

# PROMISING CATHODE MATERIALS FOR RECHARGEABLE LITHIUM-ION BATTERIES: A REVIEW

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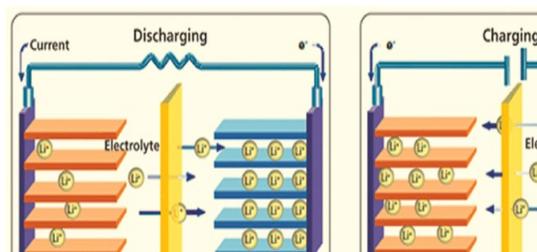
**Abstract:** The lithium-ion battery (LIB) technology is getting particular attention because of its effectiveness in small-scale-electronic products such as watches, calculators, torchlights, or mobile phones through to large-scale power systems such as automobiles, trains, ships, submarines, or airplanes. 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. 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 impact of the electrode surface and a brief review of the advanced cathode materials for LIBs have been also reported. This work aims to review the latest research works and the progress of advanced cathode materials helping to make higher-performance LIBs for future generations.

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

## 1. INTRODUCTION

The fast development of Li-ion battery technology has paid a lot of attention to researchers. This particular regard is directed to the innovation of high-performance LIBs. Therefore, recent investigations were made in the manufacturing of new smart LIBs for large-scale applications [1]. 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 battery. 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 [2-4]. A

LIB is made with an anode, an electrolyte, a separator, and a cathode (shown in Fig.1).

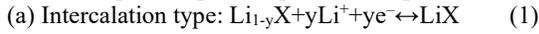


**Fig. 1. Mechanism of charging and discharging in a LIB**

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,  $\text{LiFePO}_4$ ,  $\text{LiCoO}_2$ , and  $\text{LiMn}_2\text{O}_4$  cathode materials incorporated in Li solar batteries exhibited fairly lesser charging capacities ( $<200 \text{ mAhg}^{-1}$ ). Nevertheless, materials with higher capacity tend to demonstrate reduced thermal stability [5]. 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  $\text{Li}^+/\text{Li}$  is the main problem faced with high voltage cathodes [6-12]. Unfortunately, LIB life span is limited due to the effect side reactions that may be noxious to the different elements of the cell, which includes 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 [13-15].

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 [16]. The different factors that contribute to electrode aging, are synergistically influencing battery aging [17]. Among these above-mentioned factors, the electrode material is considered one the most important factor that influences LIB performance, including capacity, lifespan, and safety. The commercialized LIB consists of a cathode made from lithium-intercalated layers using an organic electrolyte, such as  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,

or  $\text{LiClO}_4$  in an organic solvent [18]. Due to the type of reaction that occurs in LIBs between the electrode material and  $\text{Li}^+$ -ions, rechargeable LIBs electrode materials can be divided into (a) intercalation electrode materials, (b) conversion electrode materials, and other types. Figure 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. The equations of the different types of reactions in (a) LiB and (b) Li-S batteries are given in Eq. (1), Eq. (2), Eq. (3), and Eq. (4).

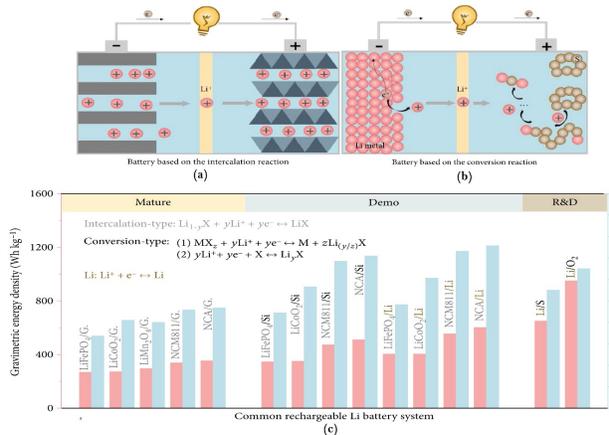


(b) Conversion type:



Where  $M$  is the transition metal

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



**Fig.2. Commonly used rechargeable Li-battery systems. (a) Interaction reaction mechanism in LIB, (b) conversion reaction mechanism in Li-S battery taken as a template, (c) Evaluation of the gravimetric and volumetric energy densities of conventional rechargeable LIB systems [19, 20].**

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 Figure 2(c) [19, 20]. Conversion-type materials are suitable for high-performance batteries because of their high specific capacity, as compared to current intercalation electrode materials [21, 22]. In particular, Li metal-based anode can aid to achieve practically a specific energy of 400 Wh kg<sup>-1</sup> and 900 Wh L<sup>-1</sup>. Nonetheless, many defies 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 performance.

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. Theoretical and experiment achievements help in understanding the basic mechanisms in LIBs and Their potential applications at different scales.

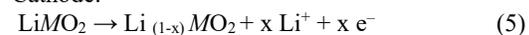
## 2. ELECTRODE MATERIALS FOR LITHIUM-ION BATTERIES

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 enable to be efficient enough to promote a high rate of electrons collection and mobility.

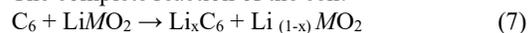
### 2.1 Working principle of LIB

In LIB, the cathode plays the role of the source of  $\text{Li}^+$ -ions and helps to determine the average voltage and specific capacitance delivered by the cell. During charge,  $\text{Li}^+$  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 Figure 3 (A). For each migrated  $\text{Li}^+$ , 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 with electricity. On the contrary, during the discharge,  $\text{Li}^+$  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 (Figure 3B). The different reactions which occur both at the positive electrode and negative electrode are given as shown in Eq. (5), Eq. (6), and Eq. (7).

Cathode:



The complete reaction of the cell:



Where  $M$  is the transition metal

During the charge and discharge process, the migration of  $\text{Li}^+$ -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/ and mass is the product of specific capacity ( $C_{\text{sp}}$ ) and the discharge voltage (V) as shown in Eq. (8):

$$E = C_{\text{sp}} \cdot V \quad (8)$$

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.

## 2.2. Positive Electrode Materials

The combination of cathode material and carbonaceous in 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,  $\text{LiCoO}_2$  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 [25]. Recent cathode materials are aimed to ameliorate the performance of LIBs. Hence, we report herein the evolution of LIBs from their birth and the marketable electrode material [26, 27]. In LIBs, cathode materials including  $\text{LiCoO}_2$ ,  $\text{LiFePO}_4$ ,  $\text{LiMn}_2\text{O}_4$ , and ternary metal oxides including  $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$  (NCM) and  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA) are principally made with transition metal oxides [28, 29].

### a) Lithium Cobalt Oxide

In 1990, LIB technology replaced hard carbon with graphite (anode material) and lithium cobalt oxide ( $\text{LiCoO}_2$ ) as cathode material. The advancement of battery technology has ameliorated the capacity by three times throughout its history. In 1980, Goodenough et al. suggested  $\text{LiCoO}_2$  as intercalation cathode material for LIB [30]. A  $\text{LiCoO}_2$ -based cell is composed of three layers in rhombohedral symmetry in space group  $R\bar{3}m$  as shown in Fig. 4. The  $\text{LiCoO}_2$ -based cell can offer a double voltage of 4.0 V better than LIB based on titanium disulfide ( $\text{TiS}_2$ ) material, showing a significant enhancement in energy density. Since Li metal shows less safety it causes its rarity in the commercial area. 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  $\text{Li}^+$ -ions [31]. In 1991, Sony Company made a

successful profit on selling LIBs because of their good safety, long cycle life and enhanced energy density of  $80\text{Wh kg}^{-1}$  and working voltage of 4.1V [32]. Theoretically,  $\text{LiCoO}_2$  based battery shows a high specific capacitance of  $274\text{mAh cm}^{-3}$  and volumetric capacity of  $1363\text{mAh cm}^{-3}$ . Nevertheless, the removal of the extra amount of lithium-ions from  $\text{Li}_{1-x}\text{CoO}_2$  lattice ( $x > 0.5$ ) implied irreversibly an architectural modification causing capacity loss [33]. The structural stability can be improved with the doping of elements and surface change owing to minimizing capacity loss [34, 35]. As a drawback,  $\text{LiCoO}_2$  (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  $\text{Li}_{0.5}\text{CoO}_2$  electrode can deliberate up to 4.2V. The cyclic behavior of LCO typically shows a reduced capacity between 3-4.2V [36]. Dahn and his co-workers [37] 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 [38-40]. 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.

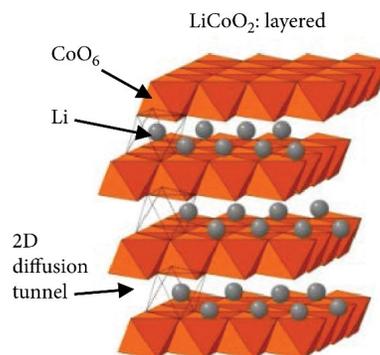


Fig. 4. Crystal structure of  $\text{LiCoO}_2$  [41].

### b) Lithium Nickel Oxide

The development of LIB for future generations needs promising cathode materials such as lithium nickel oxide ( $\text{LiNiO}_2$ ) and its derivatives [42]. In 1954, Dyer designed the first  $\text{LiNiO}_2$  (LNO) which was intensively studied by Dahn and his team to change LCO. The synthesized  $\text{LiNiO}_2$  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 [43]. The LNO material exhibits a high capacity of around  $200\text{mAh g}^{-1}$ . The cycling stability of LNOs is relatively low, which might be attributed to the cation mixture [44]. Lithium and nickel have 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  $\text{Li}[\text{Ni}_{1-x-y}\text{Co}_x\text{Al}_y]\text{O}_2$  (NCA) and  $\text{Li}[\text{Ni}_{1-x}$

$_{y}\text{Co}_x\text{Mn}_y\text{O}_2(\text{NCM})$  due to the structural modifications while charging and discharging [45]. 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 [46], which features the space change of lithium slab that has a powerful influence in comparison to electric repulsion [46]. The created vacancies of nickel located at the cation sites can be ionized to produce  $\text{Ni}^{3+}$ -ions. The structure of layered cathodes used in LIBs including LNO crystallizing into rhombohedral of R-3m space group (Fig.5). In  $\text{LiNi}_x\text{O}_2$  cathode material, the withdrawal of lithium over the range ( $0.4 < x < 0.75$ ) conducts to monoclinic phase, which is usually assigned to Jahn-Teller distortion, assisted by lithium vacancies [43]. The LNO properties can be improved by doping with some chemical elements using several approaches such as Mg [47], Al [48], Co [49-52], Ga [53], 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 [54]. The  $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$  material works well with the eventual reversibility of the lithium formula [55].  $\text{LiNiO}_2$  is a potential material for the next generations due to its affordable price and higher specific capacity of 170–200  $\text{mAh g}^{-1}$  [56].

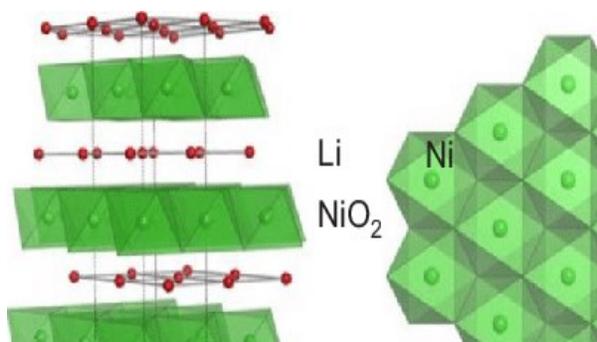


Fig. 5. The crystal structure of  $\text{LiNiO}_2$  [57].

### c) Lithium Manganese Oxide

Spinel lithium manganese oxide ( $\text{LiMnO}_2$ ) has drawn attention as an inexpensive, sustainable and basic substitute material to LCO and LNO. Although  $\text{LiMn}_2\text{O}_4$  has many profits capable of replacing LCO, its cycle stability and high rate discharge performance at high temperature remain the major problems limiting their extensive use.  $\text{LiMnO}_2$  is a strong candidate for sustainable cathodes but cycles poorly owing to the destabilization of the lattice framework caused by the Jahn-Teller deformed  $\text{Mn}^{3+}$  ions. In 1996, Delmas and Bruce [58-60] used independently a cation exchange to obtain a layered  $\text{LiMnO}_2$  (LMO) to improve the voltage stability for commercial use [58]. LMO can be promising material since Mn is relatively less costly than Co and Ni. Since the last two decades [61], the preparation of dehydrated and stereochemistry layered LMO was better than aqueous methods causing impurities, various ratios, poor crystallinity, and unwanted change of structuring in cycling [62]. Nevertheless, LMO still shows a poor cycling performance (a) because of the trend of its layered structure which turns into spinel structure through lithium

extraction [62], and (b) owing to the Mn removal from LMO throughout cycling [63]. 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  $\text{LiCoO}_2$  [64],  $\text{Al}_2\text{O}_3$ , [65, 66],  $\text{V}_2\text{O}_5$  [67],  $\text{MgO}$  [68] and  $\text{CeO}_2$  [69]. A three-dimensional (3D)  $\text{Al}_2\text{O}_3$  nanosheet was made by Li and his team to cover the  $\text{LiMn}_2\text{O}_4$  electrode [70]. The covered electrode exhibited an initial specific capacity of 128.5  $\text{mAh g}^{-1}$  at 0.1C rate, with a capacity retention of 89.8% even after 800 cycles at a 1C rate [70]. 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  $\text{LiMn}_2\text{O}_4$  heterostructure based on a Mn-rich multilayered coating surface of space group R3m [71]. As a result, this  $\text{LiMn}_2\text{O}_4$  heterostructure demonstrated an initial capacity of 123  $\text{mAh g}^{-1}$  with a capacity retention of 85% after the 100<sup>th</sup> cycle at a 1C rate, which was found to be better than the spinel  $\text{LiMn}_2\text{O}_4$  showing only 56% of retention for 131  $\text{mAh g}^{-1}$  at 60°C [71]. This enhanced performance of  $\text{LiMn}_2\text{O}_4$  heterostructure was assigned to its lower impedance as well as increased kinetics, the faster diffusion rate of lithium-ion, and lesser activation energy. Figure 6 shows the structure of spinel  $\text{LiMn}_2\text{O}_4$ .

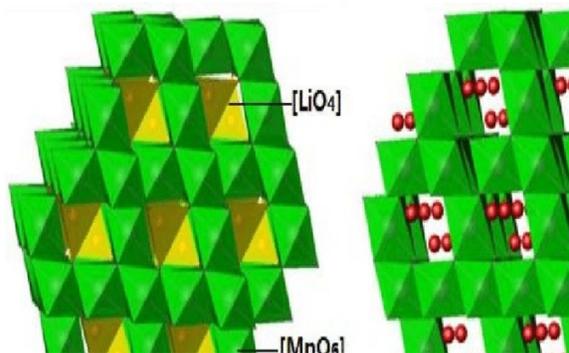
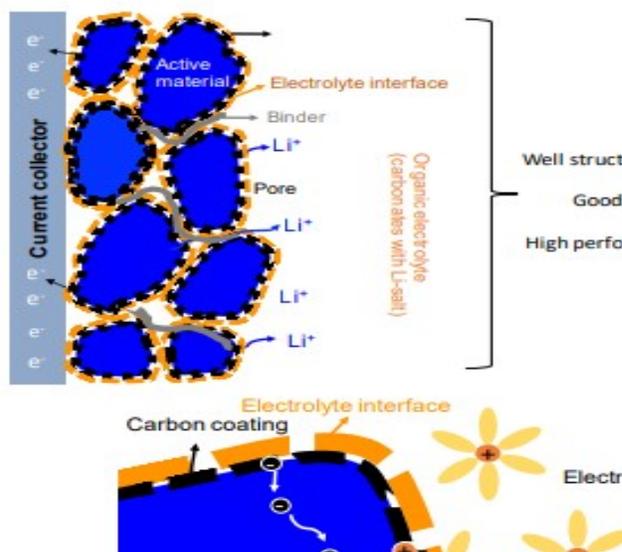


Fig. 6. The structure of spinel  $\text{LiMn}_2\text{O}_4$  [72].

### d) Lithium Nickel Manganese Oxide

Spinel lithium nickel manganese oxide ( $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ) is found to be a potential choice to replace  $\text{LiMn}_2\text{O}_4$  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 [73]. 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  $\text{Ni}_{1-x}\text{Li}_x\text{O}$  impurity phase [74]. 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<sub>2</sub>O<sub>3</sub>, etc) for enhanced cyclic stability and rate performance have been applied both to stop the development of the impurity phase [75]. Dahn was the first to report the use of LiNi<sub>1-x</sub>MnO<sub>2</sub> as cathode materials in LIBs [76]. But 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 [77] and Dahn [78] synthesized LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> and Li [Ni<sub>x</sub>Li<sub>(1/3-2x/3)</sub>Mn<sub>(2/3-x/3)</sub>]O<sub>2</sub> 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<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> 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 [79]. 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 [80].**

The modification of layered LNMO cathode materials via a coating, doping, synthesis approach, lithium-rich materials, and nanostructured materials leads to increasing 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. LNMO are promising, low-cost, and clean materials with the additional benefit of having high thermal stability. However, LNMOs are prominent cathode materials to be potential substitutes for the commercial LiCoO<sub>2</sub> electrode.

#### e) 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 [81]. The product obtained was the pristine material Li<sub>1.2</sub> Mn<sub>0.52</sub>Co<sub>0.13</sub>Ni<sub>0.13</sub>O<sub>2</sub> (LMCN). Li-rich oxide layer materials could be outlined as xLi<sub>2</sub>MnO<sub>3</sub>.

(1-x) LiMO<sub>2</sub> 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<sup>-1</sup>[82-86].

## 4. CONCLUSION

Several types of research on electrode materials have been conducted to enhance the performance of LIBs including the energy density, working voltage, safety, and lifespan. In this work, a brief introduction of the functional cathode materials is issued, as well as profound comprehension, and contrivance of the battery configurations. Moreover, the prominent cathode materials that may meet the requirements of next-generation energy are discussed, aiming to address the advantages 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 reinforce the cathode structure, increase the electrical conductivity, and limit the cathode degradation. The promising cathode materials which are used in the revolution of the advanced LIBs for EVs include LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiMnO<sub>2</sub>, LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, and Li<sub>1.2</sub> Mn<sub>0.52</sub>Co<sub>0.13</sub>Ni<sub>0.13</sub>O<sub>2</sub>. This study reveals the use of all these approaches together contributes to the development of high-performance cathode materials, leads not only to overcoming challenges faced by the cathode materials LIBs but also enhances the performance of the rechargeable LIBs.

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