

Technologies for the Use of Positive Electrode Materials for New Energy Vehicles

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Abstract. Under China's relevant policies, the focus on civilian vehicles has shifted from fuel vehicles to new energy vehicles. However, there are a variety of choices for the positive electrode materials of battery systems, and different positive electrodes have different advantages. This paper investigates three cathode materials used in new energy vehicles, describes their preparation methods, and compares their performances. The results are that the highest first discharge specific capacity is for a lithium-ion battery prepared from $\text{LiNi}_{0.94}\text{Co}_{0.04}\text{Al}_{0.02}(\text{OH})_2$ as the cathode material, and the highest first coulomb efficiency and cycle capacity retention is for a lithium iron phosphate battery prepared from a LiFePO_4/C composite. The purpose of studying the three materials in this paper is to understand the advantages and disadvantages of the batteries used in the current new energy electric vehicles, and in the follow-up research, try to further improve their characteristics according to these their battery capacity and thermal stability.

1 Introduction

As the risk of global climate change persistently increases, and energy shortages become increasingly severe, the willingness of countries around the world to promote the use of green, low-carbon energy sources increases further. In the "Action Plan for Peak Carbon Emissions by 2030", China has proposed to optimise its industrial and energy structure, and significantly improve energy efficiency in key industries. By 2030, the consumption of non-fossil energy will be roughly 25%. The plan also aims to cut CO_2 emissions per unit of GDP by more than 65% from 2005 levels, successfully achieving the goal of peaking carbon emissions before 2030 [1]. As cars continue to grow in popularity, their energy consumption is also increasing year by year, while traditional fuel cars not only have a large demand for energy but also cause serious pollution to the ecological environment, so the development of new energy vehicles is also an inevitable choice for the future development of the automotive industry [2]. However, the traditional lithium-ion battery cannot fully satisfy the requirements of electric vehicles (EVs) in terms of price, energy density, rate performance, cycle stability, and safety, so there are still some limitations and challenges in developing electric vehicles [3].

The current urgent need to improve the range of electric vehicles has prompted the development of high specific energy power batteries. Among all components

in lithium ion batteries, cathode materials play a significant part in battery performances. The introduction of composite cathodes can meet the requirements for high specific energy, high safety, long life, and low cost in order to achieve a balanced and coordinated performance of power batteries [4]. Tesla and Volkswagen have introduced Li-ion battery new energy vehicles with ternary cathode materials as the cathode in the market, which are nickel-cobalt aluminium and nickel-cobalt manganese, respectively. They are regarded as the most promising lithium-ion battery cathode materials due to their benefits of long cycle life, high energy density, and low environmental contamination [5-7]. BYD uses lithium iron phosphate batteries in its EVs, which have the advantages of high safety, low cost, stable discharge voltage, and long life.

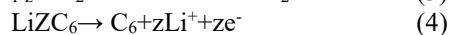
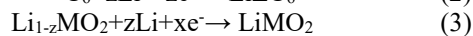
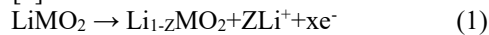
This paper will introduce the cathode materials used by these three companies in new energy vehicle batteries and compare their performance, advantages and disadvantages, and try to suggest possible improvement methods and prospects for the future.

2 Working mechanism of lithium-ion batteries

In essence, the process is a lithium ion enrichment tank. In the process of charge and discharge, the negative electrode's lattice contains embedded Li^+ that is retrieved from the positive electrode, so that the positive electrode

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shows the characteristic of "lack of lithium". In the process of charge and discharge, Li^+ is extracted from the positive electrode and embedded in the positive electrode, which makes the positive electrode show a lithium-rich state. In order to maintain the charge balance, it is necessary to move the same amount of electrons and Li^+ between the positive and negative electrodes during charge and discharge, so that the positive and negative electrodes produce oxidation-reduction, thus maintaining the potential [8].



(M is a transition metal element)

3 Three battery materials for the cathode

3.1 Nickel-cobalt aluminium batteries

3.1.1 Advantages of nickel-cobalt aluminium batteries

The advantages of nickel-cobalt aluminium batteries over the commercially available rechargeable lithium cobalt-acid batteries are as follows.

(1) It is safer because its electrolyte is non-flammable, whereas the electrolyte in lithium cobaltate batteries is flammable and explosive.

(2) Nickel-cobalt-aluminium batteries have a longer life because their cathode material structure is more stable and less prone to swelling and dissolution.

(3) Higher energy density because its cathode material has a higher specific capacity and can store more electrical energy.

(4) Lower cost because the raw materials are cheaper and the production process is simpler.

(5) Better environmental friendliness, as it contains less cathode material and is less polluting to the environment.

3.1.2 Preparation of nickel-cobalt-aluminium cathode materials

$\text{Ni}_{0.94}\text{Co}_{0.04}\text{Al}_{0.02}(\text{OH})_2$ and $\text{LiOH}\cdot\text{H}_2\text{O}$ (battery grade) prepared by co-precipitation method were mixed in a stoichiometric ratio of 5% lithium excess and heated to a set temperature of 745 °C in an oxygen atmosphere to obtain $\text{LiNi}_{0.94}\text{Co}_{0.04}\text{Al}_{0.02}(\text{OH})_2$ cathode material powder (Fig 1) [9].

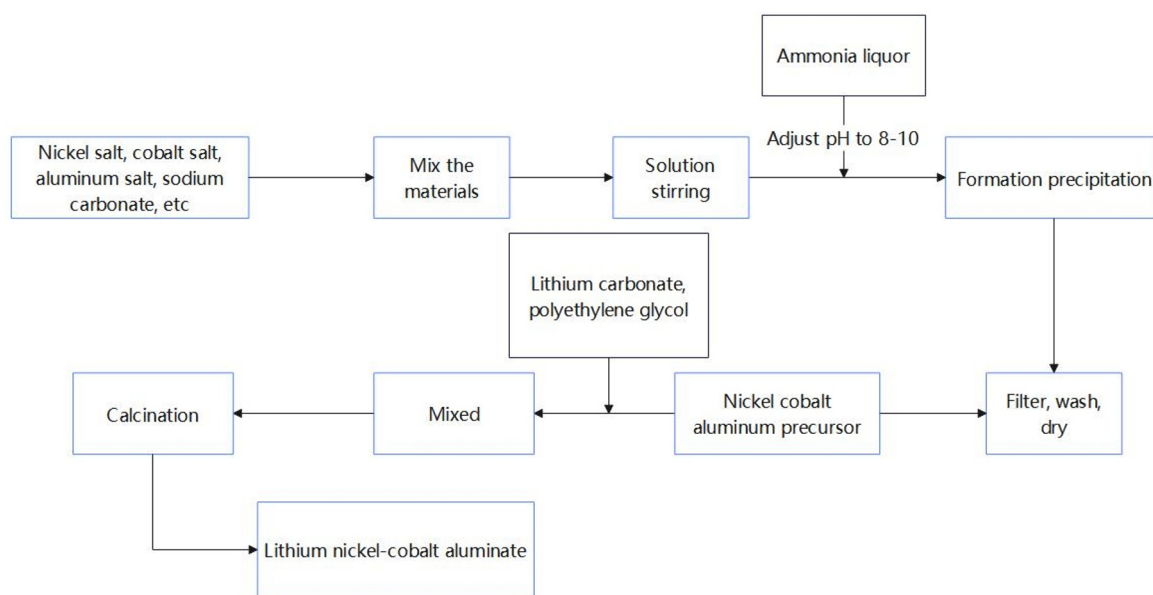


Fig. 1. Flow chart of co-precipitation of $\text{Li Ni}_{0.94}\text{Co}_{0.04}\text{Al}_{0.02}(\text{OH})_2$ preparation

3.1.3 Positive electrode preparation

Battery assembly and encapsulation were carried out in a glove box filled with argon. The positive electrode sheet was composed of 94wt% active substance, 2wt% acetylene black and 4%wt polyvinylidene fluoride (PVDF) by mass, which was mixed with moderate N-methylpyrrolidone (NMP) to form a slurry, stirred well and then evenly coated on 0.02 mm aluminium foil

and dry it in a vacuum of 120 degrees Celsius to obtain the positive electrode sheet.

3.1.4 Battery assembly and electrochemical testing

Lithium metal flakes were used as the negative electrode, Celgard 2400 was used as the diaphragm and the electrolyte was an EC/DEC (1:1, V/V) solution of 1 mol/L LiPF_6 . Constant current charge/discharge cycles were performed in a CT2001ALAND battery test system in a constant temperature room at 25 °C, with a

charge/discharge voltage range of 2.8 to 4.3 V and charge/discharge multipliers of 0.1 C and 1 C.

3.2 Nickel-cobalt-manganese batteries

3.2.1 Nickel-cobalt-manganese battery characteristics

Both NiCoM and NiCoAl are ternary cathode materials, they have similar characteristics and have the same advantages when compared to traditional lithium cobalt acid batteries, the difference between the two is that the energy density of NiCoM batteries is lower compared to NiCoAl batteries, but their raw materials are cheaper than them [10].

3.2.2 Preparation process of $Li_{1.167}Ni_{0.4}Mn_{0.383}Co_{0.05}O_2$

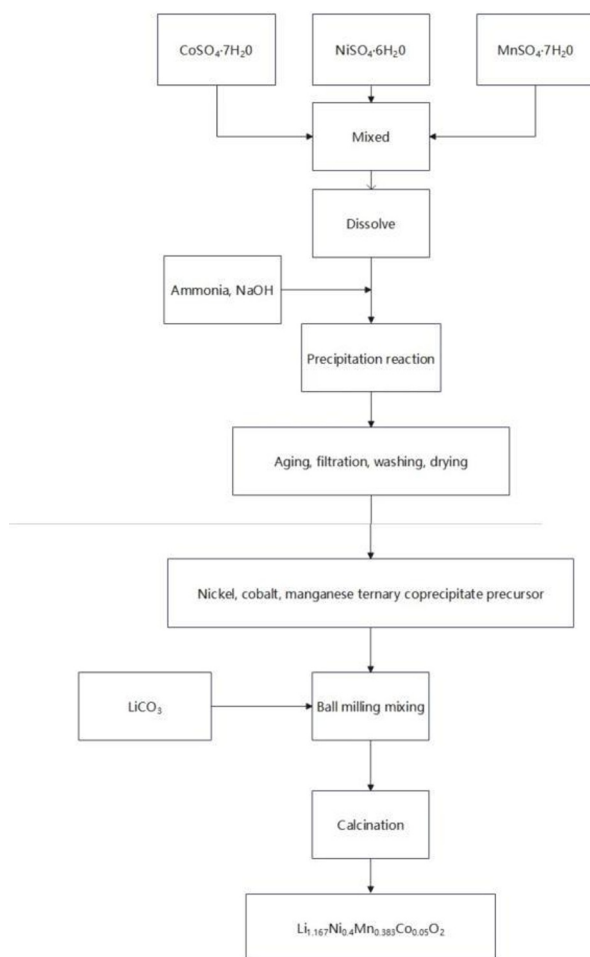


Fig. 2. Preparation process of $Li_{1.167}Ni_{0.4}Mn_{0.383}Co_{0.05}O_2$

Ni, Mn, and Co ternary co-precipitated precursors were prepared using the hydroxide co-precipitation method and mixed with Li_2CO_3 for grinding and then calcined to obtain $Li_{1.167}Ni_{0.4}Mn_{0.383}Co_{0.05}O_2$ cathode material powder (Fig 2) [11].

3.2.3 Positive electrode preparation

(1) The active substance and acetylene black were put into a mortar and ground thoroughly.

(2) PVDF/NMP was added to the mixed raw materials, then they were coated on an Al foil.

A lithium metal sheet was used as a counter electrode in a glove box at a relative humidity of not more than 5%, a Celgard 2400 type diaphragm (20 μ m thickness, 15 mm diameter) was used and the electrolyte was 1 mol/LiPF₆/EC+DMC+EMC (1:1:1 volume ratio).

The batteries were then tested for electrochemical impedance and cyclic voltammetry on an electrochemical workstation, followed by a charge/discharge test on a LAND cell test system.

3.3 Lithium iron phosphate batteries

3.3.1 Lithium iron phosphate features

Lithium iron phosphate and traditional lithium cobalt-acid batteries have the following characteristics compared to each other.

(1) Safety: Lithium iron phosphate batteries have better safety compared to lithium cobalt acid batteries. This is because lithium iron phosphate batteries use cobalt-free materials, which are relatively stable and less prone to thermal runaway reactions under high temperature, overcharging or physical damage.

(2) Lifetime: Lithium iron phosphate batteries have a longer cycle life compared to lithium cobalt acid batteries. Lithium iron phosphate batteries perform better in high-temperature environments, while lithium cobalt acid batteries are prone to polarisation and life decay in high-temperature environments. Therefore, $LiFePO_4$ is a better choice for applications that require prolonged use and high ambient temperatures.

(3) Energy density: $LiCoO_2$ has a higher energy density than $LiFePO_4$. This means that a lithium cobalt battery can store more energy per unit weight or volume [12,13].

3.3.2 $LiFePO_4/C$ composite preparation

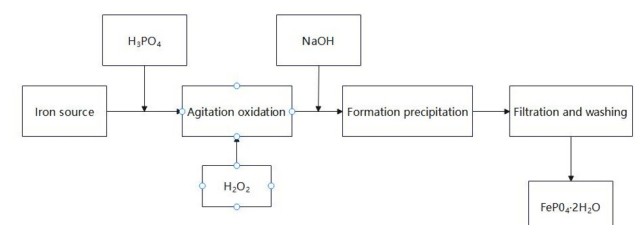


Fig. 3. Preparation of $FePO_4 \cdot xH_2O$

The method of preparing $FePO_4 \cdot xH_2O$ material by liquid phase non-oxidative co-precipitation using Fe(III) polymerised iron sulphate as the iron source is as follows (Fig 3).

H_3PO_4 was added dropwise to polymerised ferric sulphate, and then ammonia was added to adjust the pH value to about 4.5. After a period of continuous stirring, a white precipitate of $FePO_4 \cdot xH_2O$ can be obtained. The

precipitate is then filtered, washed and dried to obtain nano-scale $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ material (Fig 4).

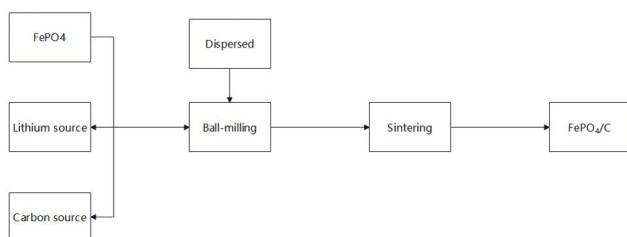


Fig. 4. LiFePO_4/C composite preparation

The $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ prepared by the above method was dried to remove the crystalline water to obtain anhydrous FePO_4 material [14].

Table 1. Initial charge specific capacity, Initial discharge specific capacity, and first coulomb efficiency data for three types of batteries

Samples	Initial charge specific capacity/($\text{mAh} \cdot \text{g}^{-1}$)	Initial discharge specific capacity/($\text{mAh} \cdot \text{g}^{-1}$)	First coulomb efficiency (%)
Nickel-cobalt aluminium batteries	256.5	221.6	86.4
Nickel-cobalt-manganese batteries	298.4	187.8	62.94
Lithium iron phosphate batteries	-	162.9	95

As can be seen from Table 1, the NiCoAl battery prepared from $\text{LiNi}_{0.94}\text{Co}_{0.04}\text{Al}_{0.02}(\text{OH})_2$ has the highest initial discharge specific capacity of $221.6 \text{ mAh} \cdot \text{g}^{-1}$ and a good first coulomb efficiency (86.4%). The Ni-Co mammoth battery made from $\text{Li}_{1.167}\text{Ni}_{0.4}\text{Mn}_{0.383}\text{Co}_{0.05}\text{O}_2$ as cathode material has the highest initial charge specific capacity of $298.4 \text{ mAh} \cdot \text{g}^{-1}$ initial discharge specific capacity of $187.8 \text{ mAh} \cdot \text{g}^{-1}$ and a lower first coulomb efficiency of about 62.94%. The LiFePO_4/C composite LiFePO_4 battery has the lowest initial discharge capacity of 162.9% but has the highest first coulomb efficiency of 95%.

Table 2. Battery capacity retention data

Samples	Capacity retention(%)
Nickel-cobalt aluminium batteries	92.9 (50 times)
Nickel-cobalt-manganese batteries	93.7 (50 times)
Lithium iron phosphate batteries	99.19 (200 times)

As can be seen from Table 2, LiFePO_4/C cathode material performs best in terms of capacity retention with 99.19% capacity retention after 200 cycles, followed by 93.7% after 50 cycles for Ni-Co manganese batteries and 92.9% after 50 cycles for Ni-Co aluminium batteries.

The anhydrous FePO_4 was weighed with the carbon and lithium sources according to a certain stoichiometric ratio, and ball milled for a certain time using alcohol or water as a dispersant. The ground stock is quickly dried in a vacuum oven at 120°C , then transferred to a tube resistance furnace and heated up under N_2 protection to reach a certain temperature and held for some time before being cooled to room temperature with the furnace to obtain LiFePO_4/C composites [14].

4 Experimental results and discussion

4.1 Performance comparison

5 Future expectations and directions for improvement

Over the years, new energy vehicles have been gradually developed through market promotion and the joint efforts of domestic and foreign scholars. In the face of fierce market competition, if the performance of vehicles is to be improved, in-depth research in these areas should be conducted in the future.

(1) Research and development of new cathode and anode materials: The cathode and anode materials commonly used for lithium-ion batteries, such as lithium iron phosphate and lithium cobalt oxide, have certain energy density limitations. Therefore, there are some developments of new positive and negative electrode materials, such as silicon-based materials and carbon nanotubes, that can improve the energy density of batteries.

(2) Optimisation of electrolytes: The current mainstream lithium-ion battery electrolytes are mainly organic solution-based liquid electrolytes, which suffer from volumetric effects and lack of stability during use. Therefore, research on new electrolytes, such as solid-state electrolytes, can improve the energy density and stability of batteries.

(3) Optimisation of electrode structure: The electrode structure of a battery has a great influence on its performance. Some new electrode structures have been proposed, such as three-dimensional electrodes, porous electrodes, etc. These electrode structures enhance the specific surface area of the electrode, thereby increasing the contact area between the electrode and the electrolyte, and improve the energy density of the battery.

(4) Research on new battery systems: In addition to lithium-ion batteries, there are many new battery systems, such as sodium-ion batteries and lithium-sulphur batteries. These new battery systems have a higher theoretical energy density and can be an important way to improve the energy density of batteries.

(5) Advanced manufacturing process: The preparation process of electrodes and electrolytes also has a great impact on battery performance, so advanced manufacturing technology, such as nano-material preparation, coating and doping technology, can be used to improve battery performance.

6 Conclusion

In this paper, the preparation processes, characteristics, and electrochemical performances of three different cathode materials, i.e., NCA, NCM, and LFP, are reviewed. Specifically, their performances including specific capacity, coulomb efficiency, and cycle stability are evaluated through constant current charge and discharge, CV, and EIS methods. By comparison. Through comparison, NCM and NiCoAl batteries have the best performance in terms of initial charge/discharge specific capacity and initial discharge specific capacity, respectively, while LiFePO₄ batteries exhibit the best performance in terms of capacity retention. Finally, future improvements are discussed, including the development of novel electrode materials, optimization of electrolytes, and research on manufacturing processes. This paper provides a comprehensive overview of typical cathode materials and gives prospective suggestions on the future development of lithium ion batteries. However, there are still some limitations in this paper. The preparation method studied in this paper is not the one used in industry and therefore the performance data presented is not representative of the performance in actual use. It is hoped that future research will lead to a process that is as advanced as preparation in laboratory and is suitable for industrial production.

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