

Cathode Materials of Lithium Ion Battery

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Abstract. Lithium ion battery (LIB) technology is getting more and more attention for its superior electrochemical property in recent years and has begun to gradually enter the market occupying a certain part of market. The cathode conducts as an important part of LIB, its material will influence the overall performance of the battery greatly. This paper classifies and introduces multiple cathode material already basic applied commercially of LIB including LCO, LMO, Ternary Lithium Oxide (mainly introduce NCM and NCA) and LFP, showing their structure, physical property, chemical property (mainly the electrochemical property working as the cathode of LIB), synthesis in the lab and manufacturing approaches in the factory. In the end of the paper, the advantages and disadvantages of each material are summarized and the reasons why some of them have got commercial applications while other not yet are discussed. Besides, the future research directions of better the cathode material are introduced briefly.

Keywords: Lithium-ion battery, cathode material, commercial application.

1. Introduction

With the worldwide industrial development, the issue about the energy resource and environment pollution getting increasingly serious. Therefore, the development of the new energy storage device is an important subject at present [1]. Lithium ion battery (LIB) technology is regarded as one of the most concerned and potential new energy storage in 21st century and since the Japanese manufacturer Sony company launched the first LIB (applied oxidate of Lithium as the cathode material and graphite as the anode material) in 1991, after the improvement for more than 30 years the LIB technology has already gotten in people's lives successfully. Moreover, it has been proved by the reality that compared with other chargeable batteries like Nickel metal hydride battery (NMHB) the high-performance LIB will be more suitable for the portable electric equipment, electric vehicles and hybrid electric vehicles as its advantages including high specific capacity, high working voltage, high efficiency and less environment pollution.

The cathode part in the LIB system mainly acts on providing Li ion, which plays a marked role in the electrochemical properties of LIB including the capacity, the thermal stability and voltage [1]. Therefore, the design and manufacture of suitable, low cost and high performance cathode material is an important topic for the Lithium ion battery technology. In this paper, the main cathode material in LIB commodity product will be introduced. The paper will present a systematic review about each material of their structure, physical property, chemical property (mainly the electrochemical property), synthesis in the lab and manufacturing approaches in the factory. Besides, some typical researches and their results will be presented to show the unique property for each cathode material. Finally, the paper will give a brief conclusion for the recent development for the cathode material of LIB and the prospect about research trend according the existing problems and challenges.

2. LiCoO₂ (LCO)

LCO is one of the most important commercial cathode materials at present. LiCoO₂ is a typical layered 2D structure material. CoO₂ stacks close to form the 2D atomic plane and Li ion move freely through the 2D atomic planes. Li⁺ and Co³⁺ are alternately distributed in the octahedral position of the dense stack of O atoms. However, the atomic force between Li⁺ and O²⁻ and the atomic force between Co³⁺ and O²⁻ are different, leading to the distorted space structure, which is a space group with less symmetry.

The theoretical maximum value of the LiCoO_2 specific capacity can reach 274 mAh/g. However, in the practical application, the excessive exfoliation of Li ion will lead to the collapse of the space structure, reducing the cyclic stability rapidly. Therefore, the actual specific capacity for LiCoO_2 could only reach around 50% performance (usually less than 140 mAh/g). In the Li ion battery products, the charging voltage should be strictly controlled under 4.35V to limit the exfoliation number of the Li ion according its change/discharge test [2].

About the preparation methods of the LiCoO_2 , different synthesis methods will lead to the different structure and electrochemical properties of the material. The synthetic methods of LiCoO_2 mainly include solid state reaction method, hydrothermal method and sol-gel method, while the high temperature solid state reaction method is the most widely used one to synthesis the commodity LiCoO_2 material [2-4]. Meanwhile, to improve the capacity and recycle performance of LiCoO_2 , there are some researches about the synthesis of LCO in nano scale. The sol-gal method is the primary method to synthesis nanomaterial in lab, and the advantages of this methods are the raw material can be mixed in atomic scale, relatively low reaction temperature, good homogeneity, high specific surface area, etc. As for the industrial process, manufacturers will choose coprecipitation method which is simple, low cost and highly efficient to meet the large-scale requirement in industrial output. Even though the nano LCO material can commonly reach the higher charge/discharge capacity, its higher chemical activity also means greater potential safety hazard, especially in high temperature [5]. Therefore, the relevant researches about nano LCO cathode material are limited in number, and researchers prefer to choose the other cathode material for the Li ion battery, like using LNO as the alternative cathode material.

3. LMO

LMO is another important commercial cathode material for the Li ion battery. Comparing with the LCO, Mn element gets the advantages of more abundant raw material, lower cost and no toxicity. LMO cathode material mainly include 3 types: LiMnO_2 with layered structure, Li_2MnO_3 with layered structure and LiMn_2O_4 with spinel structure. Among these 3 types, LiMn_2O_4 with spinel structure is regarded the most potential type. Hence study on the LiMn_2O_4 cathode material accounts for the majority of the total researches. LiMn_2O_4 spinel structure is tetragonal symmetric crystal system and the space group is Fd_3m structure. Each unit cell gets 8 Li atom, 32 O atom and 16 Mn atom (50% Mn^{3+} and 50% Mn^{4+}) and each O atom is surrounded by 3 Manganese atoms and 1 Lithium atom to form tetrahedral structure. In the LiMn_2O_4 , the extraction of Li ion will not lead the change the symmetry of the structure but around 3V working voltage the Li ion will prolapse from its original location and lead the volume shrinkage of the unit cell and decrease the cycle stability of cathode [6,7].

The theoretical maximum value of the LiMn_2O_4 specific capacity can reach 148 mAh/g and the actual reachable capacity is around 120 mAh/g. There are mainly 2 issues about the LiMn_2O_4 : at the end of the discharge phase, the excessive Mn ion concentration will lead to the disproportionation of Mn^{3+} creating Mn^{2+} and Mn^{4+} , while Mn^{2+} could dissolve in the electrolyte and loss from the cathode. At the end of the charge phase the concentration of Mn^{4+} with strong oxidation is very high and will react with electrolyte. Therefore, the stabilizer and the surface modification technology is necessary for the battery manufacture [7, 8].

As for the preparation of the LiMn_2O_4 , the primary methods to synthesis LiMn_2O_4 are solid state reaction method, hydrothermal method, one-pot route method, mould method, etc. In the laboratory, researchers mainly apply the hydrothermal method and the mould method to synthesis nanometer level LiMn_2O_4 and carry out relevant research [9,10].

Wu et al used $\text{LiOH}\cdot\text{H}_2\text{O}$ (99% pure), MnO_2 (EMD, $\geq 97.5\%$) and $\text{Mn}(\text{NO}_3)_2$ (50% aqueous solution) as the starting material one-step synthesis LiMn_2O_4 using hydrothermal method. The sample obtained stable spinel structure and particle sizes were controlled under 50-300nm. According its

electrochemical test, the initial charge specific capacity and discharge specific capacity was 131mAh/g and 121mAh/g respectively and the capacity retention was about 95.7% at 40th cycle [9].

Beside the hydrothermal method, the mould method can overcome the shortage of wide aperture distribution and discontinuous holes and the mould can be easily eliminated by thermal treatment, getting applied particularly. Hua firstly synthesized the PMMA microspheric colloidal crystal mould with methyl methacrylate monomer and polyvinylpyrrolidone dispersant, after chemical cleaning and surface treatment. According to the ESEM and XRD analysis to the prepared sample, the synthesized LiMn_2O_4 materials were obtained with three-dimensional porous structure.

LMO nano particles have the analogous issue with the LCO nano particles. Particle size in nano scale means higher surface activity and in LMO Mn element consequently dissolve in electrolyte, which will bring the loss of Mn ion. Therefore, the researchers are trying to find suitable stabilizer to create stable surface coating to solve relevant issues [11].

4. Ternary Lithium Oxide

Both LCO or LMO that have been widely used commercially, and the LNO that is still in the development phase waiting for more programme to improve its performance, they all get significant advantages in some respects and get some limits in some of their properties. Based on this fact, researchers try to design the new type of materials composed with multiple elements and get advantages from multi types of materials. Ternary Lithium Oxide is the typical material designed on the basis of this thought [12]. At present, Ternary Lithium Oxide material considered to have great application potential include $\text{LiNi}_x\text{Co}_y\text{Mn}_{(1-x-y)}\text{O}_2$ (NCM) and $\text{LiNi}_x\text{Co}_y\text{Al}_{(1-x-y)}\text{O}_2$ (NAM).

On the current situation, NCM relying on its relatively low cost and high comprehensive performance has occupied a certain part of LCO battery market and the NCM material with high capacity, high security and long life cycle recently become a research topic drawing widely attention. NCM remain the $\alpha\text{-NaFeO}_2$ layered 2D structure generally (material mainly studied recently including NCM111, NCM811, NCM523 are all $\alpha\text{-NaFeO}_2$ layered structure). In the unit cell, Co atom will stable the layered structure and suppress the migration phenomenon of transition metal ion into Li sites. Besides, partial substitution of Ni by Mn will be helpful for the material safety and thermal stability --- Ni ion can inhibit the decomposition of electrolyte and help the diffusion of Li ion while Mn can improve the structural stability [13,14].

Up until 2020, NCM111 and NCM523 have already developed to a relatively mature stage and gotten preliminary commercial application. In the power battery, their specific capacity will be able to reach around 170mAh/g. As for other materials which are mainly the material with high Nickel content like NCM811, they were mainly troubled by the incomplete reaction and mixed ion discharge. These phenomena will lead to the security issue in the industrial process and that is the main issue researchers are trying to overcome [13].

About the synthesis method of NCM, there are actually not very special method for the ternary lithium oxide material. The primary methods for NCM are still high temperature solid state reaction method, hydrothermal method, coprecipitation method, etc. [15]. However, it is worth mentioning that as the special properties of NCM material, there will usually be some extra modification treatment for the NCM material product like surface covering or doping other element to improve the chemical properties of the material or solve some existed issues:

Hu et al. take a Li_2SiO_3 covering coat for NCM and the test shows that the initial specific capacity reach 182.3 mAh/g and the capacity retention is about 88% at 200th cycle while the raw material only get 52.1% retention [16]. Vu et al. used the solution with 0.2 wt% Na^+ doping in the NCM811, showing that Na ion was able to improve the layered structure stability and help the diffusion of the Li ion. The electrochemical test showed that under 1C and 4.5V voltage, the capacity remained 132mAh/g for 100th cycle and the retention is 69.1% while capacity of the raw material only remains 90.6mAh/g and the retention is only 49.5% [17].

$\text{LiNi}_x\text{Co}_y\text{Al}_{(1-x-y)}\text{O}_2$ (NCA) is another important type of ternary lithium oxide material. It is actually the cathode material developed at the same period with NCM. In structure, as the ionic radii of Al^{3+} and Mn^{3+} got little difference (Al^{3+} radius is around 0.0535nm and Mn^{4+} radius is around 0.053nm), NCA and NCM are almost similar and are both layered $\alpha\text{-NaFeO}_2$ structure [18]. According to the relevant research, when the Nickle content is constant, the structure stability of NCM is better than NAM while when the element scale is $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, NCA get the best electrochemical performance [19].

NCA is a material which actually achieves the commercial application, American EV manufacturer Tesla is the first company applied NCA as the cathode material for the electric vehicles power battery in the world, and according to their announcement, they have achieved profitability in 2013 for the electric vehicles with NCA cathode material power battery. After that, Japan and Korea achieved commercialized production of NCA cathode. However, in China, even some factories have already got the ability to produce the NCA material, there is still some difficulty with some precursor materials to synthesis and they highly depend on imports.

Similar to NCM, the modification treatment of the NCA material is an important topic for the researchers. Zhang et al. applied reaction sintering method synthesis NCA and dope the material with the Nb, Mo and Ti. Through the electrochemical test, the effects on electrical performance of different element were showed directly that Nb most increased the specific capacity of the battery while the Mo did least [20]. T. Fu et al. researched the LiTiO_2 covered coat's effect to the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. The specific discharge capacities of NCA, 0.2% LT-NCA, 0.5% LT-NCA and 1.0% LT-NCA at 0.2C rate were 186.7mAh/g, 190mAh / g, 192. 4mAh/g and 184.5mAh/g respectively, and the coulomb efficiencies of the first cycle were 83.6%, 83.9%, 84.9% and 83.1%, which mean that with a small amount of LT covered the coulomb efficiency of the NCA could be highly improved and when the LT content was around 0.5% the electrochemical performance showed the best [21].

5. LFP

In 1996, LFP materials with olivine structure were first reported as the potential material for the lithium ion battery cathode and in 1997 it showed the possibility about reversible insertion and removal of Li ion and firstly applied as the cathode of Lithium ion battery. According to the relevant research, LiFePO_4 has the advantages of high specific capacity, high structure stability, high security, environment friendly and lower cost. In crystal structure, LFP with olivine structure belongs to orthogonal crystal system, the existence of $[\text{PO}_4]$ tetrahedron limit the volume change of the LFP, which will affect the diffusion rate of the Li ion in the unit cell. Meanwhile, the movement of electron can only proceed in c direction, directly decreasing the electronic conductivity of the LFP. Therefore, how to improve the performance of LFP cathode Li ion battery is a highly concerned topic for researchers and up to now the main improving method include ionic doping, surface coating and synthesis nanomaterial [22].

The theoretical maximum value of the LFP can reach 170mAh/g and the discharge plateau is relatively lower (the discharge plateau of the LFP is around 3.4 V while the usual value of discharge plateau is around 3.6V). In view of its low conductivity and diffusion rate, researchers tried to apply the methods like ionic doping, surface coating and synthesis nanomaterial as introduced before to achieve the improvement [23].

Chung et al. show that some metal ion doped in the LFP will be able the replace the location of lithium in the LFP lattice, which could accelerate the electron transmission rate and improve the LFP's rate capacity. Their research modifies the LFP by doping high value metal ion like Mg, Ti, Nb and so on, leading the electron unbalance. At the charge phase, the LFP form the N-type semiconductor and at the discharge phase, the LFP form the P-type semiconductor. This special function highly improved LFP's rate capacity (increased seven to eight orders of magnitude) [24]. Shi found when LFP is covered by a small amount of Carbon, the electrochemical property of LFP could be greatly improved under the discharge plateau on 3.5V. The experiment showed the result of

the electrochemical test to the LFP with 5wt%, 10wt% and 15wt% carbon covered and according to the measured data, the LFP with 10wt% carbon covered get the best electrochemical performance in both long term cycling performance and the rate cycling performance while the LFP with 5wt% carbon covered get the poorest [23].

The larger the LFP particle is, the longer the lithium ion diffusion path and the smaller the diffusion rate will be. On the basis of this fact, applying the nano technology on LFP and synthesis the LFP material in nano scale will be an effective way to improve the conductivity of LFP. Huang et al. synthesized the LFP/C composite in nano scale. Its specific capacity reached 156.3 mAh/g under 0.2C rate and under 5C and 10C rate it could still reach 133.9mAh/g and 109.9mAh/g, showing excellent electrochemical and recycle performance [25].

6. Conclusion

Various cathode materials of LIBs have been introduced in the paper. LCO gets the relatively ideal electrochemical property but its resource is scarce, increasing its cost and Co is toxic leading to the problems about security. LMO with spinel structure solve the issue about the cost and toxicity but gets poor cycle performance. Ternary Lithium Oxide is of high commercialization potential but still in the technical breakthrough stage about the manufacture. LFP material treated by relevant technology gets good electrochemical performance and is friendly both for cost and environment, but it still has the problems like sensitive to temperature.

In terms of the current research situation, the future research direction will mainly focus on two points: On the one hand, researchers will try to keep applying the different technology like the element doping, surface coating to do the chemical modification for the materials we mentioned in the paper which has already get the relatively mature relevant technology and the basic commercial production with considerable scale. On the other hand, researchers will try to find some new material or some derivatives of the existing materials to replace the cathode in recent Lithium ion battery products, but the questions is that these materials like LNO, V_2O_5 , Li_2FeSiO_4 and so on even get the unique significant advantages working as the cathode of LIB and are regarded highly potential to become the new cathode materials. They all get some issues in property or limited area which prevent their large scale commercial production. Therefore the other research direction is to develop these materials in the experimental stage and their relevant technology. Besides, some collateral technologies like the recycle technology for the metal element in LIB and material precursors synthesis technology are also important for the final commercial application and getting more and more attention from the researchers. With the further development of the LIB technology and better electrode material with higher performance designed, lithium ion battery technology is bound to get wider application and occupy a more important position in the market and people's daily life.

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