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# Review on surface engineering of NMC for high performance of lithium-ion batteries

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**Abstract**

The lithium-ion battery stands as a highly promising energy storage system. Among its key components, the cathode material—particularly lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$), or NMC—is of great importance due to its high specific capacity and cost-effectiveness. Despite its advantages, NMC faces certain challenges, with limited cycle performance being one of the most critical issues. To address this issue, extensive research has been dedicated to surface modification strategies for NMC materials. Studies have identified two primary approaches, doping and coating, both of which have proven effective in enhancing the material's long-term stability. This work systematically examines, categorizes, and compares recent advancements in NMC surface engineering. Additionally, potential future research directions for optimizing NMC cathode materials are proposed.

## 1. Introduction

The development of electric vehicles (EVs) and hybrid electric vehicle (HEVs) are the most important driving force for sustainable technology. An essential energy source for EVs and HEVs is lithium-ion batteries. Lithium-ion batteries provide significant benefits such as high energy density, high galvanic potential, low self-discharge rate, and low maintenance [1]. These advantages are based on the fundamentals of lithium base battery. Lithium has the lowest reduction potential which gives lithium-ion batteries high cell potential. The superior power, gravimetric and volumetric density of lithium-ion batteries is due to the fact that lithium has one of the smallest ionic radius. Lithium-ion batteries could also significantly decrease the amount of greenhouse gas emissions compared to hydrocarbon energy sources [2]. These advantages of lithium-ion batteries lead to their current applications in many fields, such as mobile electronic equipment, increasing the efficiency of renewable energy systems and aviation. Therefore, lithium-ion batteries are one of the topics receiving great interest and funding from both academic and industry.

Although lithium-ion batteries are being used in various applications, there are some problems that need to be addressed for using lithium-ion batteries as portable energy storage in the long term. Lithium-ion batteries still did not satisfied the industry-threshold for at least 500 km of driving for each charge [3]. The short life cycle of lithium-ion batteries is also an important issue which occurred due to many factors such as short circuit from dendrite, tearing of membrane between cathode and anode, and dissolving of some transition metals in the system [4]. The current price of lithium-ion batteries is also considered high for some applications like portable electronics and transportation and will continue to increase as the demand is growing but the availability of lithium and other transition metals used in lithium-ion batteries may eventually become limited [5].

To solve the mentioned problems of lithium-ion batteries, various cathode materials have been researched. Among all of the cathodes material developed in the past decade, lithium-ion batteries based on nickel rich cathode, in particular, nickel–cobalt–manganese cathode (NMC) are the most promising cathode due to their high operating potential and structural stability [6]. Although they have cobalt as one of the component metals, NMC is considered to be more environmentally friendly and cheaper when compared with others cathode due to its low cobalt content. However, the cycling performance of NMC is still not enough for long term usage in many applications [4,7]. Although the increase in nickel content in the cathode can further enhance the capacity to more than 200 $mAh\cdot g^{-1}$, it will greatly affect the cycle performance of the system [8]. The increase in nickel content can create cation disordering, reducing of thermal stability, microcracks in the cathode layer, and oxygen release, which led to degradation phenomena in NMC structures and failure in battery performance [4,7]. The cation disordering from high nickel content also blocks the diffusion of lithium, resulting in the reducing of charge/discharge rate [9]. There are various research strategies for solving these issues and further enhance the lithium-ion batteries such as cathode coatings, cathode

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doping, modified electrolytes and using single crystal materials [10-13]. Although most of the strategies provides benefit to lithium-ion batteries, the doping and coating strategies are by far the most effective methods in term of solving the problem of NMC based batteries [11,14]. This is the result of more than a decade of research on surface modification and its proven result in earlier cathode material such as $LiCoO_2$ and $LiMn_2O_2$. In this work, the two main modification methods - doping and coating - are summarized, compared and analyzed. Although the main focus of the work is the NMC cathode, some of the information are also analyzed from other layered oxide cathodes, such as NCA, $LiCoO_2$ and $LiMn_2O_2$.

## 2. Lithium nickel cobalt manganese oxide, $LiNi_xCo_yMn_zO_2$ (NCMxyz)

The layered lithium transition metal oxide with formula $LiNi_xCo_yMn_zO_2$ is one of the most successful categories of cathode materials for LIBs. The NMC layered structure provides numerous diffusion paths for lithium ions, which is the main reason for its superior electro-chemical performance.

The first layered rock-salt (α-$NaFeO_2$) oxide, $LiCoO_2$, as shown in Figure 1(a), was investigated by John B. Goodenough from Oxford University in 1980 and serves as the best fundamental example for understanding the NMC layered structure. In this structure, the octahedra $CoO_6$ units share the edges to form layers of $CoO_6$. The lithium ions are positioned between each layer and also occupy the same sites as Co ions, the octahedral sites. From this event, the structure can be considered as layers of octahedral $LiO_6$ and octahedral $CoO_6$, which also share the same edges with each other. The characteristics of this structure allow for small changes in the interlayer distance, from 4.24 Å in the fully delithiated state (charging) to 4.68 Å in the fully lithiated state (discharging). The difference in charge and size between $Li^+$ and $Co^{3+}$ ions provides strong support for fast two-dimensional lithium-ion diffusion between the planes of the transition metal oxide (Figure 1(b)), which is also the fundamental principle of the NMC cathode [4,7,15].

Although $LiCoO_2$ has excellent electrochemical performance, it has significant drawbacks related to thermal stability and the toxicity of cobalt. This has led to the development of alternative layered oxide cathodes, such as $LiNiO_2$ and $LiMnO_2$. While nickel has strong potential as replacement for cobalt, $LiNiO_2$ suffers from severe cation mixing of $Ni^{2+}$and $Li^+$ during repeated charge/discharge cycles. Similarly, $LiMnO_2$ has a structural stability problem, which eventually lead to its transformation into a spinel structure. Although these cathodes offer certain advantages, they are also constrained by their own chemical limitations. To overcome these challenges, researchers explored the combination of cobalt, manganese and nickel as transition metal oxides, leading to the development of the NMC cathode. The NMC structure remains similar to that of $LiCoO_2$, but with nickel and manganese partially substituting cobalt [15-17]. The number following "NMC" represents the molar percentage of each element, for example, NMC811 corresponds to $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$. These new NMC cathodes can combine the advantages of $LiNiO_2$, $LiMnO_2$ and $LiCoO_2$ while minimizing their limitations by adjusting the ratio of each element. As shown in Figure 2, cobalt, nickel and manganese provide synergistic effects which can both increase the battery performance and stability for the NMC cathodes [16].

In Table 1, the performance and characteristic trend of NMC can be estimated based on the ratio of the elements. For example, while manganese has a problem with its structural stability, it acts as a stabilizer that stabilizes $Ni^{2+}$ in NMC. The two main characteristics of the cathode are chemical stability and structural stability, which are both very difficult to achieve due to the need to balance the ratio between cobalt and manganese. The interesting element is nickel, which always positions itself in between cobalt and manganese. $Ni^{3+}$ can be charged all the way to $Ni^{4+}$ without disrupting the $O^{2-}$ 2p band, which means that more capacity can be utilized without raising the potential. While nickel inherits poor cycling ability from $LiNiO_2$ due to the weaker Ni-O bond compared to Co-O bond, manganese helps stabilize nickel as mentioned above. These are the reasons why higher nickel content in NMC, such as NMC811 or higher, is one of the most interesting trends in NMC cathode [17]. NMC811 can provide a discharge capacity as high as 200 mAh·g$^{-1}$, 3.0 V to 4.3 V at 0.1 C rate, however, its cyclability decreases compared to cathodes with lower nickel content. One of the solutions to overcome this limitation is surface modification of the NMC cathode material [8,17].

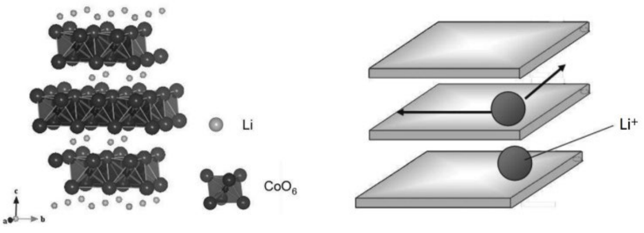

**Figure 1.** (a) $LiCoO_2$ crystal layered structure and (b) Lithium ion diffusion path between transition metal oxide layered [15].

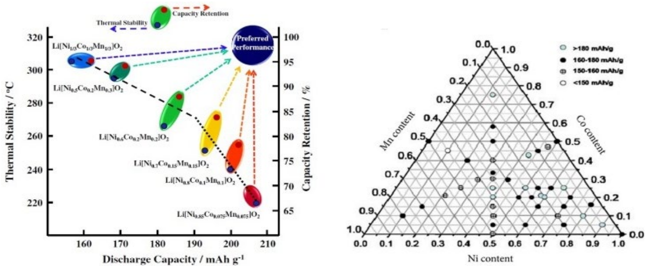

**Figure 2.** The aspect capacity from the ratio of NMC [16].

**Table 1.** The trend of cathode characteristics between the ratio of nickel, manganese and cobalt.

| Characteristic | Trend |
|---|---|
| Electrical conductivity | Co > Ni > Mn |
| Chemical stability | Mn > Ni > Co |
| Structure stability | Co > Ni > Mn |
| Toxicity | Co > Ni > Mn |

## 3. Modification methods

The research in surface modification methods can be roughly classified into two categories, internal modification and external modification. The internal modification primarily aims to stabilize the crystal structure, addressing issues caused by diffusion of lithium ion, such as cation mixing, phase transitions and metal dissolution. In contrast, the external modification focuses on protecting the cathode material from external factors like electrolyte reactions and heat. Recently, doping has emerged as the predominant approach for internal modification. While some studies are undoubtedly questionable, most of the results are well studied and informed. The external modification is mainly achieved by coating NMC with a protective layer. This approach can serve as a complete alternative to electrolyte modifications, such as the use of solid-state electrolytes, more stable electrolyte salts, or additives because they directly solve the same problems. The coating approach remains of interest due to its simplicity and effectiveness.

In early studies, there was confusion between the approaches of doping and coating. Figure 3 shows the expected outcomes of both methods. The doping method directly affects or alters the crystal structure of the NMC cathode. One of the good examples for doping in NMC is the incorporation of manganese, which can be considered a dopant in $LiNiCoO_2$. On the other hand, the coating approach focuses on the NMC cathode by forming a continuous or discontinuous protective layer or particle coating. Unlike doping, coating offers a wide range of methods and materials. Another clear difference between the two approaches is the state of the NMC material during processing. While doping occurs before the calcination process, coating is always applied after the NMC has been synthesized. This difference can greatly affect the scalability of the technology. While doping has the potential to integrate into the existing manufacturing process, coating introduces additional production steps, which can substantially increase the overall cost of NMC.

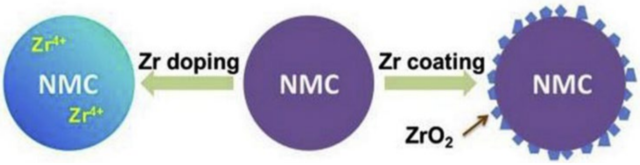

**Figure 3.** The aspect outcome of doping and coating Zirconium [10].

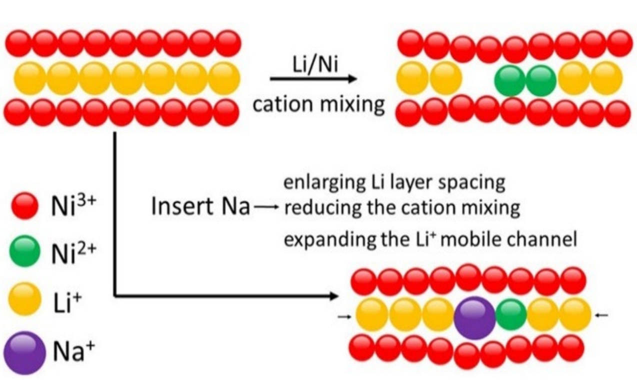

**Figure 4.** The aspect mechanism of doping [20].

### 3.1 Doping

The main goal of doping is to enhance the stability of the cathode material during charging and discharging. There are many factors that can damaged the batteries, including surface reconstruction, parasitic reaction between $Ni^{4+}$ and the electrolyte, and $M^{n+}/O^{2-}$ self- redox reactions [7]. Most of these reactions result from overcharging, the formation of rock-salt structure, heat generation and crystal instability, which become more critical as lithium ions are removed from the metal oxide layer during charging [18]. These factors are the main factors which prevent the complete movement of lithium ion from happening, making it impossible to achieve the theoretical capacity. For this reason, the percentage of lithium that can be removed is partly dependent on the type of cathode material. In a typical LCO cathode, only about 50% of the lithium can be removed, whereas in the NMC333 cathode, about 70% can be removed [18,19].

The doping elements, or dopants, help support the structure during the movement of lithium ion due to their inactive nature which can enhance the capacity. By partially replacing lithium ions with dopants, the lithium layer spacing is enlarged, leading to increased lithium-ion diffusion speed and reduced cation mixing during charging and discharging, as shown in Figure 4 [20]. Additionally, some dopants are also known to prevent lattice changes, which can reduce micro-cracking and improve cycle life. However, in some cases, doping can lead to cation mixing, where other metal ions migrate into the lithium layer, decreasing structural stability [21]. Therefore, doping should be carefully optimized to achieve an overall performance enhancement in the lithium-ion batteries.

The doping process is highly compatible with cathode materials due to its long support history and its nature which are like the NMC. The success of NMC cathode itself can be considered as the testament to the effective doping of nickel and manganese into LCO [14,22]. Moreover, the mainstream doping process is also simple and seamlessly integrates with the cathode synthesis. It does not require additional equipment beyond standard synthesis procedures, which is a significant advantage from an industrial perspective [22]. Although there are many reports (Table 2) about the advantages from doping various elements such as V [23], Al [24], Ti [25], Zr [26], Mg [27], Mo [28], Na [29], Sn [30], B [31], Fe [32], Cr [33], Cu [34], Zn [35], and Ga [36] on various cathode material, there are also limitations and disadvantages. For example, Zn and Ga doping have been associated with certain disadvantages that must be carefully considered.

To further improve the effectiveness of the doping method for NMC-based materials, various aspects of doping based on recent research will be explored. This review provides a comprehensive summary of doping elements, methods, and comparisons from recent studies.

#### 3.1.1 Method of doping

In early research, two main effective approaches for doping were commonly used. The first approach involves doping during oxidation and lithiation. Since doping is implemented at the later stage of the manufacturing process, only a limited number of doping elements can be incorporated into the surface of the particle. Although many dopants can be introduced through this approach, they often exhibit

**Table 2.** Report of doping elements on lithium-ion battery cathode.

| Doping element | At 0.1 C | | Cycling |
|---|---|---|---|
| | **Capacity [mAh·g$^{-1}$]** | **Working voltage [V]** | |
| V | 204.4 | 3.0 to 4.3 | cycling retention of 88.1% after 80 cycles at 2C |
| Al | 215 | 3.0 to 4.5 | cycling retention of 90% after 200 cycles at 10C |
| Ti | 205.7 | 2.8 to 4.5 | cycling retention of 86.9% after 200 cycles at 5C |
| Zr | 160 (0.2C) | 2.8 to 4.3 | cycling retention of 96% after 50 cycles at C/3 rate |
| Mg | 202.5 | 2.7 to 4.3 | cycling retention of 84.8% after 50 cycles at 5C |
| Mo | 152 (0.5C) | 3.0 to 4.3 | cycling retention of 97% after 50 cycles at 8C |
| Na | 180 | 3.0 to 4.3 | cycling retention of 81.6% after 300 cycles at 1C |
| Sn | 190 | 3.0 to 4.3 | cycling retention of 97% after 50 cycles at 0.5C |
| B | 237 | 3.0 to 4.3 | cycling retention of 91% after 100 cycles at 0.1C |
| Fe | 178.5 | 3.0 to 4.3 | cycling retention of 87.1% after 30 cycles at 0.1C |
| Cr | 209.9 | 2.7 to 4.3 | cycling retention of 76.1% after 50 cycles at 5C |
| Cu | 181.7 | 2.7 to 4.4 | cycling retention of 77% after 350 cycles at 5C |
| Zn | 121 | 3.0-4.4 | cycling retention of 97% after 60 cycles at 0.2C |
| Ga | 124.5 | 3.4-4.3 | cycling retention of 69% after 50 cycles at 0.2C |

issues related to poor distribution of doping elements on the surface of the particle [28]. Other approach is to add a dopant in the early stage of production, such as co-precipitation during the precipitation of the base precursor in aqueous metal solution [37]. Although this method limits the choice of doping elements compared to the first method, the result is generally a much more uniform distribution of dopants throughout the precursor particles.

### Solid solution doping

Although there are many synthesis approaches for doping, the solid-state reaction stands out from the others due to its simplicity and scalability. The doping elements in this synthesis method are usually identified as transition metals. The key idea is for the dopant to form a solid solution with NMC, preserving the layered α-$NaFeO_2$ structure. In this process, the dopant occupies the same position as the cobalt atom, specifically within the $MeO_6$ octahedra [38]. This method mainly aims to increase the strength of the metal-oxygen bonds, which is the key factor to stabilize the structure during charge and discharge cycles. The properties of a doped NMC are influenced by the size of the dopants and their valence electrons. There will be charge balance reactions between the different transition metal ions to maintain stable oxidation states so that the energy of the system is minimized. Some of the common elements for this method are aluminum, magnesium and tin, which will be discussed in the next section.

### Lithium site doping (Cation doping)

Dopants with low oxidation number cations can directly replace transition metal atoms in the lithium position. This will greatly enlarge the interlayer of NMC as the lithium ions are much smaller in comparison. The common effect of this approach is an increase in lithium diffusion speed during charging and discharging, however, excessive doping leads to the opposite result. Due to the inactive nature of the dopant, too big or too many dopants will interfere with lithium diffusion and this significantly reduced the capacity of NMC [39]. The current trends suggest that doping levels of 1% to 4% appear to be the optimal condition.

While the lithium site doping usually has the benefit of enhancing the diffusion speed, some unique elements like titanium also increase the capacity of the battery despite its size. In the voltage range of 3.0 V to 4.3 V, the initial capacity of titanium doping shows an increase of capacity by 9.2% compared to the standard sample. This is expected to be the result of enlarging lithium ions lattice space when doping with $Ti^{4+}$, which increases the unit cell volume and enhances the diffusion rate of lithium [39]. Further research also shows similar result with the investigation on SEI layer resistance, which reduce the resistance of the film from 31.1 Ω to 24.2 Ω [40].

### Oxygen site doping (Anion doping)

Similar to lithium site doping, oxygen site doping aims to replace some of the oxygen in the structure with others anion. The list of dopants is much less compared to other approaches and is mostly halogen group elements due to the structural limitations. Halogens, such as fluoride, are known to enhance the cathode performance. The mechanisms of anion doping involve complicated orbital energy level changes combined with the effects of the dopants, which lead to the unpredictable outcomes [38]. Doping a small amount of fluoride into NMC333 shows improved cycle life at 4.6 V and better efficiency compared to the undoped specimen. This is expected to be the results from the increased bonding strength of the lithium-fluoride bond, which enhances the lattice parameters [41]. Although the benefits of dopants such as fluoride are well known in this field, their implementation in real applications remains limited. From an academic point of view, there are two main suspected reasons for this. First, while the lithium-fluoride bond helps stabilize the structure, it also reduces the initial capacity due to the strong bond with lithium. Second, there is research suggesting the formation of new phase as the amount of fluoride increases. The suspicion is that increased repulsion in the oxygen layer occurs due to the lithium-fluoride bonding [41].

### 3.1.2 Dopant element

Many elements have been used for doping cathode materials, however, they can be categorized into two types, single doping and co-doping/multiple doping, based on the number of doping elements [22]. Both types aim to improve the electrochemical property and stabilize the NMC structure. Doping can reduce the reactions on the cathode surface and further increase the diffusion rate of lithium.

The reactions during the heat treatment process may also lead to volume shrinkage, which helps stabilize the NMC structure [4]. The type of doping element may also add other effects depending on the fundamental characteristics of each element.

### Single doping

The main purpose of doping NMC-based cathode is to enhance the crystal structure stability and electrochemical performance. However, depending on the doping element, there is also a chance that doping will have no effect on electrochemical performance at all. The method of doping is also important to the properties, however, by neglecting the method of doping, some of the dopants show interesting outcomes as trends can be independent of the doping method.

Lithium itself was considered as doping element in the early stage; however, the results were mostly negative and unstable, leading to a decrease in electrochemical performance. This may be related to the forming of nonstoichiometric $Li_{1+x}$, which has been reported as unfavorable for electrochemical performance [42].

Vanadium-doped NMC, through solid solution doping, exhibits remarkable structural stability leading to better cycling stability (88.1% after 80 cycle) and rate capability (86.2% at 2C). However, it does not differ much in terms of initial discharge capacity when comparing with pristine sample [23].

Aluminum is one of the most interesting doping elements for many researchers due to its uniform doping structure, unique enhancement of thermal stability and the significant improvement in electrochemical performance [24,43,44]. Comparing the pristine and Al-doping samples, the doped samples showed a significant improved in the capacity retentions (Figure 5(a)) and a better rate capability (Figure 5(b)). Aluminum has also been successfully doped into the precursor during precipitation, making industrial manufacturing of uniformly aluminum-doped cathodes feasible, hence the development of NCA. $LiAlO_2$ by itself has a -$NaFeO_2$ structure that greatly aligns with the NMC structure. The experiment from Un-Hyuck Kim (Figure 6) confirms the superior performance in terms of cycling and thermal stabilities of doped sample when compared to pristine NMC with the same amount of nickel [45]. Due to the fundamental characteristics of aluminum as an inert heteroatom, it rarely disrupts the structure of NMC under overcharge conditions. The strong aluminum-oxygen bond is also a key reason for this result. The thermal stability effect of aluminum doping helps reduce the chance of exothermic reaction during the working cycle, thus increasing the stability of the system [24,42].

Similar to aluminum, titanium also received a lot of interest from researchers, however, there are mixing results from titanium doping. Although the small amount of aluminum (0.2%) has been proven to greatly enhance the cycle performance of NMC, with 93.4% capacity retention after 200 cycles, the results for initial discharge capacity vary. These results show either a slight decrease of about 7% or an increase of about 10%, compared to the benchmark material [25,42].

The bond energy of boron-oxygen (809 kJ·$mol^{-1}$) is much larger than that of nickel-oxygen (380 kJ·$mol^{-1}$) and lithium-oxygen (78 kJ·$mol^{-1}$), which results in a more stable structure for the doped material. The initial capacity slightly decreases compared to the pristine material [22,42]. Lately, a revisit of boron doping in NMC has shown significant improvements in both capacity and cyclability by adjusting the doping method and the amount of boron [31,46,47]. This approach is similar but slightly better than iron doping through solid solution doping which has good capacity in the early cycle. However, the final performance lacks both cycle stability and capacity retention [22]. The iron doping from combustion method shows the different result, emphasizing on the importance of doping method. Although the discharge capacity and cycle performance are higher than those with solid solution doping, the overall enhanced properties still fall short compared to others elements [32,42].

Recent experiments such as zirconium doping in bulk structure show unique improvements at high temperatures. Zirconium-doped material demonstrates superior cycling performance at high temperature compared to pristine NMC. This is the result of the surface stability. Another unique benefit of zirconium doping is the stability of cathode electrolyte interfacial layer during cycling which when combines with the surface stability, further enhances the cycling performance at high temperatures [26].

A small amount magnesium can improve cycling performance as it can substitute for $Ni^{2+}$. However, this effect becomes negligible as the amount of magnesium increases and it begins substituting for nickel instead [42]. The enhancement in cycling performance of magnesium is largely related to the reduction of dendritic lithium deposition during cycling, which has been reported to be one of the root cause of short cycle life in lithium batteries [27].

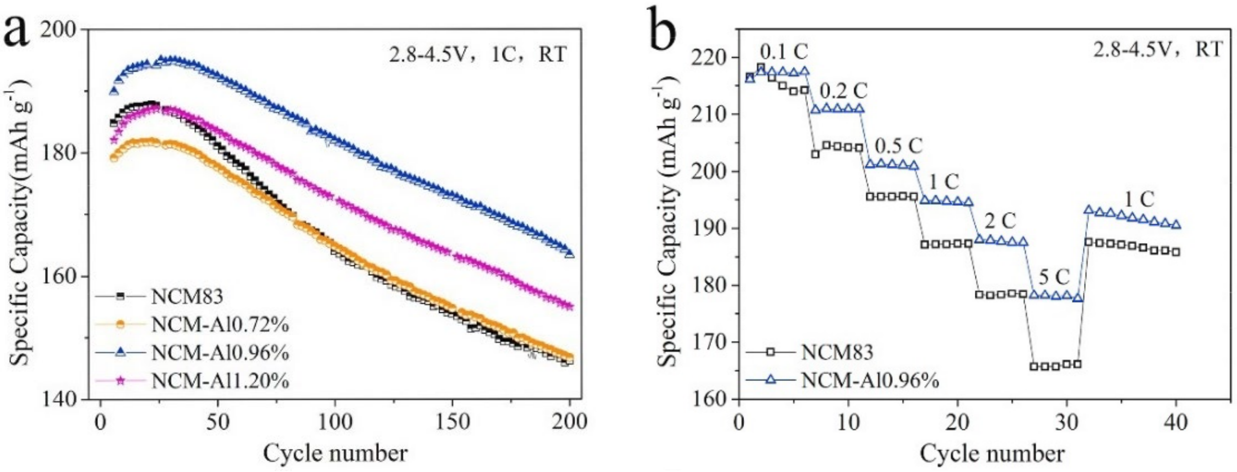

**Figure 5.** Electrochemical performances of samples, (a) cycle stability and (b) rate capability [43].

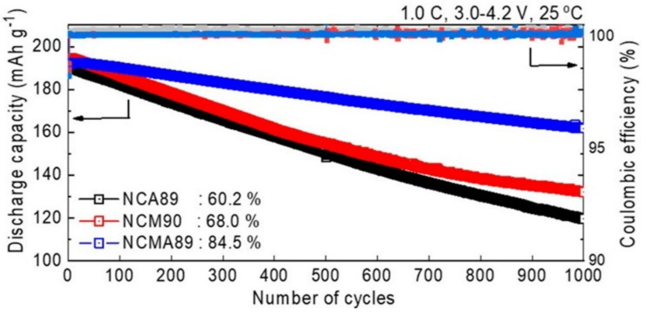

**Figure 6.** Long-term cycling performance of various cathodes [45].

The appropriate amount of molybdenum has the potential to improve crystal stability and electrochemical performance, likely due to the inherent high conductivity of molybdenum. However, the initial discharge capacity and capacity retention in experiments do not show significant improvements compared to doping with other elements [28].

Not all elements enhance the electrochemical performance and cycle performance of NMC. The elements such as sodium, tin, copper and zinc show very little improvement in early research and have an unbearable drawback. For example, copper doping shows the sign of unstable crystal structure which lead to a decrease in cycle performance [34,42]. Although sodium can substitute for lithium, which should theoretically increase the potential capacity due to the weakening of lithium-oxygen bonds, it requires precise control of the primary particles during the synthesis process [29].

The doping of heteroatoms shows both benefits and drawbacks, depending on both the methods and elements used. However, there are clearly similar effects between different elements that share certain characteristics. Doping with elements such as iron, sodium, and molybdenum can occupy the $Li^+$ sites, which directly reduces electrochemical properties and increases the energy required for charging NMC by disrupting lithium during charging and discharging [4]. The mechanism of positive doping effect is far more complicated than the negative one. The elements such as aluminum, gallium, or even cobalt itself can form an inert layer that help stabilize the crystal structure during high voltage or overcharging. The elements such as vanadium and nickel help stabilize the crystal structure through mechanical behavior similar to the effect of defects that increase hardness in metals. Titanium and magnesium do not directly affect cycling performance but instead influence or prevent the formation of sharp dendrites during charging and discharging of lithium.

### Co-doping or Multi-doping with heteroatoms

As mentioned in single heteroatom doping method, the results of doping greatly depend on the characteristic of doping elements. This leads to further improvement of doping strategies which use more than one heteroatom to dope the cathode [42]. The combined effect of various elements has already been proven by the existence of NMC, which can be considered as doping cobalt and manganese into lithium nickel oxide cathode [14]. In this section, not all co-doping research is discussed due to the large number of combinations between two or more elements and the different setups in the experiments. In fact, we aim to discuss some potential co-doping combinations that have been reported in NMC and other layered oxide cathodes.

As mentioned above, the existence of NMC is also the success of cobalt and manganese co-doping into $LiNiO_2$ cathode. Although there are many approaches for doping methods, the overall results from solid solution doping method are by far the best. The adjustment between the ratio of nickel, cobalt and manganese helps resolve some of the fatal disadvantages of $LiNiO_2$, making it one of the most promising cathode materials currently [4,14,42].

The co-doping of titanium and magnesium can enhance the reversible capacity of $LiNiO_2$ based cathodes to 190 $mAh\cdot g^{-1}$ while still maintaining the benefits of improved cycling performance. With a certain amount of titanium and magnesium ($X \geq 0.25$; $LiNi_{1-X}Ti_{X/2}Mg_{X/2}O_2$), the normal exothermic peak, which is usually noticeable at 220°C, significantly decreases to the point of being unnoticeable even at 400°C [42]. This effect has not been reported in single heteroatom doping [25,27].

Aluminum and cobalt co-doping by solid solution doping process significantly enhance the crystal structure stability and cycling performance of $LiNiO_2$. The optimal composition of cobalt and aluminum is $Li(Ni_{0.84}Co_{0.16})_{0.97}Al_{0.03}O_2$, which provides a reversible capacity of 185 $mAh\cdot g^{-1}$ with an initial irreversible capacity of only 25 $mAh\cdot g^{-1}$ [42]. In this case, the benefits of single aluminum doping are further enhanced by adjusting the cobalt content, resulting in good electrochemical and cycling performance while maintaining the thermal stability provided by aluminum doping [14,23,24].

In single iron doping, the performance is still not on par with that of other elements. However, the improvement from the combination of cobalt and iron co-doping is noticeable. This combination reduces overall polarization and increases the reversible capacity of $LiNiO_2$ [42].

The co-doping approach has shown promising results for lithium-ion batteries. Many research demonstrate improvements in both chemical performance and cycling performance [48-51]. However, the synthesis process itself becomes much more complicated. Even in single heteroatom doping, there is no fixed rule for doping except the aspect from fundamental properties of the doping elements. Factors such as heating rate, solid ratio, and material preparation play an important role in the outcome of the doped product.

## 3.2 Coating

To overcome some of the limitations of NMC cathode that cannot be easily solved by doping method, coating has been introduced due to its simplicity and the long success history in other industries. Although various materials have been used for this approach, there are common principles shared among them. Firstly, the coating material is required to have good electronic transmission performance while remaining non-reactive with the electrolyte. Lithium ions must be able to diffuse through the coating layer with ease. Lastly, although not clearly stated, there is a limit to the thickness of the coating layer due to the mechanism of LIBs which requires the diffusion of ion [14,42]. The results of coating are already shown in Figure 3, where the coating layer acts as a protective barrier, shielding NMC from external factors [26,52].

In the early stages of development, there were similarities between doping and coating. For example, some of the synthesis methods, such as sol-gel, can be used for both coating and doping [53]. However, at present, the distinction between these two approaches is much clearer.

While doping focuses on crystal structure modification, coating, as mentioned, emphasizes the macroscopic level by creating a protective layer over the cathode particles. Coating layers are reported to have two main functions: reducing or preventing the dissolution of transition metals by HF during cycling and protecting the cathode material from adverse effects, such as heat generated at high voltages, which can damage the system [53]. The most common coating materials are metal oxides as they exhibit good resistance, such as $ZrO_2$, $SiO_2$ and ZnO [54].

In order to ensure good performance after coating, several factors must be taken into consideration, including chemical and physical properties of both the cathode and coating materials, the thickness of the coating layer and the coating method. These factors will determine the final performance of the coating layer and affect the overall performance of the cathode material. In the next section, the notable coating materials are reviewed and compared.

Coating materials can be roughly categorized into metal oxides, metal fluorides and phosphates, lithium conductive materials, carbon group coatings and others. The oxides like $Al_2O_3$, $SiO_2$, $SnO_2$, $ZrO_2$, $SiO_2$ and ZnO are known for providing a good protective layer between NMC and the electrolyte, but they also decrease the lithium ions diffusion rate, thus reducing the battery performance. Carbon group coatings and lithium salt coatings can increase the conductivity of NMC.

### 3.2.1 Oxide coating

$Al_2O_3$ has been studied since the development of LCO. There are many methods for $Al_2O_3$ coating such as sol-gel, spray, and chemical deposition. $Al_2O_3$ coating usually has three main benefits: 1) it acts as a protective barrier with high lithium ion diffusion rate, 2) the coating can withstand a wide range of lattice parameters, and 3) it has been reported to not only protect the NMC but also reduce the decomposition of the electrolyte. It also one of a few modification methods that increase the cycling ability without decreasing the initial capacity [40,55,56].

$SiO_2$ has been coated by simple mechano-thermal coating using only ethanol. Although its inactive nature provides excellent corrosion resistance for NMC, it also significantly reduces the capacity of the battery. This can be solved by optimizing the amount of coating thickness to be less than 1%. Studies have also shown an interesting effect when nano $SiO_2$ is used. In this case, $SiO_2$ not only coats the surface but also diffuses into the bulk structure of NMC, enhancing structural stability. It is often chosen as a coating material for high-nickel-content NMC due to its specific thermal properties and ability to protect NMC from HF, a common byproduct of the reaction between residual $H_2O$ and $LiPF_6$ salt in the electrolyte. In high-nickel NMC, the degradation of NMC is much worse than in lower-nickel content due to Ni cation mixing, a reaction further accelerated by temperature. After coating, the main exothermic peak of decomposition of the charged electrode at 4.3 V decreased from 275°C to 288°C. Additionally, $SiO_2$ suppresses the decomposition of electrolyte at the contact surface with the mechanism of HF scavenging [57].

MgO has been a well-known coating material for layered oxide cathode since the development of LCO due to its performance and the scalability of the coating method, which is simple heat treatment. MgO coating usually has two main benefits: 1) magnesium ions can diffuse into NMC during heat treatment, noticeable from XRD peak intensity, thereby giving the advantages of magnesium doping, and 2) it forms a protective layer that prevents the dissolution of nickel and cobalt. Although it significantly enhances the cycling ability of battery, it also reduces the initial capacity [58,59].

ZnO can easily grow on NMC surface due to its structural similarity, which reduces the stress between the substrate and coating material. While ZnO itself does not exhibit any noteworthy electrochemical performance beyond the general benefits of oxide coating, ZnO doped $Al_2O_3$ (AZO) demonstrates remarkably enhancements. In this case, the small amount of $Al_2O_3$ is doped into ZnO via magnetron sputtering. The role of $Al_2O_3$ is to enhance the conductivity of ZnO and significantly enhance the cycling performance of the battery which almost double at 150 cycle as shown in Figure 7. It is believed that in addition to acting as a physical barrier and forming conductive networks, AZO coating also plays an important role in HF scavenging, similar to silica [60,61].

### 3.2.2 Carbon coating

Carbon coating is a simple and flexible method that can improve the ionic conductivity and cycle performance of NMC materials under different C-rates by increasing the electrical conductivity and changing the transmission mechanism. There are various methods for carbon coating, such as mechanical milling with NMC. In this approach, a graphene layer is prepared by milling at 200 rpm under an argon atmosphere for one hour. This method significantly improves performance compared to an uncoated NMC cathode. The surface resistance of NCA coated with graphene decreases by about 40% while both the initial capacity and cycling performance increase by around 5% compared to the uncoated material. The graphene layer also serves as a protection barrier for the cathode material [62].

Despite its simplicity and effectiveness, the amorphous carbon coating can accelerate the degradation of NMC due to the in-situ carbonization of the carbon source. This process can lead to the reduction of $Ni^{3+}$ to $Ni^{2+}$, causing the cation mixing and decreasing the structural stability of the material [63].

### 3.2.3 Lithium coating

Lithium coating is one of the latest coating approaches using lithium salt like LFP, LTO and $Li_2SiO_3$ as coating materials. This approach offers a unique advantage of enhancing the lithium ion conduction as the coating layer functions as an active coating. The reported NCM811 coated with $Li_2TiO_2$ provides a great protective layer for NMC, as shown in Figure 8. The coated NMC can withstand the decomposition of $LiPF_6$ in the electrolyte. In addition, the transmission of lithium ions through the cathode surface benefits from the more stabilized surface of the coated NMC. The microstructure of coated NMC remains stable compared to the uncoated NMC even after 170 cycles [64].

Similar to $SiO_2$ coating material, NMC coated with $Li_2SiO_3$ provides both a stabilized structure of the bulk NMC and enhanced lithium-ion conduction. The research on $Li_2SiO_3$-coated NMC523 and NMC811 show improvements in both capacity and cycling performance [63,64].

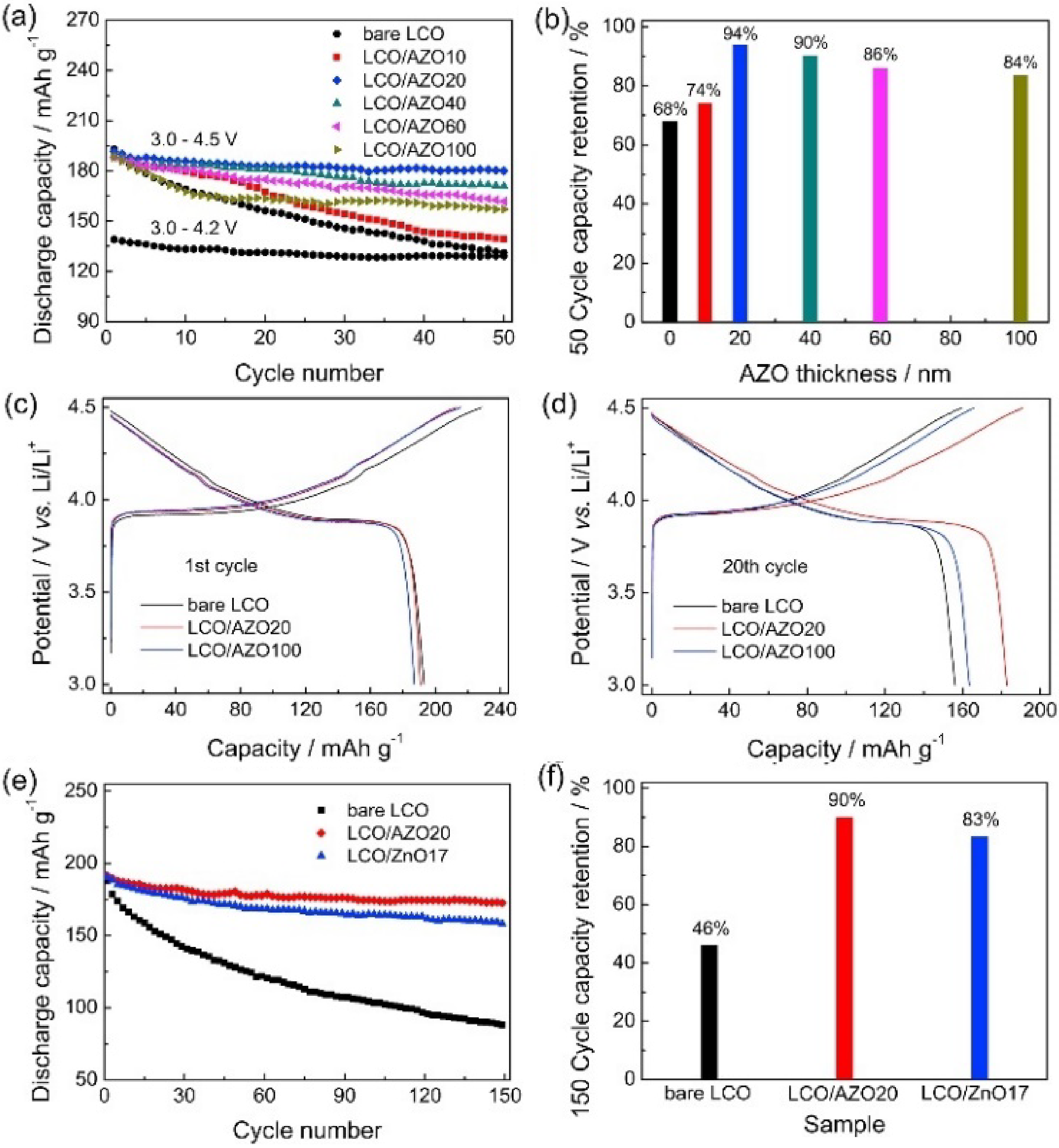

**Figure 7.** Electrochemical performance of the bare and AZO-coated LCO electrodes [60].

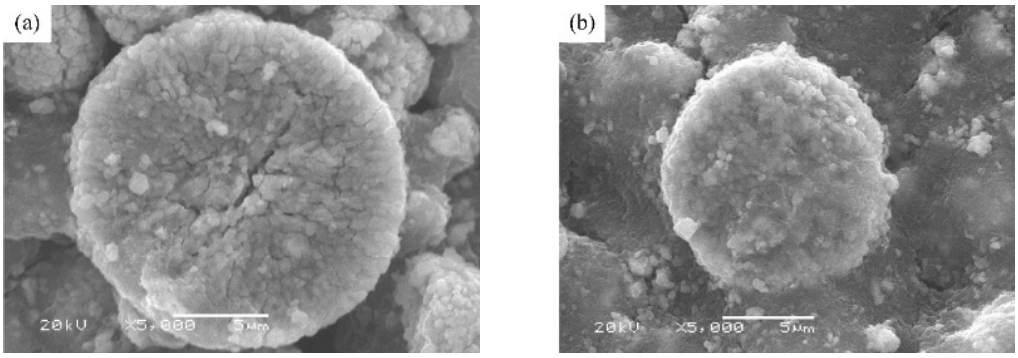

**Figure 8.** Comparison of uncoated NMC811, left, and $Li_2TiO_3$ coated NCM, right, after 170 cycles [25].

### 3.2.4 Others coating

There are still many coating approaches that provides significant enhancements. However, they do not exhibit unique coating performances like the previously mentioned coatings. Some of these methods involve very limited materials, making them difficult to categorize.

Phosphate coatings have been extensively studied over the past decade; however their principles and mechanisms are nearly identical to those of oxide coatings. They offer good thermal resistance, corrosion resistance, and improved cycling performance. Additionally in some materials such as $AlPO_4$, they provide good ion transfer. Some of the common phosphate coating materials are $AlPO_4$, $Li_3PO_4$, $Ni_3(PO_4)_2$ [65].

Fluoride coating is also widely used for NMC materials. The main mechanism for fluoride groups involves reducing the dissolution rate of transition metals caused by the decomposition of the electrolyte. Some studies have also reported that fluoride coatings help mitigate volume changes in NMC during cycling, which indirectly stabilized the NMC structure [66].

Polymer coating is also widely studied due to their diverse properties depending on the type of polymers used. However, their performance does not differ significantly from previously discussed coatings. The good conductive coating share mechanisms and properties similar to the conductive coatings such as AZO and carbon, however, they also act as binders that prevent cracking in NMC. Among the conducting polymers, polyaniline (PANI) is particularly popular due to its ease of coating and environmental stability [67]. NMC coated with PANI exhibits good cycling performance. In addition, emerging polymers such as Poly(3-hexylthiophene-2,5-diyl) (P3HT) offers an unique advantage by acting as an artificial SEI layer. The dense P3HT coating provides a very limited spacing for ion transport of the bulky reactants generated from the electrolyte decomposition [68].

## 4. Research gap analysis

In this section, I would like to analyze the gap between the research and practical applications together with pointing out the weaknesses from the reported studies.

The laboratory-scale LIB experiment is a highly sensitive system where numerous internal and external factors can influence battery performance. For example:

1) In a lab-scale battery setup, the deviation of capacity of around 5% can easily occur due to factors such as poor electrical contact, moisture, variations in material weight or even the defects of raw material.

2) The temperature of the testing environment can greatly affect the battery capacity. Generally, higher temperatures facilitate lithium-ion to diffusion, leading to an increase in capacity. There are many reports which show that the shifting of temperature from 22°C to 30°C, caused by temperature control errors, can increase the cycling performance up to 80%. From these reasons, there is high chance that the results from the research may be influenced by uncontrolled variables.

While the effects of the morphology and NMC particle size on battery performance are well-established, microstructural differences between modified and unmodified specimens should always be taken into consideration for both before the battery testing and after degradation, similar to Figure 8. This will ensure a direct correlation between the observed results and their root causes. Many studies focus solely on electrochemical performance characteristics, such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and cycling performance, without adequately considering the microstructural aspects of the material.

Although surface modification is confirmed to enhance performance, the associated increase in cost is an unavoidable factor to be concerned. As shown in Figure 9, the cathode material constitutes the majority of the battery's cost. The cost of simple surface modification in simple application can easily cost up to 10% of the material cost, meaning that the cost of the modification method can possibly be higher than other important parts such as anode. This raises concerns and may limit future research trends, especially when considering scalability. Another key factor supporting this concern is the ratio between raw material costs and processing costs from 2011 to 2017, as shown in Figure 10. While it is common that the raw material cost decreases at a faster rate than the processing cost, surface modification presents a unique challenge. The increased cost from the modification method may not be easy to reduce due to the processing cost being the main cost.

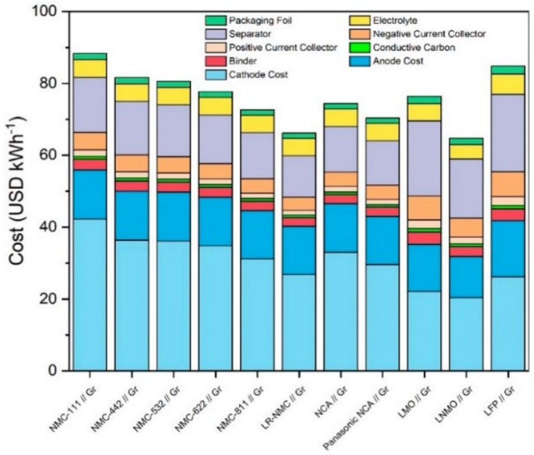

**Figure 9.** Total material costs of all 10 considered cell chemistries plus Panasonic NCA Use Case differentiated in combined CAM cost, anode cost, and secondary material costs [69].

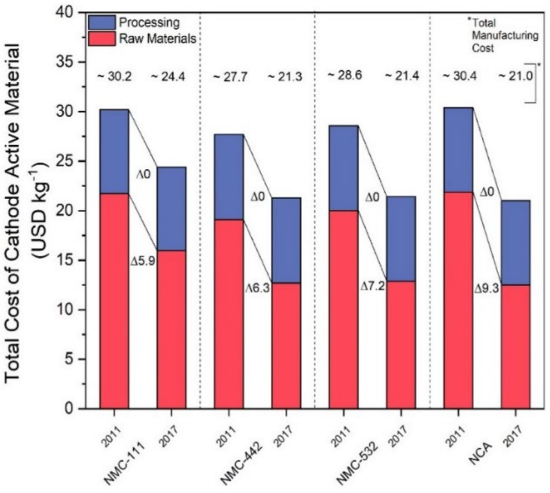

**Figure 10.** Comparison of cost breakdowns of NCA, NMC111, NMC442, and NMC532 cathode active materials into raw material and processing costs between 2011 and 2017 [69].

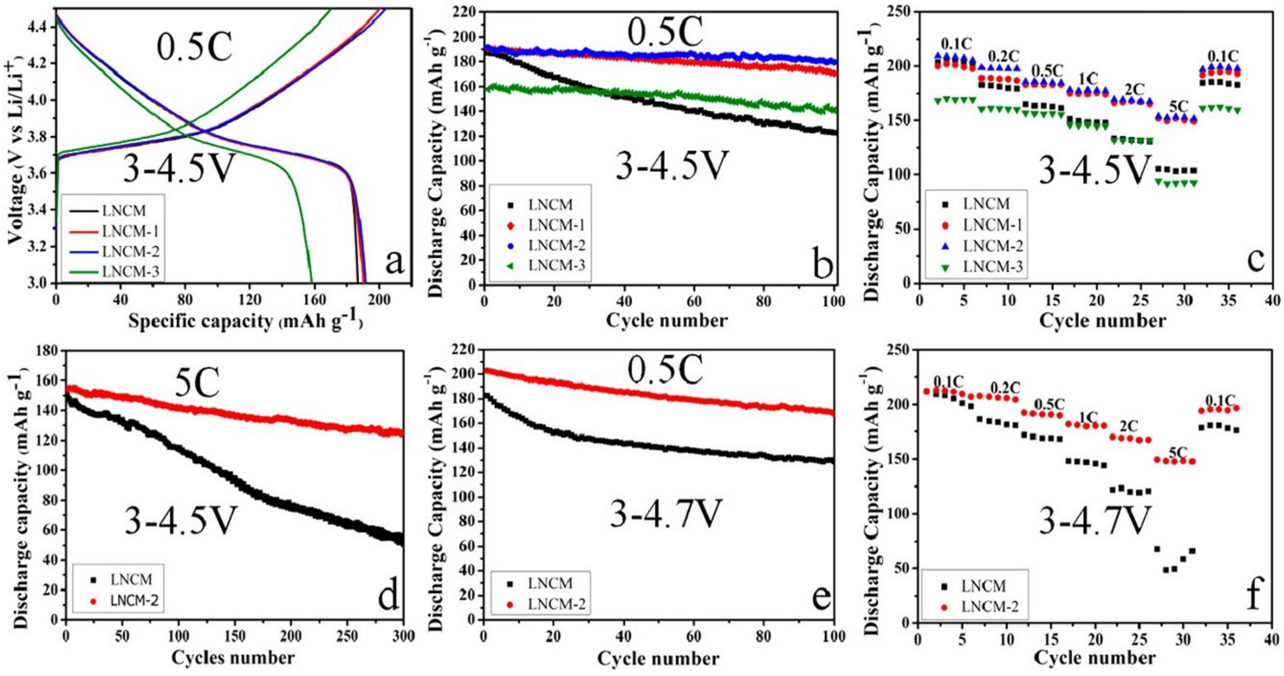

**Figure 11.** Electrochemical performance of the modified LNCM cathode [70].

From the academic point of view, the different effects from the same element in different methods present an intriguing topic for further investigation. A comparative studies of zirconium doping and coating on $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ shows the different outcomes from using the same element [10]. In this research, zirconium doping exhibited superior cycling performance compared to zirconium coating. The zirconium-doped sample retained 98% capacity retention after 50 cycles between 3.0 V and 4.5 V, whereas the zirconium-coated sample performed even worse than pristine NMC. Although it can be argued that the condition for zirconium coating may not be optimized for this experiment, this finding highlights the different mechanisms and influencing factors between doping and coating.

Another interesting concept in surface modification is the synergistic effect between doping and coating [70,71]. The combination of fluorine doping and LiF coating on NMC523 demonstrated remarkable stability, maintaining 93.7% of its initial capacity and delivering 179.4 $mAh \cdot g^{-1}$ at 0.5°C even after 100 cycles at 3.0 V to 4.5 V (Figure 11). This effect is expected to result from the replacement of some metal-oxygen bonds with stronger metal–fluorine bonds, which partially triggers the reduction of $Ni^{3+}$ to $Ni^{2+}$ [70].

## 5. Conclusion and outlook

As lithium-ion batteries continue to emerge as a promising energy solution, it is of great importance that we focus on one of the most expected enhancement methods for cathode materials. The materials such as NMC are known for their limitations in cycling performance. In order to overcome this, the doping approach is designed with practicability in mind. Studies have shown that various doping elements can effectively improve the lifespan of NMC, and with certain elements such as titanium, it also enhances electrochemical properties. However, it is important to consider the compatibility of the doping approach with the entire lithium-ion battery system, including the cathode, electrolyte, separator, anode, and the manufacturing process.

To successfully overcome the limitations of lithium-ion batteries, the modification process must be as simple as possible, ensuring ease of scalability and accessibility to a wide range of raw materials. Future research should explore the effects of combining multiple modification approaches to provide essential insights into material improvements. Additionally, integrating different cathode modification techniques, such as a combination of coating and doping, may help achieve the desired performance for next-generation lithium-ion batteries.

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