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Applying different nanomaterials to improve the performance of lithium-ion batteries

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Abstract. Due to their superior qualities, lithium-ion batteries (LIBs) have lately taken the top spot among rechargeable secondary batteries. To achieve the increasing demand for electricity in the related industries, its improvement and development are in full swing, especially the nanomaterials have become an important direction of improvement because of their special structure matching with charging-discharging mechanisms. This paper focuses on the application of nanomaterials in the LIBs. It briefly introduces carbon-based and silicon-based nanomaterials, metal (alloy), metal oxide (sulfide), MOFs nanomaterials, and Mxenes in lithium-ion batteries and lithium-sulfur batteries by reviewing the pertinent literature from recent years. including the reasons for their application, the application mechanism and the effectiveness of their improvement. It has been discovered that nanoparticles have numerous and intricate uses in the LIBs. It is hoped that this study can provide new ideas for the structural design and functional modification of nanomaterials in battery applications in the future.

Keywords: Lithium-Ion Batteries, Nanomaterials, Metal-Organic Frameworks, Mxenes.

1. Introduction

Lithium is a key component of rechargeable and dischargeable secondary batteries since it has the lowest density of all the metals and a relatively low oxidation potential, making it an excellent battery material. With the gradual increase in demand, lithium-ion batteries (LIBs) inevitably produce bottlenecks, with problems such as insufficient theoretical energy density, dendrite generation leading to cracking and a decrease in the number of cycles ensuing, and in the process of improving LIBs, nanomaterials, with their higher specific surface area, better mechanical properties, and lower diffusion lengths stand out as being essential to enhancing the LIBs performance.

At present, among the nanomaterials for the LIBs, the most widely used and mature one is carbon-based nanomaterials. High charge mobility and high specific surface area are just a few of carbon-based nanomaterials's exceptional structural qualities, providing a large number of lithium-ion embedded sites and fast charge/discharge channels. In addition, it has exceptional thermal and electrical conductivity as well as solar radiation absorption, which can be used for the subsequent development of solar LIBs.

With the development of electric vehicles and even electric airplanes, the theoretical energy density of lithium batteries has greater requirements, and conventional graphite anodes have increasingly reached their physical limits. Silicon, a member of the same family, has attracted attention for its high theoretical capacity, but the actual use of Si anodes is nevertheless constrained by a number of issues. The biggest one is the sizeable volume shift that takes place during full lithiation, which shortens the cycle life of the battery with creates severe cracking of Si and pulverization of the Si electrode. Nanosized silicon, on the other hand, reduces the mechanical stress caused by volume expansion, avoids structural cracking, and improves the number and stability of cycles.

Graphene can also work in tandem with other anode materials to enhance battery performance. For example, adding graphene to the sulfur cathode can be used to enhance the electrochemical performance of LSBs because it can be used to greatly boost conductivity, decrease sulfur volume fluctuation, regulate polysulfide and avoid the shuttle effect. The addition of noble metal nanoparticles to carbon nanomaterials can significantly increase the efficiency of LSBs batteries. In addition, there are some metal oxides (sulfides) nanomaterials that can be used as anode materials for the LIBs. Other research suggests that the molecule $CuLi_2(H_2O)_2HEDP$ (HPCuLi), which has a complicated hydrogen bonding interaction, may provide a stable route for Li^+ ion migration [1]. It can be seen that the application of nanomaterials in the LIBs is extensive and complicated. Therefore, integrating and categorizing them into distinct groups has significant practical implications and assists newcomers to understand how the associated systems are progressing as well as to learn from the past and create new paths. This research will be divided into several parts based on relevant literature in recent years, starting from the carbon-based and silicon-based nanomaterials, and gradually discussing the performance enhancement of carbon-based nanomaterials-doped, metal (alloy), metal oxide (sulfide), and metal-organic frameworks nanomaterials in the LIBs.

2. Application of different nanomaterials in LIBs

2.1. Carbon materials

Carbon-based nanomaterials used in the LIBs can be categorized into four types according to dimension: fullerene, carbon nanotubes, graphene and porous carbon. In fact, when they are used individually, the results are not very satisfactory, and only when compounded with other materials doped with more satisfactory results. Among them, the use of fullerene is actually very small, its single-crystal nature leads to its very small electric capacity, and the reversibility of lithium storage is very poor, even if it can be doped or hybridization modification of the way to improve the electric capacity and lithium storage reversibility, but subject to its own structural stability and preparation costs, its commercial use is still quite uneconomical.

The specific capacitance of carbon nanotubes is greatly affected by the structure and morphology, and there is a relatively high voltage hysteresis, so it is also generally used in composite with other materials, and currently there are studies with Fe_2O_3/C composites, MoS_2/TiO_2 composites, and V_2O_5 materials, and the results obtained are relatively good. Although graphene shows excellent physical and chemical properties such as high charge mobility, it often suffers from voltage hysteresis and low specific capacitance. And many metal oxides have large specific capacitance but poor conductivity, so the two complement each other to get the composite material can meet the needs of lithium batteries, TiO_2, Fe_3O_4, ZnO and other common metal oxides materials can be used in conjunction with it. Porous carbon is commonly used in the disciplines of energy storage and catalysis due to its plentiful pore structure, high specific surface area, and affordable manufacture. Micropores can be used to increase the charge storage capacity, and mesopores provide a fast channel for the transport of electrolyte ions to improve the electrolyte penetration, and macropores provide shorter diffusion distances for the electrolyte ions to facilitate the diffusion of the ions. This graded porous carbon can also be doped with heteroatoms such as nitrogen and phosphorus to change the internal charge distribution and create defects thereby adjusting the physical and chemical properties.

Unlike carbon-based materials, silicon-based materials face problems with structural stability. Graphite anode absorbs the largest amount of lithium ions can form a compound with the apparent chemical formula LiC_6, while the capacity of silicon is much higher, theoretically 10 times that of graphite, and can form a compound with the chemical formula $Li_{4.4}Si$, which stems from the fact that they absorb Li by a different mechanism, graphite for the insertion mechanism, and silicon for the alloying mechanism, and because of this, the transformation of its charging by the crystallization of silicon into an amorphous lithium Si process there is a considerable volume change of about 300%-

400%, and after discharge silicon becomes delithiated amorphous silicon, again there is a significant volume contraction, and the effect of these two mechanical stresses leads to cracking and powdering of the electrodes. Additionally, the electrolyte will be reduced at a lower potential during the battery's charging process and interact with Li^+ in a side reaction to form a layer of solid electrolyte membrane (SEI), which can transfer Li^+ and practically ensure the stability of Li^+ in the electrode. However, the silicon electrode, in the process of volume expansion and cracking, will continue to generate a fresh silicon surface, which continuously consumes electrolyte and lithium, generating more and more thick and inhomogeneous SEI film, which reduces the reversible capacity, the Coulombic efficiency and the ionic conductivity. And all these can be largely improved by reducing the size of silicon and using nano-silicon materials, which have been studied from zero-dimensional to three-dimensional silicon nanomaterials, although essentially, nano-silicon is electrochemically very similar to bulk silicon, with the same alloying mechanism and the same lattice changes, but nano-silicon is quite a bit superior to bulk silicon in fracture resistance due to the increase in yield strength, and therefore does not have a significantly larger volume cracking and no significant amount of SEI film generation. Additionally, Si/C composites have the important benefit that the carbon skeleton may effectively buffer the dimensional changes of the structure while simultaneously improving the material's electrical conductivity.

Along with carbon and silicon, germanium is a member of the carbon family and it is a substance that is utilized as an anode in the LIBs. Compared to carbon, germanium has a higher theoretical capacity of 1600 mAh/g, while silicon has an electrical conductivity that is about 100 times lower and a lithium-ion diffusion efficiency that is about 400 times lower [2]. it looks like an excellent material that draws on the strengths of both, however the lithium storage mechanism is the alloying mechanism of it, which is similar to silicon will be affected by the volume expansion problem, which is also similar to silicon can be solved by nanosizing. In addition, to slow down the volume expansion, another approach is to use AB intermetallic phase instead of B single metal phase, lithium involves the displacement of one metal, to generate Li_xB, where metal A is electrochemically inactive to buffer the change of the volume, for example, the combination of Ni_3Sn_4 with Li to generate Ni and $Li_{4.4}Sn$.

Lithium-sulfur batteries (LSBs) are an important type of LIBs that have arisen in recent years. Unlike the intercalation mechanism of the LIBs, LSBs follow a multistep electrochemical process. It belongs to the conversion reaction mechanism, in which sulfur is converted to Li_2S_2 and Li_2S_4 by the long-chain polysulfides Li_2S_8-Li_2S_6-Li_2S_4. Under this mechanism, compared to commercial $LiCoO_2$/graphite batteries, which have an energy density of just 387 Wh/kg, LSBs have the maximum energy densities approximately 2600 Wh/kg [2]. For this reason, the industry has paid close attention to it due to its greater energy density advantage. However, because of its much attention, many problems have been found in the commercialization process, such as the poor conductivity of S, which is only 5×10^{-30} S/cm, and the Li_2S_4-Li_2S_8 compounds generated in the discharge process are soluble substances that can migrate to the anode of Li to react directly to produce self-discharge phenomenon, making the Coulomb efficiency low. At the same time, the final stabilization product Li_2S is an insoluble substance, which will be encapsulated in the lithium electrode and cause passivation, a process known as the "shuttle effect". In addition, there is significant volume expansion and structural damage due to the difference in density. To solve these problems, researchers used graphene nanocomposites as sulfur hosts instead of the original pure sulfur cathode, with good results.

Graphene itself has excellent electrical conductivity, which can greatly alleviate the problem of poor sulfur conductivity. It has a sizable specific surface area, allowing scattered reactive sites to lessen the effect of volume expansion. With various patterns such as planar, sandwich, core-layer, and curl-like, Graphene can provide appropriate physical hindrance to slow down the degree of shuttle effect, A caterpillar-like graphene with 363 mAh/g at 1675 mA/g for 200 cycles was created by Xu et al. [3]. It may include polysulfides in graphene cages with high cycling stability. All of the above rely on the physical structure to improve the performance, but due to the absence of polar groups on graphene, the anchoring effect on Li_2S_x is weak to inhibit the shuttle effect, This can be strengthened by the inclusion of polar doping groups such as boron, nitrogen, hydroxyl carbonyl, and carbon to make the adsorption of polysulfides more effective at blocking the shuttle effect. Cheng et al. used CV, galvanostatic discharge-charge, and EIS to evaluate the performance of the developed battery [4]. They found that the original discharge capacity of 977 mAh/g was still maintained with around 76% capacity after 300 cycles. Alternately, by adding metal compounds to adsorb and catalyze the intermediate polysulfides, the shuttle effect can be further reduced. By adding Fe_2O_3 nanoparticles (NPs) to graphene sheets, Zheng et al. demonstrated how to create a three-dimensional (3D) Fe_2O_3-graphene hybrid material (referred to as Fe-PGM) and further suppress the shuttle effect. In this work, the cyclic voltammetry was used to assess when long-chain soluble polysulfides changed into short-chain insoluble polysulfides when Fe_2O_3 was added, possessing higher intensity and narrower peaks implying the enhancement of the reaction. And this catalytic enhancement of the anodic in-situ greatly reduces the occurrence of shuttle effects, 565 mAh/g of high capacity with a very low capacity fading rate over 1000 cycles at 5 C [5], as shown in Figure 1.

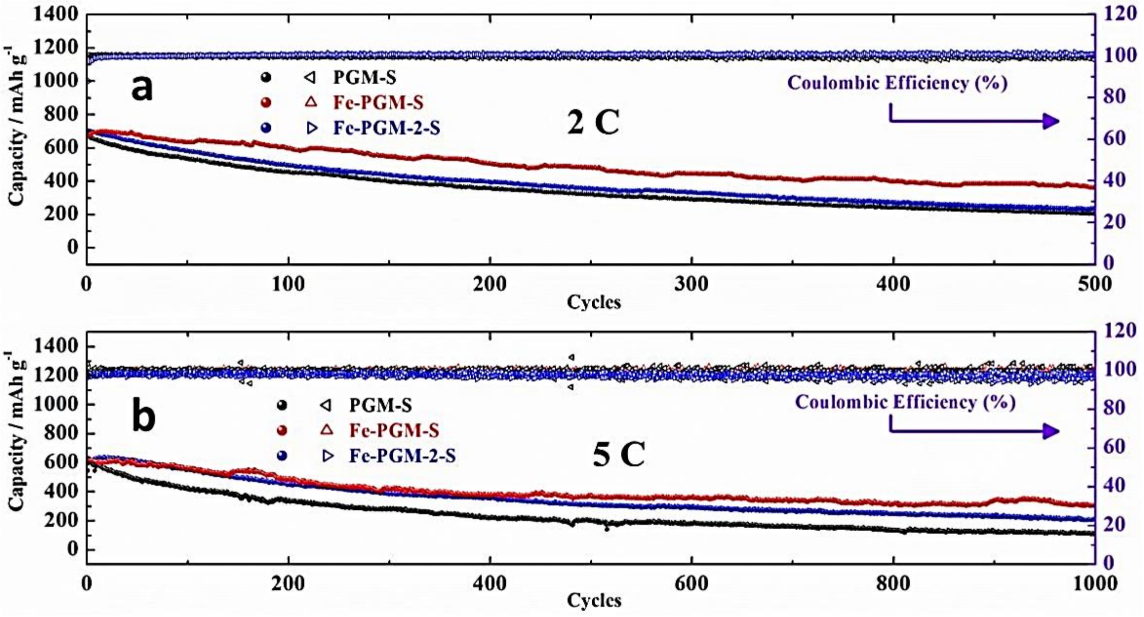

Figure 1. Cycling performance for the battery [5].

2.2. *Transition metal and porous materials*

Transition metal compounds are also widely used in lithium-ion electrode materials, it has good performance both in the anode and cathode, thanks to its corrosion resistance, high safety and low toxicity and low cost. However, this type of material also experiences a significant volume shift. The current treatment is comparable to that used on silicon and germanium and involves the use of composites modified with carbon nanomaterials or nanometallic compounds. Within this type of materials. Due to its enormous availability, cheap processing cost, and structural stability during charging and discharging, titanium dioxide is the most often utilized substance in anodes. In addition, due to its high working voltage of 1.75 V, TiO_2 can lower the likelihood of safety problems by inhibiting the development of lithium dendrites. Its lithium storage mechanism is also an intercalation mechanism. With its edge-sharing TiO_6 octahedra and chalcopyrite-like windows between sites, the crystal structure of TiO_2-(B) makes it simple for lithium ions to intercalate and has a storage capacity of 300 mAh/g [6]. Another material that has caused great interest is CuO, thanks to its extremely high theoretical capacity, in addition to its environmental friendliness and high abundance. Due to its low conductivity and high volume expansion, it has poor electrochemical properties; fortunately, these drawbacks can be overcome by nanosizing the material. Su et al. synthesized CuO nanowire arrays on copper foils, and they were able to achieve high capacities of 639 mAh/g at 100 mA/g and 520 mAh/g at 20 mA/g [7].

Metal-organic framework complexes (MOFs) are a type of polymeric nanomaterials with porous structure coordinated by organic ligands to metal clusters, which have big specific surface area, abundant pores, a lot of reactive sites and can adapt to the volume changes during lithiation and delithiation. It also can achieve different operating voltages by adjusting the types of ligands or central ions. Both the metal ions and organic ligands have a strong electron transfer capacity and loading capacity, which are stable and relatively more flexible in terms of their properties and performance, all these advantages have made it an excellent anode material for batteries. This is one of the areas in which the present high-performance LIBs are being developed. By adjusting the proportion of water to DMF in the solvent, Chen et al. created five cobalt-based metal-organic framework (Co-MOF) precursors with benzene tetraacetic acid as the ligand. The derivative D-1:5 obtained after firing under an Ar atmosphere continued to exhibit excellent electrochemical performance after 200 cycles. They believed that the calcination was the cause of the excellent electrochemical performance of the derivative D-1:5. They explained it by the production of a certain structure during the calcination process, where the inner layer of the material preserves the porous MOFs and the outer layer of the MOFs is wrapped in a thin layer of oxide and carbon. Without carbonization, the porous structured Co-MOFs' core was shielded [8]. This demonstrates the excellent performance of MOFs as well as their enormous potential.

Mn+1XnTx (n=1-4) is the fundamental chemical formula of mxenes, a novel class of 2D nanomaterials that has just emerged. The Tx indicates for the termination of the plane, which is typically related to the solvent under the synthesis circumstances. The more common ones are -F, -OH and -Cl. M is the transition metal, and X is carbon or (and) nitrogen. It can generally be prepared by breaking the weaker M-A bond through the MAX phase precursor.

MXene is mostly accordion-like multilayer or monolayer structure with conductivity up to 6000-8000 S/cm. Ti_3C_2Tx MXene nanosheets have a low Li diffusion barrier (0.07 eV), according to calculations using the density-functional theory (DFT) [9]. They also have a high ion diffusion capacity. Different and controllable architectures and morphologies, including 0- and 3-dimensional materials, are possible. It also has a large specific surface area. Chen et al. generated $MoS_2/Mo_2TiC_2O_2$ by in-situ sulfurization reaction of $Mo_2TiC_2O_2$ MXene to improve the cycling problem of MoS_2 , and first-principle calculations of it found that the interaction of Li_2S generated in the electrode reaction with $Mo_2TiC_2O_2$ is stronger than with pure MoS2, with greater variation in bond length and bond angle, having better adsorption properties, and this strong interaction makes the self-generation and shuttling effects, which are commonly found in pure MoS2, much weaker, and improves the Coulombic efficiency and cyclic stability [10].

3. Conclusion

Through the summarization of this paper, it can be found that different elements, different morphology of nanomaterials have different reasons for application, and there are cases of significant improvement in the anode and cathode, with three different application mechanisms, namely, alloying, intercalation and conversion reaction. The application of nanomaterials in the LIBs is indeed extensive and complex. The summary of this research can help the beginners in the related fields to understand the development of the field briefly and quickly, and hopefully can also play a minor help for the future development. Nanomaterials have become an excellent choice of electrode materials due to their high adaptability to volume changes in the charging and discharging process, strong electrical conductivity and ionic conductivity, abundant specific surface area and reaction sites and regional restriction of electrode reactions. From the perspective of development, nanomaterials are more inclined to develop into composites combining a variety of materials, a variety of morphologies, and a variety of mechanisms with the passage of time. It is believed that in the future, there will be more excellent composite nanomaterials to shine in LIBs.

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