Nanotechnology used in Li-ion Battery for Electric Vehicles

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Abstract. In recent years, environmental issues have been given increasing attention, and electric vehicles have replaced conventional combustion engined vehicles as a critical focus for development. In order to win the market, electric vehicles (EVs) must have sufficiently good performance, such as a longer mileage range, long cycling life, and time-saving charging, and the performance of the battery is one of the essential factors determining the performance of the EVs. In order to make more environmentally friendly electric vehicles available, the performance of lithium-ion batteries, which are the mainstream EV batteries, must be improved, and nanotechnology can facilitate this process. This report summarizes four promising materials for the cathodes and anodes of lithium batteries for electric vehicles and how nanotechnology can improve them. For $LiMn_2O_4$ (LMO), $LiNi_{1-x-y}Mn_xCo_yO_2$ (NMC), and $LiNiCoAlO_2$ (NCA) as cathode materials and $Li_4Ti_5O_{12}$ (LTO) as anode material, nano-doping, nano-structuring, and surface coating are effective techniques to enhance the stability and rate capacity, and cycle performance of the battery. In the case of LMC, nanotechnology can help solve the Jahn-Teller distortions and stabilize the structure; for NMC, nanotechnology can suppress ion dissolution and chemical reactivity. For NCA, it can strengthen conductivity and capacity. And finally, for LTO, nanotechnology can faster charge/discharge rate. This paper looks forward to the maturation of these nanotechnologies and their practical application, and the identification of more nanotechnologies that can enhance the performance of Li-ion batteries to help make electric vehicles more usable and contribute to environmental development.

Keywords: Nanotechnology, Li-ion Battery, cathode and anode materials, electrical performance.

1. Introduction

Electric vehicles have many advantages compared to traditional internal combustion engined cars. For example, it has approximately zero emission in the driving process, environmental protection, stable operation, and is noise-free. Moreover, for the government, introducing electric vehicles is necessary and beneficial for the long-term development of the environment. Customers have many expectations about electric vehicles, like a longer mileage range, longer cycling life, and more time-saving charging. These aspects can be improved by having a larger battery capacity, better cycle performance, and rate capacity. Nanotechnology can be used for improvement. Currently, the lithium-ion battery is the most commonly studied and used battery for electric vehicles. For EV batteries, there are several optional materials for cathode and anode. The three commercialized cathode materials are LMO, NMC, and NCA, and LTO is a promising line of research for the anode material. Each of these materials has its pros and cons as an EV battery material in the study conducted up to now. Furthermore, using nanotechnology to improve their performance in different ways is essential for the long-term development of electric vehicles.

Over the last decade, a large body of literature has accumulated a wealth of experience through experiments and data measurements of nanotechnology applications on different battery materials. However, the combination of battery cathode and anode materials and the direction of nanotechnology enhancement for them need to be systematically summarized and integrated in order to indicate the future direction of nanotechnology improvement for materials with different advantages and disadvantages.

The main objective of this article is to analyze ways in which the performance of lithium batteries for electric vehicles can be improved. Firstly, four alternative materials for the cathode and anode of the battery are listed and presented, including their advantages and disadvantages and the reasons why they can be used in electric vehicle batteries. Nanotechnology is then analyzed to improve the

performance of the available materials and the specific ways they can be improved. These four materials are then analyzed for their most fatal performance drawbacks as cathode and anode materials for lithium-ion batteries, and a variety of different nanotechnologies are listed to address these drawbacks. This is followed by comparing the performance of the nanotechnology-improved materials with those that have not been manipulated to investigate the impact of nanotechnology improvements to electrode materials considering the battery capacity, rate capability, cycling performance, and consequently on the range and charging efficiency of electric vehicles. Finally, a summary of promising electrode materials and corresponding nanotechnologies to enhance their performance is presented.

2. Cathode LMO

2.1. Bi3+ and La3+ doping

LMO($LiMn_2O_4$) has already been commercially used in vehicles like Chevy Volt and Nissan Leaf. It has numerous advantages like its rich resources resulting in low costs; it's environmentally friendly and has good safety and high rate capacity. However, it is not stable and easy to decompose gas. Its high-temperature performance is not good as well. Meanwhile, it has an ordinary energy density and acceptable cycling life.

The main reason LMO has been considered as a cathode material used in EV batteries is that the 3-D structure of $LiMn_2O_4$ providing a framework that is well-connected for the insertion and de-insertion of Li+ ions during the process of charging and discharging the battery, which makes it suitable for high rate capability [1]. Batteries based on $LiMn_2O_4$ cathodes have shown a better rate-capability than materials with two-dimensional frameworks as a result of this structural arrangement. However, the unexpected Jahn-Teller distortions is present in the LMO. The Jahn-Teller distortions describes the geometrical distortion of molecules and ions that result from specific electron configurations [2]. After the electronic configuration splits, the z-axis force that nuclei act on electrons becomes smaller, and the octahedron has been vertically stretched (Figure 1).

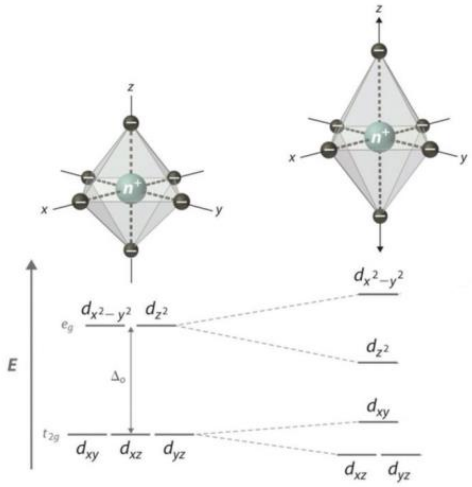


Figure 1. Illustration of tetragonal distortion (elongation) for an octahedron complex [2].

For the LMO battery, during the charge and discharge process, the Mn^{3+} is formed at a low state of charge, and the Jahn-Teller distortions is present in the MnO_6 Octahedron (Figure 2) [3]. The distortion changes its structure and therefore has negative impacts on its performance.

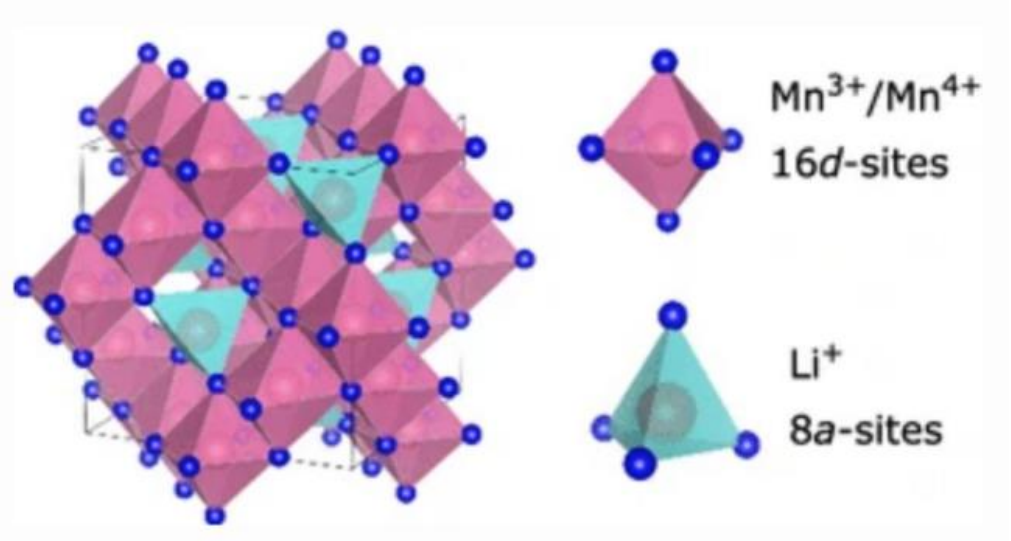


Figure 2. Schematic 3D structural model for stoichiometric $LiMn_2O_4$ [3].

This problem can be solved using nanotechnology by doping Bismuth and Lanthanum to the LMO; as Mn^{3+} is replaced with an equal amount of Bi^{3+} and La^{3+}, the structural stability of the material could be greatly improved, and the Jahn-Teller distortions could be suppressed, leading to improved electrochemical characteristics [4]. The $LiBi_xLa_xMn_2O_4$ sample delivered a high initial discharge capacity and remained 95% for the following 80 cycles. Therefore, the doping strategy severely improves the lithium-ion battery performance by stabilizing its cathode material structure.

2.2. LiMn2−xTixO4 surface coating

Mn ions dissolving into the non-aqueous electrolyte is another issue with LMO. These Mn ions will eventually accumulate on the surface of the graphitic anode, which will lead to a decrease in the anode's electrochemical performance [5]. This can be solved by nano-coating technology. Titanium ions are solely integrated into the surface of the spinel, which causes the formation of a cation-doped $LiMn_{2-x}Ti_xO_4$ surface layer (Figure 3).

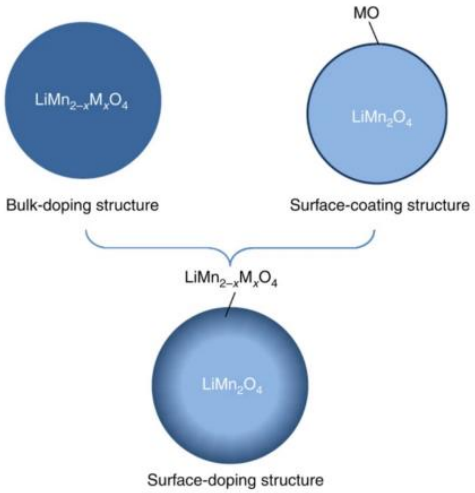


Figure 3. The combination of bulk-doping and surface-coating: surface-doping [5].

This strategy combines the technologies of bulk doping and surface coating in order to stabilize the material structure throughout the particle while simultaneously preventing the electrolyte from coming into direct contact with the $LiMn_2O_4$ and therefore reducing the pace at which the Mn ions dissolve. In addition, the vast majority of the surface coatings are made out of insulator material. Contrarily, in contrast to the physical barrier that is imposed by those surface coatings, this specific coated layer is capable of electrochemical activity, as a result, it keeps the channels for the transport

of ions and charges on the surface [5]. By comparing the cycling life for unmodified $LiMn_2O_4$ with the titanium-coated materials at relatively high temperatures, the nano-coating technology servilely improves its performance.

3. Cathode NMC

3.1. Hierarchical nanostructure

The $LiNi_{1-x-y}Mn_xCo_yO_2$ battery has already been commercially used by some companies like Renault due to its relatively high capacity and power. However, it still suffers from weak rate capability and rapidly diminishing capacity since of Jahn-Teller distortions. Furthermore, the migration of metal ions and release of oxygen causes lattice shrinkage and leads to capacity drop. Hierarchical nanostructure materials have the potential to improve the electrochemical performance of NMC because they provide shorter lithium-ion diffusion pathways, which in turn enables quick rates of lithium-ion intercalation and deintercalation as well as rapid electron transfer, and because they have a larger surface area, which ultimately results in enhanced rate capability. In the meantime, the hierarchical nanostructure offers not only excellent structural stability but also a reduction in side reactions; to be specific, it prevents the Jahn-Teller distortions, which guarantees better cycle performance. One valuable nanostructure is the Peanut-like Hierarchical nanostructure $Li_{1.2}Ni_{0.18}Mn_{0.54}Co_{0.08}O_2$; it is synthesized by using facile solvothermal method combined with a calcination process, which has a Peanut-like shape with a length of 2–3 um and a width of 1–2 um, composed of numerous primary nanoparticles with sizes less than 50 nm [6].

After the lattice has shrunk, the channel of Li-ions and electrons may close, and a structure with distinct layers that is well-formed and excellent crystallinity of Peanut-like Hierarchical nanostructure contribute to better structural stability and cycle performance, as well as a high initial discharge capacity coupled with good capacity retention and demonstrates higher rate capabilities. The unmodified MNC batteries have an initial discharge capacity of 174.1mAh. After 100 cycles, the discharge capacity is 155.3mAh, and the capacity retention is around 89.2%. While the Peanut-like NMC has an initial discharge capacity of 229.9mAh, after 100 cycles, the discharge capacity is 216.5mAh, and 94.2% of the capacity is maintained. By comparison, the nanostructure material has much better discharge capacity as well as capacity retention.

3.2. Nano coating

Furthermore, another nanotechnology that can be used for improvement is NMC coated with nanostructured fumed metal oxide like Al_2O_3, TiO_2, and ZrO_2. The metal oxide is broken up into smaller size and interacts with cathode powder surface during mixing process. Following the completion of the necessary mixing, a layer of solid coating that is both relatively continuous and sticky is produced [7]. In order to suppress dissolutions with electrolytes and avoid the formation of cracks and particle disintegration, the coated layer is a useful concept. ZrO_2 has the ability to effectively inhibit the chemical reactivity of NMC, while Al_2O_3 and TiO_2 also have the ability to concurrently prevent the cathode particle from breaking and disintegrating. During cycling, the physical barrier provided by the coated layer precludes the creation of the electrolyte interface by electrolyte breakdown products on the untreated NMC surface, which prevents increased resistance, providing a better rate capacity. However, the thickness of coated layer needs to be tightly controlled to enhance lithium-ion transport and achieve best result.

4. Cathode NCA

NCA is considered a cathode material because $LiNiCoAlO_2$ battery can provide a high energy density and voltage, long cycle life, good cycling performance, low self-discharge, thermal stability, and no memory effect. However, it has low capacity retention and rate capacity in cycling. The capacity fading and rate reducing mechanisms are the result of two factors: as the transition of the

inactive phase grows, the battery's resistance also increases, resulting in a proportional decline in capacity. Moreover, throughout the process of charging and discharging, particles are often coated with a surface layer as a result of the breakdown of electrolytes; the deposition on the surface of electrodes is also the cause of enhanced polarization [8]. Graphene has been explored as a cathode material in this instance because to its high strength, wide surface area, and great conductivity. The nano-material composite G-NCA can be introduced to improve NCA in many aspects like higher capacity, higher charging rate, and long cycling life. The composite G-NCA is a 3D nanostructure NCA/ graphene based on a simple template self-assembly approach that is applicable on a large scale. Figure 4 illustrates the method of preparing the G-NCA composite. With the use of high-powered ultrasonic stirring technology and absolute ethanol dialysis, the NCA particle and graphene self-assemble. The electrostatic interaction helps better combine NCA and graphene. This technology has many innovations; for example, a subsequent increase in the surface area significantly improves the electrochemical performance of the battery, such as electrochemical stability, reversibility of electrochemical reaction, magnification ability, and cycle stability, and it can also reduce the polarization of the electrode in the electrochemical process. In large-scale lithium battery applications, obtaining electrode materials with a long lifespan and a high rate of discharge is the most crucial factor. The graphene-supported NCA nano-composite can therefore form a three-dimensional network, leading to enhancement in electrochemical efficiency.

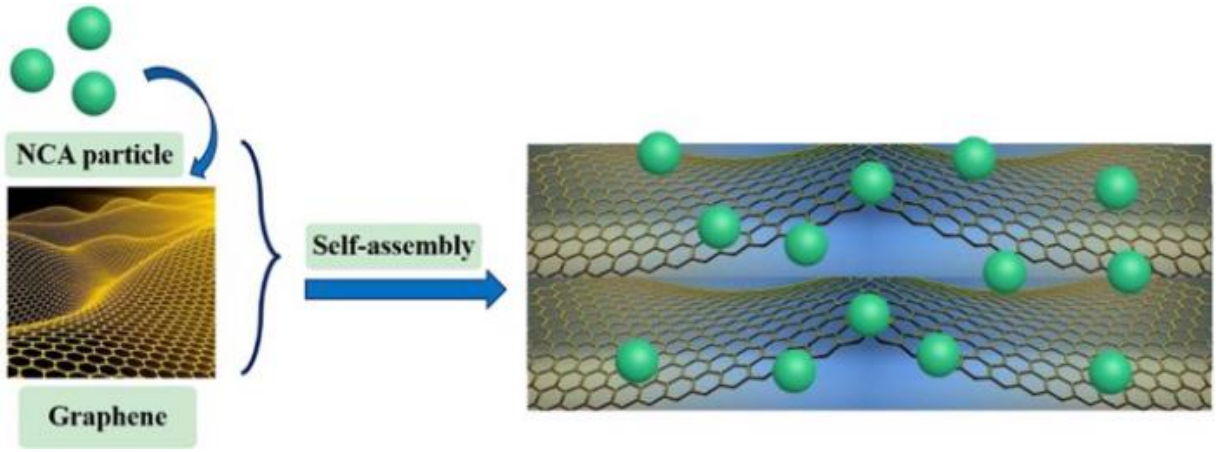


Figure 4. The self-assemble process of the G-NCA composite [8].

As the graphene and NCA particle are self-assembled from 0.5% to 5% percentage of graphene, the close stacking of graphene and NCA can increase the interaction between molecules and enhance synergistic effect. However, this structure was destroyed when the rate increased to 5% due to the heavily stacked graphene.

The G-NCA composite cathode's reversible capacity and discharge retention rate are significantly higher than those of the original NCA. At the 5C discharge rate, G-NCA showed a reversible capacity of 153.6mAh/g with a retention rate of 82%, while the original NCA showed only 125mAh/g with a retention rate of 77%. However, when the graphite content reaches 5%, due to the severely stacked material structure of graphene, the unique 3-D structure will be destroyed, and the battery performance will not significantly improve. The template self-assembly G-NCA composite offers a practical and scalable technique for high-rate and long-lasting lithium-ion battery applications, while future development of the G-NCA composite should focus on a deep investigation of composition manipulation.

5. Anode LTO

$Li_4Ti_5O_{12}$ provides exceptional structural stability and safety during cycling; however, it has low ionic and electronic conductivity. Gas swelling also exists in the usage. $Li_4Ti_5O_{12}$ is known to be a zero-strain anode material since it exhibits a minor volume change of only 0.2% during lithiation due

to a tiny change in lattice parameter [10]. Lattice stresses during cycling are one of the primary reasons of capacity deterioration in battery cathode and anode, hence this property of $Li_4Ti_5O_{12}$ anodes is the reason behind their exceptional cycling life [11]. Besides the reduction of diffusion pathways and the improvement of the intercalation kinetics due to larger electrode/electrolyte contact area provided by nanostructure, nanotechnology of Carbon Nano-composites is also a helpful strategy to eliminate limitations of poor electrical conductivity of $Li_4Ti_5O_{12}$ and therefore enhance electrical performance. Carbon has a lower mass density than metal additions and is less expensive. The use of carbon with high conductivity into $Li_4Ti_5O_{12}$ to create $Li_4Ti_5O_{12}$-carbon nanocomposites should enhance the rate capability performance of $Li_4Ti_5O_{12}$ anode [11]. Carbon nanocoating enhances the electrical conductivity of the surface and the contact surface with electrolyte solution, hence boosting electrochemical performance. Consequently, carbon coating has been shown to increase the electrical conductivity of $Li_4Ti_5O_{12}$. In addition, the carbon coating strategy prevents particles from aggregating into larger clusters and drastically lowers the resistance of contact between individual particles; it can also limit the production of gas evolution by preventing the electrode from direct contact with the electrolyte. The carbon coating raises the electrical conductivity, but the thickness of the carbon layer limit the rate capability. As a result, the ideal carbon layer needs to be as thin as feasible while simultaneously maintaining its integrity and homogeneity.

6. Conclusion

Considering the future energy and environmental issues, electric vehicles are the way forward and therefore the application of nanotechnology to electric vehicle batteries is well worth an in-depth study. This paper lists four materials that can be used as electrode of Lithium-ion battery in electric vehicles, LMO, NMC, NCA and LTO; there are three areas in which nanotechnology can improve electrical performance of them. First, doping and metal oxide coating in LMO and NMC can stabilize the material structure and prevent Jahn-Teller distortions. Then the Hierarchical and 3D nanostructure material in NMC and NCA can increase contact area and reaction rate. Finally, the Carbon coating in LTO can increase conductivity. All these lead to the enhancement of battery performance. As a result, LMC and NMC have high rates capability and remain at 95% after 80 cycles. For LMC, it is not stable and easy to decompose gas; for NMC, the effect of coated layer thickness still needs to be investigated. For NCA material, nanotechnology makes it have a higher capacity and retention rate. However, if there is a high enough concentration of graphite (5%), this unique structure will be destroyed. Although LTO has high thermostability, excellent cycling stability, and high power density, it still not been commercially used yet due to its short cycling life. The nanotechnology strategy is not perfect, and some limitations need further work. The performance in extreme weather, the manufacturing difficulty, and the deep investigation of composition manipulation must be considered in actual production and application. Furthermore, LTO is relatively new and still in the research process; more experiments must be done before being used in large-scale commercial production. This paper summarizes and concludes the contribution of nanotechnology to the performance enhancement of battery cathode and anode materials and indicates the future development of lithium batteries in electric vehicles.

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