Research of Different Materials Used in Lithium Batteries and Combination with Nanomaterials

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Abstract. Ever since the 2nd industrial revolution, people's demand of energy has increased a lot not just high power but also convenience and security. Batteries have been popular among people of all ages since it was invented for it satisfied most of them. However, most of them can only be used once so that is the reason why lithium-ion rechargeable batteries are invented. Lithium-ion batteries hold well on their mass and volume, which solves the bulks' obstacles over centuries. More importantly, they own wonderful voltage as well as capacity. With the development of lithium-ion batteries, people's demand of better materials became more and more stronger. Graphite material has had a dominant position in both commercial and industrial area. However, there are more extraordinary compounds whose properties like capacity and potential are better than those of carbon. Therefore, several new materials that scientists researched about are introduced below to compare them with carbon. Meanwhile, nanomaterials have caught people's eyes because they are newborn subject for science. By modification, they can improve properties of different materials. This article is a literature review of lithium-ion batteries. Moreover, it will combine batteries with nanomaterials together to explore better methods to use in lithium-ion batteries.

Keywords: Lithium-ion batteries; Nanomaterials; Anode; Cathode.

1. Introduction

Traditional fuels like petrol that are often used always have a large amount of greenhouse gas emission, which do a large harm to the environment and global warming [1]. Therefore, the governments tried to solve the problems by changing the original bunkers into electric charges [2].

Lithium batteries have been trying to be created since the last two decades. Due to traditional batteries' low efficiency and limited energy, they could not satisfy the requirements of the power supply in the industrial fields [3]. After lithium batteries were invented, they later emerged in Japan for the use in cameras, laptops and cell phones, which first turned lithium-ion chemistry into commercial products [4].

Compared to other sorts of charges, for instance Ni-Cd and Ni-MH, Lithium-ion batteries (LIB) own better energy as well as density. However, it is impossible to put them into use especially in industrial applications due to the high power. Therefore, there's still a long way to go in order to spread LIB across [5,6].

The word 'nano' has been used in many kinds of fields of knowledge and refers to the low weight and height of a person initially, which finally represents the material whose size is among 1-100nm materials. Based on in-common physical and chemical properties, they can be divided into five main categories [7]. With the development of nanomaterials, they have been applied to different fields as well as the batteries. For example, carbon nanomaterials are widely used, and they are famous for microscopy structure, which has low density, high intensity, extraordinary conductivity and flexibility [8].

The working principles of LIB are quite similar to traditional ones, and they have three main components: anode, cathode and electrolyte. The positive charge is where reduction reaction happens, and its component are often lithium metal oxide while the negative charge is the opposite. We use carbon anode as an example to describe the working function of LIBs [9] (Fig 1).

Charge reactions:

At the anode: $Li_nC_6 \longleftarrow Li_0C_6 + nLi^+ + ne^-$;

At the cathode: $Li_{m-n}MO_2 + nLi^+ + ne^- \longleftarrow Li_mMO_2$;

Global reaction: $Li_nC_6 + Li_{m-n}MO_2 \longleftarrow Li_0C_6 + Li_mMO_2$.

Fig 1. Charge reactions of carbon anode LIBs [9].

The cathode gives out the electrons and the anode receives them and thus the current is formed. The whole LIB battery component is shown below **Fig 2**.

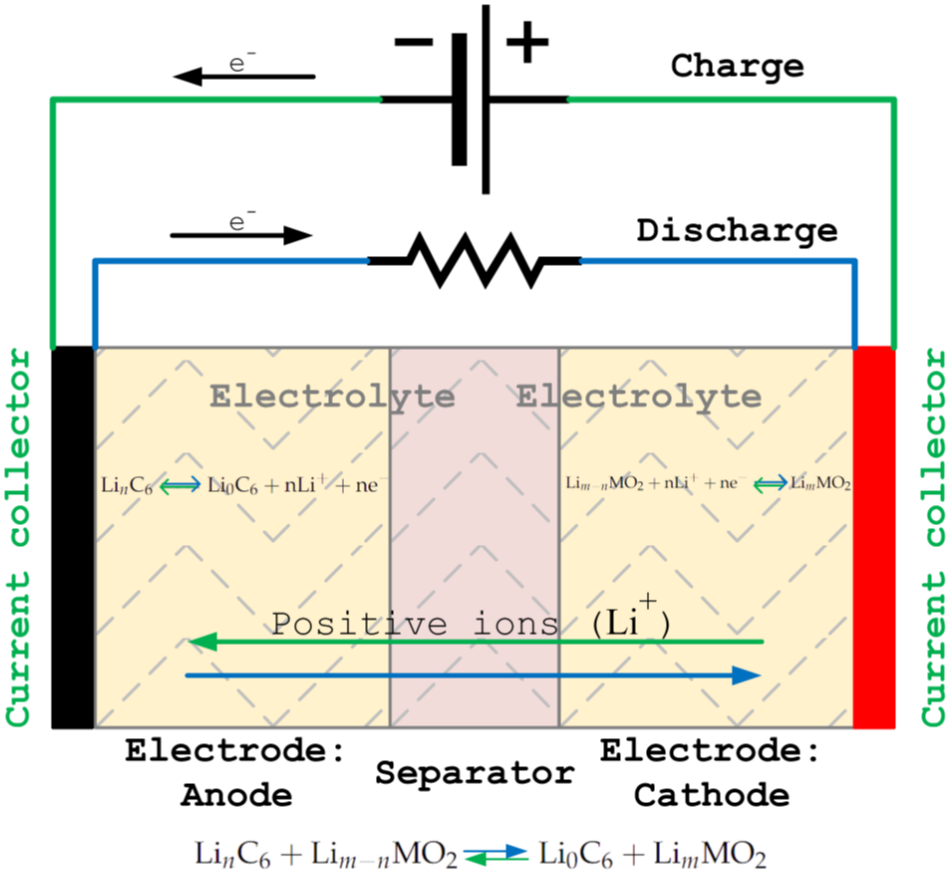

Fig 2. The formulas as well as the processes of charging and discharging [9].

It is known to us all that LIB can be divided into three essential parts: anodes, cathodes and electrolyte. Therefore, this article will mainly talk about the anode and cathode materials that have been used in LIBs and it will be described in the order of the batteries' parts.

2. Materials of the Electrodes

2.1. Anode Materials

The anode is where oxidation reactions happen and they are the most important to measure whether a battery is effective enough, so they should not be active material such as metals. For this reason, lots of high-performance and novel materials are found and three stable anode materials: carbon, silicon and metal sulfide compounds are chosen to be discussed. Carbon and graphite are widely used because of their low cost as well as high ion conductivity. However, silicon has been regarded as one of the best alternatives because of their wonderful capacity in theory and perfect working voltage [10].

2.1.1 Graphene or Graphite material (Carbon nanomaterial)

Carbon nanomaterials are the foundation during the development of LIB after they replaced the firstly used hard carbon. Graphite material has low de−/lithiation potential and specific capacity of 372 mAh g^{-1}(theory), as a consequence, it improves the density of LIBs [11].

Carbon nanomaterials offer exceptional electrical conductivity and a large theoretical surface area. Meanwhile, because of the different sorts of nanomaterials, carbon nanomaterials have different categories as well, such as carbon nanotubes and graphene with a single layer of carbon atoms. Therefore, various morphologies lead to the flexibility of the batteries, which means they can be wearable in biology [12].

Carbon nanotubes can be fabricated into distinct dimensional microscopy structures owing to the ultrahigh length-to-diameter ratio. Moreover, graphene is one of the newest stuff among carbon materials. When used in anodes, graphene can facilitate rapid lithium-ion diffusion, leading to improved rate performance.

It seems that there are still shortcomings for carbon nanomaterials to improve. For example, their cycle stability should be enhanced, and the production cost must be lower [13]. Even though carbon nanomaterials may not the best choice for LIBs, they still occupy the majority position of the market share, which shows the fact that they keep well balance between their costs and their properties. Fortunately, Kaiser and Smet have tried to improve the graphite performance. It claimed that they found reversible superdense ordering of graphene layers with over -372 mAh/g potential [14]. The research reported by Zhu et al. shows graphite intercalation compounds (GICs) can increase the ability for Li storage [15]. Moreover, Dahn et al. claimed that specific electrolytes could provide plating Li thus leading to higher LIBs density [16]. As a matter of fact, these reports are not enough, there is still a long way to go for carbon nanomaterials [17].

2.1.2 Silicon and Silicon Oxide Nanoparticles

Silicon has been treated as next-generation LIB anode for it has a much higher capacity than graphite especially in the gravimetric capacity potential field. It has 4200 mAh·g^{-1} in theory, more than 11 times that of graphite of 372 mAh·g^{-1}. What's more, Si is the second most abundant element in soil and more eco-friendly, which makes it an attractive alternative for anode material [11,18].

Scientists called Xinzhi Li, Meng Zhang, Prof. Shuxia Yuan and Prof. Chunxiang Lu have proved that silicon is better than graphite because it can definitely shorten the transmission distance of lithium ions, thus raising the capacity of nanostructured anodes. They recognized that though graphite ones have better electrical conductivity than silicon, they offer much more safety issues due to higher voltage. Silicon's potential is much lower when operating. However, it cannot be applied to practical use for following reasons. Firstly, while being alloyed and dealloyed with ions, the crystal structure of the silicon will be destroyed. Consequently, voltage will change and be unstable [11].

However, A.M. Wilson and his colleagues noticed silicon's large volume expansion upon lithium insertion is around 360% for $Li_{4.4}Si$ that leads to poor cyclability [19]. To alleviate the problem, we can try to nanosizing silicon by reducing the mechanical stress and altering strategies to enhance the electrode's structural integrity [18].

2.1.3 Metal and metal oxides

Metal and metal oxides, such as lithium itself and tin oxide (SnO2), have been explored for their high theoretical capacities. Graphite anodes are on their bottlenecks for they are heavy and have limited densities. As for LIBs, theoretical specific capacities are the higher, the better while negative electrochemical potentials are the opposite. Therefore, lithium itself can definitely be taken into consideration as it has capacities of 3860 mAh g^{-1} and 2061 mAh cm^{-3} and −3.04 V negative potential compared to hydrogen electrodes [20].

Metal oxide anodes have been regarded as another choice to take the place of carbon anodes because they are not poisonous and with special properties [10]. Take iron as an example, it naturally has two common oxides: Fe_2O_3 and Fe_3O_4. The report by Tarascon and co-workers shows the transition formula: $Fe_2O_3 + 6Li^+ + 6e^- \leftrightharpoons 2Fe + 3Li_2O$ owns 1006 mAh g^{-1} in theory [21], which is also several times of carbon. Moreover, Fe_2O_3's expansion voltage is range to 0.005−3.0 V, much smaller than both silicon and graphite. Fe_3O_4 has raised the people's interest since decades ago. It has extraordinary capacity as well (~926 $mAhg^{-1}$).

However, they both have drawbacks which have not been solved. Because of oxygen's physical properties and its limited weight, while the metal is covered by its small thickness the whole battery will stop reacting gradually and LIBs' efficiency will be decreased consequently. More importantly, lithium is one of the most active metals among all the elements, so it is quite hard to control the reaction speed, and the techniques are still immature [20]. Besides, it is known to all that transition metal oxides and sulfides have poor electrical conductivity compared to metals [10].
One practical method is to nanostructure these materials can improve their electrochemical performance by increasing the active surface area and reducing the diffusion length for lithium ions.

2.2. Cathode Materials

The cathode material is crucial for the battery's energy density and voltage and it accounts for more than 40% in rechargeable LIBs. Interestingly, the 2019 Noble Prize in Chemistry is presented to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino to award their efforts for the development of LIBs [22]. Using nanomaterials in the cathode can improve the battery's overall performance by enhancing the redox reaction kinetics.

2.2.1 Layered structures LiCoO2

$LiCoO_2$ has been applied to commercial usage long time ago, which is the earliest among all cathodes. Its crystal structure ensures the stability of the cations and lithium ions with octahedral structures and six oxygen atoms closely around them **Fig 3**. Besides, its theoretical capacity is as high as 274 mAh g^{-1}. Nevertheless, though $LiCoO_2$ has a high capacity in theory, it can only release more than half of it during the reaction (140 mAh g^{-1}). That is because when the charge voltage reaches to 4.2 V, the amount of lithium ion will decrease and be released, leading to LIBs low efficiency [23]. For $LiCoO_2$ seems to be an ideal cathode material, scientists made plenty of efforts in order to cope with lithium ions lost. One doable way is to $LiCoO_2$'s surface modification with carbon. It can keep the cathode away from the electrolyte and prevent the decomposition of lithium.

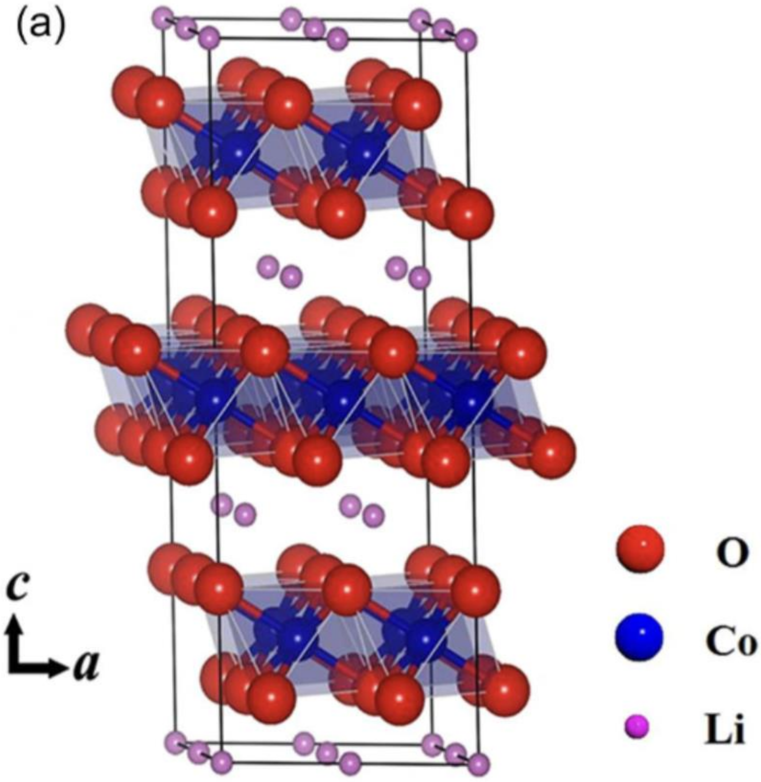

Fig 3. Crystal structure of $LiCoO_2$ [23].

2.2.2 Lithium Manganese Oxides (LiMn2O4)

Spinel-structured lithium manganese oxides are known for their thermal stability and safety profile. It was brought forward by Thackeray et al.in 1983 and had application in both academic and industrial filed. It is popular among people by several reasons: Firstly, it has a specific three-dimensional structure which equally contains Mn^{2+} and Mn^{3+}. Secondly, the capacity is around 148 mAh g^{-1} lower than both theoretical and discharge ones of $LiCoO_2$ (Figure 4).

Although it has many advantages, there still exists some problems. Both $LiMn_2O_4$ and $LiCoO_2$ have phase transitions during battery reactions, and they have capacity loss especially under high temperature. What's more, short cyclable life is another difficulty to conquer. The happening reason can be concluded as follows: Jahn-Teller effect, Corrosion effect from electrolyte and Dissolution of Mn. Jahn-Teller effect has the largest influence among three effects. During this period, the structure will change which contribute to particle collapse collide with each other then reduce the conductivity.

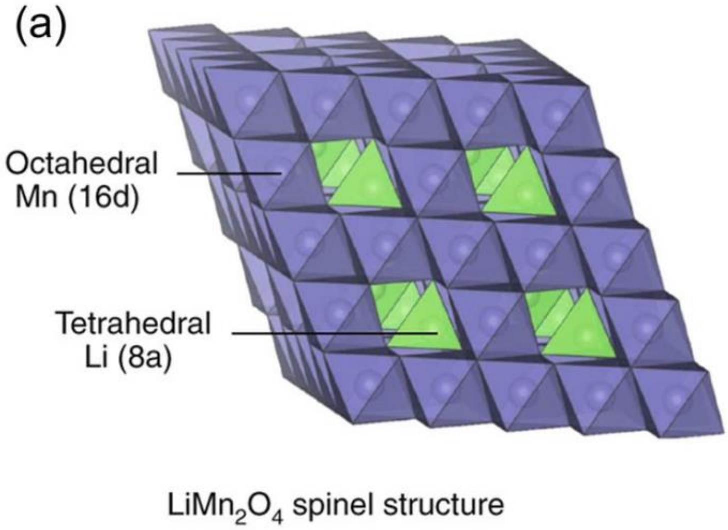

Fig 4. $LiMn_2O_4$ spinel structure [23].

2.2.3 Lithium Iron Phosphate (LiFePO4)

The research about lithium iron phosphate came much later than the other materials not until it was firstly found by the Goodenough group in 1997 [24]. However, compared to other traditional cathodes which are mentioned above, it is more promising with its 170 $mAhg^{-1}$ perfect capacity even at room temperature and longer cyclable life [25]. Meanwhile, with an olivine structure, LiFePO4 offers a stable platform for lithium ions. Consequently, it seems one of the best to match the mechanisms of the LIBs while using as the cathode (Figure 5).

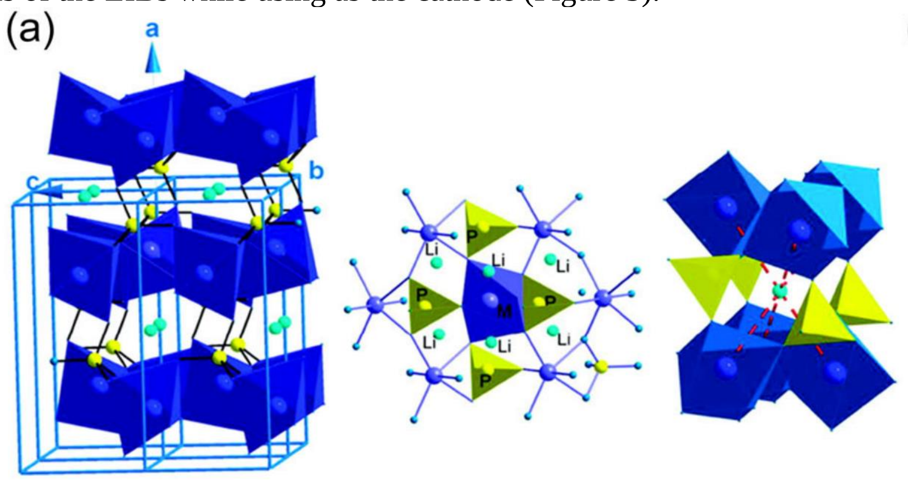

Fig 5. $LiFePO_4$'s crystalized structure [23].

Nevertheless, it has lower electricity conductivity. Researchers have been trying to figure it out by modification. Several sorts of these methods have been included and take surface modification as an example. The definition of this noun phrase is to change the material on the surface and carbon coat is one of the most famous. After covering, it appears great electrochemical properties but prevents lithium ions' transition, so it is hard to say whether the efficiency has been improved or not. Fortunately, reduced metal oxides (RGO) came out. By its porous structure, lithium ions will have faster diffusion. Some scientists have tried to mis these two cathode materials together and studies have been done on this considerable theory [25].

2.2.4 Lithium rich Layered Metal Oxides (LRLOs)

The name of this kind of cathode is quite similar to the three examples above and that is because the only distinction of them is their structure. Unlike traditional ones which rely on redox action that transits metal ions, its mechanism includes oxygen and redox actions both.

However, it can accelerate LIBs' corrosion thus reducing the life span of the batteries. High-voltage cathode materials like lithium nickel manganese cobalt oxide (NMC) and lithium nickel cobalt aluminum oxide (NCA) faced the same situation of voltage decay. When comes to this case, nanostructure can have a huge impact. LRLOs can benefit a lot while reacting in a crystal structure [26].

2.3. Nanostructured Electrodes

Apart from choosing electrode materials, it is recommended that make some changes based on those materials. In recent years, nanostructures have raised people's interest and attracted more research. Nanostructure can be defined by different scale sizes: one, two or three dimensions which ranges from 1-100 nm [27].

Beyond individual nanomaterials, the design of nanostructured electrodes is critical for maximizing the densities of nanomaterials. Moreover, security and cost should also be taken into consideration.

Techniques such as nanocomposites, where nanomaterials are combined with conductive agents and binders, can create a synergistic effect that further improves battery performance.

2.3.1 Surface structures

Surface structures mean fibrining materials into different nanostructures. As we all know, nanomaterials own large surface-to-volume ratio, which can increase the active material's exposure to the electrolyte then accelerate the reaction process and reduce the impact of side reactions. Moreover, there are ligands that can be attached to the surface. Those connections are important components to improve LIBs' properties [28]. In this part, three commonly usedexample will be discussed in detail.

2.3.2 Composite Structures:

Composite structures mean combining different nanomaterials together then leverage their individual strengths. For example, a silicon nanoparticle anode can be combined with graphene to enhance conductivity and mechanical stability. Nanosizing can increase the tap density and improve the structural stability during charge-discharge cycles.

2.3.3 Porous Nanostructures:

Porous Nanostructures are another method to make more material explore to the electrolytes thus reducing the consumption of raw materials.

3. Conclusion

Porous nanomaterials can provide additional benefits, such as increased electrolyte accessibility and reduced diffusion path lengths for lithium ions, leading to improved rate performance and capacity. The integration of nanomaterials in the anode and cathode of lithium-ion batteries offers a pathway to overcome current limitations and achieve the next generation of high-performance energy storage systems. Continued research into material synthesis, nanostructure design, and understanding of lithium-ion transport mechanisms will be pivotal in realizing the full potential of nanomaterials in LIBs. This paper has provided an overview of the role of nanomaterials in enhancing the performance of anodes and cathodes in lithium-ion batteries. The unique properties of nanomaterials, when harnessed effectively, can lead to significant improvements in energy density, power density, cycle life, and safety of LIBs. As research progresses, the development of novel nanomaterials and their strategic integration into battery architectures will continue to push the boundaries of energy storage technology.

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