Development of Anode Materials for Lithium Batteries

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Abstract: As the most promising secondary energy storage equipment, lithium batteries have been successfully commercialized. Compared with the existing new energy systems, it has the advantages of small size, light material, high voltage, long service life, and low pollution. Anode as the important part of lithium batteries, how its advantages are expanded is the research focus in future. Miniaturization of the negative electrode, nanometer, solved volume expansion problem and slowed down the lithium dendrite problem; Composite materialization provided higher cyclic stability; Alloying of materials made SEI film more stable. This article reviews the research progress on the properties, advantages and disadvantages, and improvement methods of C, Si, and Li-based anode materials.

1. Introduction

Natural resources are limited, and the utilization rate of energy is getting higher and higher, so it is accompanied by the depletion of future energy. Therefore, the society has invested a lot of energy in developing new and secondary energy sources, the most representative of which is the lithium battery. Among all new energy systems, lithium batteries are the most complete and widely used energy source. The shape, volume, and composition of lithium batteries are flexible. At present, they have been applied to various types of industrial production and daily life, occupying most of the energy market. Therefore, on the basis of the existing ones, the development of lithium batteries with higher energy, which can be applied in a larger field, is an important direction for researching lithium batteries. The anode, as an integral part of the lithium battery composition, has been divided into a separate field to study. The material, shape, volume, production method, and whether the reaction with the electrolyte are all important factors affecting the performance of the lithium battery. So the research on the anode of lithium battery also means the exploration of the future of lithium battery energy.

2. Carbon-Based Anode Material

C-based anode material is currently the most widely used in commercial lithium-ion batteries. It has a good charging and discharging platform, electrochemically inert and low price. It also can reduce the formation of lithium dendrites and improve safety [1]. However, due to the lower theoretical capacity of C-based anode materials, only about 372mAh/g, and the narrow layer spacing, its application in high-density energy fields is limited. C-based anode materials are mainly divided into two categories: Graphite materials and Non-graphite materials.

Graphite materials: Graphite as a negative electrode material has a good interlayer structure,Li^+ interposed between graphite layers to form an interlayer compound--Li_xC_6[2]. However, graphite is highly anisotropic, and its directivity is strong when lithium ions are intercalated, which makes graphite's large current charging and discharging ability worse[3].In addition, the electrolyte can also enter between the layers, causing a large change in the interlayer distance, which eventually leads to the shedding and crushing of the graphite layer[4], thereby reducing the cycling performance and service life of the graphite material. But graphite materials have flexibility, it can be subjected to various modification treatments to prepare graphite composite materials with better electrochemical performance. Modification methods include structural modification, coating treatment and element doping[5].

Non-graphite materials: Amorphous carbon (soft carbon and hard carbon). Soft carbon is represented by mesophase carbon materials. Its smooth surface forms a uniform and dense SEI film, reducing the capacity loss for the first charge[6]. Hard carbon is Refractory carbon, and has many advantages, such as high specific capacity and good cycle performance. However, shortcomings in the first week, such as low efficiency, potential lag, and poor rate performance of low-potential lithium storage, which have affected the application of hard carbon. (Improved methods include: extending the calcination time, reducing the content of H heteroatoms in hard carbon, etc.)[7]

The huge market demand for high specific capacity lithium batteries urgently requires negative electrode materials with high lithium storage capacity. Due to the limited capacity of carbon-based materials, new non-carbon materials such as silicon alloys, tin alloys, and lithium metals have become hot research topics.[8]

3. Silicon-Based Anode Material

The theoretical capacity of silicon is up to 4200mAh / g, which is more than ten times the capacity of graphite. Silicon and lithium can form alloys (Li_xSi) . Its charging platform is low, and it is difficult to cause lithium dendrites during charging, so that it has high safety[9]. Silicon is the most abundant element in the earth's crust, so it has a wide range of sources and low prices.

Although silicon is an ideal material in terms of capacity, it will have a severe volume expansion phenomenon during the charge and discharge process, and its change can reach 300%[10]. This will cause the material to fall or even smash, resulting in a rapid decline in capacity and poor cycle performance. Another major obstacle hindering the commercial application of Si anode materials is the unstable SEI film[11].

Aiming at the above problems, various research methods have been proposed in recent years, such as nanomaterialization of silicon materials, preparation of porous silicon elements, compounding of materials, and improvement of electrolytes, etc[12].

Nanocrystallization of silicon: Nanometer silicon can reduce the degree of change in absolute volume and can also insert the diffusion distance of lithium ions, which improves the electrochemical reaction rate. However, when the size drops below 100 nm, agglomeration is easy to occur, that is, “chemical sintering” phenomenon, which can accelerates the capacity loss[13].

Wang et al[14]. A silicon hollow sphere structure material with a diameter of 90 ~ 110nm was synthesized by solvothermal method. This hollow-structured nano-silicon, while effectively buffering the volume change of silicon, also increases the active point of reaction with lithium ions and Shorten the diffusion path of lithium ions, which make it have high specific capacity and excellent cycle performance.

Compounding of silicon: In silicon metal composite silicon carbide, silicon has strong adhesion to the substrate, stable electrode structure, and better cycling performance[15]. Using the unique properties of core-shell structure stability and controllability, composite electrodes with graphite as the shell and alloy particles as the core can better weaken the crushing of active particles and the destruction of the electrode structure during the charge and discharge cycle[16]. During the delithiation process, silicon undergoes an irreversible transformation from crystalline to amorphous[17]. That is, an empty “graphite shell” is formed, which provides sufficient migration channels for lithium ions.

The high capacity of silicon cannot be ignored. Based on this, researching a more effective structure to buffer volume changes and reduce capacity loss will be the future development of silicon.

4. Lithium-Based Anode Material

Li is the metal with the smallest specific gravity and good electrical conductivity. Its theoretical capacity is up to 3860mAh / g, which is much higher than the widely used electrode materials such as C, Si, Zn and so on. And its exchange current density is large, so the degree of polarization is small[18]. However, Li anode materials cannot be widely used because of their great safety issues.

The “lithium dendrite” problem. The phenomenon is common in all kinds of lithium batteries, but it is especially serious when Li is used as the anode material, which is also the biggest problem of Li anode materials. This is because the existence of “lithium dendrite” may pierce the separator, cause a short circuit of the battery, which may cause thermal runaway of the lithium battery and cause an explosion[19]. The “lithium dendrite” may break from the root, thereby forming “dead lithium”, which increases the resistance of the lithium battery and reduces the electrode life[20]. Overcharging and overdischarging may also cause an explosion. On the other hand, complex interfacial reactions lead to lower charge and discharge efficiency of the battery.

SEI film is also an important factor affecting Li anode material batteries[21]. The SEI film produced by the in-situ reaction of the electrolyte and the lithium negative electrode will passivate the lithium surface and protect the lithium negative electrode. However, the SEI film with poor physical and chemical properties is fragile, and the electrolyte and lithium salt are continuously consumed during the cycle, which results in a decrease in battery capacity and a decrease in coulomb efficiency.

For Li-based anode batteries, existing research has often improved from two aspects:

SEI film: The purpose of improving the SEI film is to improve the efficiency of lithium batteries by improving the electrolyte. Organic solvents are an important part of the electrolyte. Current research shows that ether solvents can achieve higher cycle efficiency[22], while carbonate solvents have a higher reactivity for lithium than ethers[23]. It is worth mentioning that the DOL electrolyte obtained from other studies is currently the best electrolyte for lithium batteries[24].

Improvement of Li electrode: Aiming at the problem of “lithium dendrite”, existing research often makes lithium into a small volume, such as nano-lithium, powder lithium, and lithium foam[25]. This increases the specific surface area of the anode, increases the number of deposition sites, and suppresses the “lithium dendrite” Formation. Other researches have made the anode into a lithium alloy, such as aluminum-lithium alloy, tin-lithium alloy, etc[26]. Compared to pure lithium materials, lithium alloys inhibit the formation of “lithium dendrites”[27]. The interface with the electrolyte is more stable, which will make the SEI film more uniform at the same time[28], making the lithium battery more stable. Therefore, lithium alloy is a more popular research direction in Li-based anode materials lithium batteries.

The safety of Li anode materials needs to be improved. Although the existing improvement methods such as lithium alloys have improved safety, they have also reduced the theoretical capacity. Therefore, in the future research road, how to optimize both aspects at the same time is the most difficult problem to overcome.

5. Conclusions

Since the successful commercialization of lithium-ion batteries, it has been widely used, and has made remarkable achievements in various fields such as automotive, industrial, and mobile communications. On this basis, in order for lithium batteries to be used in large-scale energy systems such as aviation and navigation, it is necessary to move towards higher capacity, higher cycle efficiency, higher energy density, and higher tolerance. And price development. Negative electrode materials have been widely studied as an important component of batteries. Among them, carbon-based materials are the most commonly used negative electrode materials but have low specific capacity. Silicon-based materials and lithium metal anodes have high specific capacities, but poor cycle stability. With the use of various modification methods, their service lives have been extended. However, whether these high-capacity negative electrode materials can be commercialized depends on whether the preparation method is suitable for large-scale production. A new form of anode material may emerge, which can break through the existing problems in the existing theory, which will also be a direction for the development of anode materials and even lithium batteries.

References

[1] Yan Xuming, Feng Guangzhu, Huang xue. Research progress of preparation and application of cathode material for lithium-ion battery[J]. New Chemistry Materials, 47(7): 22-25.

[2] Zhou Guanwei, He Yushi, Yang Xiaowei, Gao Pengfei, Liao Xiaozhen, Ma Zifeng. Graphene-containing composite Materials for lithium-ion batteries applications[J]. Progress In Chemistry, 2012, 24(2/3): 235-245.

[3] Wang Li. Synthesis of Graphene and Graphene-based Nanocomposites and Applications in Energy Storage[D]. Changchun: Jilin University, 2010.

[4] Wu Shenghui, You Jinkua, Lin Dangeng. Study on carbon negative electrode for lithium ion batteries[J]. ChineseJourhalofPowerSources, 1998,22(1):35-39.

[5] WU Ming-hao , CHEN Jian , WANG Chong , YI Bao-lian. Research progress in anode materials for Li-ion battery[J]. BATTERY BIMONTHLY, 2011, 41(4): 222-225.

[6] Wang Jincai, Li Feng, Liu Chang, Li Hongxi. Research status and development of carbon negative electrode materials for lithium ion batteries. Corrosion Science And Protection Technology, 2004, 16(5): 300-303.

[7] WU Ming-hao , CHEN Jian , WANG Chong , YI Bao-lian. Research progress in anode materials for Li-ion battery[J]. BATTERY BIMONTHLY, 2011, 41(4): 222-225.

[8] Wang Li. Synthesis of Graphene and Graphene-based Nanocomposites and Applications in Energy Storage[D]. Changchun: Jilin University, 2010.

[9] Gao Pengfei, Yang Jun. Si-Based Composite Anode Materials for Li-Ion Batteries[J]. Progress In Chemistry, 2011, 23(2/3): 264-274.

[10] Chen Jingbo, Zhao Hailei, He Jianchao, Wang Mengwei. Si-Based Composite Anode Materials for Lithium-ion Batteries[J]. Progress In Chemistry, 2009, 21(10): 2115-2122.

[11] Luo Fei, ChuGeng, Huang Jie, Sun Yang, Li Hong. Fundamental scientific aspects of lithium batteries(Ⅷ)——Anode electrode materials[J]. Energy Storage Science and Technology, 2014, 3(2): 176-163.

[12] Zhao Tiepeng, Gao Deshu, Li Zhaohui, Lei Gangtie, Zhou ji. Improvement progress of the Si-based materials for lithium-ion batteries[J]. Chinese Journal of Power Source, 2009, 33(1): 65-68.

[13] Gao Pengfei, Yang Jun. Si-Based Composite Anode Materials for Li-Ion Batteries[J]. Progress In Chemistry, 2011, 23(2/3): 264-274.

[14] Wang Hongbo, Zhou Yanhong, Tao Zhanliang, Chen Jun.Research progress of silicon--based anodes for lithium --ion batteries[J].Chinese Journal of Power Source, 2009, 33(11): 1029-1032.
[15] Wen Zhongsheng, Wang Ke, Xxie Jingying, Yang Jun . Research on high capacity silicon—containing anode material for lithium—ion batteries[J]. Chinese Journal of Power Source, 2004, 28(11): 719-722.
[16] Chen Jingbo, Zhao Hailei, He Jianchao, Wang Mengwei. Si-Based Composite Anode Materials for Lithium-ion Batteries[J]. Progress In Chemistry, 2009, 21(10): 2115-2122.
[17] Wang Hongbo, Zhou Yanhong, Tao Zhanliang, Chen Jun.Research progress of silicon--based anodes for lithium --ion batteries[J].Chinese Journal of Power Source, 2009, 33(11): 1029-1032.
[18] Ding Fei. Study on Lithium metal anode material of high specific energy Lithium secondary battery[D]. Harbin: Harbin Institute of Technology, 2006.
[19] Wang Xiao. A brief discussion on the lithium metal anode material in the two lithium battery with high specific energy[J]. Electronic Test, 2017, (1): 151-152.
[20] Yan Xuming, Feng Guangzhu, Huang xue. Research progress of preparation and application of cathode material for lithium-ion battery[J]. New Chemistry Materials, 47(7): 22-25.
[21] Geng Yaoyao, Sang Lin, Ding Fei, Qin Xiujuan, Shao Guang-jie. Development of lithium anode for rechargeable lithium metal batteries[J]. Chinese Journal of Power Source, 2019, 43(1): 158-162.
[22] Cheng Qi, Deng Hemin, Lan Qian, Liu ran , Tang Shun, Liang Jiyuan, Wei Feng, Tu Ji, Cao Yuancheng.Research Progress of Lithium Metal Cathode Materials for High Energy Batteries[J]. J. Jianghan Univ. (Nat. Sci. Ed.), 2018, 46(3): 197-204.
[23] Sun Qidi. Structural Design and Study of High-performance Lithium Metal Anodes[D]. Jinan: Shandong University, 2019.
[24] Wang Xiao. A brief discussion on the lithium metal anode material in the two lithium battery with high specific energy[J]. Electronic Test, 2017, (1): 151-152.
[25] Ding Fei. Study on Lithium metal anode material of high specific energy Lithium secondary battery[D]. Harbin: Harbin Institute of Technology, 2006.
[26] Gao Hongquan, Wang Hongqiang, Li Qingyu, Lv Bao-in, Huang Youguo. Development of Super-high Capacity Negative Electrode Materials for Lithium Ion Batteries[J]. Mining And Metallurgical Engineering, 2005, 25(5): 57-62.
[27] Tang Zhiyuan, Zhuang Xinguo, Zhai Yumei. Progress in studies on negative material for lithium ion battery[J]. Chinese Journal of Power Source, 2000, 24(2): 108-111.
[28] Geng Yaoyao, Sang Lin, Ding Fei, Qin Xiujuan, Shao Guang-jie. Development of lithium anode for rechargeable lithium metal batteries[J]. Chinese Journal of Power Source, 2019, 43(1): 158-162.