery cycles. The liquid electrolyte has a very high ionic conductivity, which makes the material closer to the theoretical energy density. However, the organic solvents in the liquid electrolyte are very flammable [14], which increases the possibility of thermal runaway of the battery and greatly reduces safety. Therefore, a complex and complete battery thermal management system must be installed in the lithium battery, which will increase the weight of the battery, thereby reducing space utilization and the energy density of the battery. In addition, the electrochemical window of the liquid electrolyte is low. When it is >4.3V, it will cause the solvent to oxidize and decompose. Therefore, it cannot be used in combination with high energy density cathode and anode materials (such as lithium-rich manganese-based) [13].

To solve the safety problem of liquid electrolytes, more electronegative substituents, such as cyanide or sulfone, can be introduced into common organic molecules to increase the reduction potential, thereby enhancing thermal and electrochemical oxidation stability and improving the initial coulombic efficiency. However, the addition of flame retardant will lead to a decrease in the performance of lithium batteries and a reduction in the number of cycles [14].

2.4 Separator

The role of the separator is to isolate the cathode and anode materials from contact and prevent battery short circuits. The pore structure allows lithium ions to pass through while blocking electrons to maintain electrochemical reactions. Its thin and light design helps to improve battery energy density while maintaining performance. The model research results from Yifu and Li Zhongchao Tan concluded that reducing the thickness of the separator by 95 μm increases the energy density for about 38.2Wh/kg [8, 15]. However, the thermal stability of the separator is relatively poor. The melting point of the common PP/PE separator is <160°C, which is very easy to melt and cause a short circuit between the cathode and anode. In addition, the separator is usually hydrophobic, which will cause uneven distribution of the electrolyte and increase the resistance of the lithium battery, reducing energy efficiency and density [16]. To address these issues, inorganic ceramics, polar groups, and carbon-based nanocomposites can be used to improve surface wettability, increase electrolyte absorption, and ionic conductivity. Ceramics can also effectively improve thermal stability.

3. Conclusion and Outlook

In order to improve the energy density of lithium batteries, there are several common issues to consider in the application of materials, namely, electrochemical window, ionic conductivity, theoretical specific capacity, thermal stability, and lightweight design. For the modification of the anode, it is necessary to focus on silicon-based composite structural materials, integrating the advantages of various structures, such as hollow porous silicon nanospheres, etc. to improve the theoretical energy density; for the modification of the cathode, the lithium-rich manganese-based materials with the highest theoretical energy density can be studied, and the problems caused by its irreversible phase change need to be solved by anion doping and spinel encapsulation; For the modification of the electrolyte, solid electrolytes need to be set as the ultimate goal, completely eliminating the flammable risk of the electrolyte, improving the compressive strength, expanding the electrochemical window, and further improving the energy density, but the problem of insufficient conductivity needs to be studied; for the modification of the separator, nanomaterials can be added to the inorganic ceramic separator, because the modification of the ceramic material will increase the thickness and weight of the separator, thereby reducing its energy density. The addition of nanomaterials can effectively maintain the energy density and can also increase the toughness of the separator and improve its strength.

The next 3-5 years will be a critical period for the development of technology routes. More research is needed to solve safety issues in the transition from semi-solid-state batteries to the interface conduction and cost control of the ultimate all-solid-state batteries, pushing lithium batteries towards a high energy density of more than 500 Wh/kg. In this way, people can further reduce the pollution of carbon dioxide to the environment and restore the “green” Earth.

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