Nanotechnology Applications in Cathode and Anode Materials of Li-Ion Battery

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Abstract. Lithium-ion batteries (LiBs), with their high energy/specific density, extended cycle life, and minimal self-discharge rate, have gained considerable popularity in the manufacturing of portable devices and electric vehicles, where space and weight constraints are of utmost importance. Additionally, LiBs have played a pivotal role in the advancement of electric vehicles, promoting sustainable energy practices, and reducing greenhouse gas emissions. However, the limitations that stem from the inherent structures and properties of the conventional component materials of batteries might pose obstacles to the application and development of LiBs, despite their numerous advantages. Nevertheless, significant strides have been made towards improving the capacity, cycling performance, and rate performance of these batteries using nanotechnology. This approach leverages the outstanding properties of nanomaterials to enhance the electrochemical performance of battery components, such as cathode materials, which includes NMC, NCA, LMO, LFP, and anode materials such as Silicon and LTO. This paper provides a comprehensive discussion of the applications of nanotechnology in lithium-ion batteries, offering insights into the future of this promising field.

Keywords: Lithium-ion batteries (LiBs), nanotechnology, applications, cathode, anode.

1. Introduction

Li-ion batteries (LIBs) have become increasingly widespread in modern society, owing to their extensive applications in portable gadgets, electric vehicles (EVs), and expansive energy storage systems. Their appeal lies in their high specific/energy density, extended cycle life, as well as minimal self-discharge rate, making them well-suited for applications where space and weight constraints are critical factors. Furthermore, LiBs have been instrumental in propelling electric vehicle development, fostering sustainable energy practices, and mitigating greenhouse gas emissions [1].

Despite their extraordinary performance and widespread use, LIBs still face several challenges, such as limited capacity, long charging time, short cycle life, and safety concerns, which severely limit their performance and hinder their widespread implementation. One promising solution for overcoming these limitations is the applications of nanotechnology in LIBs. Integrating nanotechnology into LIBs has demonstrated significant promise in enhancing the performance of various battery elements, including cathode and anode materials, which can be attributed to the extraordinary properties of nanomaterials, e.g., high surface area, enhanced reactivity, superior mechanical and thermal properties, which can be harnessed to develop high-performance LIBs [1]. The use of nanostructured materials, such as nanoparticles, nanowires, and nanotubes, allows for the creation of materials and structures with unique properties that can enhance the battery's performance. Moreover, the use of advanced nanostructured materials and techniques has significantly improved the performance of battery components. Nano-coating, nano-doping, hierarchical structures like core-shell and yolk-shell structures, and matrices are some of the popular nanotechnology-related strategies that have demonstrated their effectiveness in enhancing the specific capacity, rate performance, and cycling performance of batteries.

This paper aims to review the current state of nanotechnology applications in LiBs and explore their potential for enhancing the electrochemical performance of battery components, mainly centering on the commonly utilized cathode materials Lithium nickel manganese cobalt oxide (NMC) battery, Lithium nickel cobalt aluminium oxide (NCA) battery, Lithium manganese oxide (LMO) battery, Lithium phosphate (LFP) battery, and the anode materials Lithium titanate (LTO) and silicon. Section 2 provides an introduction to the fundamental components of LiBs and elaborates on the distinctive characteristics of several electrode materials. Section 3 discusses the nanotechnology applications in various cathode materials for the enhancement of electrochemical properties and ultimately the overall battery performance, with section 4 discussing in similar topic. Finally, a comprehensive conclusion of nanotechnology applications in LiBs electrode materials and their effectiveness are drawn from the literature review and research findings, in order to provide insights into the future of nanotechnology applications in lithium-ion batteries.

2. Battery Structure

Rechargeable batteries comprise three essential components: cathode, anode, and electrolyte. Table 1 shows the cathode materials, theoretical specific capacities, range of specific energies in experimental and commercialized cell, and the degree to rate performance, cycle retention, stability/safety of LiB mentioned above [1]. Generally, a higher specific capacity and high working voltage would render a higher cost due to expensive metals utilization and a worse cycling performance and stability, where a trade-off between these factors should take into consideration.

Regarding to working mechanisms, anode materials can be classified into intercalation/de-intercalation materials, including graphite and LTO, alloy/de-alloy materials, including Si, Al, Sn, and conversion materials. Compared to graphite, alloy/de-alloy materials offer higher theoretical capacity as LiB anode materials; however, one main challenge for such materials is the severe volumetric changes during cycling, which leads to structural instability [1]. Another factor that significantly affects the capacity and power performance of a battery is the diffusion of Li^+ in the anode during the charging/discharging process. A shorter diffusion time (and higher diffusion coefficient) is favored by a better capacity and power performance of the battery system.

Eletrolyte is the medium that allows ion transportation between the two electrodes. An ideal electrolyte is expected to offer high ionic conductivity for Li^+ that enables efficient transportation of charges between the electrodes, and also possesses a chemical inertness to the electrode materials that prevents dissolution of the electrodes and loss of electrolyte, which is crucial to the safety and reliability of a battery.

Table 1. Cathode materials, theoretical specific capacities, range of specific energies in experimental and commercialized cell, characteristics of LCA, NMC, NCA, LMO and LFP cathode.

Cathode	Theoretical Capacity ($mAh\cdot g^{-1}$)	Capacity ($mAh\cdot g^{-1}$)	Voltage (V)	Advantage	Limitation
NMC	279	147~200	3.7	Specific energy, operating voltage	Cycling, high cost
NCA	279	125~227	3.7	Specific energy, operating voltage	Cycling, high cost
LMO	148.2	90~135	4	Voltage, rate performance, low cost	Cycling, rate performance
LFP	169.9	116~162	3.4	Cycling, low toxicity, low cost	Rate performance

3. Nanotechnology in Cathode Materials

3.1. NMC

NMC, with $LiNi_xMn_yCo_zO_2$ (x+y+z=1) as cathode material, is one of the most dominant classes of LiBs especially for large electronic devices especially EVs due to its outstanding specific energy up to 200 mAh·g-1, high voltage, and excellent structural stability during cycling [1].

In pursuit of NMC batteries' high theoretical capacity, rich-Ni NMC offer increased Li^+ utilization at a ralatively low voltage window, resulting in higher specific energy. However, even within a reasonable voltage range, rich-Ni cathode still suffers from undesirable cycling performance. This can be attributed to the lattice oxygen release, which subsequently result in rock-salt NiO layer forming on the cathode surface, revealing the loss of nickel and the lattice shrinking. To inhibit the formation of NiO layer as well as lattice shrinking, implementation of nanostructured NMC cathode is a practical solution [1]. Furthermore, hybrid nanostructured NMC cathode has also been investigated, as which not only provides the structural backbone to prevent lattice shrinking but also suppression of side effects [2].

Additionally, high Ni content also conduces to increased chemical reactivity between the cathode material and non-aqueous electrolyte [1]. Such property would render severe capacity lost, power density loss, and substantial reduction of safety characteristics. Basically, a protective layer is extremely necessary to avoid contact between the electrode materials (especially the active materials) and electrolyte and their further reaction. Formation of the protective layer can be realized via techniques e.g., nano-coating and atomic layer deposition (ALD) to produce nanoscale coating layers with oxides and fluorides. However, it is worth noticing that these coating techniques still have room for improvement as neither of them could offer a complete and conformal layer within reasonable efforts.

Coban et al. fabricated a hybrid nanostructured NMC battery system incorporating a carbon nanotube (CNT) conductive framework. After undergoing 1000 cycles, the specific capacity demonstrated is 150.7 $mAh\cdot g^{-1}$, maintaining a relatively high retention rate of 69.6%, significantly outperforming the unmodified NMC with a capacity of merely 84.9 $mAh\cdot g^{-1}$ [2]. Zhang et al. developed an NMC battery with a ZrF_4 coating. Following 100 cycles, the capacity of the modified NMC reached 185 $mAh\cdot g^{-1}$, boasting a retention rate of 89%, and this considerably surpasses merely 97 $mAh\cdot g^{-1}$ obtained by the unmodified NMC. These findings suggest a substantial enhancement in cycling performance for the modified NMC batteries [3].

3.2. NCA

NCA, with $LiNi_{0.8}Co_{0.15}Al_{0.05}$ as cathode material, exhibits similar advantages of extraordinary specific energy and high operating voltage as NMC. The commercial applications of NCA battery, however, has been impeded by the limitation of relative short lifespan presented by rapid capacity loss and poor cycle performance. Following the thread of the development of NCA, additional nano-doping can also be implemented to current NCA cathode for enhancement in capacity and electrochemical stability window as it integrates the desirable properties of the doping elements and reduces cation mixing [4]. Additionally, doping atoms also contributes to expansion of diffusion pathway, which expedites the kinetics of Li^+ diffusion and improve electronic conductivity. Various doping elements have been investigated and proven the effectiveness in pursuit of better capacity, conductivity, and cycle performance, including cations Nb, Ti, and F as substitute for oxygen, and the combinations of the different elements [4].

Besides, side reactions can be observed between the O^{2-} on the surface region of NCA cathode and the non-aqueous electrolytes, with by-products depositing on the battery separator and expedite electrolyte hydrolysis. The contact between H_2O and CO_2 in the external environment also facilitate the formation of lithium compound layer, which locates on the surface of cathode that blocks the diffusion of Li^+ [1]. These side reactions can significantly deteriorate the electrochemical performance of battery. Furthermore, such undesirable characteristics would be amplified due to the thermochemical instability of NCA cathode. In order to prevent the undesirable side reactions that deteriorates the battery performance, as well as the formation of SEI, it is imperative to insulate the cathode and electrolyte to prevent direct contact between the active materials. This can be achieved by surface modification on cathode particles with coating materials such as oxide, phosphate, carbon, and glass, which can be explained by the coating layer offering protection to the cathode against the HF attacks from the electrolyte and ultimately minimizing the formation of by-products [5]. However, it is crucial to manage the thickness of this layer to circumvent any hindrance to Li^+ diffusion that may lead to a reduction in rate performance.

He et al. introduced Nb doping into the NCA cathode material, resulting in 94.2% retention rate under the condition of 0.5C and 100 charging cycles, which is significantly higher than the 69.5% retention rate observed for the unmodified NCA [4]. In another study, Li et al. employed a nano-scale phosphate coating on the NCA cathode material. Following 500 cycles, the phosphate-coated NCA exhibited a retention rate of 90.3%, a notable improvement over the 67.2% retention rate of the unmodified NCA [5].

3.3. LMO

LMO featuring spinel $LiMn_2O_4$ as cathode material have gained interest for their high operating voltage, rate performance, and eco-friendliness, as they contain no Nickel or Cobalt, unlike NCA and NMC. Despite lower capacity, these advantages appeal to EV manufacturers like Nissan, Chevrolet, and BMW, resulting in successful commercial applications.

However, structural instability has deteriorated the cycle performance and impeded the further development of LMO battery, which is presented by the Jahn-Teller distortion, which is shown in Fig 1. The strategy of substituting Mn^{3+} with lower-valence elements through nano-doping has been demonstrated to be a successful method for reducing the impact of Jahn-Teller distortion, which can be explained by the increased average valence state of Manganese due to the reduction of Mn^{3+} in the system via element replacement. Studies shows that the Jahn-Teller distortion can be significantly inhibited via doping, leading to a greatly improved structural stability [6].

Figure 1. Two forms of Jahn-Teller distortion [6].

Another issue of LMO battery lies on the dissolution of Mn^{2+} into the electrolyte, causing structural degradation of LMO battery that contributes to quickly fading capacity and poor cycle performance [1]. Similar to NMC, to mitigate the dissolution of Mn, it is crucial to implement protective measures on the interface bewteen the electrode and the electrolyte to avoid their direct contact (especially between the materials that can occue side reactions) further prevent the dissolution of Mn^{2+}. Series of metal oxides, phosphates, and carbon has been investigated and proven to be effective nano-coating materials [7,8]. Besides, modifying the electrolyte with functional additives to facilitate the forming of a nano-layer on the cathode surface can also enable an effective protection to the cathode during charging/discharging process, which results in a significantly improved stability and cycle performance.

Tao et al. doped the LMO battery with a combination of Ni and B, resulting in a retained specific capacity of 92.8 $mAh \cdot g^{-1}$ under the condition of 1C, long cycles (1000 cycles), which signifies enhanced stability [6]. Zhang et al. applied a Gd oxide coating to the LMO cathode material, achieving a specific capacity of 90 $mAh \cdot g^{-1}$ and 81.5% retention rate under a 5C cycling condition [7]. Furthermore, Qing et al. utilized a phosphate coating on the LMO cathode, yielding a specific capacity of 78 $mAh \cdot g^{-1}$ under the condition with an elevated temperature of 55°C, in contrast to 33 $mAh \cdot g^{-1}$ obtained by the unmodified LMO [8]. These investigations demonstrate that nano-coating techniques can significantly improve battery performance under high current and high temperature conditions.

3.4. LFP

LFP has exhibited an upward trend in current EV industry. Despite the relatively low energy density of LFP battery, its incomparable electrochemical and thermal stability enable an excellent cycling performance and improved safety. Similar to LMO battery, LFP battery is free of Ni and Co and that renders a low cost. These benefits have prompted manufacturers, such as Tesla, to adopt LFP batteries in standard range EVs where energy requirements are met.

However, one main challenge LFP battery encountered is its undesirable rate performance, which is correlated to the slow electron movement in LFP crystal structure during charging/discharging process. To overcome this drawback and enhance rate performance, one effective approach is to reduce the particle size to a nano-scale to form nanostructured $LiFePO_4$ and hierarchical nanostructures, which renders a shortened transport length of electrons and inhibited anti-site defects. This method, however, does not address the limitation of low electronic conductivity, and also significantly compromises the outstanding stability of LFP battery as nano-particles entail increased exposure to external atmosphere for its extremely larger surface area. One feasible solution to both problems is nano-coating $LiFePO_4$ nano-particles with conductive mediums i.e., oxide, carbon, and conductive polymer [9,10].

Additionally, the enhancement of rate capability and capacity in LFP cathodes can be achieved through nano-doping with diverse elements, whose advantages have been discussed in the section of nanotechnology application in NCA cathode. A number of dopants have proven its effectiveness in the improvement of electrochemical property of LFP cathode, including metal (Nb), glass (B), and different co-doping strategies [11].

Zhang et al. applied a carbon coating to the LFP cathode material and incorporated it into a hierarchically structured MXene matrix, resulting in a significant increase in the diffusion coefficient by 10^2 [9]. Besides, a greatly increased specific capacity of 165.1mAh·g^{-1} at the initial stage of cycling, in contrast to 122.9 mAh·g^{-1} initial capacity achieved by the unmodified LFP [9]. Mo et al. employing a poly(aminobenzylamine) (PAB) polymer coating on the LFP cathode. Under high current cycling conditions at 10C, the coated LFP cathode exhibited remarkable stability, retaining 125.5 mAh·g^{-1} specific capacity after long cycles (1000 cycles), corresponding to an 83.7% capacity retention rate [10]. This result is notably superior to the control group, which utilized glucose as the coating material and obtained a capacity of merely 85 mAh·g^{-1} under identical cycling conditions [10]. Furthermore, the PAB-coated LFP cathode demonstrated an elevated diffusion coefficient, reaching an order of magnitude of 10^{-10} cm^2·s^{-1} [10], significantly surpassing the measured range for uncoated LFP cathodes. Teng et al. employed Nb doping for the LFP battery, leading to a substantial enhancement in the diffusion coefficient by 10^3 [11]. The specific capacity of 169.87 mAh·g^{-1} at the initial stage of cycling is also observed in the modified LFP battery system, compared to 137.49mAh·g^{-1} with unmodified LFP [11].

4. Nanotechnology in Anode Materials

4.1. LTO

LTO is an alternative for graphite as LiB anode material offering remarkable cycling stability and safety, which presents by a meager volumetric change of 0.2% due to the tiny variation of lattice diameter [1]. However, LTO suffers from low theoretical capacity, poor rate performance due to its large electronic bandgap and crystal lattice structure, and lower battery operating voltage due to its high electrochemical potential relative to lithium.

To resolve such limitations, nanostructured LTO are investigated and have demonstrated the effectiveness on improve the rate performance and electronic conductivity, resulting from significantly miniatured diffusion path of Li^+, and increased contact between electrode/electrolyte due to large surface area. Additionally, attempts to the incorporation of LTO into materials with high capacity and electronic conductivity have also undertaken, usually categorized by nano-doping and nano-coating. A number of studies have demonstrated the effectiveness of nano-doping to achieve higher conductivity. In terms of surface coating, various materials e.g., silver, carbon, and oxide that have been studied for the improvement of graphite anode have also been reported to be effective in facilitating electron transportation on the electrode/electrolyte interface, leading to improved conductivity and rate performance [12-14]. Besides, the implementation of the coating layer can effectively mitigate particle aggregation, leading to improved anode protection against degradation and enhanced electrochemical performance.

Both methods mentioned are typically employed in conjunction with nanostructured LTO to improve the performance of batteries. Zou et al. employed Al and Mn doping in conjunction with a graphene coating for the LTO cathode material, achieving an impressive specific capacity of 261.7 $mAh\cdot g^{-1}$, in comparison to 169.4 $mAh\cdot g^{-1}$ obtained by the unmodified LTO [12]. Additionally, the diffusion coefficient increased by 10^3 [12]. Bai et al. employed nano-coating with a composite layer of Li, Mg, and silicon oxide. The modified LTO anode exhibits a capacity of 155 $mAh\cdot g^{-1}$at the initial stage of cycling, which is notably greater than the 139.6 $mAh\cdot g^{-1}$ obtained by the uncoated LTO [13]. Moreover, the capacity retention of the modified LTO system stands at an impressive 89.6% after long cycles (900 cycles) under a 2.85C rate, whereas the unmodified LTO suffers from a significant decline in performance, retaining only 5.4% of its capacity after a mere 700 cycles [13]. This enhancement in stability and performance can also be observed through the increase in the diffusion coefficient, which demonstrates a remarkable 10^2 improvement [13]. Chen et al. employed nano-coating on the LTO with graphene and incorporated it into a hierarchical pore structure, resulting in a desirable specific capacity of 250 $mAh\cdot g^{-1}$ and a diffusion coefficient increase by 10^2 [14].

4.2. Silicon

Silicon has garnered significant interest and is acknowledged as alternative anode materials with most promising future, due to its exceptionally high theoretical capacity of 3572 $mAh\cdot g^{-1}$, in contrast to graphite with only 372 $mAh\cdot g^{-1}$. However, the severe volumetric change of up to 300% in the anode structure during the cycling can contribute to particle pulverization and structural degradation. Additionally, this pulverization isolates active materials, impeding electron transport necessary for oxidation reactions, resulting in unused active materials, rapid capacity fading, and undesirable cycling performance [15].

To address the challenge of volumetric change, a number of studies have placed efforts in the design and fabrication of nanostructured silicon. Nanostructured silicon e.g., nanoparticles (SiNPs), nanowires (SiNWs), and nanotubes (SiNTs) also demonstrated their capability. Studies have shown that regardless of the occurrence of volume change, particle pulverization can be efficiently suppressed when the silicon particles size diminished to nanoscale [15-17]. Furthermore, instead of bulk materials (nanoparticles), SiNWs and SiNTs are more favored for not only stronger adaptability to the volume change but more efficient electron transfer. Porous silicon (PSi) has also been investigated. Accordingly, a microscale pore structure provides sufficient room for volume fluctuations during the charge/discharge cycle, thereby preserving the structural integrity of the anode. Besides, the nanoscale wall in the PSi structure provides not only an increased surface area that facilitates the access between anode and electrolyte, but also short diffusion path that accelerate the Li^+ diffusion, which results in high rate performance [18].

Regarding to the conductivity, it should be emphasized that silicon is semiconductor. In addition, the amorphous property of silicon also results in undesirable electronic conductivity. Hybrid nanostructures can address such limitation by enabling the combination of nanostructured silicon/PSi and conductive materials (usually carbon). One intuitive method is to incorporate silicon nanotubes with the conductive materials as the core of the structure, or coating on the surface, the other is to synthesize nanocomposite of silicon and conductive materials to form hybrid structure to buffer the volume change. One example is presented by the utilization of secondary architecture structures, with silicon nanoparticles encapsulated in the shells with reserves extra voids to accommodate anode expansion and further assembled into a larger sphere, forming a yolk-shell structure. Aside from buffering volume change, this design enables a significantly improved cycle performance by enabling a stable and spatially constricted SEI on the electrode/electrolyte interface [18].

Typically, such incorporation strategies are accompanied by the fabrication of nanostructured silicon, resulting in the collective advantages of both nanostructured silicon and carbon incorporation and ultimately enhancing the efficacy of batteries. Qiu et al. employed a carbon coating on SiNPs and decorated them with cobalt, subsequently integrating these SiNPs into a CNT framework. This approach resulted in 1191 $mAh\cdot g^{-1}$ under 0.5A after 200 cycles, which is a remarkable specific capacity that far surpasses the 400 $mAh\cdot g^{-1}$ specific capacity observed in the unmodified anode after only 100 cycles [17]. Xiang et al. utilized a yolk-shell structure by encapsulating porous silicon nanospheres (PSSs) within graphene layers. This configuration maintained a specific capacity of 1034 $mAh\cdot g^{-1}$ under the rigorous condition of 2.1A (0.5C for Silicon), long cycles (1000 cycles), whereas the specific capacity of the unencapsulated PSSs diminished to zero after 500 cycles [18]. These findings demonstrate the significantly enhanced stability and performance achieved through the modification of silicon-based anode materials.

5. Conclusion

LiBs provide a reliable and efficient source of energy for a broad range of applications. The high specific/energy density, minimal self-discharge rate, extended cycle life, adaptability, and low maintenance demands of these batteries make them an attractive option for energizing a wide variety of devices. Despite the numerous advantages of LiBs, the intrinsic structures and properties of component materials result in various limitations that hinder their widespread implementation and advancement.

The utilization of nanotechnology has demonstrated significant improvements in capacity, cycling performance, and rate performance, providing promising avenues for the development and innovation of high-performing lithium-ion batteries in the future. This is achieved via the utilization of nanotechnology improving the electrochemical performance of battery components, including cathode materials such as NMC, NCA, LMO, LFP, and promising anode materials that are already commercialized such as LTO and silicon, as comprehensively discussed in this paper, with the approaches and common effects concluded as follow: (i) nanostructured electrode: with the use of nanostructured materials, e.g., nanoparticles, nanowires, nanotubes and porous materials, (ii) nano-coatings: with the use of the deposition of thin nanoscale coatings on the electrode materials, usually aiming to provide substantial protection to electrode materials for better cycling performance, and offer high electronic conductivity., (iii) nano-doping: with the introduction of small amounts of nanoscale dopants into the electrode materials, which integrates the desirable properties of the doping elements and improve the intrinsic characteristics of the electrodes, (iv) hierarchical structure: with core or yolk material to provide coating layer, and secondary structure offering thin and stable SEI; nano-matrices: with the use of nanomaterials (usually carbon) to form a matrix for the electrode materials to improve their mechanical stability and enhance their electrochemical properties.

As research into nanotechnology continues to progress, it is expected that more advanced and sophisticated methods of applying nanotechnology to lithium-ion batteries will emerge and ultimately lead to the development of more efficient and high-performing batteries in the future.

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