Applications of Nanotechnology: lithium-ion based batteries in electric vehicles

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Abstract. With the benefit of zero emissions, free noise and stable operation, the electrical vehicle market has grown dramatically. More expectations are raised for electric vehicles to achieve a better user experience of long-range, long-lifespan and time-saving charging. Thus the capacity, cycling ability and rate capability of electric vehicle batteries are aimed to be improved. Since the advent of nanotechnology, it has made great contributions to various industries and is also believed to be a breakthrough in battery performance. This article introduced nanotechnologies, summarised and discussed its application that could improve lithium-ion-based electric vehicle battery performance. Three typical commercialised cathode materials (Lithium Manganese Oxide (LMO), Lithium Nickel Manganese Cobalt Oxide (NMC), and Lithium Nickel Cobalt Aluminium Oxide (NCA)) suffer capacity fading due to lattice distortion, ion dissolution, and electrolyte decomposition, which can be mitigated by nano-doping, nanocoating, and special nanostructure to certain extents. Two promising anode materials (Lithium titanate (LTO) and silicon) face problems of poor electrical conductivity and volumetric expansion during cycling. Nanotechnologies provide solutions that greatly accelerate their commercialisation. In the future, quantitative composition manipulation is the key point to further promoting cathode material performance. And anode materials still need to be improved to be genuinely used in life. This article combines nanotechnology with the electric vehicle industry and provides innovative ideas for their development.

Keywords: nanotechnology, electric automobile, Circulation capacity.

1. Introduction

In recent years, as a milestone in the automobile industry, the importance of vehicle electrification has grown dramatically. Meanwhile, concerns about the environmental consequences of conventional vehicles have been raised. According to the United States Environmental Protection Agency, Transportation takes 27% of 2020 CO_2 emissions, which are primarily resulting from the combustion of petroleum-based products, in internal combustion engines [1]. One of the most effective solutions to reduce emissions is switching fuels to cleaner energy sources. Therefore, electric vehicles (EVs) are considered the best alternative to conventional vehicles, with the most significant advantage of zero emissions. Moreover, EVs also provide a better driving experience with stable operation and free noise. It is precise because of these advantages that the market share of electric vehicles has increased exponentially, and by the year 2021, the number of electric cars has exceeded 10 million in the world [2]. On this basis, consumers have more expectations for the performance of electric vehicles, which require EVs to have a long mileage range, use period and flexible charging time. To achieve these expectations, research on electric vehicles batteries performance has subsequently gained attention.

Lithium-ion battery dominates the EVs battery market for the reason that compared with other rechargeable batteries like Ni-Cd and Lead-acid batteries, it offers excellent energy and power density and relatively service life. As mentioned above, lithium-ion battery is aimed to have desirable properties of large capacity, acceptable capacity retention, and high rate performance to achieve expectations of EV performance. Electrode conductivity is crucial for battery capacity and charging/discharging rate. Structure deformation is a critical issue leading to capacity drops in EV lithium-ion batteries [3]. In addition, lithium-ion and electrons diffusion rates are considered to be closely related to the charging/discharging speed. Therefore, plenty of research has been carried out on these topics, including capacity enhancement by stabilised lithium metal powder (SLMP) and performance promotion with electrolyte additives [4, 5].

Nanotechnology and nanomaterials have made significant contributions to various industries due to their excellent mechanical properties, unique surface mo morphology and high surface ratio. In the vehicle field, nanotechnology has already been applied to achieve better performances in all aspects. Bayerische Motoren Werke AG (BMW) enable their car to have both lightweight and rigidity by using nanocarbon fiber composite as frames [6]. And the addition of nanoparticles could improve the tyers wear resistance [7]. Thus, the application of nanotechnology is also expected as an effective way to promote the lithium-ion battery performance of electric vehicles. And there are research has already shown that special nanostructures could play a crucial role in battery performance promotion [8, 9].

This article is aimed to discuss nanotechnologies and their applications to Li-ion batteries of EVs. Basic concepts of nanotechnologies are introduced first. Then, existing problems of battery materials and more specific technologies that can be applied to commercialised cathode and promising anode materials are summarised and discussed. In the end, the future works and expectations in this area are concluded.

2. Nanotechnology and Nanomaterials

Nanotechnology (nanotech) is defined by the United States National Nanotechnology Initiative as the manipulation of matter having at least one dimension scale ranging from 1 to 100 nanometers [10]. The major benefit of nanotechnology is based on the ability to customize the structures of materials at extremely tiny sizes to obtain specified properties, significantly increasing the materials science application range. Current research in nanotechnology mainly focuses on areas of bottom-up approaches (assemble individual components into larger complexes), top-down approaches (create smaller devices by directing their assembly with larger ones) and nanomaterials.

Nanomaterials describe materials in which a single unit is between 1 and 100 nm in at least one dimension. At the nanoscale, matter can exhibit unusual properties that differ significantly from the properties of bulk materials. As shown in figure 1, from the perspective of shape, nanomaterials can be divided into nanoparticles (nanoscale includes all three dimensions), nanofibers (nanoscale of two dimensions) and nanoplates (nanoscale of one dimension). Moreover, nanostructured materials are commonly categorised by their contained phases of matter. Nanoporous materials are materials with pores in size less than 50 nm. A nanocomposite is a solid that contains at least one distinct region or collection of regions with at least one nanoscale dimension.

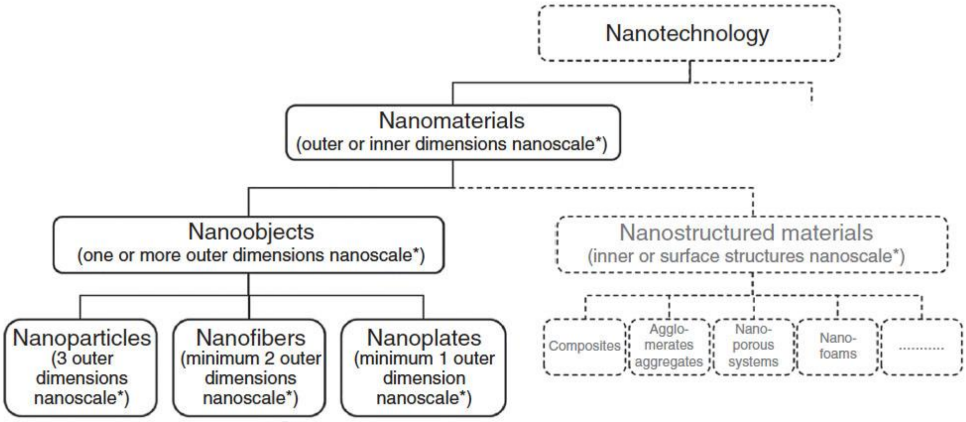

Figure 1. Classification of nanomaterials and nanostructured materials [11].

3. Lithium-ion battery materials

3.1. Cathode materials

The dominant electronics cathode material in the market is $LiCoO_2$. However, it is not suited for EV batteries due to its high cost and capacity fade under relatively high voltage. Currently, common commercialised EV battery cathode materials are LMO, NMC and NCA.

3.1.1 LMO

$LiMn_2O_4$ (LMO) is the first commercialised cathode material that has a 3D Li-ion channel, allowing for efficient Li^+ diffusion mechanisms during the charge/discharge process. It has the strengths of affordable cost, high potential and good safety and has already been commercially used in EVs like Chevy Volt and Nissan Leaf. However, there are two mean problems that cause the capacity drop of LMO cathode batteries: Jahn-Teller Distortion and Mn-ion dissolution into electrolyte during cycling.

During discharging, especially at high rates, Li-ions diffuse faster in the electrolyte than inside LMO and heap at cathode surfaces, inducing Jahn-Teller distortion that causes an irreversible cubic-to-tetrahedral phase transition. This phase transition results in lattice damage of LMO, and the mismatch between two lattices significantly impacts the Li-ion diffusion pathway, leading to capacity fading. An effective way to improve this problem with nanotech is substituting Mn^{3+} with equimolar Bi^{3+} and La^{3+}. To be more specific, Bi and La are codoped, and complex $LiBi_x$-$La_xMn_{2-2x}O_4$ is used as the cathode material. With the increase of x from 0.002 to 0.005, the lattice parameter increased, indicating the entry of Bi and La ions into the LMO spinel structure, which can stabilise the structure, resulting in an enlarged Li^+ diffusion channel [12]. Research confirmed that this nanotech could effectively improve LMO capacity retention from 89% to 95% at 1C over 80 cycles. However, when the x value is enlarged from 0.005 to 0.01, impurities are detected, affecting the performance even negatively [12].

For the Mn-ion dissolution issue, nanoscale surface doping could improve a lot. As shown in figure 2, surface doping is a nanotech that combines bulk doping and surface coating, which can both avoid direct interaction between the electrolyte and cathode and maintain the inside structure of LMO. Research reported that surface doping by Ti^{4+} can form a uniform $LiMn_{2-x}Ti_xO_4$ spinel structure layer that blocks Mn-ions dissolution by inhibiting the electrolyte erosion of LMO particles [13]. Moreover, it also offers a consecutive phase transformation from surface to bulk, which minimises phase mismatches, improving battery cycling performance significantly [13].

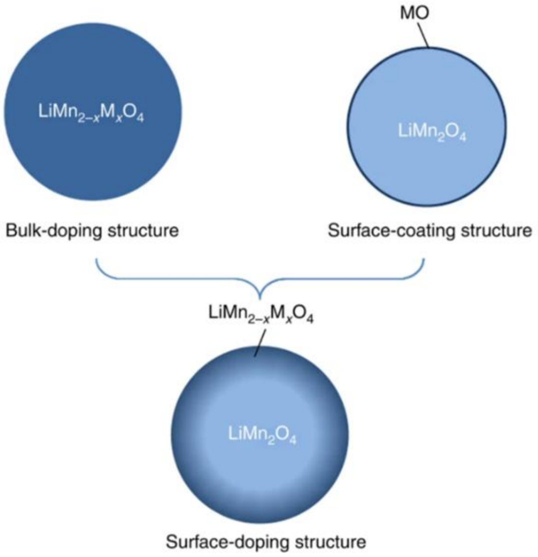

Figure 2. Structures of particles with various doping and coating technics (M is the dopant ion) [13].

3.1.2 NMC

Lithium Nickel Manganese Cobalt Oxide ($LiNi_{1-x-y}Mn_xCo_yO_2$ NMC) is also a cathode material with 3D Li-ion channels. It has already been commercially used as EV cathode material by automobile companies like Renault, Hyundai and Chevrolet. Although it has high capacity and high power, it is still afflicted with rapid capacity fading and poor rate capability.

Same as LMO, Jahn-Teller Distortion and Mn-ion dissolution can lead to capacity fading of NMC. In addition, the release of oxygen is also a reason for NMC capacity loss. As shown in figure 3 that at a high charging state, there is a repulsive force between the lattice layers and increased capacity. Nevertheless, during charging and discharging, because of the migration of metal ions and the release of oxygens, there is a shrinkage between metal ion layers, leading to a lattice failure [14]. This shrinkage closes the Li-ion channel and causes capacity drops during cycling. Synthesis of NMC particles into a special nanostructure is considered a method to solve this problem. For example, research shows that Peanut-like hierarchical nanostructure can effectively improve capacity retention from 89.2% to 94.2% after 100 cycles [15]. This is because the well-formed layered structure and excellent crystallinity of hierarchical nanostructure contribute to better structural stability, suppressing lattice distortion and shrinkage. However, synthesis conditions of hierarchical nanostructures are strict and hard to control, which might be a problem for this nanotech to be applied in EVs in scale.

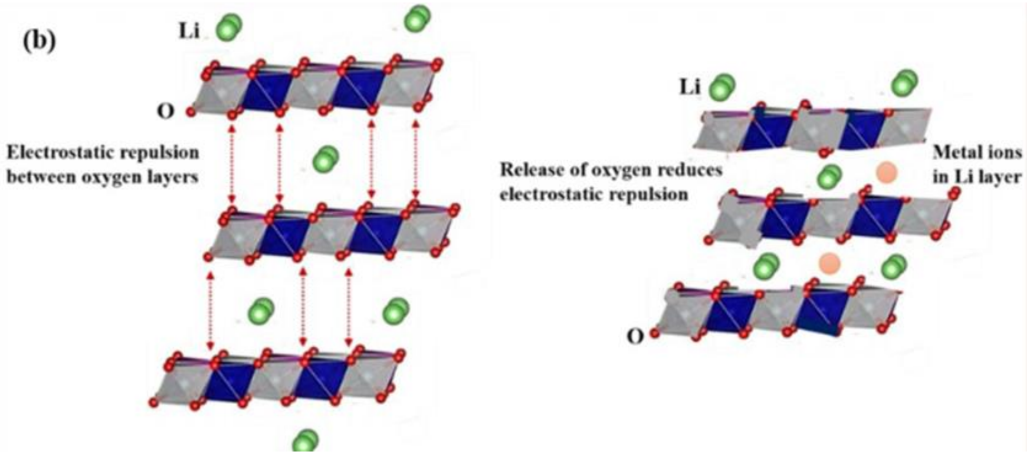

Figure 3. The schematic representation of NMC shrinkage during cycling [14].

The other strategy to improve NMC performance is the surface coating with nanostructured Fumed Metal oxides. Just as mentioned in the LMO section, it can prevent the Mn-ion dissolution by separating cathode material with electrolyte, thus improving the capacity fading issue. This nanotech also achieved 95% capacity retention after 100 cycles with coated material of Al_2O_3 [17]. Moreover, this nanotech could also improve the rate capability of NMC material. Electrolyte decomposition and Solid electrolyte interface(SEI) formation are two main reasons for unfavorable rate performance. During cycling, the electrolyte is easy to decompose, and the decomposed product interacts on the NMC surface, forming a solid electrolyte interface, which hinders the migration of lithium-ions and electrons and impacts the rate. However, the coated metal oxide layer prevents the SEI formation by reducing direct contact between electrolytes and NMC surfaces, enabling an excellent rate capability [16]. Research also mentioned that the coated thickness and materials also affect the battery performance, but the best value thickness and factors caused by materials differences still need to be investigated [16].

3.1.3 NCA

$LiNiCoAlO_2$ (NCA) is an EV battery cathode material that is rare and currently only limited to Tesla. NCA batteries have high energy density and voltage. Compared with NMC, it has an improved lifespan as it swaps the manganese with aluminum. While the pure NCA cathode material still suffers problems of noticeable capacity drop during long-time cycling and poor rate capacity at a high discharging rate.

Similarly, the electrolyte decomposition, which forms an SEI and covers the active cathode particle surface, and undesirable phase transition are significant issues that affect NCA battery performance [17]. In order to solve these issues, NCA-based composites have been used as a practical approach to enhancing electrochemical performance. Three-dimensional nanostructured NCA/graphene composite synthesised with a facile template self-assembly methode (figure 4) can greatly enhance capacity retention and rate performance. Because the three-dimensional network enhances the synergistic effect of NCA particles with graphene, and nanostructure increases surface area, a higher electronic conductivity can be achieved. Graphene sheets also reduce the contact surface with electrolytes and suppress electrode oxidation. Moreover, the layered composite structure provides better structural stability and less phase distortion. Research data also confirmed this, in which 1G-NCA (graphene-supported NCA composite with a mass fraction of 1%) promoted reversible capacity retention from 77% of pristine NCA to 82.1% at 5C after 100 cycles [17].

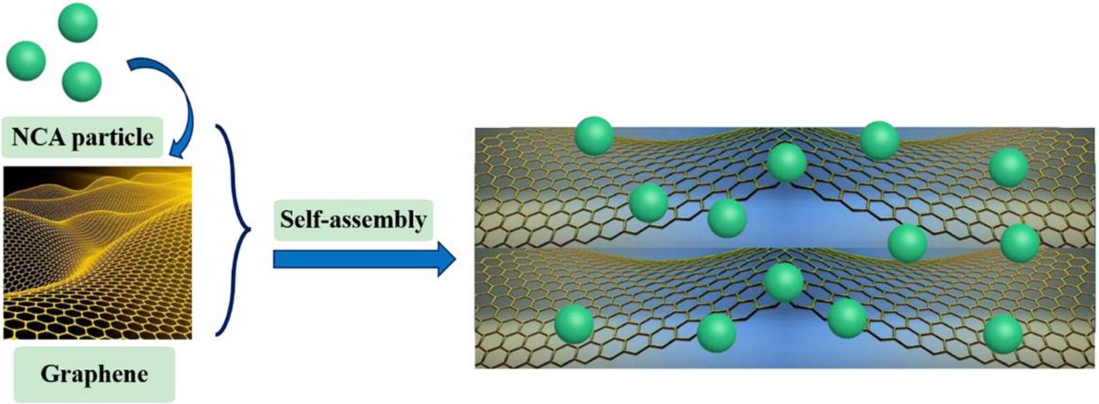

Figure 4. Schematic illustration of the G-NCA composite preparation process [17].

This nanostructured NCA/graphene composite paves the way for a long-lasting, high-rate electrode material in large-scale EV battery applications. However, this nanotech still has problems that excessive graphene (e.g. 5% mass fraction) could squeeze NCA particles and break the structure, causing a negative impact on battery performance [17].

3.2. Anode materials

The anodes in rechargeable batteries act as hosts, allowing lithium-ion intercalation/deintercalation to occur reversibly during cycling. The predominant anode material used in virtually all EV batteries is graphite due to its chemical inertness, good electrical conductivity and affordable cost. However, it is easy to undergo irreversible reactions with commonly used organic electrolytes. LTO and silicon are the two most competitive alternatives for it.

3.2.1 LTO

$Li_4Ti_5O_{12}$ (LTO) with spinel structure is regarded as a promising competitive replacement for conventional graphite anode material because of its higher voltage and safety. But compared with graphite, it suffers low electronic and Li-ion conductivity, which greatly affects the electrochemical performance.

Nanostructures are considered to enhance the electrochemical properties of LTO material, which can considerably reduce the diffusion pathway of lithium-ions within particles and increase active surface area, achieving more efficient electrochemical reactions [18]. Moreover, recent research shows that LTO nanocomposite anode can achieve outstanding capacity retention and rate capability. LTO/reduced graphite oxide (rGO) composite anodes demonstrated outstanding cycling performance with 97.2% capacity retention at a rate of 10C after 1000 cycles, and good specific discharge capacity can be delivered at 20℃, even 40℃ [19]. LTO/rGO composite (shown in figure 5) was fabricated by a controlled self-assembly method, by which rGO is distributed lamellarly all through the composite, and LTO nanoparticles are wrapped and spread evenly within the rGO sheets, forming a hierarchical structure. The rGO sheet avoids the agglomeration of LTO particles, providing a better surface activation. The synergistic effect of rGO and featured morphology shorten the Li-ion path length, resulting in higher electrical conductivity. Moreover, the layered hierarchical structure keeps good structure stability and layer-stacked channels for ion diffusion [19].

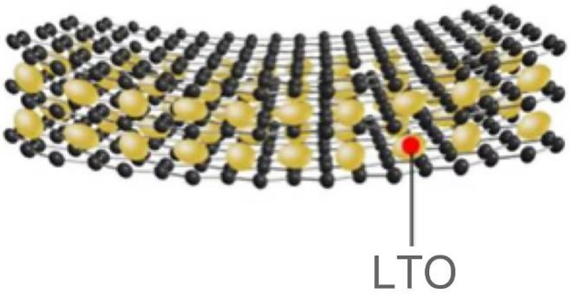

Figure 5. The schematic representation of the LTO/rGO composite [20].

Although with the help of nanotech, the problem of low conductivity has been improved, LTO could go further in the process of large-scale commercialization. It still faces the disadvantage of having a theoretical capacity (175 mAh g^{-1}) which is smaller than graphite (372 mAh g^{-1}) [18]. On that account, LTO is most appealing for high-power systems, which are mainly hybrid electric vehicles (HEVs).

3.2.2 Silicon

Silicon is an anode material under the spotlight for its huge theoretical capacity which is 3572 mAh g^{-1}. Nevertheless, it suffers the problem that an undesirable volumetric expansion of more than 300% occurs during cycling, causing the anode structure to expand and contract repeatedly, which results in silicon particle cracking, isolation and ultimately capacity loss, even stopping working [18].

Technology company Amprius discovered a nanotech to deal with the unfavorable expansion of silicon anodes, which uses pure silicon nanowire anode to replace graphite anodes directly [21]. Because the mechanical properties improved a lot for materials in the nanoscale, silicon nanowires have better tolerance to mechanical stress. Moreover, as shown in Figure 6 that the gaps between silicon nanowires can also accommodate the volumetric change, preventing the anode contraction.

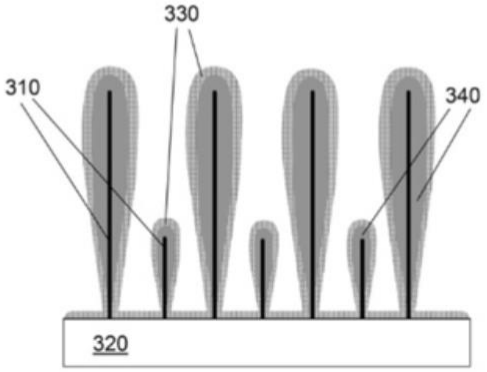

Figure 6. The cross-sectional illustration of Amprius nanowires [21].

Recently, transition metal doping to silicon nanoparticles is also reported as an efficient way to boost the silicon anode performance. Research shows that 0.5% Mn-doped silicon nanoparticles, as well as 0.5% Ni-doped nanoparticle anodes, accomplished impressive capacities, which are 2324 mAh g^{-1} and 2561 mAh g^{-1}, respectively. In addition, they also show great cycling ability that can maintain 88% and 86% capacity after 100 cycles [22]. The better mechanical properties of transition metals strengthen silicon nanoparticles and mitigate volume expansions. Moreover, the doped metals with high conductivity create necessary ionic channels for more rapid lithium-ion diffusion while shortening the length of lithium-ion diffusion through the host silicon nanoparticles, achieving excellent improvements in the electrochemical properties.

Both nanotech mentioned above confirm that silicon anode can reach excellent capacity performances, and the structure expansion issue could be solved by nanotech to a large extent. However, compared with commercialised graphite anodes, the cycling ability of silicon is still someway behind, and it can not alternate the graphite yet.

4. Prospective and Further works

Nanotechnology is expected to continue to drive advancements in lithium-ion batteries and beyond. It is also envisaged that rational designs for nanomaterials are going to continuously contribute to developing high-energy-density, great cycling ability and good rate performance lithium-ion batteries, which will eventually enable electric vehicles to achieve long-range, long-lifespan and flexible charging time.

The immediate challenge is to investigate the best composition of surface/bulk doping and self-assembling of already commercialised safe cathode materials, such as LMO, NMC and NCA, to suppress lattice distortion to a further extent. In the case of LTO anode, with its excellent safety and improved conductivity, it is expected to be commerciallised and used in HEVs in the near future. Same as LTO, silicon will significantly improve the EV performance after the expansion problem is completely solved in the future.

5. Conclusion

Electric vehicles are considered the best alternative to conventional vehicles to reduce environmental hazards, which significantly promotes the development of electric vehicle battery performance. Nanotechnologies provide solutions to existing problems of Li-ion batteries to a large extent. An overview of nanotechnologies and their application to lithium-ion electric vehicle batteries is provided in this article, including the three most common commercialised cathode materials (LMO, NMC and NCA) and two promising competitive anode materials (LTO and silicon). Nano-coating technology can suppress the lattice distortion and prevent electrolyte decomposition of LMO and NMC. Well-formed layered 3-D nanostructured composites could promote conductivity and hold ion diffusion channels of NCA and LTO. And the strong mechanical property of nanomaterials mitigates the phase swelling of silicon anode. However, further research still needs to investigate the quantitive effects of nanocoating thickness and composite composition to achieve the best performance. Moreover, although silicon can offer excellent charge capacity, the cycling ability still needs to be improved to reach ideal performance. Nanotechnology and electric vehicles are combined in this article, and it is proposed to provide innovative ideas for their development.

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