Effect of Layered, Spinel, and Olivine-Based Positive Electrode Materials on Rechargeable Lithium-Ion Batteries: A Review

Azemtsop Manfo Theodore  
Dept of Electrical and Electronics Engineering,  
Recep Tayyip Erdoğan University,  
Rize, Turkey.

Abdullahi Abbas Adam  
Department of Physics,  
College of Natural and Applied Sciences,  
Al-Qalam University Katsina, Nigeria.

Pawan Singh Dhapola  
Center for Solar Cells and Renewable Energy,  
School of Basic Sciences and Research,  
Sharda University, Greater Noida, India

Abstract: The lithium-ion battery (LIB) technology is getting particular attention because of its effectiveness in small-scale electronic products such as watches, calculators, torchlights, or mobile phones through to large-scale power systems such as automobiles, trains, ships, submarines, or airplanes. LIBs are widely applied due to their advantages which make them unique. They exhibit greater energy density than other types of rechargeable batteries. LIBs are lightweight with a limited rate of charge loss, a greater number of charge/discharge cycles, no complete discharge is needed, and LIBs function at a higher voltage than other rechargeable batteries. However, LIB is suffering from many disadvantages such as the high risk of bursting, high cost compared to other batteries, battery deterioration after a complete discharge, high sensitivity to high temperatures (fast degradation when exposed to heat), poor rate of capability, very limited lifespan (2-3 years) and not available in standard cells sizes like others. Basic science research combining solid-state chemistry and physics has been at the heart of this endeavor, particularly throughout the 1970s and 1980s. With the awarding of the 2019 Nobel Prize in Chemistry to the creation of lithium-ion batteries, it is instructive to examine the evolution of cathode chemistry that enabled modern lithium-ion technology. A good choice of cathode materials leads to enhanced performance in LIBs. This work involves a deep comprehension of Li-ion transport, as well as the mechanism of charge and discharge in LIBs. The paper provides a fundamental study on layered, spinel, and olivine-based cathode materials and their benefit for LIBs. The study also gives details about optimization techniques needed to improve the cathode performances. The advantages and disadvantages of these prominent cathode materials for rechargeable LIBs are also discussed to emphasize the importance of choosing and/or optimizing the right cathode materials to lead to enhanced LIB performance.

Keywords: Lithium-ion battery, Anode, Cathode, Voltage, Energy density.

Nomenclature

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIB</td>
<td>Lithium-Ion Battery</td>
</tr>
<tr>
<td>EVs</td>
<td>Electric Vehicles</td>
</tr>
<tr>
<td>LiFePO4</td>
<td>lithium iron phosphate</td>
</tr>
<tr>
<td>LiCoO2</td>
<td>lithium cobalt oxide</td>
</tr>
<tr>
<td>LiMn2O4</td>
<td>lithium manganese oxide</td>
</tr>
<tr>
<td>Li1.2Mn0.54Ni0.13Co0.13O2</td>
<td>lithium manganese nickel cobalt oxide</td>
</tr>
<tr>
<td>LiNi0.8Co0.15Al0.05O2</td>
<td>lithium manganese nickel cobalt oxide</td>
</tr>
<tr>
<td>Li [Ni0.8Co0.1Mn0.1] O2</td>
<td>lithium nickel cobalt manganese</td>
</tr>
<tr>
<td>LiPF6</td>
<td>lithium hexafluorophosphate</td>
</tr>
<tr>
<td>LiBF4</td>
<td>lithium tetrafluoroborate</td>
</tr>
<tr>
<td>LiClO4</td>
<td>lithium perchlorate</td>
</tr>
<tr>
<td>LiNiO2</td>
<td>lithium nickel oxide</td>
</tr>
<tr>
<td>LiNi0.5Mn0.5O2</td>
<td>lithium nickel manganese oxide</td>
</tr>
<tr>
<td>Al2O3</td>
<td>aluminum oxide</td>
</tr>
<tr>
<td>V2O5</td>
<td>vanadium pentoxide</td>
</tr>
<tr>
<td>MgO</td>
<td>magnesium oxide</td>
</tr>
<tr>
<td>ZnO</td>
<td>zinc oxide</td>
</tr>
<tr>
<td>CeO2</td>
<td>cerium dioxide</td>
</tr>
<tr>
<td>LiNi0.7Co 0.3O2</td>
<td>lithium nickel cobalt oxide</td>
</tr>
<tr>
<td>Ga</td>
<td>gallium</td>
</tr>
<tr>
<td>Mn</td>
<td>manganese</td>
</tr>
<tr>
<td>Co</td>
<td>cobalt</td>
</tr>
<tr>
<td>Ni</td>
<td>nickel</td>
</tr>
<tr>
<td>E</td>
<td>specific energy</td>
</tr>
<tr>
<td>Csp</td>
<td>specific capacity</td>
</tr>
<tr>
<td>V</td>
<td>discharge voltage</td>
</tr>
<tr>
<td>Li+</td>
<td>lithium-ion</td>
</tr>
<tr>
<td>e-</td>
<td>electron charge</td>
</tr>
</tbody>
</table>
1. Introduction

Energy is a critical aspect of the development of any society [1][2]. The fast development of Li-ion battery technology has paid a lot of attention to researchers. LiBs have dominated the market for advanced energy sources in today’s society because they are widely used in a variety of applications such as electronics, electric vehicles, and energy storage systems [3].

This particular regard is directed to the innovation of high-performance LIBs. Therefore, recent investigations were made into the manufacturing of new smart LIBs for large-scale applications [4]. The Sony Company developed its first commercial LIB that was largely sold on the market for about thirty years. In this advanced technology, lightweight and efficient electrodes are needed to promote excellent batteries. In today’s research, many parameters such as size, weight, life span, security, and low cost are taken into account in the fabrication of batteries [5-7]. LiBs are also expected to be essential in enabling the broad replacement of fossil-fuel-based power generation with renewable energy sources such as solar and wind, resulting in a cleaner, more sustainable world. The 2019 Nobel Prize in Chemistry awarded to John Goodenough, Stanley Whittingham, and Akira Yoshino strengthens this claim. Since roughly 50 years ago, there has been a focused effort on understanding the fundamental solid-state chemistry of materials, leading to the current advancement of LIB technology. The discovery of new materials, as well as a deeper understanding of their structure-composition-property-performance linkages, has played a significant role in improving the area. Among the several components in a lithium-ion cell, the cathodes (positive electrodes) currently limit energy density and dominate battery cost. The evolution of LIB technology is ultimately dependent on a fundamental understanding of the electrical, chemical, and structural changes in battery elements that drive the charge-discharge cycle [8]. A LIB is made with an anode, an electrolyte, a separator, and a cathode (shown in Fig.1). The potential difference is minimal for anodes depending on their type, but very large for cathodes in general. As a result, the cathode is crucial in determining the voltage of the battery. The necessity for a rechargeable battery with a higher energy density, i.e., a higher voltage, necessitated the development of the Li-ion battery. Because H+ is exclusively mobile in water, Li+ was selected as the working ion in a nonaqueous electrolyte.

LIB which shows higher specific energy, poor self-discharge, and greater coulombic efficiency is required for electric automobiles, trains, and spatial technologies. Therefore, the LIB performance counts on the Li-ion intercalation mechanism within the cell. For this reason, the choice of materials should be appropriate to enhance the properties of the whole cell. For example, LiFePO4, LiCoO2, and LiMn2O4 cathode materials incorporated in Li solar batteries exhibited fairly lesser charging capacities (<200 mAhg⁻¹). Nevertheless, materials with higher capacities tend to demonstrate reduced thermal stability [9]. The use of voltage-active cathode materials, anode materials, and electrodes in LIBs can commonly increase energy density, but the electrolyte decomposition beyond 4.2V Li⁺/Li is the main problem faced with high-voltage cathodes [10-16]. Unfortunately, LIB life span is limited due to the effect side reactions that may be noxious to the different elements of the cell, which include a binder, the separator, electric bridging components (current collectors), conducting salt and solvents, and these reactions lead to reduce capacity and increase the cell resistance [17-19].

Deep comprehension of the mechanism of electrode aging in LIBs is of high standing to direct the challenges of durability and safety, to make an accurate prediction regarding the life span, and to enhance the battery performance [20]. The different factors that contribute to electrode aging, are synergistically influencing battery aging [21][17]. Among these above-mentioned factors, the electrode material is considered one the most important factors that influence LIB performance, including capacity, lifespan, and safety. The commercialized LIB consists of a cathode made from lithium-intercalated layers using an or-
ganic electrolyte, such as LiPF₆, LiBF₄, or LiClO₄ in an organic solvent [22]. Due to the type of reaction that occurs in LIBs between the electrode material and Li⁺-ions, rechargeable LIB electrode materials can be divided into (a) intercalation electrode materials, (b) conversion electrode materials, and other types. Fig. 2 shows the different LIB systems based on their respective reaction and the performance of popular LIB systems achieved in terms of energy densities with such electrode materials. In commercialised LIBs, intercalation electrode materials are frequently used. Li ions reversibly intercalate/de-intercalate without a considerable volume change in the intercalation electrode, displaying steady cycling but a restricted specific capacity (Fig. 2(a)). The charge/discharge process is a conversion reaction in conversion electrode materials that is always accompanied by phase transitions, which not only efficiently raise the specific capacity but also create additional stability difficulties, such as structural collapse and poor reversibility. (Fig. 2(b)). The reasonable matching of cathode and anode materials can meet current and future needs for high energy and power density (Fig. 1(c)) [23,24].

The equations of the different types of reactions in (a) LIB and (b) Li-S batteries are given in Equation (1), Equation (2), Equation (3), and Equation (4).

(a) Intercalation type

\[ \text{Li}_{1-y}X + y\text{Li}^+ + ye^- \leftrightarrow \text{Li}X \]  

(b) Conversion type

\[ M_{Xz} + y\text{Li}^+ + ye^- \leftrightarrow M + z\text{Li}_{(y/z)}X \]  
\[ y\text{Li}^+ + ye^- + X \leftrightarrow \text{Li}_yX \]  

Where \( M \) is the transition metal

For the Li metal anode, the equation is given as follows:

\[ \text{Li}: \text{Li}^+ + e^- \leftrightarrow \text{Li} \]  

(a) Intercalation type

It should be noted that intercalation in LIBs occurs only during the charging and discharging processes, not during the idle state or when the battery is dead. LIB like any other battery, is made up of a positive electrode, a negative electrode, and electrolytes. During discharging, the positive lithium ion flows from the negative electrode (typically graphite) to the positive electrode (commonly lithium oxide) via the electrolyte solution (a solid or liquid organic solvent). The entire reverse of this process occurs while charging, which is why this is characterized as a reversible process.

(b) Conversion type

In conversion electrode materials, the charge/discharge process is a conversion reaction that is always accompanied by phase transitions, which not only efficiently increase the specific capacity but also introduce additional stability difficulties, such as structural collapse and poor reversibility. Conversion reaction materials have been identified/proposed as prospective high-energy-density intercalation-based materials substitutes. Conversion reaction materials, on the other hand, react during lithiation to generate wholly new products, frequently with significantly altered structure and chemistry, via reaction processes that are currently poorly understood. This makes it difficult to differentiate the restrictions imposed by the mechanism and actual losses from initial particle morphology, synthetic techniques, and electrode preparations.
The demand of the current and next generation of LIB systems with high energy density and power density can be covered using the corresponding potential cathode and anode materials shown in Fig. 2(c) [23,24]. Conversion-type materials are suitable for high-performance batteries because of their high specific capacity, as compared to current intercalation electrode materials [25,26]. In particular, Li metal-based anode can aid in achieving practically a specific energy of 400 Wh kg⁻¹ and 900 Wh L⁻¹. Nonetheless, many challenges remain to define the prominent electrodes used to ameliorate the device’s performance. A high number of electrons can be collected from the cell only if the active material remains stuck on the electrode surfaces, which contributes to increasing the cell’s performance. It is worth noting that John Goodenough’s group at the University of Oxford in England and the University of Texas at Austin (UT Austin) in the United States invented the three major oxide cathode chemistries currently in use (layered, spinel, and polyanion families). The goal of this review paper is to examine and reflect on the progress of lithium-ion battery cathode chemistry. The essay will demonstrate how collaborative efforts can produce wonders in science and technology, inspiring future generations to make discoveries through fundamental science research.

This work aims to provide the details and report recent works accomplished with some advanced electrode materials in the growth of energy-efficient LIBs. Meanwhile, emerging electrode materials that can be used for a long lifetime, contributing to more safety and enhanced performance LIBs are discussed. We first present an overview of electrode materials and their improvements in LIBs. Secondly, we provide details about promising cathode materials with their outstanding properties that are needed for rechargeable LIBs, and finally advantages and drawbacks between the proposed electrodes. The study provides a clear understanding of the impact of the properties of elements that consist of promising cathode materials and the choice of the right materials in manufacturing advanced positive electrodes that meet high-performance rechargeable requirements. This article analyzes and addresses the variables that determine the electrochemical potential of cathode materials. Increased electrical and ionic conductivities of phosphate polyanion cathodes can be accomplished through surface coating, particle size reduction, doping, and morphological engineering. These achievements help in understanding the basic mechanisms of LIBs and their potential applications at different scales.

1.1 Literature Review: Cathode Improvements

The development of positive electrodes is also promising. The author [27] offered a comprehensive assessment with a historical perspective. [28] has offered a review of performance data from the literature. The greatest capacities given were in the range of 190 mAh/g for Ni₁/₃Co₁/₃Mn₁/₃O₂ materials. Near-term development has included the “layered-layered” cathode material, which consists of Li₂MnO₃ layered within another material. This combination has demonstrated capacities greater than 250 mAh/g [29] [30] [31] [32] and offered an overview of the theoretical capacities of many materials based on first-principles calculations; the results included numerous materials with capacities greater than 300 mAh/g and voltages greater than 4.0 V, showing that there is plenty of potential for further research.
In addition to the aforementioned performance enhancements, the sector is looking for cost-cutting alternatives. One area of development has been the lowering of cobalt concentration. Cobalt, nickel, and manganese were employed in about equal proportions in early lithium-ion batteries. Industry has drastically lowered cobalt content, with some cells using less than 10%. Some anticipate that cobalt will be practically extinct. Cobalt is more than $50/kg at the time of writing, compared to less than $20/kg for nickel, $2.60/kg for aluminum, and less than $0.10/kg for manganese. These price disparities underline the financial incentive for cobalt removal. These are raw material pricing; processed powders with regulated particle shapes will cost more.

Another method to save money is to have a more fulfilling life. Some investigations in the literature have shown that cathode particles with a pristine crystalline structure can have a very long cycle life. It is uncertain whether such particles can be produced at a low cost.

The layered lithium cobalt oxide electrode is now the dominant positive electrode technique for lithium-ion batteries. Recent advancements in this field suggest that the LiNi$_x$Co$_{1-x}$Mn$_2$O$_4$ materials may provide significant performance improvements, particularly in terms of specific capacity. The layered -NaFeO$_2$ structure is maintained in compositions where the transition metal layers contain Ni$^{2+}$, Co$^{3+}$, and Mn$^{4+}$[33]. The LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ material, in particular, stands out for its exceptional electrochemical performance, with a reversible specific capacity reaching 200 mAh g$^{-1}$[34]. This advancement has permitted the commercialization of lithium-ion batteries with higher energy density than existing technology. Importantly, diffraction measurements on this phase show that inter-site mixing of the lithium and transition metals is low. To improve these qualities, researchers have used stoichiometry control, cation substitution, surface coatings, and partial fluorine/oxygen replacement. The effect of fluorine substitution in cation-substituted (Ti, Ni) manganese spinels has recently been studied in depth [35]. Working with positive electrode materials at higher operating voltages is one definite option for increasing the energy density of lithium-ion batteries. Several 5 V lithium insertion materials based on the manganese spinel, LiM$_{6/3}$Mn$_{1/3}$O$_4$ (M=3d transition metal), for example, have been presented [36]. All of these cycles keep the manganese in the tetravalent state, avoiding the problems caused by the Jahn-Teller distortion of Mn$^{3+}$ at the six-coordinate sites. The LiNi$_{1/3}$Mn$_{1/3}$O$_4$ spinel has gained special attention for its reversible capacity of roughly 140 mAh g$^{-1}$ at 4.7 V vs. Li. As a general statement, it should be emphasized that because of the higher operating voltages, these 5 V materials do not yet work well in lithium-ion designs and that other components of the cell infrastructure will need to be improved.

2. Electrode Materials for Lithium-Ion Batteries

Most of the electrode materials commercialized for LIBs manufacture are selected for their good withstanding via the test of time. The performance of new-generation LIBs would be seen to increase considerably if particular attention is given to the type of electrode materials. The electrode materials used should be enabled to contribute to the increased energy density of LIBs. Because of some drawbacks such as low energy density, some materials cannot be used in LIBs. As a consequence, the higher polarization increases intensively during charging and discharging within the poor cycling life owing to declining capacities. LIBs are facing many defies which affect their performance. The low conductivity and thermal pathway of most of the electrode materials limit the collection of electrons throughout the external circuit due to the poor capability of storage of LIBs. For this reason, LIBs need electrode materials with the capacity to be efficient enough to promote a high rate of electron collection and mobility.

2.1 Working principle of LIB

In LIB, the cathode plays the role of the source of Li$^+$-ions and helps to determine the average voltage and specific capacitance delivered by the cell. During charge, Li$^+$ is detached from the cathode and migrated across the electrolyte along with solvent molecules to the negatively charged electrode (generally graphite) where they are stored. The schematic diagram of LIB is given in Fig. 3 (A). For each migrated Li$^+$, an electron will be freed in the anode and a charge is created at the positive current collector. The free electrons will flow through the external circuit and supply a load of electricity. On the contrary, during the discharge, Li$^+$ is extracted from the graphite and migrated back to the cathode. Meanwhile, electrons will circulate back oppositely from a negative to a positive current collector (Fig. 3B). The different reactions that occur both at the positive electrode and negative electrode are given as shown in Equation (5), Equation (6), and Equation (7).

**Cathode:**

\[
\text{LiMO}_2 \rightarrow \text{Li} \,(1-x)\text{MO}_2 + x \, \text{Li}^+ + x \, e^- \tag{5}
\]

**Anode (Graphite):**

\[
C_6 + x \, \text{Li}^+ + x \, e^- \rightarrow \text{Li}_xC_6 \tag{6}
\]

The complete reaction of the cell:

\[
\text{LiMO}_2 + C_6 \rightarrow \text{Li}_x\text{MO}_2 + x \, \text{Li}_xC_6
\]
\[
C_6 + LiMO_2 \rightarrow Li_xC_6 + Li_{(1-x)}MO_2
\]  
(7)

Where \(M\) is the transition metal.

During the charge and discharge process, the migration of \(Li^+\)-ions obeys the principle of the rocking chair. The LIB performance reduces due to the aging development occurring in the cell which depends strongly on the way of use and the cell chemistry. Particular attention was directed towards building high energy-density LIBs with a good lifetime and high safety for automobiles. The specific energy \(E\) stored in the battery per unit volume/unit mass is the product of specific capacity \(C_{sp}\) and the discharge voltage \(V\) as shown in Equation (8):

\[
E = C_{sp}V
\]  
(8)

This energy can be either increased or reduced due to the type of electrolytes and electrode materials used to build the cell. To optimize this energy, high-voltage cathode material-based LIBs with and/or high capacity reinforce the design of the naturally stable electrolytes. However, the choice of a new cathode material remains the best way to run for increased energy density. Although many works have been conducted with different cathode materials, this current research focuses on studying the impact of new positive electrode materials that may be more appropriate for high-performance LIBs.

![Fig.3. (A) Schematic drawing of the LIB components[37] and (B) Schematic of the operating mechanism of LIBs [38].](image)

### 2.2 Positive Electrode Materials

The combination of cathode material and carbonaceous wherein there is a reversible process of insertion and extraction led to generating a voltage over 3.5V in LIB. According to equation 8, a higher-density battery can be obtained using a higher voltage and higher capacity material. In LIB, LiCoO_2 as cathode material- is typically used to increase the rate capability and capacity. However, the control of particle shape helps in increasing the rate capability and improved charge voltage leads to an increase in the rate capability [39]. Recent cathode materials are aimed at ameliorating the performance of LIBs. Hence, we report herein the evolution of LIBs from their birth and the marketable electrode material [40,41]. In LIBs, cathode materials including LiCoO_2, LiFePO_4, LiMn_2O_4, and ternary metal oxides including LiNi-Co-MnO_2 (NCM) and LiNi_0.8Co_0.15Al_0.05O_2 (NCA) are principally made with transition metal oxides [42,43].

#### 2.2.1 Lithium Cobalt Oxide

In 1990, LIB technology replaced hard carbon with graphite (anode material) and lithium cobalt oxide (LiCoO_2) as cathode material. The advancement of battery technology has ameliorated the capacity by three times throughout its history. In 1980, Goodenough et al. suggested LiCoO_2 as intercalation cathode material for LIB [43]. A LiCoO_2-based cell is composed of three layers in rhombohedral symmetry in space group R 3’ m as shown in Fig.4. The LiCoO_2-based cell can offer a double voltage of 4.0 V better than LIB based on titanium disulfide (TiS_2) material, showing a significant enhancement in energy density. Since Li metal shows less safety, it causes its rarity in commercial areas. In 1985, Yoshima and his team reported that the replacement of Li metal with carbonaceous material (petroleum coke) can stabilize and secure the intercalation and de-intercalation of Li^+-ions [45]. In 1991, Sony Company made a successful profit from selling LIBs because of their good safety, long cycle life enhanced energy density of 80Wh kg^{-1}, and working voltage of 4.1V [46]. Theoretically, the LiCoO_2-based battery shows a high specific capacitance of 274 mAh cm^{-3} and a volumetric capacity of 1363 mAh cm^{-3}. Nevertheless, the removal of the extra lithium-ions from the Li_{1-x}CoO_2 lattice \((x > 0.5)\) implied irreversibly an architectural modification causing capacity loss [47]. The structural stability can be improved with the doping of elements and surface change owing to minimizing capacity loss [48][49]. As a drawback, LiCoO_2 (LCO) material is highly costly and poorly thermally stable which limits their application in electric vehicles (EVs). However, LCO is
being utilized in small-scale devices because of its high tapped density. In general, good cycle stability is achieved when the charge of the Li0.5CoO2 electrode can deliberate up to 4.2V. The cyclic behavior of LCO typically shows a reduced capacity between 3-4.2V [50]. Dahn and his co-workers [51] showed that poor cyclic behavior observed over a potential range of 4.5 V is related to the rise in impedance. It has been reported that the coating of metal oxides into LCO leads to increased cycle stability over a working voltage of 4.2V [52-52]. Although LCO is relatively costly, and non-stable at high voltage during charge with low capability, its high conductivity remains the principal advantage. Moreover, recent studies reveal that cathodes containing a low ratio of Co demonstrate interesting properties.

![CoO6](image)

**Fig.4. Crystal structure of LiCoO2 [55].**

### 2.2.2 Lithium Nickel Oxide

The development of LIB for future generations needs promising cathode materials such as lithium nickel oxide (LiNiO2) and its derivatives [56]. In 1954, Dyer designed the first LiNiO2 (LNO) which was intensively studied by Dahn and his team to change LCO. The synthesized LiNiO2 using the solid-state reaction approach showed a diminished discharge capacity and low cycling performance because of its low degree of crystallinity and non-uniformness of particle size caused by the impurities [57]. The LNO material exhibits a high capacity of around 200 mAh g⁻¹. The cycling stability of LNOs is relatively low, which might be attributed to the cation mixture [58]. Lithium and nickel are typically the same size and when the lithium membrane is drained during the charge, nickel can fill the lithium vacant sites. Capacity fading can remain in Li[Li1−x−yNixCo3−yAlx]O2 (NCA) and Li[Li1−x−yNixCo3−yMnx]O2 (NCM) due to the structural modifications while charging and discharging [59]. The migration of Li-ions creates a strong electrostatic repulsion which increases the charge of nickel. This result was confirmed by Ceder and his team [60], which features the space change of lithium slab that has a powerful influence in comparison to electric repulsion [60]. The created vacancies of nickel located at the cation sites can be ionized to produce Ni²⁺ ions. The structure of layered cathodes used in LiBs including LNO crystallizing into rhombohedral of R-3m space group (Fig.5). In LiNiO2 cathode material, the withdrawal of lithium over the range (0.4 < x< 0.75) conducts to the monoclinic phase, which is usually assigned to Jahn-Teller distortion, assisted by lithium vacancies [57]. The LNO properties can be improved by doping with some chemical elements using several approaches such as Mg [61], Al [61], Co [63-66], Ga [67], etc. These substances are commonly used due to their ability to facilitate the synthesis of active materials. Solid solutions are exemplified by LNO and LCO over the composition range [68]. The LiNi0.3Co0.7O2 material works well with the eventual reversibility of the lithium formula [69]. LiNiO2 is a potential material for the next generations due to its affordable price and higher specific capacity of 170–200 mAh g⁻¹ [70].
2.2.3 Lithium Manganese Oxide

Spinel lithium manganese oxide (LiMnO$_2$) has drawn attention as an inexpensive, sustainable, and basic substitute material for LCO and LNO. Although LiMnO$_2$ has many profits capable of replacing LCO, its cycle stability and high-rate discharge performance at high temperatures remain the major problems limiting their extensive use. LiMnO$_2$ is a strong candidate for sustainable cathodes but cycles poorly owing to the destabilization of the lattice framework caused by the Jahn–Teller deformed Mn$^{3+}$ ions. In 1996, Delmas and Bruce [72-74] used independently a cation exchange to obtain a layered LiMnO$_2$ (LMO) to improve the voltage stability for commercial use [72]. LMO can be a promising material since Mn is relatively less costly than Co and Ni. For the last two decades [75], the preparation of dehydrated and stereochemistry layered LMO was better than aqueous methods causing impurities, various ratios, poor crystallinity, and unwanted changes of structuring in cycling [76]. Nevertheless, LMO still shows a poor cycling performance (a) because of the trend of its layered structure which turns into a spinel structure through lithium extraction [76], and (b) owing to the Mn removal from LMO throughout cycling [77]. Stoichiometric LMO showed a remarkable deficit in micro-fractures and improved structural and cycle stability. Significant progress has been made to overcome the Mn-ion dissolution issue by developing coating materials to avoid direct interaction with the electrolyte. These materials used for surface coating and which are enabled to remove the acidic outgrowth from side reactions with electrolytes decelerate the deterioration and the Mn-ion dissolution at the cathode include LiCoO$_2$ [78], Al$_2$O$_3$ [79,80], V$_2$O$_5$ [81], MgO [82] and CeO$_2$ [83]. A three-dimensional (3D) Al$_2$O$_3$ nanosheet was made by Li and his team to cover the LiMn$_2$O$_4$ electrode [74]. The covered electrode exhibited an initial specific capacity of 128.5 mAh g$^{-1}$ at a 0.1C rate, with a capacity retention of 89.8% even after 800 cycles at a 1C rate [84]. These coating layered exhibited a high specific area and were used to protect the electrode against the growth of acidic species created by side reactions during the operation of charging and discharging, limiting the interaction between Li-ions and the active material.

Cho and his team developed a LiMn$_2$O$_4$ heterostructure based on an Mn-rich multilayered coating surface of space group R3m [85]. As a result, this LiMn$_2$O$_4$ heterostructure demonstrated an initial capacity of 123 mAh g$^{-1}$ with a capacity retention of 85% after the 100$^{th}$ cycle at a 1C rate, which was found to be better than the spinel LiMn$_2$O$_4$, showing only 56% of retention for 131 mAh g$^{-1}$ at 60°C [85]. This enhanced performance of LiMn$_2$O$_4$ heterostructure was assigned to its lower impedance as well as increased kinetics, faster diffusion rate of lithium-ion, and lesser activation energy. Fig. 6 shows the structure of spinel LiMn$_2$O$_4$.

![Fig. 5. The crystal structure of LiNiO$_2$][71].

![Fig. 6. The structure of spinel LiMn$_2$O$_4$][86].
2.2.4 Lithium Nickel Manganese Oxide

Spinel lithium nickel manganese oxide (LiNi$_{0.5}$Mn$_{1.5}$O$_4$) is found to be a potential choice to replace LiMn$_2$O$_4$ because it delivers a high working voltage of about 4.7V and increased cyclability that can significantly lead to enhanced energy density for traditional LIBs [87]. Nevertheless, the usage of a high-voltage cathode causes the nonstability of the organic electrolyte when it exceeds 4.2V and also the creation of a Ni$_{1-x}$Li$_x$O impurity phase [88]. Two approaches were to be accomplished to solve this issue. The cationic substitution of either Ni or both (Ni and Mn) and surface change using oxide materials (e.g. ZnO, Al$_2$O$_3$, etc.) for enhanced cyclic stability and rate performance have been applied both to stop the development of the impurity phase [89]. Dahn was the first to report the use of LiNi$_{1-x}$MnO$_2$ as cathode materials in LIBs [90]. However, these materials are less attractive because of their poor electrochemical properties. Because of that, lithium nickel manganese oxides (LNMO) were subjected to research. Previous to 2021, Ohzuku [91] and Dahn [92] synthesized LiNi$_{0.5}$Mn$_{0.5}$O$_2$ and Li[Li$_{x}$Ni$_{(1/3-2x/3)}$Mn$_{(2/3-x/3)}$]O$_2$ respectively at 800°C to ameliorate the performance of LNMO and found to be distinguished materials with outstanding electrochemical properties. The effect of carbon coating on LiNi$_{0.5}$Mn$_{0.5}$O$_2$ cathode was studied by Good–Enough et al. and revealed that the coating prevented the capacity loss by improving the electronic conductivity and diminishing the polarization, which increased the discharge capacities at fairly high current densities [93]. An example of carbon coating on the cathode is illustrated in Fig. 7.

![Fig. 7. An illustrative representation of a cathode, composed of active material, carbon, and a binder. Including the transfer track of Li-ions, and electrons as well [94].](image)

Modifying layered LNMO cathode materials via a coating, doping, synthesis approach, lithium-rich materials, and nanostructured materials increases stability during the charge/discharge cycle and enhances the electrochemical properties. However, the application of only one of these above methods shows some restrictions for LNMO cathode materials. LNMOs are promising, low-cost, clean materials with the additional benefit of high thermal stability. However, LNMOs are prominent cathode materials to are potential substitutes for the commercial LiCoO$_2$ electrode.

2.2.5 Lithium Manganese Cobalt Nickel Oxide

The Li-rich oxide layer cathode material was developed via a liquid process communicated by B. Li and his coworkers[95]. The product obtained was the pristine material Li$_{1.2}$Mn$_{0.52}$Co$_{0.13}$Ni$_{0.13}$O$_2$ (LMCN). Li-rich oxide layer materials could be outlined as xLi$_2$MnO$_3$ (1-x) LiMO$_2$ where, M= Mn, Co, Ni, etc., was recognized as potential material to be used for enhanced energy density batteries because of its high specific capacity over 250 mAh g$^{-1}$[96-100].

2.2.6 Phosphate Polyanion Materials

Due to their high electrochemical potential (4.8-5 V vs Li/Li$^+$), long cycle stability, low cost, and achieved specific capacity (165 mAhg$^{-1}$) close to the theoretical limit (170 mAhg$^{-1}$) phosphate polyanion materials (LiMPO$_4$, where M is a single metal or a combination of metals) demonstrated promising candidacy.[101]. Aside from increasing C_sp, researchers are focusing on increasing the electrochemical potential of cathode materials in order to create a lithium-ion battery with a working potential of 5 V versus Li/Li$^+$. Numerous attempts have been made in this direction, resulting in the development of cathode materials. LiVOPO$_4$, [102,103], MxVO(HPO$_4$)(C$_2$O$_4$)[104], LiNi$_{1.0xyCoxMnyO2}$[105,106], and others have working potentials greater than 4 V vs Li/Li$^+$. 
Polyanionic materials such as phosphates (LiMPO$_4$) [107], fluorophosphate (LiM(PO$_4$)F) [108,109], pyrophosphate (Li$_2$MP$_2$O$_7$) [110,111], orthosilicates (Li$_2$M(SiO$_4$)) [112], borates (LiMBO$_3$) [113], and tsavorite fluoro sulfates (Li$_2$M(SO$_4$)$_2$F) [114,115], (M = Fe, Co, Ni, Mn, etc.) have been recognized for their high charge-discharge potential. The origin of high electrochemical potential energy at cathode (c) for polyanion materials is described elsewhere [116]. In summary, when the covalent link between a transition metal and oxygen (Mo) is strong, considerable splitting energy between bonding and antibonding orbitals are reached. As the antibonding orbital approaches the vacuum, the redox potential of the material aligns with that of a Li metal, lowering the working potential. In polyanion materials, the M–O bond is weakened by introducing another anion (P, Si, B, etc.) with stronger electronegativity, lowering the splitting energy between bonding and antibonding orbitals [117, 118]. Such an effect is visible between iron- and cobalt-based materials, where the discharge voltages of layered LiFeO$_2$ (2.98 V against Li/Li$^+$) and LiCoO$_2$ (3.9 V vs Li/Li$^+$) are raised by polyanionic couplings to 3.5 V vs Li/Li$^+$ (LiFePO$_4$) and 4.8 V vs Li/Li$^+$ (Li-CoPO$_4$), respectively [119]. The addition of fluorine increased the discharge voltages of these polyanions [120]. The addition of fluoride to anions decreased the covalency of the M−O bond, further stabilizing the energies of the metal ions in antibonding d-orbitals and increasing Li insertion potentials [121-123].

Phosphate-based polyanion cathodes are more beneficial than other polyanion materials due to their high working potentials and accordingly high specific energy densities of 700 Wh kg$^{-1}$ with LiCoO$_2$ [124]. The unusual atomic arrangement, in the case of LiFePO$_4$, and periodic interval of the FeO$_6$ octahedron (electrochemically active) and PO$_4$ tetrahedron (electrochemically inert) also contributed to enhanced mechanical integrity throughout prolonged charge-discharge cycles. Furthermore, phosphate polyanions are a low-cost cathode contender when compared to LiCoO$_2$ and other prominent players such as lithium nickel cobalt manganese oxide and lithium nickel cobalt aluminum. Due to its rarity in the earth's crust, the availability of cobalt has long impeded the expansion of lithium-ion batteries, generating a significant increase in cobalt costs during the preceding decades. In response to the increased cobalt price, attempts were made to develop nickel-rich NCM cathode materials that used as little cobalt as possible. These efforts, however, were insufficient, and the total elimination of cobalt from cathode materials was encouraged in order to develop lower-cost and more sustainable lithium-ion batteries [125]. Without a doubt, phosphate-based polyanions meet the condition of cobalt-free cathodes, with LiMnPO$_4$ and LiNiPO$_4$ having comparable high working potentials to LiCoPO$_4$ [126,127], and LiMnPO$_4$ having equivalent gravimetry-specific capacity to LiFePO$_4$ and slightly higher than LiCoPO$_4$ [128].

Recently, orthosilicate (Li$_2$M(SiO$_4$)) counterparts have received a lot of attention since they have higher theoretical gravimetry-specific capacities (>300 mAh g$^{-1}$ for LiFeSiO$_4$) and practically equal working potentials (3.1 V vs Li/Li$^+$ for LiFeSiO$_4$) as phosphate analogs [129]. The ability of orthosilicate Polyanions to host two lithium ions within a single cell, as opposed to phosphate analogs, results in their high theoretical gravimetry-specific capacities.

Phosphate-based materials such as LiMnPO$_4$, LiCoPO$_4$, and LiNiPO$_4$ have attracted substantial research attention among polyanion cathodes due to their capacity to produce much higher energy densities than LiFePO$_4$ due to their high operating voltages. However, these materials have not yet been fully commercialized, owing to metal ion dissolution and electrolyte disintegration at high working voltage windows (>4.8 V versus Li/Li$^+$). Most typical LIB electrolytes (nonaqueous organic electrolytes) are unstable and disintegrate at >4.8 V versus Li/Li$^+$, limiting the possible specific capacity (167 mAhg$^{-1}$) and cycle stability of high-voltage polyanion cathode materials such as LiCoPO$_4$ and LiNiPO$_4$. Table 1 summarizes the electrochemical performances of some promising polyanion cathode materials.

<table>
<thead>
<tr>
<th>Polyanion compounds</th>
<th>Theoretical capacity (mAh g$^{-1}$)</th>
<th>Average discharge potential (V vs Li/Li$^+$)</th>
<th>Potential range (V vs Li/Li$^+$)</th>
<th>Redox couple</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_3$V$_2$(PO$_4$)$_3$</td>
<td>197</td>
<td>3.8</td>
<td>3.0−4.8</td>
<td>V$^{3+/4+}$</td>
<td>[130]</td>
</tr>
<tr>
<td>LiCoPO$_4$</td>
<td>167</td>
<td>4.8</td>
<td>3.0−5.1</td>
<td>Co$^{2+/3+}$</td>
<td>[131]</td>
</tr>
<tr>
<td>LiNiPO$_4$</td>
<td>167</td>
<td>~5.1</td>
<td>3.0−5.5</td>
<td>Ni$^{2+/3+}$</td>
<td>[132]</td>
</tr>
<tr>
<td>LiNiOSO$_4$</td>
<td>152</td>
<td>5.0 (theoretical)</td>
<td>-</td>
<td>Ni$^{3+/4+}$</td>
<td>[133]</td>
</tr>
<tr>
<td>LiCoOSO$_4$</td>
<td>152</td>
<td>5.1 (theoretical)</td>
<td>-</td>
<td>Co$^{2+/3+}$</td>
<td>[133]</td>
</tr>
<tr>
<td>Li$_2$NiOSO$_4$</td>
<td>152</td>
<td>5.0 (theoretical)</td>
<td>-</td>
<td>Ni$^{3+/4+}$</td>
<td>[133]</td>
</tr>
<tr>
<td>Li$<em>2$Cr$</em>{0.5}$Mn$_{0.5}$O$_4$</td>
<td>151</td>
<td>~4.5−4.8</td>
<td>3.4−5.4</td>
<td>Cr$^{3+/4+}$, Mn$^{3+/4+}$</td>
<td>[134]</td>
</tr>
<tr>
<td>LiCoSO$_4$F</td>
<td>149</td>
<td>4.7−4.9 (theoretical)</td>
<td>-</td>
<td>Co$^{2+/3+}$</td>
<td>[135]</td>
</tr>
<tr>
<td>LiNiSO$_4$F</td>
<td>149</td>
<td>5.2−5.4 (theoretical)</td>
<td>-</td>
<td>Ni$^{2+/3+}$</td>
<td>[135]</td>
</tr>
<tr>
<td>LiFe$<em>2$Mn$</em>{1.5}$O$_4$</td>
<td>148</td>
<td>4.5</td>
<td>3.0−5.3</td>
<td>Fe$_{2+/3+}$, Mn$^{3+/4+}$</td>
<td>[136]</td>
</tr>
<tr>
<td>LiNi$<em>{0.5}$Mn$</em>{1.5}$O$_4$</td>
<td>147</td>
<td>4.7</td>
<td>3.5−5.0</td>
<td>Ni$^{2+/3+}$</td>
<td>[137]</td>
</tr>
<tr>
<td>LiCu$_{0.5}$SO$_4$F</td>
<td>145</td>
<td>5.1 (theoretical)</td>
<td>5.15−5.40</td>
<td>Cu$^{2+/3+}$</td>
<td>[138]</td>
</tr>
<tr>
<td>LiCu$<em>{0.5}$Mn$</em>{1.5}$O$_4$</td>
<td>145</td>
<td>~4.3</td>
<td>3.3−5.1</td>
<td>Cu$^{2+/3+}$, Mn$^{3+/4+}$</td>
<td>[139]</td>
</tr>
<tr>
<td>Li$_2$NiPO$_4$F</td>
<td>143</td>
<td>~5.1</td>
<td>3.0−5.5</td>
<td>Ni$^{2+/3+}$</td>
<td>[140]</td>
</tr>
</tbody>
</table>
As a result, strategies for enhancing the electronic conductivities of polyanion materials have been extensively investigated, including (1) conductive carbon coating, (2) particle size reduction, and (3) metal ion doping (such as Mg\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), and Co\(^{2+}\) ion doping). Indeed, these solutions successfully enhanced the storage capacity and charging voltage of olivine-type cathodes, as discussed below.

### 2.2.6.1 Surface Coating

Coating the surface of cathode materials with a thin coating (nanometer thickness) of metal or metal oxide such as AlPO\(_4\), ZrO\(_2\), LiNbO\(_3\), carbon, or conductive polymers has proved to greatly improve the electrical conductivity of the active materials on most occasions [144-148]. Carbon coating was extensively researched among coating materials due to its inexpensive cost, strong conductivity even at low concentrations (0.52 wt%), and simple coating techniques during or after active material creation. Numerous studies have linked such improvements in electrochemical performance to enhanced electrical conductivity and the lithium-ion diffusion coefficient following carbon coating [149,150]. However, the adjustment of the surface carbon coating in terms of volume, thickness, and quality of carbon is essential to provide superior electrochemical performance of the cathode.

### 2.2.6.2 Control of Particle Size

Aside from surface coating, the olivine cathode’s capacity can be increased by modifying the lithium-ion diffusion pathway. Reduced particle size of active materials is one of the most successful and extensively used techniques. The electrode particle size was reduced primarily for two reasons: (1) to reduce the ion diffusion pathway and (2) to improve the surface area of the active material. A significant improvement in rate capability was found by lowering particle size. Reducing particle size greatly decreased the diffusion pathway for lithium ions to reach the innermost parts of the cathode materials, improving the cathode materials’ rate capabilities [151]. Yang et al. next employed sol-gel techniques to produce LiMn\(_{0.8}\)Fe\(_{0.2}\)PO\(_4\) with varying secondary particle sizes, observing a rise in electrode polarization during charge-discharge as particle size increased [152]. Increases in electrode polarizations in active materials with large particle sizes are caused by longer lithium-ion diffusion routes. Furthermore, the size reduction resulted in less volume expansion during lithiation, which directly contributes to increased cycling stability [153][154].

### 2.2.6.3 Metal Ion Doping

Metal ion doping was also important in increasing the electrical and ionic conductivities of phosphate-based polyanion cathodes by changing their crystallographic and electronic environment. Doping LiNiPO\(_4\) with low concentration cobalt resulted in a small increase in crystal volume due to higher ionic radii of 72 nm (compared to 69 nm for Ni\(^{2+}\)), allowing for greater lithium-ion diffusion to/from Li-NiO\(_0.3\)CoO\(_{0.7}\)PO\(_4\). Crystal growth was observed when LiFePO\(_4\) was doped with additional heteroatoms such as titanium, zirconium, vanadium, niobium, and tungsten, according to previous research [155-157]. Due to the difference in oxidation state, replacing phosphorus with silicon introduces a hole into the crystal structure, converting Si-doped LiMPO\(_4\) to a p-type material [158]. The inclusion of a hole into the crystal structure would improve the electronic conductivity of Si-doped LiMPO\(_4\) but would hinder lithium-ion diffusion at greater concentrations.

The phosphate-based LiMnPO\(_4\) cathode material is regarded as a possible contender for next-level high-voltage LIBs due to its cost-effectiveness, environmental friendliness, and acceptable energy density. Similarly, the electrochemical performance of multicomponent LiMPO\(_4\) (M = Fe, Mn, Co, and Ni) is superior to that of single-component LiMPO\(_4\) [159]. LiFe\(_{0.2}\)Mn\(_{0.8}\)PO\(_4\) (4.6 V vs Li/Li\(^+\)) and LiFe\(_{0.8}\)Co\(_{0.2}\)PO\(_4\) (4.8 V vs Li/Li\(^+\)) solid solutions surpass LiFePO\(_4\) in terms of higher rate capability, cycle stability, and working potential. The most often used binary olivine-type solid solution is LiFe\(_{0.5}\)Mn\(_{0.5}\)PO\(_4\), which has a higher rate capability and energy density than LiMnPO\(_4\) and LiFePO\(_4\), respectively [160][161]. Metal doping in LiMPO\(_4\) (M = Fe, Mn, Co, Ni, etc.) could only improve electrical and ionic conductivities to a limited amount, with surface coating and particle size reduction (shortening the lithium diffusion pathway) playing the most important roles in assuring high-rate capability.

### 2.2.6.4 Synthesis of Coprecipitation

Coprecipitation is a low-temperature, low-cost synthetic approach that produces ultrafine and uniform particles. This approach also avoids difficult processes like alkoxide reflexing. Transition metal hydroxides, oxalates, and carbonates were used as metal precursors with suitable precipitating agents such as ammonium hydroxide, ammonium oxalate, ammonia, ammonium persulfate, oxalic acid, and citric acid [162][164]. Surprisingly, a coprecipitation technique has been widely used in large-scale applications to

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle Size</th>
<th>Oxidation State</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LizCoPO(_4)F</td>
<td>~4.9</td>
<td>2+/3+</td>
<td>[141]</td>
</tr>
<tr>
<td>LizMnP(_2)O(_7)</td>
<td>4.45</td>
<td>2.0–4.7</td>
<td>Mn(^{2+})–(^{3+})</td>
</tr>
<tr>
<td>LizCoP(_2)O(_7)</td>
<td>4.9</td>
<td>2.0–5.5</td>
<td>Co(^{2+})–(^{3+})</td>
</tr>
</tbody>
</table>
prepare spherical high tap density precursors for high volumetric energy density cathode materials. Ternary Li$_{Fe_{0.5}Mn_{0.3}Co_{0.2}}$PO$_4$/C composite (5 V vs Li/Li$^+$) cathode materials were synthesized using a stepwise coprecipitation and ball-milling method, yielding an initial capacity of 163.3 mAh g$^{-1}$ at 0.1 C and high-rate capacities of 110 and 140.7 mAh g$^{-1}$ after 100 cycles at 0.5 and 1 C, respectively[164]. As a result, the preceding results demonstrate that coprecipitation is an efficient method for producing scalable and low-cost phosphate-type composite cathodes with excellent LIB electrochemical performances.

2.2.6.5 Sol-gel Synthesis

The sol-gel method has also been used for the synthesis of phosphate-based polyanion cathode materials due to its considerable benefits of good raw material homogeneity, low calcination temperature, and rapid reaction time. For example, nanosized Li$_{Mn_{0.5}Fe_{0.5}}$PO$_4$/C composite cathode materials synthesized via high-energy ball-milling-assisted sol-gel deliver much better discharge capacities of 129 mAh g$^{-1}$ and 116.3 mAh g$^{-1}$ with retentions of 93.5% and 90.3% for 100 cycles at 1 and 2 C, respectively, when compared to only LiMnPO$_4$/C[165]. Furthermore, nanocomposites of Li$_{Mn_{x}Fe_{1-x}}$PO$_4$/C (x = 1, 5/6, 2/3, 1/2) cathode materials with varied mole ratios of Fe substitution were produced and tested at 4.5 V versus Li/Li$^+$[166] using freeze-drying-assisted sol-gel techniques.

2.2.6.6 Solid-State Synthesis

The planetary or high-energy ball-milling technique is the most commonly used equipment for a solid-state reaction to synthesize LIBs cathode materials, and it is also a more straightforward route for a scalable application. It is also one of the most prevalent ways for shrinking primary particles on the nanoscale to reduce intraparticle-transport resistance and provides uniform carbon coating on an individual nanocrystal surface to reduce interparticle transport resistance. The solid-state synthesis method was also used to prepare a 5 V vs Li/Li$^+$ Li$_{Fe_{0.3}Mn_{0.3}Co_{0.2}}$PO$_4$/C cathode; the initial discharge capacity and rate capabilities are noticeably improved when spinel Co$_3$O$_4$ nanoneedles are used as the precursor for Co substitution instead of conventional Co$_3$O$_4$ microspheres[167]. Nanostructured materials with large surface areas, according to the research, can allow for better Li$^+$ ion penetration and storage capacity. According to the published literature, the solid-state synthesis route using a dual-time ball-milled process can control the secondary particle size and uniform distribution of nanocrystals with residual carbon content, improving overall electrochemical performance in high-voltage LIB applications.

This study focused on three main aspects, namely electrochemical potential, electrical conductivity, and synthetic methodologies, as shown schematically in Fig.8, to improve the specific capacities and voltage windows of the aforementioned polyanion materials; factors contributing to each section are thoroughly discussed.

**Fig.8.** The overarching goals of this study are divided into three categories (denoted by the outer circle)[168]. The inner parts depict the focus locations.

### 3. Advantages and Disadvantages of the Oxide Cathodes

The various types of oxide cathodes listed above have advantages and disadvantages. The layered and spinel classes of oxides have strong electronic conductivity, but the polyanion oxide class has weak electronic conductivity. As a result, polyanion oxide cathodes necessitate small particle synthesis and coating with conductive carbon, which frequently raises processing costs and produces irregularities in performance. Close-packed structures with high densities characterize both layered and spinel oxides, whereas the polyanion class of oxides has lower densities, which is further lowered by the requirement to manufacture them as microscopic particles covered with carbon, resulting in a lower volumetric energy density.
As a result, polyanionic cathodes are frequently less desirable than multilayer oxide cathodes for applications needing high volumetric energy density, such as portable electronic devices and electric vehicles. Furthermore, unlike layered and spinel oxides, polyanionic cathodes have abundant transition metals such as Fe, which provides sustainability benefits. As a result, they are advocating for grid storage of renewable energy sources such as solar and wind.

However, the polyanion class of cathodes has a significant advantage in terms of thermal stability and safety over multilayer and spinel oxide cathodes because the oxygen is strongly attached to P, S, or Si by strong covalent bonds [170]. Furthermore, despite having a lower volumetric energy density, polyanionic cathodes with appropriately small carbon-covered particles can maintain high charge-discharge rates due to their structural integrity.

Because standard synthetic processes have trouble stabilizing highly oxidized $M^{3+/4+}$ states in spinel oxides, layered oxides with a wider range of compositions are more appealing. Spinel cathodes are generally confined to LiMn$_2$O$_4$, but even this is hampered by Mn dissolution and the resulting poisoning of graphite anodes, as well as capacity fade, especially at high temperatures. However, replacing a small amount of lithium (e.g., 5 atoms%) for Mn helps to alleviate some of the difficulties. However, while LiMn$_{1.5}$Ni$_{0.5}$O$_4$ is appealing due to its high working voltage of 4.7 V and hence power capability, its practical feasibility is hampered by a lack of adequate electrolytes capable of operating at such high operating voltages.

Layered materials are used as cathodes in high-energy systems [171][172], whilst spinel oxides and olivine are being studied for high-power Li-ion batteries due to their low cost and extended life [173][174]. These lithium-insertion compounds, on the other hand, must have particular features such as chemical stability, capacity, rate capability, toxicity, cost, and safety. All of them, however, reach a theoretical specific capacity greater than 140 mAh g$^{-1}$ at a potential greater than 3.4 V vs. Li$^0$/Li$^+$. The electrochemical properties of the three groups of insertion compounds are summarized in Table 2.

The promising cathode materials that are used in the revolution of the advanced LIBs for EVs include LiCoO$_2$, LiNiO$_2$, LiMnO$_2$, LiNi$_{0.5}$Mn$_{1.5}$O$_4$, and Li$_{1.2}$ Mn$_{0.52}$Co$_{0.13}$Ni$_{0.13}$O$_2$ [175].

### Table 2. The electrochemical properties of three kinds of insertion chemicals.

<table>
<thead>
<tr>
<th>Framework</th>
<th>Compound</th>
<th>Specific capacity (mAh g$^{-1}$)</th>
<th>Average potential (V vs. Li$^0$/Li$^+$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layered</td>
<td>LiCoO$_2$</td>
<td>272 (140)</td>
<td>4.2</td>
</tr>
<tr>
<td>Layered</td>
<td>LiNi$<em>{0.5}$Mn$</em>{1.5}$O$_2$</td>
<td>272 (200)</td>
<td>4.0</td>
</tr>
<tr>
<td>Spinel</td>
<td>LiMn$_2$O$_4$</td>
<td>148 (120)</td>
<td>4.1</td>
</tr>
<tr>
<td>Spinel</td>
<td>LiMn$<em>{3/2}$Ni$</em>{1/2}$O$_4$</td>
<td>148 (120)</td>
<td>4.7</td>
</tr>
<tr>
<td>Olivine</td>
<td>LiFePO$_4$</td>
<td>170 (160)</td>
<td>3.45</td>
</tr>
<tr>
<td>Olivine</td>
<td>LiFe$<em>{1/2}$Mn$</em>{1/2}$PO$_4$</td>
<td>170 (160)</td>
<td>3.4/4.1</td>
</tr>
</tbody>
</table>

*Value in parenthesis indicates the practical specific capacity of the electrode.

### 4. Conclusion and Perspectives

In summary, coordinated fundamental science research led to the identification of three types of transition-metal oxide cathodes with substantially higher operating voltages than previously investigated sulfide cathodes for lithium-based batteries in the 1980s. They are layered oxides, spinel oxides, and polyanionic oxides, and these three classes remain feasible practical cathodes and serve as the foundation for future advances. Several types of research on electrode materials have been conducted to enhance the performance of LIBs including energy density, working voltage, safety, and lifespan. As we progress with large-scale applications, there is a desire to increase energy density while lowering costs. In this regard, layered oxide cathodes with high nickel content have become intriguing, but smart bulk and surface stabilization techniques are required to overcome the cycle, thermal, and air instabilities associated with them and realize their full potential. Moreover, the prominent cathode materials that may meet the requirements of next-generation energy are discussed, aiming to address the advantages and disadvantages as well as the beneficial approaches including cationic substitution, surface modification, coating, and doping to overcome the permanent issues encountered in the LIB cathodes. The cationic substitution using the transition metals including Mg, Al, Co, Ga, etc., and the surface modification using oxide materials enhance the stability and rate capability. Carbon coating prevents the capacity fade, limits the polarization effect, and increases the discharge capacities at relatively high currents, and doping leads to reinforcing the cathode structure, increasing the electrical conductivity, and limiting the cathode degradation. The promising cathode materials that are used in the revolution of the advanced LIBs for EVs include LiCoO$_2$, LiNiO$_2$, LiMnO$_2$, LiNi$_{0.5}$Mn$_{1.5}$O$_4$, and Li$_{1.2}$ Mn$_{0.52}$Co$_{0.13}$Ni$_{0.13}$O$_2$. This study reveals the use of all these approaches together contributes to the development of high-performance cathode materials.
leading not only to overcoming challenges faced by the cathode materials but also enhancing the performance of the rechargeable LIBs. Alternatively, because insertion-reaction oxide cathodes have a capacity limitation due to a limited number of available crystallographic sites for lithium insertion/extraction and experience large voltage steps when switching from one redox couple to another, there is a lot of interest in conversion-reaction cathodes like sulfur and oxygen. Finally, newer synthesis and processing methods, as well as improved characterization tools and computer analysis, may aid in the identification of new materials as we work toward a cleaner, more sustainable planet.

Compliance with Ethical Standards

Conflicts of interest: Authors declared that they have no conflict of interest.

Human participants: The conducted research follows the ethical standards and the authors ensured that they have not conducted any studies with human participants or animals.

References

Effect of Layered, Spinel, and Olivine-Based Positive Electrode Materials On Rechargeable Lithium-Ion Batteries: A Review

Effect of Layered, Spinel, and Olivine-Based Positive Electrode Materials On Rechargeable Lithium-Ion Batteries: A Review


Effect of Layered, Spinel, and Olivine-Based Positive Electrode Materials On Rechargeable Lithium-Ion Batteries: A Review


[95] Li, Bing, Y. Yu and J. Zhao, “Facile Synthesis of Spherical xLi2MnO3 (1-x)Li(Mn0.33Co0.33Ni0.33)O2 as Cathode Materials for Lithium-Ion Batteries with Improved Electrochemical Performance,” Journal of Power Sources, Vol. 275, pp.64-72, 2015.


[100] Dai, Dongmei, B. Wang, B. Li, F. Li, X. Wang, H. Tang and Z. Chang, “Li-Rich Layered Li1.2Mn0.54Ni0.13Co0.3O2 Derived from Transition Metal Carbonate with a Micro–Nanostructure as a Cathode Material for High-Performance Li-Ion Batteries,” RSC Advances, Vol. 6, No. 99, pp. 96714-20, 2016.


Effect of Layered, Spinel, and Olivine-Based Positive Electrode Materials On Rechargeable Lithium-Ion Batteries: A Review


Effect of Layered, Spinel, and Olivine-Based Positive Electrode Materials on Rechargeable Lithium-Ion Batteries: A Review


[168] Huang, Z. Gen, J. T. Li, K. Wang, W. F. Ren, Y. Q. Lu, L. Deng, L. Huang and S. G. Sun, “Synthesis of LiFe0.4Mn0.4Co0.2PO4/C Cathode Material of Lithium Ion Battery with Enhanced Electrochemical Performance,” Journal of Alloys and Compounds, Vol. 782, pp. 413-20, 2019.


