Methods for improving negative electrode performance of lithium-ion batteries under low-temperature conditions

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Abstract. The benefits of lithium-ion batteries (LIBs), one of the most popular secondary batteries, include their high specific energy, prolonged cycle life, minimal self-discharge, lack of memory effect, and green environmental protection. Although they are now widely employed in a variety of industries, including new energy vehicles, digital devices, aviation, and aerospace, the present range of mainstream commercial products' applications is restricted to settings of normal temperature. Their uses are severely constrained at high temperatures because of a large decrease in energy density and an increase in resistance. One of the crucial factors is the deterioration in the performance of negative electrode materials. This article first explores the problems faced by the negative electrode of lithium-ion batteries under low-temperature conditions. Then, the research progress of common negative electrode materials and their reaction mechanisms during LIBs charging were introduced. In addition, methods for improving the performance of low-temperature anodes were emphasized. Finally, prospects for future LIBs under low-temperature conditions were presented.

Keywords: Lithium-ion battery, low temperature, negative electrode.

1. Introduction

With the economy's continued growth and the level of industrialization and urbanization rising, issues like old energy sources' high pollution and low efficiency have gotten progressively worse. In recent years, a number of novel energy power generating and energy storage technologies have arisen to address this issue. One of the most significant outcomes of these research efforts is the development of lithium-ion batteries.

Lithium battery development started in the 1950s, and it was first used as a main battery in the 1970s. Reusable secondary batteries were introduced in the 1980s. However, the pace of its civilian usage was frequently hampered until the 1990s because of several fire mishaps. Lithium batteries entered the civilian market after the development of safer LIBs. High specific energy, minimal self-discharge, long cycle capacity, no memory effect, and environmental preservation are all benefits of lithium-ion batteries (LIBs). They are currently widely utilized in spacecraft, mobile phones, new energy vehicles, and other industries as one of the fastest-growing and most prevalent new energy batteries.

Positive electrodes, negative electrodes, and electrolytes make up the majority of LIBs. The primary components of the positive electrode are layered oxide, spinel oxide, and polyanionic oxide [1], whereas the negative electrode is made of materials such as graphite, lithium titanate, alloys, etc. LIBs are usually composed of three parts: electrolyte, positive electrode, and negative electrode. The primary components of the positive electrode are layered oxide, spinel oxide, and polyanionic oxide [1], whereas the negative electrode is made of materials such as graphite, lithium titanate, alloys, etc. decrease electrical potential substances. This kind of battery operates on the "rocking chair" theory. Important parts of lithium batteries are the positive and negative electrode materials used to intercalate lithium. Both the oxidation-reduction reaction and the intercalation-deintercalation reaction are active simultaneously during the charge and discharge process.

As of today, temperature has a significant impact on lithium-ion batteries. The typical working temperature range of commercial lithium batteries is between -10°C and 60°C (using Tesla lithium iron phosphate batteries as an example). Due to lower energy densities or safety concerns, it is sometimes difficult to use in harsh climates (like Russia and other frigid locations). One major factor affecting battery efficiency is the impact of temperature on the negative electrode. Under low-temperature conditions, the negative electrode of lithium-ion batteries often reduces efficiency due to reasons such as decreased ion conductivity and increased resistance [2]. This article mainly introduces the negative electrode materials and related modification strategies for LIBs.

2. Dilemma of lithium batteries under low-temperature conditions

As of today, temperature has a significant impact on LIBs. The typical working temperature range of commercial lithium batteries is between -10°C and 60°C (using Tesla lithium iron phosphate batteries as an example). Due to lower energy densities or safety concerns, it is sometimes difficult to use in harsh climates (like Russia and other frigid locations). One major factor affecting battery efficiency is the impact of temperature on the negative electrode. The electrolyte is the largest obstacle in this area since it must have a lower melting point and the capacity to sustain relatively high conductivity at low temperatures because its ionic conductivity is liquid > gel > solid [3]. Additionally, it is impossible to overlook the issues brought on by electrodes.

The most common problem with the negative electrode of lithium-ion batteries under low-temperature conditions is the increase in resistance. The lithium plating formed when lithium metal is charged on the graphite surface will cause a decrease in capacity, and lithium dendrites will cause safety issues.

In addition, the conductivity, volume expansion, capacity loss, and safety issues that commonly plague negative electrode materials must also be taken into consideration, and it is worth noting that the impact of these problems is sometimes exacerbated under low-temperature conditions. The above factors need to be comprehensively considered to select anode materials suitable for use under low-temperature conditions.

3. Currently common negative electrode materials

Up to now, the research on anode materials for LIBs has been quite in-depth, which can be mainly divided into five categories: carbon-based compounds, lithium titanate, alloy materials, transformation transition metal compounds, and silicon-based compounds [4]. Lithium titanate has the benefits of zero strain (does not expand with charge and discharge) and high reduction potential, but has poor energy density. Carbon-based compounds primarily have the advantages of high conductivity and low cost, but they have low energy density and are harmful. They are now widely used in commercial batteries because they are less expensive and less expensive than carbon-based compounds, but the disadvantages of the latter three types of batteries include significant irreversible capacity loss, poor conductivity, and significant strain before and after charging and discharging.

3.1. Carbon-based compounds

Carbon-based compounds are currently the most widely used commercial electrodes. They have extremely low cost, excellent electronic conductivity, and a layered structure that facilitates the entry of lithium ions. However, the theoretical capacity is low (about one-tenth of metallic lithium), and natural stone The surface activity of the ink is not uniform, and there is a certain dendrite phenomenon.

Carbon electrodes can be divided into two forms: graphitic carbon and non-graphitic carbon. The reaction mechanism during the charging process of both is the same, that is, multiple carbon atoms are combined with one lithium-ion. As shown in the following equation:

$$Li^{+} + e^{-} + nC \rightarrow LiC_{n}$$

As the amount of Li embedded increases, Li-GIC undergoes a phase transition in the order of 4th order → 3rd order → diluted 2nd order → 2nd order → 1st order, and the value of n gradually decreases from 24 to 6, finally forming 1 The order intercalation compound LiC_6 is also the direct reason for the low energy density of carbon electrodes [1].

At present, the research on carbon-based compounds has been quite complete, and various modified graphites have been widely used in commercial applications. However, many new results have still appeared, such as carbon nanotubes, graphene, and three-dimensional shell-sphere structures at the microscopic scale [5]. Currently, extensive research has been carried out on its application under low-temperature conditions, and great progress has been made.

3.2. Lithium titanate

Lithium titanate is another electrode widely used commercially. It has the huge advantage of "zero strain", that is, the volume difference during charge and discharge is only one percent, the irreversible loss of capacity is extremely low, and the cycle life is very long. Carbon batteries are less dangerous but also less theoretically capable, more costly, and subject to the phenomena of flatulence brought on by the reaction of the embedded lithium state with the water.

The chemical formula of a single lithium titanate lattice is $Li(Li_{1/3}Ti_{5/3})O_4$. The charge and discharge process is also insertion-extraction. Only one lithium ion can be embedded in a lattice. As shown in the following equation:

$$Li(Li_{1/3}Ti_{5/3})O_4 + Li^+ + e^- \rightarrow Li_2(Li_{1/3}Ti_{5/3})O_4$$

Simplified to:

$$Li_4Ti_5O_{12} + 3Li^+ + 3e^- \rightarrow Li_7Ti_5O_{12}$$

3.3. Alloyed negative electrode material

Alloyed negative electrode materials include aluminum (Al), tin (Sn), magnesium (Mg), silver (Ag), antimony (Sb), silicon (Si), antimony (Sb), etc., and their alloys. The mechanism of the lithium-ion combination is different from that of carbon and lithium titanate. The charging process is essentially to form a lithium-containing alloy. The charging reaction equation is as follows:

$$M + xLi^+ + xe^- \rightarrow Li_xM$$

It can be seen from the mechanism that its specific capacity is higher than that of carbon-based compounds and lithium titanate. Taking silicon as an example, its specific capacity reaches 4200 mA*h/g. However, it currently has the disadvantages of large volume expansion, poor conductivity, low lithium ion diffusion rate, and substantial irreversible loss of capacity after the first cycle, and it is not yet commercially available. Although the current specific capacity of commercial electrode anode materials is already higher than that of cathode materials, further improvement in the specific capacity of anode materials can still improve electrode efficiency, while carbon-based compounds and lithium titanate have almost no room for improvement in this area. If the above problems can be solved solution, its commercial value will be fully reflected.

3.4. Transformation transition metal compounds

Transformation transition metal compounds (CTAM) mostly consist of selenides, phosphides, nitrides, sulfides, and oxides of transition metals.

The process involves a redox reaction as opposed to the concentrated materials indicated above. The material performs a redox reaction with lithium ions during charging to produce metal elements and a salt that contains lithium. During discharge, the metal elements are oxidized into metal cations, and then the ions in the lithium salt recombine to the initial state. The reaction equation is as follows:

$$M_aX_b + (b * n)Li^+ + (b * n)e^- \rightarrow aM + bLi_nX$$

Among them, M represents metallic elements, and X represents non-metallic elements such as oxygen and sulfur. The advantages of this material are lower production cost and higher theoretical capacity. The disadvantages are similar to alloyed negative electrode materials. In addition to poor conductivity, electrolyte decomposition, and large volume expansion, there is also serious voltage lag.

4. Methods to improve negative electrode performance

In response to the problem that electrodes are difficult to use under low-temperature conditions, researchers have proposed a variety of solutions, which can be mainly divided into five aspects: surface coating, composite materials, preparation of polymer materials, preparation of new materials, and improvement of electrolytes, all of which have achieved considerable results. The numerous and significant results have largely overcome the shortcomings described above. These methods are not independent of each other and are often used in combination during experimental and commercial processes.

4.1. Surface covering

One of the most popular ways to modify graphite electrodes is surface coating. Its primary purposes include reducing the specific surface area of natural graphite, covering the active areas on the surface, and preventing irreversible side reactions. To enhance their conductivity and other qualities, different negative electrode materials are occasionally coated with substances like graphite on the surface.

The graphite negative electrode of Samsung's commercial 18650 lithium battery was coated with Al_2O_3 by Friesen et al. [6]. The adherence of the coating significantly lowers irreversible deposition in the first cycle of the lithium battery, minimizing capacity fading, and the coating structure stays intact after several cycles, according to research. This coating also has a high thermal stability. However, there is still a flaw in that a thick layer of lithium metal deposits in the Al_2O_3 holes, reducing capacity.

Two-dimensional Fe_3O_4 nanorods with a nitrogen-doped carbon matrix layer were created by Chen et al. [7] and tested for electrochemical conductivity and material characterization using X-ray diffraction. It performs exceptionally well in terms of lithium storage at low temperatures and maintains a high reversible capacity of 760mAh/g after 900 cycles at -172°C and 1000 mA/g.

4.2. Composite materials

Composite materials refer to the combination of two or more materials on a microscopic scale. They are often combined with metal materials and carbon to achieve the purpose of combining the advantages of both and relatively avoiding the disadvantages. Generally speaking, this approach can achieve higher lithium storage performance and smaller resistance, and the performance under low-temperature conditions may be better than that of a single material.

Liu et al. prepared a MoS_2/C hybrid in which MoS_2 nanosheets and carbon layers are uniformly combined, which can be used as the negative electrode of low-temperature high-performance lithium-ion batteries [8]. The discharge-charge curves, ion diffusion rate, and its function relationship with discharge or charge time at 25°C and -20°C were measured respectively, as well as the morphological and structural evolution of MoS_2/C lithium transport under a scanning electron microscope. The results show that this MoS_2/C hybrid with a large interlayer spacing has excellent performance as a negative electrode for lithium-ion batteries under low-temperature conditions.

Ge et al. prepared two molybdate materials, $LiCr(MoO_4)_2$/C and $Li_3Cr(MoO_4)_3$/C [9]. The study found that both materials have multi-dimensional ion transport channel structures similar to those of fast ion conductors, which can increase the transmission efficiency of lithium ions. The conductive carbon was compounded with molybdate in a ratio of 9:1 and its charge and discharge performance was measured using electrochemical measurements such as XRD. It showed good results in the range of 0.01 to 3.00 V relative to Li and showed high cycle stability.

4.3. Polymer Materials

Research demonstrates that polymer carbon anodes, like graphene, can greatly enhance the performance of LIBs in comparison to hard carbon and soft carbon, which are easy to produce. The diffusion distance of lithium ions is decreased and the contact area between the electrolyte and the active material is increased as a result of the smaller particle size and thickness, but this has the drawback of creating lower contact density, which lowers volume capacity [10].

Up to now, common methods of using polymer materials to improve low-temperature performance include graphene, carbon nanofibers, etc. In addition, there are also related studies on materials such as lithium titanate, such as the preparation of hydrogen titanate nanotubes, intercalation materials, etc. Research on the material itself has become more and more complete, and the cutting-edge research direction is mainly focused on doping and making composite materials to further improve performance.

Tan et al. prepared Co_3O_4@graphene composite anode [11]. The researchers first compared pure Co_3O_4, intercalated graphite, lithium titanate, SiC, and other substances, and concluded that Co_3O_4 has the best cycleability in low temperature environments. After measuring the crystal structure of Co_3O_4@graphene, it was found that the main structure did not change but some smaller crystal grains appeared, inhibiting the agglomeration of Co_3O_4. Subsequent electrochemical measurements further proved its excellent capacity retention and cycle stability.

4.4. New material

There are currently relatively few studies on new non-carbon-based materials that meet specific needs under low-temperature conditions, mainly because such materials cannot yet be commercialized under normal temperature conditions. However, this research idea is also an important one for researchers. New directions to try.

Xiong et al. studied InSb as an anode material and found that it has both high capacity and high cycle stability under low-temperature conditions [12]. It still has a high degree of structure and cycle stability after 700 charges and discharges at -30°C and -50°C. The scientists postulate that this results from the creation of Li3Sb during the embedding of lithium ions in the negative electrode. Because of its structural resemblance to InSb, it protects the negative electrode from deterioration, preserves the crystal's structural integrity, and enables the 2500 mAh commercial soft-pack battery to run satisfactorily at -30°C for an extended period. Graphite must be doped into this material to increase electrical conductivity because it is a semiconductor material with weak electrical conductivity.

4.5. Electrolyte improvements

The method to improve the performance of the negative electrode can not only start from the negative electrode material but also operate through indirect methods. For example, on the surface of the negative electrode, the performance of lithium-ion batteries under low-temperature conditions is limited by the resistance interface caused by deposits produced by the decomposition of the electrolyte. This phenomenon can be alleviated by improving the composition of the electrolyte solution.

Dimethyl sulfite (DMS) was added by Lan et al. to the electrolyte to create a low-resistance anode surface [13]. They performed temperature analysis, scanning electron microscopy for morphology and color analysis of electrode surface, and electrochemical experiments using a multi-channel battery cycler. Following cycle testing and other techniques, it was determined that, in comparison to other marketed DTD additives, the discharge performance at low temperatures is quite good. The initial capacity of the battery is compared to the baseline electrolyte at 0.2C in the electrolyte containing 0.5% DMS at -20C. The retention rate is 82.13% and 74.28% at 0.5C; the cycle stability has also been significantly improved. It can still maintain 98.84% of the capacity after 50 charge and discharge cycles at -10°C (DTD can only maintain about 81%).

Yin et al. replaced ethylene carbonate (EC) in the lithium-ion battery electrolyte with the five-membered heterocyclic compound isoxazole (IZ), which not only circumvented the high melting point defect of EC but also showed a weaker solvent [14]. It exhibits high ionic conductivity and generates an inorganic-rich interface phase with a low activation barrier. Its cycle stability is also excellent, retaining 98.4% after 150 cycles at -20°C.

5. Summary

Up to now, there has been much research progress on improving the performance of carbon-based anodes for lithium-ion batteries under low-temperature conditions. The research directions are diverse and the achievements are remarkable. It is expected that these research results will enter the market in the not-too-distant future. However, for other anodes that have not yet been commercialized, the improvement of the anode itself has not yet been completed. The small amount of research that has been done so far has not been achieved, and further research may take a long time to show results. In addition, current major research is focused on the range of -10°C to -30°C, which is sufficient to cope with winter in most areas, but lacks response to more extreme climate conditions (such as Russia, polar regions, and outer space). ability, which is also an important research direction in the future.

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