

Emerging Electrode Materials for Lithium-Ion Batteries

Han Zhang*

Earl Warren College, The University of California, San Diego, 92093, US

* Corresponding Author Email: haz046@ucsd.edu

Abstract. In the past, engine combustion vehicles are one of the most popular traffic tools for people to consider when they want to go out. Developed technologies provide people with more options, such as hybrid and battery electric vehicles. This paper includes a discussion of the applications of nanotechnology in electric vehicles. The paper is divided into two big parts: cathode and anode materials. After researching many resources online, the significance of nanotechnology applications in electric vehicles can be understood better now. One of the most known batteries people use today is the Li-ion battery. The most common one used in the cathode is phosphates, and the most common one used in the anode is graphites. Phosphates also have many alternatives like cobalt, iron and nickel. They all have advantages and disadvantages, and the mission of scientists is to convert disadvantages into advantages. Graphites also play an important role in running a Li-ion battery, but scientists today are looking for better options to replace graphites. Although it is still difficult to achieve the goal of applying nanotechnology in every area of electric vehicles, today's study of nanotechnology in electric vehicles has reference significance, encouraging people to study further.

Keywords: Electric vehicles, Li-ion batteries, Cathode, Anode.

1. Introduction

As more new energy sources are introduced to our daily life, people are becoming increasingly independent from fossil fuels. The action of searching for more new energy sources brings many benefits to the environment. In the past, people had no choice when they bought a car. The only choice was a combustion engine vehicle. However, People today are different from the past. They have more choices now, like hybrid vehicles, fuel-cell vehicles or pure battery vehicles. These days, Li-ion batteries have become a hot topic for scientists. For Li-ion batteries, electrons are formed when a lithium ion moves from the cathode to the anode [1]. The cathode will release lithium ions when the battery is charging; however, when the battery is discharging, the anode will release lithium ions [1].

Moreover, increased people choose electric vehicles because they release less carbon dioxide emissions than conventional vehicles and cost fewer maintenance fees. However, today's commercial Li-ion batteries face some obstacles, such as safety problems, immature markets, etc. Among these obstacles, alternative cathode and anode materials are the most significant. Right now, the widely used cathode is $LiCoO_2$ and the widely used anode is graphite; however, with the development of the technology, they should be obsoleted for several reasons such as unfriendliness to the environment and high cost. Thus, new materials like $LiFePO_4$ have been introduced to replace the position of $LiCoO_2$ due to its suitable capacity and low cost; $Li_4Ti_5O_{12}$ has been introduced to replace graphite due to its high safety and good cycle ability. Although these alternatives are not perfect enough, and they all have their defects, it is still significant for scientists to keep seeking new alternatives and studying them. The rest paper will be divided into four big sections. First, the reasons why people seek new energy sources will be presented. Secondly, the characteristics and developments of cathode material- $LiFePO_4$ will be discussed. Then, the third section will talk about how to upgrade graphites and the alternative anode material- $Li_4Ti_5O_{12}$. The last part will summarize the above information and discuss their future potential [2].

3.1. Characteristics of LiFePO_4

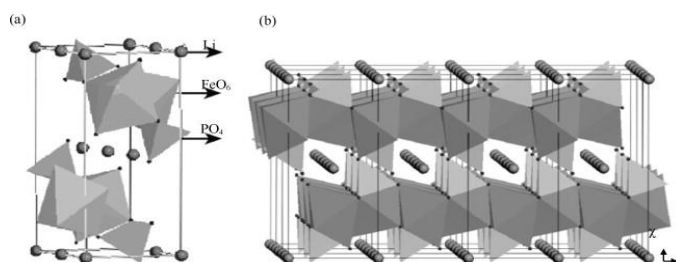


Figure 2 LiFePO_4 crystal structure (a) and the olivine's structure (b) [5].

LiFePO_4 is a phosphate when Fe^{2+} is oxidized to Fe^{3+} and it delithiates to FePO_4 . Its crystal structure can be shown in Figure 2 [5]. LiFePO_4 has different cation structures. Tetrahedral sites include element P, which is also in a hexagonal framework, while octahedral sites include elements Li and Fe [5]. Octahedron LiO_6 and tetrahedron PO_4 are sharing edges in FeO_6 with no continuous connection [5]. In that case, there are Li^+ flowing in the tunnel formed by this special structure. Comparing with LiCoO_2 , LiFePO_4 has a suitable discharge capacity which is 170 mA hg^{-1} , a compatible voltage at 3.4 V versus Li^+/Li , cheap price and environmental friendliness [6]. Although LiFePO_4 has many advantages, it still has its disadvantages that need to be overcome, such as low electronic conductivity and ion diffusion rate [7].

3.2. Development of LiFePO_4

To explain this weakness, scientists attribute this characteristic to the frameworks of poly anions [1]. To develop better conductivity and enhance efficiency, nanocoating like polymer even has been introduced into this study [1]. Studies show that polymer nanocomposites can improve conventional properties at macro and micro scales [8]. This finding allows batteries to complete their charge or discharge in a few minutes. Different carbon sources play different roles in their electrochemical performances. Carbon nanotubes are nanometer-scale diameters forming a tubular structure [9]. It is shown in Figure 3. Due to this incredibly special structure and its C-C covalent bonding can have good heat conductivity, outstanding durability and great electrical conductivity. Moreover, different walls of carbon nanotubes make them function differently. Many pieces of research have concluded that different types of carbon sources and amounts of carbon sources can result in different coating thickness, density and discharge capacity [5].

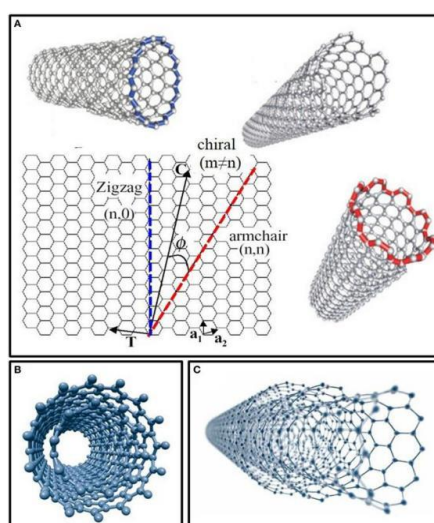


Figure 3 Different structures with different walls in carbon nanotubes. (A) Single-walled carbon nanotubes. (B) Double-walled carbon nanotubes. (C) Multi-walled carbon nanotubes [9].

Another way to enhance the low diffusion rate and small electronic conductivity of LiFePO_4 is to add metal dispersion. The way that the metal coating improves the electrochemical performance is

not to change LiFePO_4 's structure, but to increase its chemical kinetic energy [5]. To make the result better, the control of composition and content of metal must be realized and understood [5]. Metal oxides like ZnO and TiO_2 also, work by improving the electrochemical performance at a high charge/discharge rate [5]. Study shows that TiO_2 can enhance the capacity of LiFePO_4 , but it also influences the cell negatively, so CeO_2 is also introduced to solve the problem of TiO_2 , making it possible to improve the performance of LiFePO_4 under room temperature and 40 degrees [5].

As nanocoating of carbon and metal or metal oxide dispersion do not work in the internal system of electrochemical conductivity and LiFePO_4 does not have a small enough particle size, increasing internal conductivity can be achieved by ion-doping method [5]. Ion-doping has influenced the proliferation of Li-ion. For example, the replacement of the Li-site by Ti^{+4} leads to the changing of the portion of Fe^{+3} and Fe^{+2} , showing that ion-doping does not only change the morphology but also LiFePO_4 's electrochemical properties [5]. Fe-doping site has also been proved as an effective method for improving internal conductivity. This Fe-doping has better discharge capacities and cyclic stability than those not doped or coated with carbon [5]. Unlike nanocoating and metal dispersion, ion dopants such as Zn^{+2} and Cu^{+2} can influence the structure of LiFePO_4 to upgrade its electrochemical properties. There are still many other technologies to affect the electrochemical conductivity of LiFePO_4 , such as heat treating, but this heat treating requires an extra conductive phase called Fe_2P [4]. During this process, it is important to take care of the amount of Fe_2P , because an excessive amount may cause the failure of running a lithium-ion battery [4].

4. Anode Materials

In Li-ion batteries, the commercialized anode material is mostly graphite in the market, with its electrochemical properties tied to Li-ion's reversible intercalation/deintercalation: $6\text{C} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{C}_6$ ($0 < x < 1$) [1]. In this case, LiC_6 has a suitable capacity of 372 mAh g^{-1} and this superiority helps it to be chosen by many electronic devices [1]. However, graphite has its disadvantages. If some organic electrolytes react with graphite, it may cause side reactions resulting in the decomposition of the electrolyte [1]. Since anode materials attach great significance to the stability and safety of Li-ion batteries, scientists are actively seeking alternatives to replace or upgrade graphite anode. One anode material that has been investigated by scientists today is $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO).

4.1. Characteristics of $\text{Li}_4\text{Ti}_5\text{O}_{12}$

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be prepared by Li_2CO_3 and TiO_2 with the formula: $2\text{Li}_2\text{CO}_3 + 5\text{TiO}_2 \rightarrow \text{Li}_4\text{Ti}_5\text{O}_{12} + 2\text{CO}_2 \uparrow$ [10]. The crystal structure is shown in Figure 4 of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 75% of lithium ions take up tetrahedral sites; the rest are in octahedral sites; 32e sites are occupied by titanium ions and oxygen ions [11]. The spinel framework gives lithium ions a channel to flow into the LTO lattice and take the sites of octahedra [1]. Since LTO has a stable voltage at 1.55 V versus Li^+/Li , and it will hardly change its volume during insertion/desertion. LTO has some great properties that others do not have, such as fast Li^+ Insertion ability, good kinetics and cycle ability [10]. LTO is different from graphite, meaning that its reaction will not result in the decomposition of the electrolyte but improves safety simultaneously. However, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is facing two major obstacles right now: (1) its capacity of 175 mAh g^{-1} is not big enough, and (2) its electrochemical conductivity is low. If $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be widely used in the future, both problems should be solved to replace graphite [1].

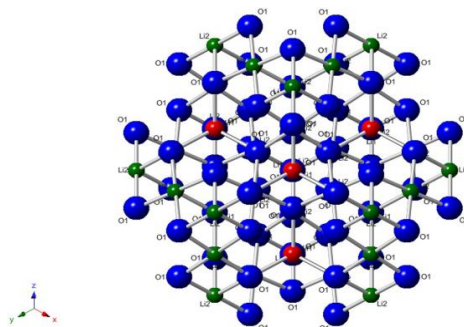


Figure 4 The crystal structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [11].

4.2. Development of $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Nanostructures can be introduced into this condition to enhance the electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by reducing the diffusion of the Li-ion and increasing the areas to the electrolyte [1]. This way, LTO will get a large current to run [1]. Today, many researchers also focus on finding new methods to create new nanostructures, and the new trial requires ion doping which can enhance the high rate of performance. Just like cathode, doping affects the structure of LTO directly. Many metals have been studied to influence the LTO, and one would be the W dopant. The $\text{Li}_4\text{Ti}_{5-x}\text{W}_x\text{O}_{12}$ with W substitution improves the capability of LTO due to the high oxidation state of W^{6+} [12]. This high oxidation state makes It possible for Ti to reduce from Ti^{4+} to Ti^{3+} and results in a higher conductivity and rate performance due to a charge compensation W^{6+} [12]. The study has proven that under a large discharge rate, W-doped LTO can have a large capacity, good reversibility and electrochemical performance [12].

Carbon coating created by thermal vapor decomposition (TVD) also provides anode in LIBs with better electrochemical performance [13]. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated with carbon has a better rate of performance than uncoated LTO because the coating can decrease the resistance of the electrode and serve as a conductive phase [13]. Another thing that needs to be aware of is the thickness of the carbon layer since the electronic conductivity depends on the thickness. While having a thicker layer, the LTO will show a better electron transfer path, leading to fewer defects but better properties [13].

4.3. Upgrade Graphite Anode

Since scientists are seeking alternatives for graphite and considering how to make it better, mild oxidation can be used to improve graphite's electrochemical performance [14]. Mild oxidation is effective for increasing capacity and enhancing lithium intercalation because it not only forms the production of nanochannels but also oxidized layers [14]. However, during the oxidation process, the rate should be paid attention to, so the reaction should not be too fast. Oxidation ability plays an important role in reversible capacity, and its stability also depends on oxidation ability. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ has shown a good oxidation ability to upgrade the reversible capacity of natural graphite, but the problem is that it is not a green oxidant to the environment, so other oxidants like $\text{Ce}(\text{SO}_4)_2$ are also introduced to this area [14]. It is shown in Figure 5.

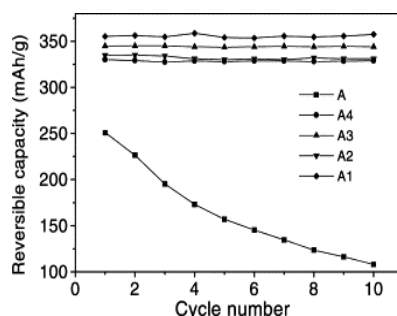


Figure 5 Different cycling behavior of common natural graphites (A) before and after oxidation by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (A1), HNO_3 (A2), $\text{Ce}(\text{SO}_4)_2$ (A3) and H_2O_2 (A4) at 60°C [14].

5. Conclusion

In summary, there are many similarities in enhancing the electrochemical performance of cathode and anode materials. For example, they both rely on nanocoating and nanostructures to directly influence the structure of materials, making it possible to improve rate performance. Even though the nanocoating materials are the same as carbon nanotubes and polymers, they apply the same effect on both cathode and anode materials. For the alternative of LiCoO_2 — LiFePO_4 , LiFePO_4 has advantages of good capacity, compatible voltages and low cost, but it also has two problems to overcome: low diffusion rate and small electronic conductivity. To this, three methods are proposed: (1) nanocoatings such as polymer 11 and carbon nanotubes can affect its density and discharge/charge capacity, and (2) metal/metal oxides dispersion applies the same effect on it, but one thing should be aware of is the amount of metal/metal oxide and (3) to influence the internal electronic conductivity directly, ion-doping is added to increase the proliferation of Li-ion. For the alternative of graphite— $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has advantages of negligible volume changing, fast Li^+ insertion ability, stable voltage, good kinetics and cycle ability; nevertheless, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has low capacity and electronic conductivity just like LiFePO_4 . To enhance both issues, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ practices similar methods as LiFePO_4 : (1) nanostructure of the $\text{Li}_4\text{Ti}_{5-x}\text{W}_x\text{O}_{12}$ with W substitution is optimized to lower the diffusion rate of the Li-ion and increase areas to the electrolyte, and (2) carbon coating by TVD will give a better electron transfer path. Another way of directly working on graphite is to upgrade itself by mild oxidation, resulting in better electrochemical performance. For all the reasons above, the path of seeking new sources should not stop even though scientists may find a better alternative, because if people want to live in a greener house in the future, some ungreen chemical materials should be replaced by better ones. It is easy to understand that the path to seeking green alternatives is still long, and only more research can contribute to a better future.

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