Prominent Selection Strategies for Metal Cathode Materials in Lithium-Ion Batteries

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Abstract. Lithium-ion batteries (LIBs) emerge as a substitute for traditional fossil fuels and become a dominating power source in portable electronics and electric vehicle markets. Recent research on improving the performance of lithium-ion batteries involves better battery lifetime, power capacity, and specific energy by the innovation of new anodes, cathodes, and nonaqueous electrolytes. However, the cathode materials are the bottleneck in the research process due to their lower capacity, which becomes the focus of development. This review presents an outlook on lithium-ion technology by introducing its basic structure and mechanism, examining four structures of LIBs, namely lithium-rich layered oxides, lithium-manganese-rich layered oxides, lithium-ion-phosphate and spinel lithium-rich oxide, as well as comparing their performances and practical use.

Keywords: lithium-ion battery; selection strategy; metal cathode; renewable energy.3.

1. Introduction

The lithium-ion battery (LIB) was first developed in Japan and then commercialized by Sony Co. in 1991 [1]. For most commercial devices, the consumers' desire for longer running time becomes the incentive to improve the capacity and energy density of the battery. Graphite is widely used as anode for LIBs owing to its high conductivity, good reversibility, low cost. It delivers a high specific capacity of 372 mAh g^{-1}, inferior to other anode materials, like silicon [2]. However, most of the current commercial cathodes can merely reach 180 mAh g^{-1}, about half that of the anode. The performance of the cathode is largely determined by the properties and characteristics of the component materials. In the past few decades, there have been substantial attempts at improving the capacity of cathode materials through methods such as increasing the operating voltage.

This review will first briefly introduce the general mechanism of lithium-ion batteries and the key components. Subsequently, four popular structures of cathodes for commercial LIBs will be examined – lithium-rich layered oxides, lithium-manganese-rich layered oxides, lithium-ion phosphates and spinel lithium-rich oxides, where various combinations of different transitional metals are used for each structure. Finally, different materials and structures will be reviewed on the atomic level, and compared by their price, power capacity, cyclability, stability in structure and other criteria.

2. Mechanism of lithium-ion batteries

2.1. Construction of a lithium-ion battery

Lithium ions are stored in the cathodes and anodes, which can flow in between in the electrolyte. The separator prevents contact between the cathode and the anode inside the battery but promotes ion movement.

The cathode consists of three components: active materials, which contain lithium ions and take part in the chemical reaction; conductive additives, which help increase electron conductivity; the binder, which binds the active material and the conductive additive together [3].

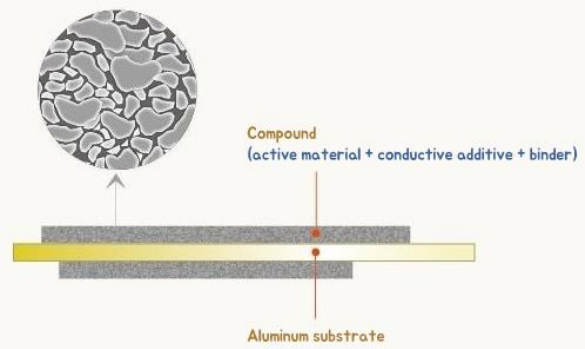


Fig.1 Structure of a cathode [3]

2.2. Charging and discharging

The movement of lithium ions in the batteries involves redox reactions at anode and cathodes. During discharge, an oxidation half-reaction occurs and produces the lithium ions, electrons and the remaining materials left in the anode. Accordingly, a reduction half-equation occurs at the cathode, where the lithium ions combine with electrons and the cathode material.

The movement of positively charged ions causes the cathode to be more positively charged than the anode. As a result, electrons are attracted to the cathode, generating a current from the anode and performing the external circuit's external work. The electrons are received at the positive current collector.

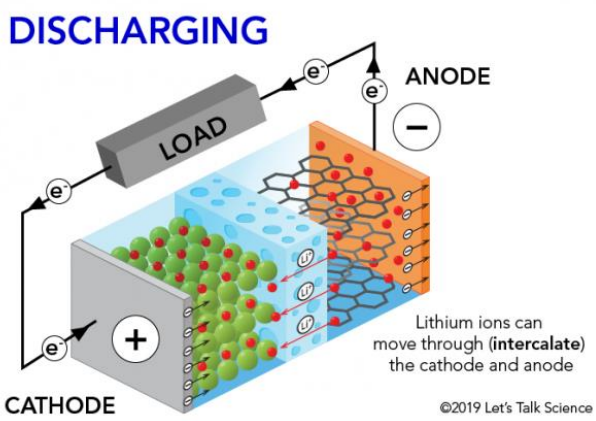


Fig.2 The discharging process of a lithium-ion battery [4]

When charging, the battery is connected to an external charger with a higher voltage, and hence a current is generated. As a result, lithium ions inside the battery are forced to be released from the cathode, transported through the electrolyte, and delivered to the anode.

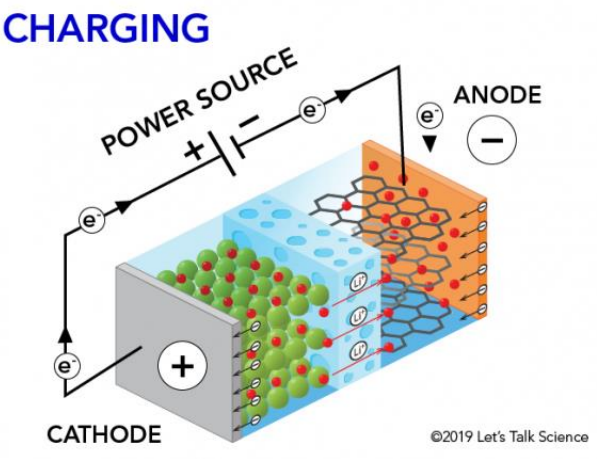


Fig.3 The charging process of a lithium-ion battery [4]

3. Choice of cathode materials

3.1.Significance of the cathode materials in terms of their capacity and voltage

As mentioned earlier, lithium ions are stored in the cathode and anode to achieve a stable form, and electricity is generated through chemical reactions involving lithium ions. The amount of lithium ions that the cathode can host during charging determines the battery's power capacity. The higher amount of lithium ions stored, the bigger the capacity.

The battery's voltage is the potential difference between the cathode and the anode, whose electric potential depends on relative materials. As a result, the higher the potential the cathode has, the higher electric potential difference the battery has, and thus the greater power while discharging.

3.2. Different types of cathode materials

3.2.1. Lithium-rich layered transition metal oxides (LiMO2 structure)

$LiMO_2$ exhibits a trigonal crystal system with $R\bar{3}m$ space group symmetry (Fig.4 (a)). The cyan layers are transitional metal (TM) oxide layers consisting of MO_6 octahedra illustrated in Fig.4 (b). Lithium ions reside in between the TM layers.

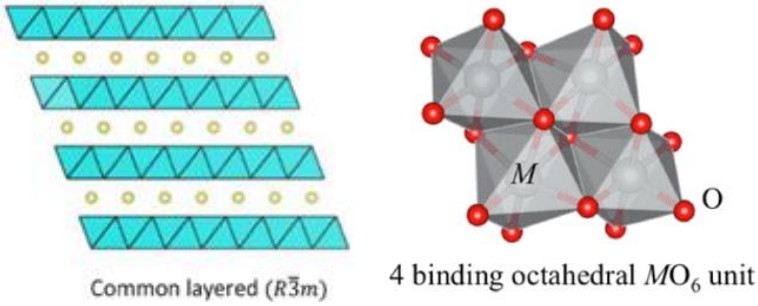


Fig.4 Schematic illustrations for (a) Crystal structure of $LiMO_2$ (M = Co, Ni) (Diagram adapted from [5]) and (b) the structure of MO_6 in TM layers [6]

$LiCoO_2$ was the first material discovered and implemented for LIBs and has been the dominant cathode material for LIBs since its invention in 1991. When <25% of lithium ions are extracted, the structure still keeps its rhombohedral shape, which indicates. When 50 % of the lithium is extracted from the structure, a monoclinic phase is instead observed. During the delithiation (removal of lithium ions) from 25% onwards to 75%, the phase changes from $R\bar{3}m$ to $C2/m$ then back to $R\bar{3}m$. Methods for enhancing the capacity retention of $LiCoO_2$ at higher voltage cycling (4.4/4.5 V) have been explored, aiming at preventing the growth of impedance at the surface caused by side reactions by heat treatment or adding oxide coatings. However, the strong oxidizing power of cobalt still causes thermal stability concerns and safety issues of this cathode material [7].

Aside from the faults mentioned above, cobalt has become the most expensive battery metal due to the massive supply chain bottleneck coming out of Africa [8]. The potential for exposure to cobalt metal dust during the production and processing of cobalt powder also poses a threat to the environment and human health [9]. As a result, manufacturers are looking into other possibilities. Nickel is used as a replacement for cobalt. $LiNiO_2$ has an identical structure to that of $LiNiO_2$. The characteristics of which during charging are also similar. It transforms into a monoclinic phase in the window of 55% to 75% loss of lithium ions while also showing poor capacity retention if a further loss occurs. Since it can be suitably used from 0% to 75%, it has a higher effective capacity of ≈200 mAh g^{-1}. However, it shares the same issue of poor thermal stability as cobalt. It is even harder to control due to difficulty preparing the desired phases without contamination of nickel ions in the Li layers [7].

The limiting sources and the resulting high prices of cobalt and nickel have prevented wider usage. Hence, the extremely low price of manganese is the main advantage of $LiMnO_2$. In addition, manganese is abundant in the Earth's crust. Currently (By September 2021), manganese sells for ≈ 30

USD per ton, which is almost 100 times cheaper than nickel (≈ 20000 USD per ton), and even more for cobalt (≈ 50000 USD per ton) [10]. Moreover, since manganese has a lower atomic mass (54.94) than nickel (58.69) and cobalt (58.93), theoretically, the specific energy of cathode materials would increase. However, $LiMnO_2$ has discharge plateaus of 4 and 3 V, which are comparatively low, leading to low energy. Furthermore, the movements of Li ions would make the structure unstable, changing into a spinel-type structure and leading to poor cyclability [7].

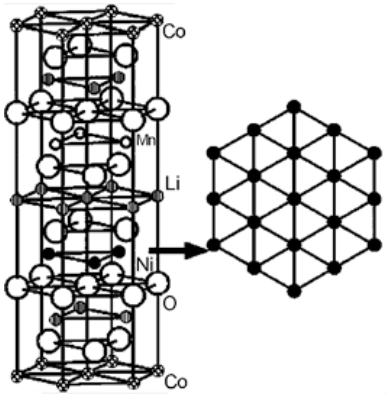


Fig.5 Illustration of a possible superstructure (not proven) of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ alternating layers [11]

These metals have been mixed and trailed at different ratios, of which the LLO containing all three common transition metals ($LiNi_{1-y-z}Co_yMn_zO_2$) is tested to a more promising cathode material (NCM) [7]. The structure $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, where all transition metals have an equal ratio, inherits the rate performance from $LiCoO_2$, the capacity from $LiNiO_2$, and the stability from Mn^{4+} ions. One assumption of the structure based on the equal proposition of the three metals is proposed, where the MO_2 $R\bar{3}m$ layers stack on one another, shown in Fig.5 [11]. It shows a high discharge capacity of over 200 mAh g^{-1} between 3.0-4.6 V and can be stored at 50 ºC for up to 50 days. It also has overall good cyclability, losing only 18% of capacity after 200 cycles at the rate of 5C. Despite that, the common issues of the uniform $LiMO_2$ of structure deformation and oxygen loss at high cycling potential still exist. The $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode has better overall characteristics than the conventional LLO cathodes [12]. With a higher content of nickel (lower "y" and "z"), the capacity of the cathode can be further enhanced, such as $LiNi_{0.8}$ $Co_{0.1}Mn_{0.1}O_2$.

3.2.2. Lithium-manganese-rich layered transition metal oxides (LMR-NMC)

Solid solutions or nanocomposites of Li_2MnO_3 and $LiMO_2$ are a type of cathode material in line with the basic layered structure [13]. The price advantage and higher specific energy of manganese compared to the other two materials have been explained in B. 1).

Fig.6 illustrates the general structure that LLOs take. Different electronic configurations are formed – (a) represents the trigonal (rhombohedra) crystal system exhibited by $LiMO_2$ ($R\bar{3}m$ space group symmetry); (b) represents the monoclinic crystal system exhibited by Li_2MnO_3 ($C2/m$ space group symmetry). It is found that the two phases of $LiMO_2$ and Li_2MnO_3-like structures coexist in the same crystalline grain. The close-packed layers in each of them have an interlayer spacing close to 4.7 Å, making them compatible to integrate at the atomic level [14].

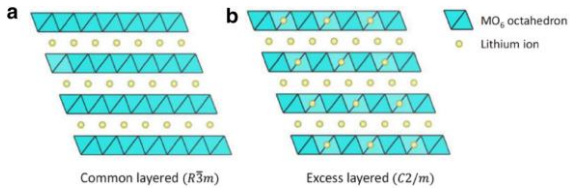


Fig.6 Schematic illustrations of idealized (a) Li_2MnO_3 and (b) $LiMO_2$ (M = Co, Ni, Mn) layered structures [5]

Between the potential 2.0-4.4 V, the Li_2MnO_3 component is electrochemically inactive, and hence it does not contribute to power capacity, where it only helps the stabilization inside the structure. The activation of Li_2MnO_3-like phases inside the lithium-rich layered oxides gives rise to large rechargeable capacities, mainly when the cells are electrochemically charged to >4.4 V during the 1st cycle [15]. The process of activation would almost go to completion with >4.8 V provided. This is mainly caused by the significant reduction in its electronic conductivity due to the formation of reaction products and oxygen loss on the cathode, and the insulating electrolyte decomposition [16]. It is reported that the cation ordering is no longer observed after 125 cycles under high voltage, which suggests that the cathodes are unstable. This is again due to the structural changes in the cathode at high charging potential [17].

Methods have been developed to mitigate the above issues. Adding cellulose nanofiber has been proven to improve the rate of performance at a high potential. It is also reported that the rate performance of Lipon-coated NMC cathodes improves by a factor of 4 or 5 compared to that of the conventional design [16].

3.2.3. Lithium-ion phosphate

In Fig.7, the green particles show the distribution of lithium ions between the TM layers, similar to the previous cases (M is represented in yellow; O is represented in red). Additionally, PO_4 tetrahedrons (P is represented in blue) are distributed between the TM layers, suggesting that this structure has strong bonding in and between layers. The 3D formation gives $LiMPO_4$ better thermal stability than other layered structures (e.g., $LiMO_2$) [19]. XRD patterns before and after cycling are tested, and there was no major deformation in its structure, which again indicates the good thermal stability of the material [20].

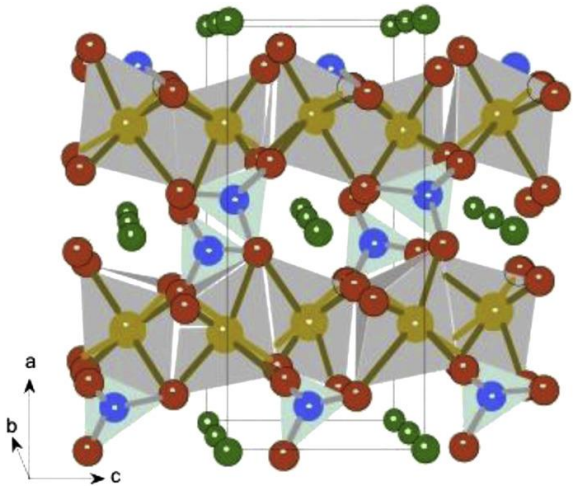


Fig.7. Schematic illustrations of the olivine structure of $LiMPO_4$ (M = Fe, Mn, Ni, Co) [19]

Lithium iron phosphate (LFP) was invented in the year 1996. As iron is abundant in the Earth's crust, it became the first cathode material with low costs and a relatively easy approach for synthesis. LFPs have good capacity retention that no obvious capacity fading was observed even after several hundred cycles. Its capacity approaches 170 mAh g^{-1}, on a comparable level to stabilized $LiNiO_2$ [21]. The availability, accessibility, and safety favor industrialization as a cathode material. Hence, carbon coatings are applied, and those materials have a conductivity ($\approx 10^{-6}$ S cm^{-1}) that is a hundredfold higher than the conventional design ($\approx 10^{-9}$ S cm^{-1}). Other methods like doping other elements such as niobium also become successful in electrochemical behavior, increasing the conductivity by 8 orders of magnitude [21].

Explorations on other metals as iron replacement are done, such as $LiMnPO_4$, but the electrochemical performance is entirely different from $LiFePO_4$It is found that manganese may also have a catalytic effect on the decomposition of PO_4, causing the loss of oxygen [20]. Overall, the poorer stability and capacity retention make $LiFePO_4$ a more favorable choice.

3.2.4. Spinel lithium-rich oxides

Spinel oxide structures are cubic close-packed oxides with eight tetrahedral and four octahedral sites per unit. The $[M_2]\ O_4$ has a framework of cubic symmetry with space group $Fd\bar{3}m$ as shown in Fig.8, where 75% of the M cations occupy alternate layers between the cubic close-packed oxygen layers just as the first three types of materials. The remaining 25% of the M cations are located in the lithium layers, which is unique to this structure, resulting in M cations in every layer. Normally, the spinel structures expand and contract in an isotropic manner during lithium insertion and extraction [22].

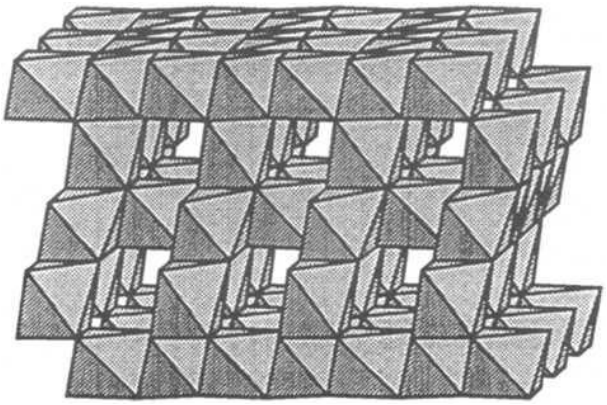


Fig.8 Schematic illustration of the $[M_2]\ O_4$ framework [22]

$LiMn_2O_4$ offers a high voltage (4 V) and provides a stable cubic $[Mn_2]\ O_4$ framework over the whole extraction process (The structure is maintained). However, during lithium insertion at 3 V, the electrode slowly changes from the phase of $LiMn_2O_4$ into a tetragonal phase of $Li_2Mn_2O_4$. The presence of Mn^{3+} ions cause the Jahn-Teller effect (deformation of the electron configuration), hence causing capacity fading [23]. These modified spinel electrodes offer higher stability in cycling behavior at the expense of slightly inferior electrode capacities [22].

Attempts at doping the spinel oxides with other metals such as Ni, Fe, Co, Ti, etc. have been made, and Li $[Me_{1/2}Mn_{3/2}]\ O_4$ (Me = Ni, Fe, Co, Ti, Cr, Cu, Zn) turns out to be the best composition. The doped materials show higher operating voltage, up to 4.8 V [24]. Additionally, doping other cations also helps increase the rate capability and its cycling. The average oxidation state of Mn is nearly 4 at the end of the 4 V region, avoiding the Jahn-Teller effect.

4. Cathode material selection strategy

In this section, different cathode materials are compared against each other in different qualities, in which the power capacity is the dominant factor. Fig.9 shows the discharge voltage and capacity of some common cathode materials (The relevant materials in this research are highlighted - purple = $LiMO_2$; yellow = $xLi_2MnO_3 \cdot (1-x)\ LiMO_2$; red = $LiMPO_4$; green = LiM_2O_4) Being the newer invention among the four, LMR-NMCs have a dominating discharge capacity, reaching 300 mAh g^{-1} at high temperature. However, with a high nickel content in NCM battery (e.g., NMC-9525), the capacity can reach 230 mAh g^{-1}, shrinking the gap with LMR cathodes. $LiFePO_4$ has a specific capacity of 165 mAh g^{-1}, while Li $[Ni_{0.5}Mn_{1.5}]\ O_4$ (and other spinel oxides) has the worst capacity due to its problem with the extraction of lithium ions [26].

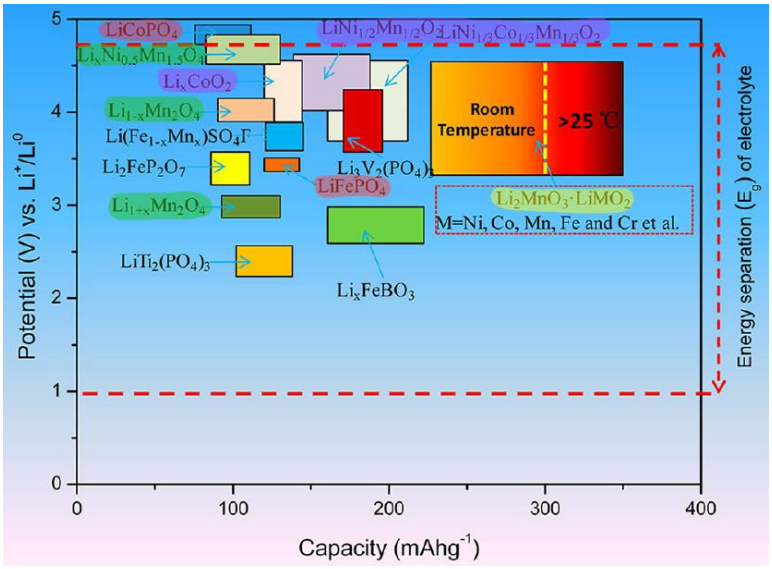


Fig.9 Voltage and capacity of common cathode materials for lithium-ion batteries [27] (Annotated by author)

The specific energy of cathodes is another key component of the performance of a battery. In Fig.10, the cathode material with the highest specific energy among each type of cathode structure is highlighted. For example, spinel $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) has a specific energy of 650 Wh kg^{-1}, arising from its high operating voltage of ~4.7 V vs Li, which is close to LFMP [28]. By increasing the nickel content ($LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$), the specific energy of NMC batteries exceeds that of LNMO and LFMP. However, it is still far from reaching the LMR cathode, nearly 1000 Wh kg^{-1} [27].

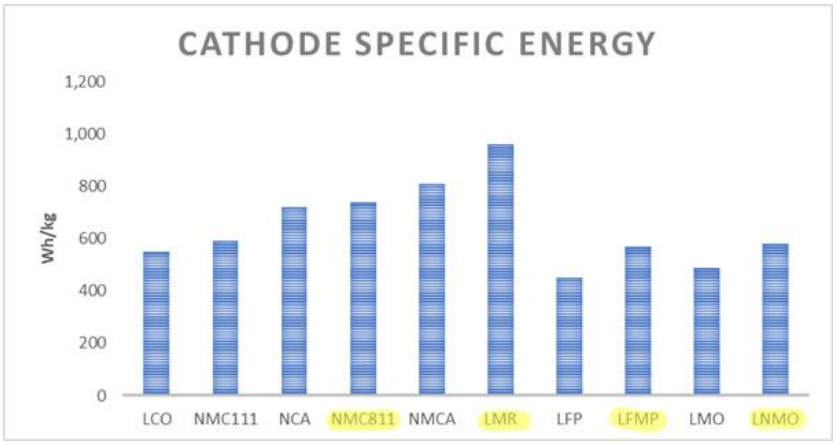


Fig.10 Specific energy of cathode materials [29] (annotated by author)

From the above discussion, it seems that LMR-NCA cathode batteries are superior in both specific energy and power capacity and thus are optimal. However, the problem of structural instability at high voltage leads to voltage fade, large initial capacity loss, poor rate capability and limited cycle life, which are problematic when it comes to practical usage. On the other hand, NMC batteries have great cyclability with decent specific energy and power capacity, making them good material for applications in LIBs in power-demanding devices such as electric vehicles.

The improved materials of all four structures have generally high thermal stability. High-voltage LNMO spinel has superior thermal stability $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ and high ionic conductivity [28]. Though the specific energy of LFP and spinel LMO is not comparable to high-nickel NMC, their costs are, in turn, lower. LFP and LMO have similar specific energy and capacity with the addition of manganese. However, the cyclability problem also occurred to spinel oxides due to their capacity decay and electrolyte decomposition at high voltage. In comparison, the good capacity retention of $LiFePO_4$ guarantees the long life and durability of the devices. In addition to its high availability,

high safety, and low costs, it would still be the optimal choice in less power-demanding areas and where durability is valued.

5. Conclusion

With the high capacities in anodes, the bottleneck in lithium-ion batteries is mainly the cathode materials. Throughout the research, it is realized that the cathode materials' capacity, specific energy, and cyclability are core elements in examining their performances. The costs and availability of the materials also need to be taken into consideration when applied to manufacture. The originally developed $LiCoO_2$ with cobalt as its transitional metal has been widely replaced with other metals such as manganese and nickel. The modern principle of designs of layered oxides for LIB cathodes is to generally decrease the cobalt content and increase the nickel content for its high specific energy. With a mixed-use of Mn, Co and largely Ni, the layered oxides are favored and become the most popular cathode material.

LFP and spinel LMO are the relative early technologies with inferior performance compared to the improved NMC material. Yet, their advantages in costs are still significant as batteries based on these technologies are still used for electric cars as economical alternatives. LFP is very stable, safe, and has better cyclability than spinel LMO and is more widely used. Meanwhile, research involving doping with other metal ions for both materials has been conducted in recent years. Therefore, they could potentially become a more cost-efficient choice than NMC in the future.

LMR-NMC batteries are still a relatively new technology, with insanely high capacity as well as specific energy. Its cyclability problem is hindering it from being widely applied in electronic devices. As there are plenty of research papers reporting the modified LMRs through nanotechnology as promising cathode materials that mitigate the issue of voltage fading in recent years, I hope to overcome such issues and replace current NMCs.

In general, the various types of lithium-ion batteries are all still under further research, in which some chemical reaction pathways and structures are not fully understood. However, with the new methods such as coating and doping experimented, I expect the cathode technology to make some huge leaps and enhance the performance of LIBs.

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