Effect of optimizing the synthesis methods of Prussian blue on its application in sodium-ion batteries

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Abstract. Prussian blue has significant advantages as a cathode material for sodium-ion batteries. First of all, it has good electrochemical stability and reversibility, and can maintain high energy efficiency and cycle stability in multiple charge and discharge cycles. Secondly, Prussian blue has rich sodium storage capacity and high specific capacity, which can effectively improve the energy density and power performance of the battery. The preparation process of Prussian blue is relatively simple and the material cost is low. But Prussian blue also has several major drawbacks as a cathode material for sodium-ion batteries. Its low conductivity can lead to poor performance at high current densities. Long-term cyclic charge and discharge process capacity attenuation is serious, affecting the life of the battery. In addition, the structure of Prussian blue may change during charging and discharging, which is poor in stability, limiting its ability to operate stably for a long time. In this research, the performance of Prussian blue is effectively improved through the improvement of manufacturing process and chemistry, and its advantages are more obvious.

Keywords: Prussian blue, Preparation, Sodium-ion batteries, Application.

1. Introduction

With the continuous development of new energy, people gradually begin to use a large number of new green energy, like wind energy, hydroenergy, solar energy, geothermal energy and a series of environmentally friendly renewable energy has been discovered and put into use. There are many ways to obtain energy, but also need to store energy, so in recent years, energy storage technology is also rapidly improving. Battery is a very common way of energy storage, which is used by converting the chemical energy stored inside the battery into electrical energy to achieve energy conversion and output. The most common type of battery is lithium battery because it has a high energy density and can store more energy in the same volume. It has a long life, which means it can carry out thousands of charge and discharge cycles. It is lightweight, so it is often used in mobile devices, such as mobile phones, computers. However, due to the extremely uneven distribution of lithium resources, since 53% of the lithium resources are distributed in Bolivia, Chile and Argentina, according to the 2021 survey, so many countries need to import a lot of lithium. Because of the large-scale use of lithium ion battery manufacturing, it has led to a shortage of lithium resources and a significant increase in prices. The emergence of sodium battery is able to solve this problem. That’s because sodium is in the same family as lithium, it has similar chemical natures and works similarly.

Compared with lithium battery, the content of sodium resources in the Earth’s crust is 2.8%, much higher than the 0.0065% of lithium resources, and the distribution is more widespread, so sodium is easier to obtain, and sodium resources are cheaper. And sodium battery is still very safe and friendly to the environment. Prussian blue, the chemical name is ferric ferrocyanide, is a blue pigment. The chemical formula is $Fe_4[Fe(CN)_6]_3 \cdot nH_2O$, which is three-dimensional structure, stable at room temperature and pressure, and it is also inexpensive. It can improve the manifestation of sodium-ion batteries by utilizing Prussian blue as the positive electrode. The disadvantages of solution coprecipitation are low crystallinity, serious aggregation of ion clusters, and large amounts of water and lattice vacancies. For the purpose of reducing the nucleation rate, aggrandizing the crystallinity of the product and reducing the vacancy content of PBAs, it is a common practice to add chelating agent to the precursor solution. The ligands of chelating agents effectively prevent the spontaneous nucleation and precipitation of PBAs by forming complexes with transition metal ions. The negatively charged ligand ions can simultaneously adsorb on the surface of the initial nucleus, limiting the growth rate of the nucleus and effectively preventing serious grain aggregation. Under the action of chelating agent, the crystal nuclei are more inclined to form well-shaped, less defective and monodisperse grains.

Now there are citrate, oxalate, ethylenediamine tetraacetate disodium, ethylenediamine tetraacetate manganese sodium and sodium pyrophosphate have been added as chelating agents in the precipitation process. With the increase of NaCl concentration, the structure of PBAs changes from cuboid to multi-level rod-like and then to porous structure, which can increase its surface area during reaction, promote electrolyte penetration, and thus accelerate Na^+ transport. In electrochemical tests, the specific capacity of PBAs remained almost constant whether at room temperature or 80 ℃. Inactive coating, which is formed by the orderly arrangement of inert and active ions, can effectively improve the stability of the cycle and improve the compatibility of the interface. Using this conductive polymer coating can significantly improve the conductivity of PBAs electrodes, and it can also prevent transition metals from breaking down to form electrolytes during long-term cycling [1]. In this research, the improvement of various properties of the positive electrode materials of sodium-ion batteries using Prussian blue is discussed in view of the improvement and application of different preparation methods.

2. Improvements in electrochemical performance of Prussian blue by using different preparation methods

2.1. Effect of reaction temperature

The crystallization, accumulation and yield of PBAs were significantly affected by the reaction temperature. With the increase of reaction temperature, the diffraction peak becomes sharper, indicating that the crystallinity of PBAs increases. At lower temperatures (50 ℃), the nucleation rate of PBAs on KB is lower, resulting in a limited number of grains. When the temperature rises to 60 ℃ and above, the nucleation and growth of PBAs grains are favorable, and the formed grains show a complete cube morphology. Upon further temperature elevation, the initially wrought PBAs grains create additional nucleation sites, facilitating the upward accumulation of PBAs crystal particles and enhancing yield. At 80 ℃, the synthetic PBAs achieved a yield of 96.5%. Electrochemical tests revealed that batteries congregated with PBAs synthesized under these conditions exhibited outstanding cyclic performance, maintaining a capacity retention rate of 93.9% after 100 charge and discharge cycles. PBAs synthesized at 65 ℃ for battery assembly demonstrated commendable rate capacity, delivering a specific discharge capacity of 48.1 mAh/g at an ampere density of 1.0 A/g [2].

2.2. Effect of reaction time

The grain size of PBAs is affected by the extension of reaction time. With the increase of time, the diffraction peak becomes sharper, indicating that the crystallization of Prussian blue can be improved by extending the reaction time. At the reaction time of 4 hours, the diameter of the grain is about 500 nm, and there is almost no accumulation phenomenon. When the reaction time reaches 6 hours or longer, the diameter range of PBAs grains increases to 1~2 μm, and accumulation phenomenon begins. From 4 hours to 6 hours, the grain size of PBAs increased with the extension of reaction time. However, after further extension of the reaction time, the grain diameter no longer increases and basically remains unchanged after 6 hours. This is because with the increase of Prussian blue grain size, its specific surface area decreases, and the grain boundary energy also decreases, resulting in PBAs grains tending to be more stable and no further growth occurs. Therefore, the grain diameter of PBAs increases from 500 nm to 1~2 μm during the reaction process of 4 to 6 hours, but after more than 6 hours, due to the influence of surface energy, the grain size does not increase. Following a 10-hour synthesis period, the battery constructed with PBAs exhibited robust cycling performance, maintaining a capacity preserving rate of 90% after undergoing 100 times' charge and discharge circulations [2].

2.3. Effect of hydrochloric acid concentration

The morphology and lattice constants of PBAs are affected by the concentration of hydrochloric acid. With the increase of hydrochloric acid concentration, the diffraction peak gradually moves to the right, indicating that the lattice constant decreases. At 0.05 M and 0.10 M concentrations, PBAs showed a complete cubic morphology with grain size less than 1 μm, and the yield at 0.10 M concentration was higher than 0.05 M. However, at 0.15 M and 0.20 M concentrations, the grain morphology of PBAs becomes irregular. In acidic environment, the proper concentration of hydrochloric acid is conducive to the separation of ferrous ions, thus increasing the yield of PBAs. If the concentration of hydrochloric acid is too high, it may corrode the PBAs formed in the solution, resulting in the loss of the original cubic shape. In general, 0.15 M and 0.20 M concentration of hydrochloric acid can change the shape of PBAs, while 0.20 M concentration can enormously boost of the battery cycle consistency and rate capacity of PBAs as a positive electrode material [2].

2.4. Surface coating

By coating Prussian blue and PBAs compounds with inorganic compounds or carbon materials, side reactions can be effectively inhibited, thus improving the long-term stability of materials [3]. Of course, the use of polymers for packaging is also an effective approach. According to the different conductive properties of polymer substances, polymer composite Prussian blue materials can be divided into conductive polymer composites and ordinary polymer composites. Conductive polymers, also known as conductive polymers or synthetic metals, have good electrical conductivity. The main function of the composite of conductive polymer and PBAs is to use conductive polymer to modify the surface of PBAs and improve its conductivity without destroying its crystal structure. The uniform conductive polymer coating can effectively inhibit the dissolution of transition metals in the electrolyte. For example, using polypyrrole (PPy) as the coating layer can not only improve the conductivity of the material surface, but also reduce the damage of Prussian blue material and improve its cycling performance. Doped PPy can increase the reversible REDOX site, thereby increasing the capacity of the composite [4]. The coating of PPy not only enhances the electronic conductivity of the material, but also effectively prevents the occurrence of surface side reactions. The composite material shows excellent rate performance [4], such as a capacity of 108.6 mAh/g at a charge/discharge rate of 200 mA/g, and a retention rate of 79% after 500 cycles.

Prussian blue-based electrodes were designed [5]. The active material, conductive agent (Kochin Black) and binder (PVDF) are mixed in a mortar at a ratio of 7:2:1. After uniform grinding, the mixture is transferred to the mixing tube, and an appropriate amount of N methylpyrrolidone (NMP) is added, and then the mixture is prepared in a high-speed homogenizer. Use a scraper to evenly apply the mixed paste on the carbon-covered aluminum foil, and then put it in a vacuum drying oven at 120 °C overnight to dry. The dried electrode is cut into a circle with a diameter of 16 mm for subsequent assembly of the CR2025 button battery. The shell layer is introduced to slow down the volume change of the structure, so as to slow down the capacity decay. The selection of nickel-based material with smaller strain can effectively inhibit the lattice distortion of MnHCF material during the process of sodium ion removal, and improve the cyclic performance of the material. A series of MnHCF materials with different metal shells were prepared by adjusting ion species and ion exchange temperature. The initial capacity and capacity decay of MnHFC-S3 (Sc^{3+}) and MnHFC-S4 (Ni^{2+}) prepared at room temperature were compared, and the cyclic stability was obviously improved. Considering the high cost of rare earth metal Sc salt, Ni salt was chosen as the ion exchange object and the experimental parameters were optimized. The results showed that the initial capacity of Ex-MnHCF-Ni material reached 122 mAh/g, and the capacity retention rate was 62% after 200 cycles. It is found that the morphology of Ex-MnHCF-Ni particles is almost unchanged, but the fracture of MnHCF material after cycling is obvious. This further proves that the nickel-rich shell can stabilize the frame structure of MnHCF, inhibit volume change, and slow down the capacity decay during the cycle [5].

2.5. Doping-based preparation strategies

Doping is an effective method to improve the electronic and ionic conductivity of PBAs by introducing other elements into the crystal structure of the Prussian blue analog, aiming to enhance the electronic conductivity of the material and the migration rate of sodium ions (Na^+). By introducing a cation with a larger radius, the lattice strain during Na^+ insertion and removal can be slowed down, thus improving the cyclic stability of the material. In addition, the introduction of some electrochemically active ions helps to increase the specific capacity of the material [3]. During charging and discharging at high rates, the C-coordinated Fe^{3+} ions in iron based Prussian blue (FeHCF) result in relatively low capacity and structural instability. In the study, it was found that the electron cloud on the Fe-C bond moves towards the CN ligand, which is equivalent to the oxidation of the C-coordinated Fe^{3+} ions to a higher valence state, indicating that the partial substitution of Ni ions can improve the diffusion rate of sodium ions and stabilize the PB lattice structure, thus improving the magnization performance and cycle life of the material [5].

Carbon materials are an important class of PBAs modified materials due to their good electrical conductivity, large specific surface area and light weight [6]. Jiang et al. grow the nanoscale Prussian blue cube directly on the carbon chain, which has rapid charge transfer and ion diffusion ability [7], and has a specific capacity of 77.5 mAh/g at 90 C (Fig. 1) and 90 mAh/g after 2000 cycles at 20 C, with a capacity retention rate of 90%. Qi et al. prepared three-dimensional carbon skeleton (3DFC) with hierarchical porous structure using sodium citrate as carbon source [8], and grew PBAs in situ on the skeleton as a sodium electrode. Compared with the Rct (752.4 Ω) of KxNayMn[Fe(CN)] (KNMF), KNMF@3DFC shows a low Rct with a specific capacity of 62 mAh/g at 3200 mA/g current density. Wan et al. combined carbon nanotubes (CNT) with Prussian blue with a layered hollow structure [9], which has a large lattice expansion tolerance, reduces the Nat diffusion path, and enhances the electronic conductivity. Lee et al. coated graphene oxide with Prussia blue (PBGO) [10], which has a high specific capacity of 165 mAh/g at 20 mA/g current density and 68 mAh/g at 4 A/g current density, the Rct values of Prussian blue and PBGO are 3300 Ω and 247 Ω, respectively. The Prussian blue coated graphene oxide not only reduces the diffusion coefficient of Nat, but also reduces the diffusion coefficient of NAT. And it increases the electrical conductivity.

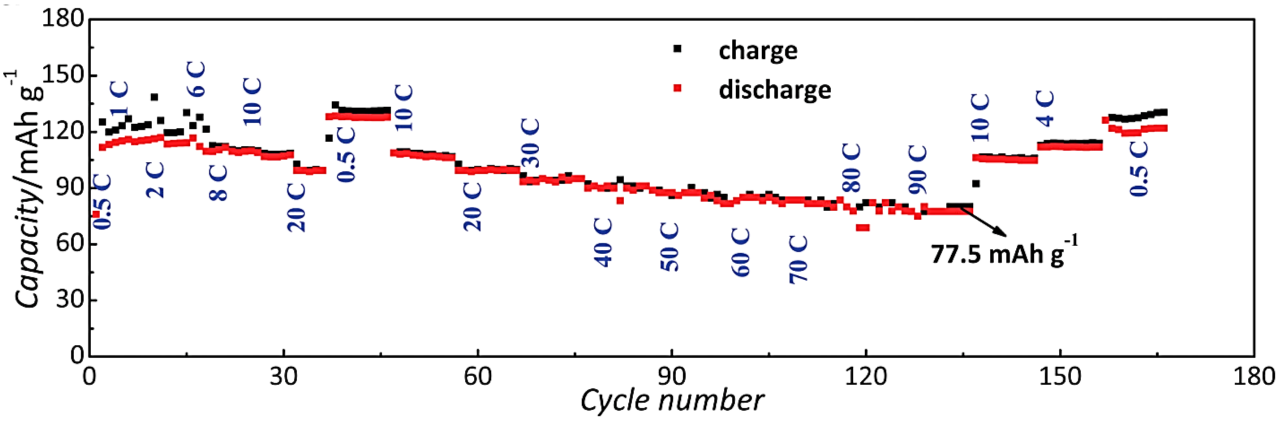

Fig. 1 Rate capability analysis [7].

At present, research has moved beyond single element doping to two or even three elements doping PBAs. For example, in previous studies, ternary NiCoFe-PB with high crystallinity, high Na content, low defects and no crystal water was synthesized by incorporating Co and Fe at the Ni site at the same time. First principles calculations verify that the double doping of Co and Fe enormously reduces the energy barrier and band gap of Ni-Prussian blue. Electrochemical tests show that in addition to high-spin Co and low-spin Fe, co-doping also improves the electrochemical liveness of low-spin Fe, and doping of Fe promotes the activity of high-spin Co. After co-doping, the thermal stability of the material is significantly improved. NiCoFe-Prussian blue can provide 120.4 mA/g discharge specific capacity. When the ampere density is increased to 1A/g, the highest theoretical capacity and good cycle performance can still be maintained. After 1500 periods of testing, NiCoFe-Prussian blue still maintains a high capacity of 68.3 mAh/g, while Ni-Prussian blue, NiCo-Prussian blue and NFEL-Prussian blue merely maintain a discharge capacity of 23.1, 41.4 and 47.3 mAh/g [1].

3. Conclusion

In the context of the era of substantial resource consumption, with the rising price of electrode raw materials, the cost of traditional lithium batteries continues to rise. In order to solve this problem, people have gradually shifted their research focus to lower cost sodium-ion batteries. Prussian blue has attracted much attention as a positive electrode material for sodium-ion batteries. Through chemical improvement and preparation process optimization, the crystallinity, yield, cycling performance, stability and magnification performance of Prussian blue can be significantly improved by adjusting reaction temperature, time and concentration of hydrochloric acid. The coating of the PBAs not only effectively prevents the dissolution of the transition metal in the electrolyte, but also significantly improves the electrical conductivity. Element doping can effectively improve the charging and discharging capacity and cycle stability of Prussian blue. Future research can explore more novel doping elements and preparation processes, and design more stable and efficient Prussian blue materials to meet the needs of sodium-ion batteries in the field of energy storage.

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