The Future Trend of Manganese Positive Electrode

Jingzhe Shi *

Wuhan-Britain China School, Wuhan, China

* Corresponding author: awyman65256@student.napavalley.edu

Abstract. The high abundance and low cost of sodium resources enabled reaserchers to pay attention and do research in the fields of smart grids and large-scale energy storage. Among them, the positive electrode material not only determines the energy density of the battery, but also directly determines the cost of the battery. Therefore, selecting suitable sodium ion electrode materials has become an important research direction at present. Among the three mainstream cathode materials currently available, polyanionic compounds with NASICON structure as the main component have become potential cathode materials for large-scale energy storage because of their high ionic conductivity, structure, and thermal stability, compared to layered transition metal oxides and Prussian blue analogues. Sodium ion batteries have attracted widespread attention and research in the fields of smart grids and large-scale energy storage due to their high abundance and low cost of sodium resources. Among them, the positive electrode material not only determines the energy density of the battery, but also directly determines the cost of the battery. Therefore, selecting suitable sodium ion electrode materials has become an important research direction at present. Among the three mainstream cathode materials currently available, polyanionic compounds with NASICON structure as the main component have become potential cathode materials for large-scale energy storage due to their high ionic conductivity, structure, and thermal stability, compared to layered transition metal oxides and Prussian blue analogues.

Keywords: Energy Density, Thermal Stability, Structural Transformation.

1. Introduction

The emergence of lithium-ion batteries can be traced back to the early 1970s. During this period, scientists in the America and the Britain began researching lithium-ion batteries, attempting to use lithium ions instead of lithium metals, and using carbon as the negative electrode material. This type of lithium-ion battery overcomes the potential risk in safty of lithium-metal batteries and has become a focus of attention. In 1980, J. Goodenough discovered that lithium cobalt oxide could be used as a positive electrode material for lithium-ion batteries, laying the foundation for modern lithium-ion batteries. Lithium-ion batteries, a new type of secondary battery with high energy density, multiple cycles, and long service life, are widely used in mobile power sources, electric vehicles, home appliances, intelligent wearable devices, 3C products, and other fields. They have gradually become the main power source for new energy vehicles and energy storage, and have attracted widespread attention in recent years. In this article, the positive electrode of lithium batteries is investigated to check out whether manganese is a suitable material for the positive electrode of lithium batteries.

2. The Energy Density of Manganese Positive Electrode

There are four large-scale commercial lithium batteries, namely cobalt lithium batteries, ternary lithium batteries, lithium iron phosphate batteries, and manganese lithium batteries. These four types of batteries. In terms of energy density, the order from high to low is cobalt>ternary>iron phosphate> manganese; In terms of price, the order from high to low is cobalt>ternary>iron phosphate> manganese The reason is also easy to understand, rare things are precious. In new energy batteries, the cost of positive electrode materials accounts for approximately 40%, and among these four positive electrode materials, cobalt has the lowest content in the crust, only 0.001%, with a unit price of around 350000 RMB. So, lithium cobalt oxide batteries are the most expensive. Lithium cobalt oxide batteries were the earliest commercially available, mainly used in products such as mobile phones and laptops; Before the invention of BYD's blade battery in 2020, the batteries used in the installation of new energy vehicles were mainly ternary lithium batteries; Lithium iron phosphate batteries are currently the most popular. This is mainly due to BYD's invention of blade batteries last year, a structural and technological innovation that allows the same volume to accommodate more battery materials, thereby improving energy density and making up for the shortcomings of lithium iron phosphate batteries. Since then, sales have increased significantly. The total installed capacity of ternary lithium batteries is lower to the lithium iron phosphate batteries'. At the same time, lithium iron phosphate is also widely used in the field of energy storage.

Lithium manganese oxide batteries are mainly used for electric bicycles and small electric tools (such as electric drills, sweeping robots, balance vehicles, and drones). Contrary to the mainstream view of all of us, the production of lithium manganese oxide has surpassed that of lithium cobalt oxide among these four cathode materials. In 2020, the production of lithium manganese oxide in China was 92900 tons, while the production of lithium cobalt oxide was 73800 tons. In terms of shipment volume, lithium cobalt oxide is still higher, with 81600 tons of lithium cobalt oxide and 62600 tons of lithium manganese oxide

3. Synthesis Method of Manganese-Based NASICON Type Cathode Materials

Due to the low intrinsic conductivity of the NASICON structure, adding carbon-based nanomaterials through different synthesis processes is a necessary way to improve conductivity, as shown in fig.1. This paper summarized several typical synthesis methods at present, including the wet chemical method, solid phase ball milling method, and spray drying method, and summarized the effects of different carbon materials and synthesis processes on the micromorphology, conductivity, and electrochemical properties of materials. It is also believed that although graphene-based materials can effectively improve the electronic conductivity and electrochemical performance of positive electrode active materials, the high cost makes it difficult for such carbon-based materials to be commercially produced on a large scale. Therefore, in response to the demand for commercialization, proposing low-cost carbon materials and continuous production strategies is the primary choice.

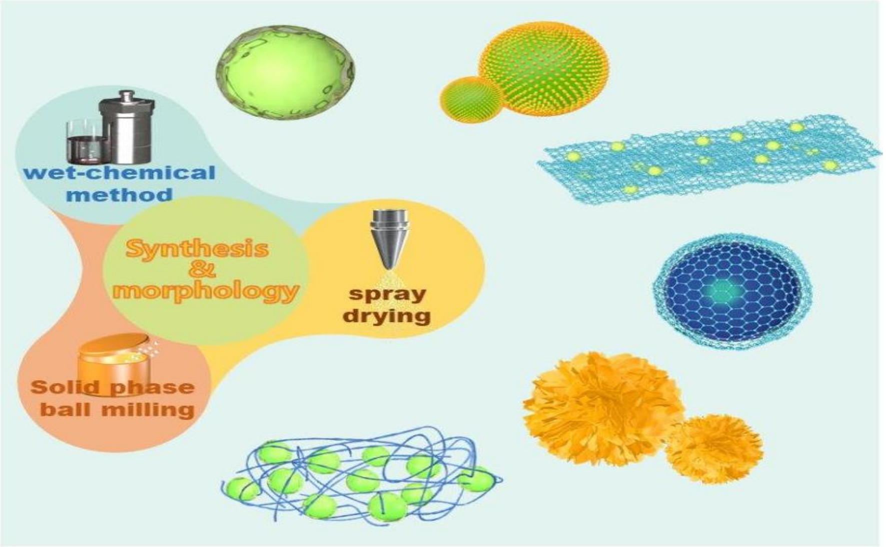

Figure 1. The products of synthesis methods [1]

4. Characterization of Thermal Stability, Oxygen Release, and Structural Transformation

To visually compare the thermal stability of lithium manganese-based cathode materials with different Mn contents, a certain mass (9 mg) of charged cathode material powder was added to a stainless-steel crucible for differential scanning calorimetry (DSC) testing, as shown in fig.2. At the same time, to reflect the actual battery situation, a certain proportion of electrolyte (7μL) is added to the material. Generally speaking, during the heating process, the reaction between the oxygen generated by material decomposition and the electrolyte will release enormous heat, causing the thermal runaway of the battery. From the DSC curve, it can be seen that when the Mn content increases, the exothermic peak temperature of the material gradually decreases and the exothermic heat gradually increases, indicating poor thermal stability.

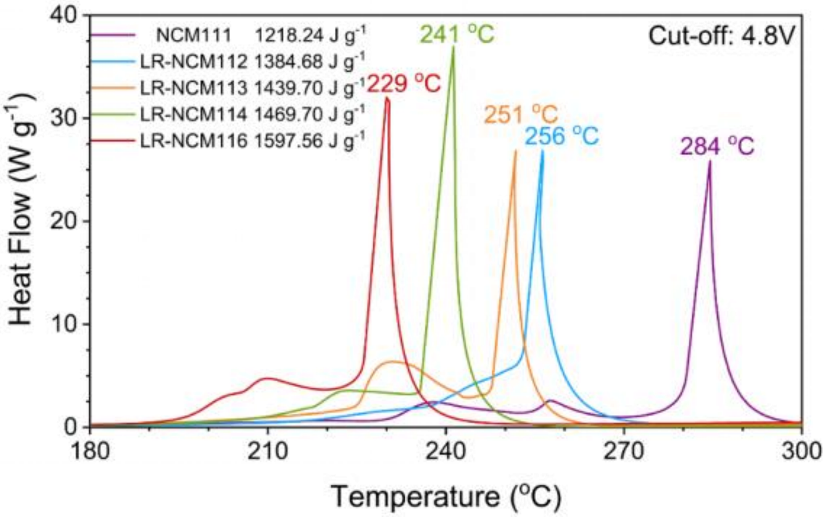

Figure 2. The heat flow of different materials [2]

Because the heat release of materials mainly comes from the reaction between oxygen and electrolyte, the ease of oxygen release can be used as a basis for determining the thermal stability of positive electrode materials. To monitor the oxygen production of the positive electrode material during the heating process, in situ thermogravimetric mass spectrometry (TG-MS) was used to characterize the mass loss and oxygen release of the electrode material during the heating process. The results in fig.3 showed that the high Mn content lithium-rich manganese-based positive electrode material released oxygen at lower temperatures, indicating its poor structural stability. Not only oxygen release, the structural transformation of the positive electrode material during heating also has strong a relationship with its thermal stability. Therefore, in situ, heated synchrotron radiation X-ray diffraction (In situ TD-SXRD) was used to detect the structural transformation of different cathode materials. During the heating process, the release of oxygen inevitably reduces the average valence state of transition metals (especially Ni^{4+}) and lowers the migration barrier of transition metals, thereby promoting the transition metal ions migrate from their octahedral positions through coplanar tetrahedra to the octahedral positions adjacent to the Li layer. In layered structures, the evolution of diffraction peaks for (003) R and (018) R/ (110) R can reflect the migration of transition metal ions. The results showed that the (003) R peak of high Mn content lithium-rich manganese-based cathode materials tended to shift towards a higher angle at lower temperatures, accompanied by a decrease in strength. At the same time, the (018) R/ (110) R diffraction peaks tended to merge. This indicates that high Mn-content lithium-rich manganese-based cathode materials are more prone to structural transformation at lower temperatures. Based on the above results, it can be found that the Mn element is not conducive to the thermal stability of lithium-rich manganese-based cathode materials, that is, the higher the Mn content, the poorer the thermal stability of the material.

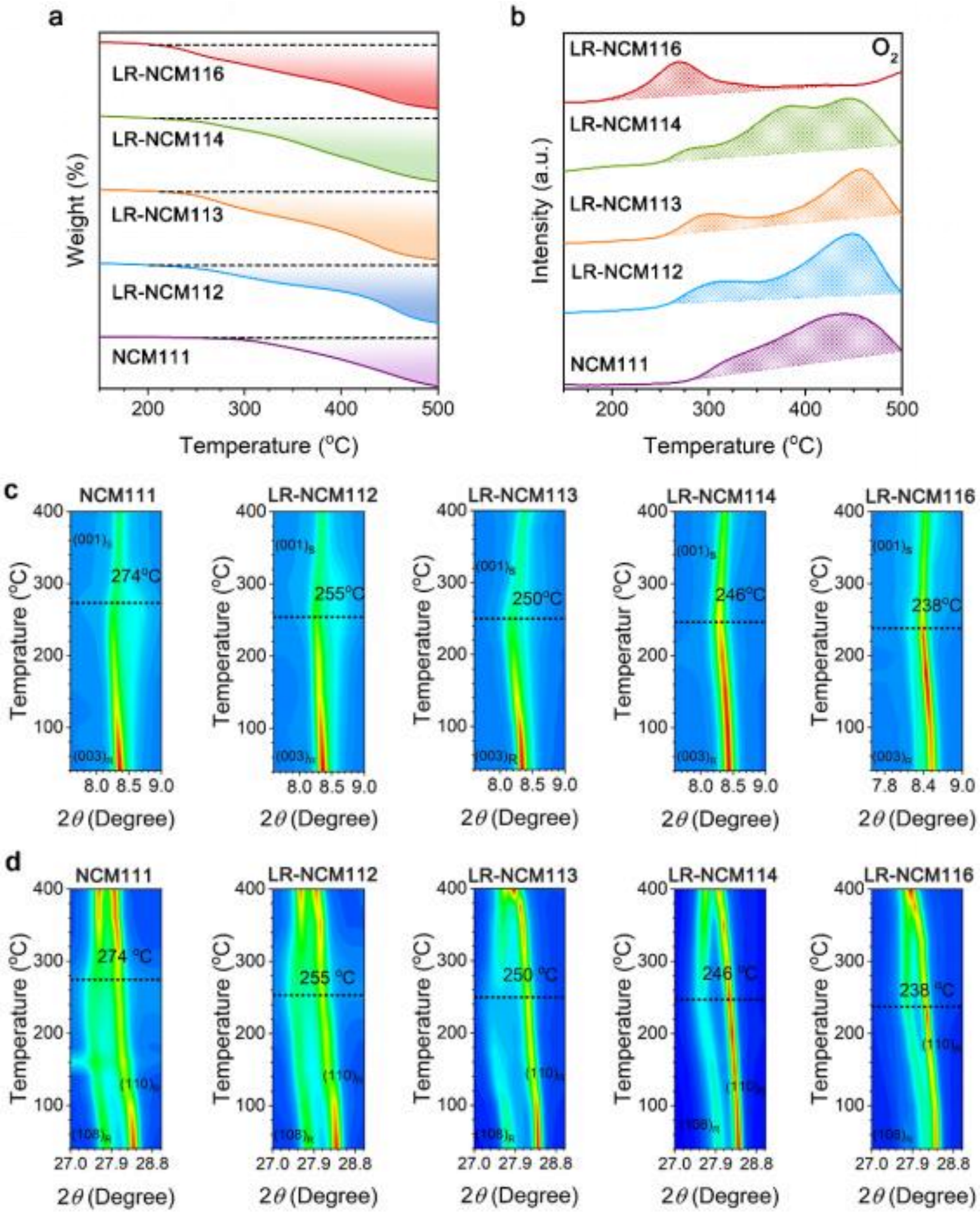

Figure 3. The weight and intensity of different materials [3]

5. The Prospect of the Production Chain of the Manganese Positive Electrode

Although there are certain shortcomings, because of the progress of material modification technology, the industrialization process of manganese-based cathode materials is accelerating. CITIC Securities expects a significant increase in the amount of manganese used in lithium batteries, which is expected to increase to over 1.3 million tons by 2035, more than 10 times the amount in 2021. Manganese will become the "fourth battery metal that cannot be ignored" [2]. CITIC Securities believes that positive electrode enterprises that are the first to develop and produce new manganese-based materials and manganese product manufacturers that extend downstream battery materials will benefit, and suggests investing around these two main lines. From the upstream manganese resource mining perspective, Qingdao Zhongcheng (300208. SZ) holds approximately 476 hectares of East Timor manganese ore, with an exploration area of 103.47 hectares and reserves of approximately 340000 tons, with a manganese content of approximately 45% -60%; Three Gorges Water Conservancy (600116. SH) has a complete industrial chain of manganese ore mining, electrolytic manganese production, processing, and sales. In terms of raw material processing enterprises, Minmetals Capital (600390) has the largest manganese tetroxide factory in Asia and the largest electrolytic metal manganese production base in China, with a market share of over 50%. The subsidiary of Red Star Development (600367), Dalong Manganese Industry, mainly produces electrolytic manganese dioxide (the main raw material of lithium manganate) for primary batteries and lithium batteries, as well as high-purity manganese sulfate for ternary cathode materials; [3] Zhonggang Tianyuan (002057) is the world's largest manufacturer of manganese tetroxide. Additionally, manganese product manufacturers have begun actively expanding their battery material business downstream. Xiangtan Electrochemical (002125) is the largest electrolytic manganese dioxide production enterprise in China, with an annual output of 122000 tons of electrolytic manganese dioxide. The company's products cover five categories: carbon zinc battery grade, mercury-free alkaline manganese battery grade, primary lithium manganese battery grade, lithium manganese oxide battery grade, and high-performance battery grade. The company is currently laying out manganese-based new energy battery materials such as lithium manganese oxide and manganese tetroxide [4]. To save capital, the company is searching for high-quality manganese ore resources with low cost and high safety in Hunan, Guangxi, and other places. It has now obtained a 51% controlling stake in Xiangtan Nanmuchong Manganese Industry Co., Ltd. and the exploration rights for the Aitun Manganese Mine in Jingxi City, Guangxi. After the resumption of production of Nanmuchong Manganese Mine, it is expected to provide a resource guarantee for the company. Among positive electrode enterprises, German Nano (300769. SZ), Dangsheng Technology (300073. SZ), Xiamen Tungsten New Energy (688778. SH), and Rongbai Technology (688005. SH) have successively carried out layout plans for manganese-based battery materials. In terms of lithium manganese iron phosphate, the German side's nano progress is relatively advanced. The company signed an investment agreement with the Qujing Economic and Technological Development Zone Management Committee of Yunnan Province in 2021 and 2022 for a new phosphate-based cathode material production base project of 10 billion yuan, with a focus on the key technology research and development of graphene composite phosphate iron manganese lithium-ion battery cathode materials. [5] The company currently has a 100-ton level pilot line, and the relevant products have been sent to the battery factory. The battery end testing has been completed, and it has entered the vehicle end verification stage. Dangsheng Technology and Xiamen Tungsten New Energy are still in the pilot stage. Industry insiders say that lithium manganese iron phosphate is currently not widely used, but it should be put on the agenda soon. [6] It is worth mentioning that "Ningwang" has quietly laid out its business in lithium manganese iron phosphate materials. In November 2021, Ningde Times (300750. SZ) first signed an equity transfer agreement with Jiangsu Litai Lithium Energy Technology Co., Ltd., followed by subscribing to newly registered capital. After some operations, Ningde Times owns 60% of the equity of Litai Lithium Energy, becoming its largest shareholder. Litai Lithium's main product is lithium manganese iron phosphate material, and it has multiple nationally registered proprietary technology intellectual property patents for lithium manganese iron phosphate. In contrast, fewer enterprises layout nickel manganese lithium materials. According to the 2021 third-quarter report of Rongbai Technology, the company's LNMO material pilot process has matured and is actively promoting performance optimization and process scaling-up experiments. In terms of lithium-rich manganese-based production, multiple domestic companies have reserved relevant production technologies. Rongbai Technology and Dangsheng Technology have now entered the small trial stage. It is reported that enterprises such as Duofu Duo and Zhenhua New Materials have also carried out research and development work related to lithium-rich manganese-based materials

6. The Advantages and Disadvantages of the Manganese Positive Electrode

The first thing to understand is that due to the industry's higher requirements for the energy density of lithium-ion batteries, such as electric vehicles, consumer (3C) electronic products, and energy storage devices, the development of high specific capacity and high voltage cathode materials to improve battery energy density has become a research hotspot. However, looking at the current commercial application of positive electrode materials, $LiCoO_2$, as the first positive electrode material used for commercial LIBs, has a high working voltage and is easy to prepare. However, its high cost and toxicity limit its large-scale application; Although some breakthroughs have been made in the research of replaceable positive electrode materials such as $Li_{1.2}Ni_{0.2}M_{0.6}O_2$, $LiMn_2O_4$, $LiFePO_4$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, and $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$, all of which have a capacity of 120-160 $mAh \cdot g^{-1}$, the energy density of these materials is usually less than 200 $Wh \cdot kg^{-1}$, making it difficult to meet the current market demand for LIBs. The lithium-rich manganese-based material $xLi_2MnO_3 \cdot (1-x) LiMO_2$ (transition metals such as $0<x<1$, M=Ni, Co, Mn, and their combinations, referred to as LMR) uses cheap manganese as the main transition metal element, and its discharge specific capacity can reach over 250 mAh/g, thus attracting widespread attention from researchers [7]. Compared with commercial cathode materials LMO, LFP, LCO, NCM, and NCA, LMR has a higher energy density, the lithium-rich manganese-based cathode material is composed of two components: LiMO (M=Co, Mn, Ni, etc.), and Li_2MnO_3, with the molecular formula written as $xLi_2MnO_3 \cdot (1-x) LiMO_2$. The two components have similar structures, both of which are α- A layered structure of $NaFeO_2$ type, in which oxygen atoms are arranged in a cubic dense arrangement. The transition metal (TM) layer in the $LiMO_2$ structure does not contain Li^+ and belongs to the hexagonal crystal space group (fig.4 a); In the Li_2MnO_3 structure, one-third of the Mn in the transition metal layer is replaced by Li (Fig. b), forming a "honeycomb" structure where Li is surrounded by six Mn atoms (Fig.4 c).

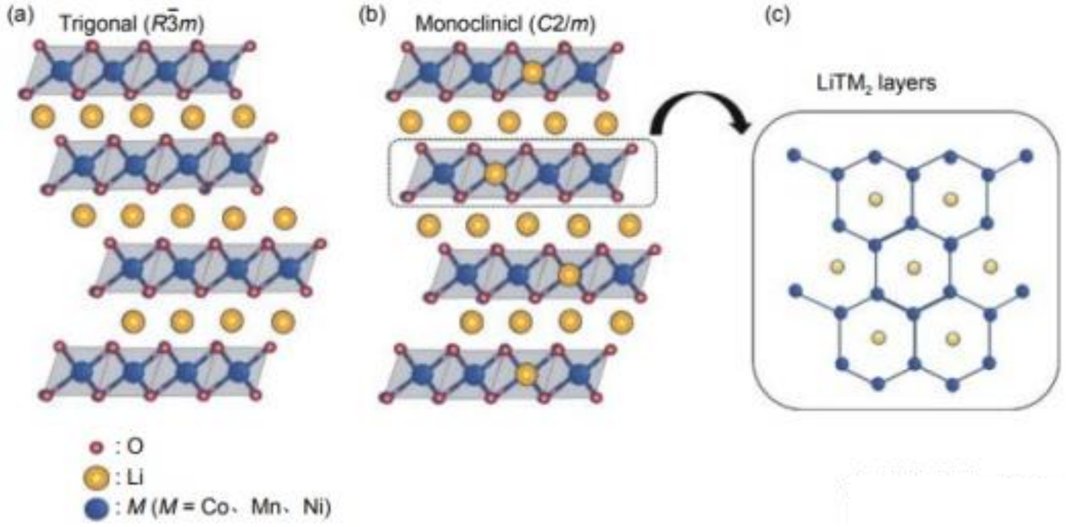

Figure 4. The formation of the LiTM2 layers [4]

LMR is different from traditional layered materials in that its charging and discharging process involves the redox reaction of transition metal ions and the charge compensation reaction of oxygen anions. The morphology and microstructure of its precursors have a very important impact on its final electrochemical performance. Common precursor synthesis methods include coprecipitation, sol-gel, and hydrothermal methods, but only coprecipitation is suitable for large-scale applications. The following figure shows the process flow diagram of the precipitation method for preparing lithium-rich manganese-based precursors. If sodium carbonate is used as the precipitant, the resulting LMR precursor is carbonate precursor $Mn1-x-yCoxNiyCO_3$. If sodium hydroxide is used as the precipitant, the resulting LMR precursor is hydroxide precursor $Mn_{1-x-y}CoxNi_y (OH)_2$ [8]. LMR is different from traditional layered materials in that its charging and discharging process involves the redox reaction of transition metal ions and the charge compensation reaction of oxygen anions. The morphology and microstructure of its precursors have a very important impact on its final electrochemical performance. Common precursor synthesis methods include coprecipitation, sol-gel, and hydrothermal methods, but only coprecipitation is suitable for large-scale applications. The following figure shows the process flow diagram of the precipitation method for preparing lithium-rich manganese-based precursors. If sodium carbonate is used as the precipitant, the resulting LMR precursor is carbonate precursor $Mn_{1-x-y}Co_xNi_yCO_3$. If sodium hydroxide is used as the precipitant, the resulting LMR precursor is hydroxide precursor $Mn_{1-x-y}Co_xNi_y(OH)_2$.

According to relevant reports, the laboratory stage of lithium-rich manganese-based materials has reached 400mAh/g, and after formal batch production, it can reach a level of approximately 300mAh/g. If matched with silicon carbon-negative electrodes, it is expected to reach 400Wh/kg. For the application prospects of lithium-rich manganese-based materials, the industry expects that if high-performance lithium-rich manganese-based materials can be applied, they can theoretically replace ternary positive electrodes and some iron lithium positive electrodes, and even create more increments. They are popular in many fields such as automobiles, energy storage, small power, and digital, with huge potential.

Due to the larger size and mass of Na^+(0.102nm; 22.99g/mol) compared to Li^+(0.076nm; 6.94g/mol), there are significant challenges in developing electrode materials for sodium-ion batteries, especially the positive electrode material that determines the energy density of the battery. Thanks to the research and application of transition metal lithium oxides in lithium-ion batteries, transition metal sodium oxides (Na_xMeO_2, Me=Co, Ni, Fe, Mn, V, etc.) have been widely studied and developed as cathode materials for sodium-ion batteries. Previous studies have shown that manganese-based ($Na_xMn_{1-y}M_yO_2$, M: doped element) materials have advantages such as abundant resources, simple synthesis process, high theoretical specific capacity, strong controllability of chemical composition and phase structure, and environmental friendliness, which have attracted widespread attention from many researchers [9].

$Na_xMn_{1-y}MyO_2$ materials can generally be divided into layered and tunnel structures. Layered $Na_xMn_{1-y}MyO_2$ ($0<x \leq 1$) materials have been widely studied due to their high sodium content and ability to provide high specific capacity.[10] However, it is prone to irreversible phase structure changes during storage and charge discharge processes, resulting in poor material stability and cycling performance. Furthermore, the presence of positive electrode/electrolyte interface reactions directly affects the positive electrode material, resulting in structural changes and the generation of new substances that can have adverse effects on the battery charging and discharging process;[11] In addition, the ordered arrangement of Na^+/vacancies in the material can lead to complex redox peaks during the charging and discharging process, hindering the transport rate of sodium ions and thereby affecting rate performance and cycling stability.

7. Problems in the Industrialization Process

Compared to graphene and graphene oxide, the industrialization process requires further research on carbon nanotubes with high packing density and low cost, as well as carbon-based materials doped with heteroatoms. To obtain high energy density cathode materials, precise synthesis technologies such as spray drying are feasible ways for future industrialization. Jahn Teller's non-active metal ion doping, construction of high entropy material systems, and introduction of anionic groups can take the advantages of different metal elements to show better performance of the sodium ion storage. Compared to liquid electrolytes, solid electrolytes not only improve safety but also prevent harmful migration of ions. Using advanced characterization technology to systematically evaluate the entire battery system, to construct a high energy density, all climate, and high safety sodium ion battery system.

8. Conclusion

NASICON Type Cathode Material has high energy density, low cost, and environmental friendliness, and is a potential development direction for positive electrode materials in the future. Its specific capacity is as high as 300mAh/g, far higher than the discharge-specific capacity of current commercial applications of positive electrode materials such as lithium iron phosphate and ternary materials. It is the key technology for the energy density of power lithium batteries to exceed

400Wh/kg. At the same time, lithium-rich manganese-based materials are mainly composed of cheaper manganese elements with low content of precious metals. Compared with commonly used lithium cobalt oxide, they not only have lower costs but also better safety. At present, there are few application cases of lithium-rich manganese-based materials in the industry. Rongbai Technology and Dangsheng Technology have developed rich lithium manganese-based cathode materials for layout; The discharge-specific capacity of the low cobalt material buckle battery produced by Rongbai Technology is no less than 245mAh/g at a current density of 0.33C at room temperature; Low cost and high capacity, suitable for liquid batteries. Currently, samples have been sent to multiple domestic and foreign home appliance core enterprises for testing. Dongcheng Technology reported in the 20th year that it will promote the development of new strategic products for solid-state lithium batteries, lithium-rich manganese-based batteries, and sodium-ion batteries, improve the strategic layout of intellectual property rights, strengthen patent risk prevention and protection mechanisms, and seize the technological highland of the next generation of lithium battery positive electrode materials.

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