Application of metal oxide-based materials for improving the performance of lithium-ion batteries

Xinghao Wang*
1Queen Mary University of London Engineering School, NPU, Northwestern Polytechnical University, Xi'an, China
*Corresponding author: wang-xinghao@mail.nwpu.edu.cn

Abstract. With the continuous development of electric vehicles, battery technology has also been developed rapidly. Lithium-ion batteries (LIBs) with a variety of advantages become the primary choice of the current battery industry. The global demand for lithium element also shows a rapidly rising trend, however, the global supply of lithium is in a relatively urgent stage. By improving the service life and efficiency of LIBs has become a hot research topic. One of the research directions is to improve the performance of battery by improving the structure of electrode materials, and metal oxide materials have become an important part of improving the performance of electrode materials by virtue of their low cost, high structural stability, high service life and high energy density. This research will introduce manganese-based oxide cathode materials, chromium oxide cathode materials, nanostructured copper oxide anode materials, and carbon/metal oxide composite anode materials. These four types of materials can improve the service life and electrochemical performance of LIBs by improving the structural stability of the materials and increasing the flow rate of lithium ions at the electrode.

Keywords: LIBs; Metal oxide; Energy density; Capacity; Lifetime.

1. Introduction

New energy vehicles have been widely supported by governments, and lithium-ion batteries (LIBs) have become the current choice of the new energy vehicle industry by virtue of their high energy density and long cycle life. The current mainstream battery technologies for new energy vehicles are lithium nickel cobalt aluminate (NCA). Ying et al. predicted the global demand for lithium to reach 17.36-21.94 million tons in 2050 in a net-zero emissions scenario [1]. However, the mine production of lithium is only 180 thousand tons. The performance of LIBs and the production of lithium will be directly related to the growth prospects of the new energy industry. The global supply of lithium still remains at a relatively urgent stage, and how to efficiently utilize the limited lithium resources in the earth has become an important research proposition in the field of LIBs, in which improving the energy density and lifetime of LIBs is an important means to enhance the utilization of lithium resources.

The main problems faced by LIBs are limited energy density of electrode materials, low battery capacity and short battery life. During the charging process, lithium ions are lost from the positive electrode, resulting in a layered structure that is easily affected by external factors, which in turn causes a decrease in battery life and energy density. Increasing the lithium storage capacity of the positive electrode or improving the structure of the oxide of the positive electrode material has become a hot research topic nowadays. Improving the lithium storage capacity of electrode materials to extend the service life of the battery has become a hot research topic nowadays. The current mainstream research routes can be divided into the following two, the first is to improve the energy density of LIBs by optimizing the structure of electrode materials. Wang et al. improved the storage capacity and service life of Li-ion batteries by introducing chemical short-range disorder (CSRD) to the cathode to reduce the impact of Li-ion loss on the structure of the cathode oxide under charging conditions [2]. The second improvement method is to increase the energy density of LIBs by improving the cathode material components. Lin et al. designed a lithium-rich compound

$Li_2[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$, which significantly increased the lithium-ion concentration in the cathode oxide, resulting in improved energy density and battery life [3].

In the research process of increasing the energy density of LIBs, metal oxides have become an important class of materials to improve the loss of lithium ions during the battery charging process. Similar to the above, metal oxides can also improve the energy density and lifetime of the battery by increasing the lithium storage capacity and improving the anode oxide structure. Meanwhile, metal oxides can also have a reversible reaction with lithium ions through a conversion reaction to form a composite structure of lithium salts and metal oxide particles to maintain the stability of the anode [4]. Nano-metal oxides can also form a composite material with carbon, which combines the advantages of two kinds of materials and can improve the energy density and service life of the electrode material by improving the flow rate of lithium ions and the stability of the material structure. This research will focus on four types of metal oxide electrode materials and discuss the principles of these four types of materials to improve the battery performance of LIBs. And combined with recent research results to give its practical application effect, hoping to provide some help for the future direction of research.

2. Application of four types of metal oxide materials in LIBs

2.1. Mechanism of LIBs

LIBs consist of other components such as positive electrode, negative electrode, electrolyte, fluid collector and diaphragm. Lithium ions will be embedded in the negative electrode during the charging process, so the material of the negative electrode will also have a large impact on the battery performance. Electrolyte is a medium for lithium-ion transfer, so the ideal electrolyte should have good ionic conductivity. The collector, on the other hand, is used to concentrate the battery current and is usually connected to the electrode. The collector for the positive electrode is usually an aluminum foil, and the collector for the negative electrode is usually a copper foil. The diaphragm is used to separate the positive and negative terminals of the battery to prevent short-circuiting. During discharge, lithium ions flow out of the negative electrode and embed themselves in the negative electrode, while during charging, lithium ions make just the opposite movement. Through this repeated process, LIBs achieve the storage and release of energy, Armand et al. likened LIBs to ‘rocking chair batteries’ [5]. During the discharge process of LIBs, lithium ions are embedded in the cathode, so the structural properties of the cathode material have a significant impact on the performance of the battery.

2.2. Manganese-based oxide cathode materials

Li-rich manganese-based oxides belong to a wide range of lithium-rich oxides, and lithium-rich oxide materials are usually denoted by $Li_{1+x}TM_{1-x}O_2$ [6]. LRMOs were first prepared in 1991 [7]. The structure of the LRMO material is an important factor affecting the flow of lithium ions when performing the intercalation reaction. Li-rich manganese-based oxides can be written as $xLi_2MnO_3\cdot(1-x)LiMO_2$, and from the chemical formulae, the structure of this material consists of two phases, with Li_2MnO_3 written to the left as the first phase and $LiMO_2$ written to the right as the second phase [8]. The left and right phases possess a very similar spatial structure, both being cubic closet packed oxygen stacks, and all the octahedral sites are occupied by lithium (Li), transition metals (TMs) or Li/TMs. Fig. 1 illustrates the compatible structure of the two phases, where the second phase is used to provide additional lithium ions [9].

Due to the complexity of the internal structure of LRMO, there is no clear conclusion as to whether the two phases coexist in solid solution or exist locally as single phases. The solid solution model of LRMO can solve most of the problems and is widely accepted, however, too low a proportion of Li and TMs will break the periodic arrangement of the two phases in solid solution model, which causes the localized separation of the two phases [10]. The structure of LRMO is a major factor affecting its use as cathode material, and lots of research have shown that the composition of raw materials, lithium-ion content, preparation temperature, and cooling rate are important factors affecting the structure of LRMO. And the concentration of lithium ions is the main factor affecting the structure of LRMO. LRMO has been in the limelight because of its excellent properties. The introduction of LRMO-like materials into battery cathode can greatly help to increase the energy density of LIBs, which represents a great potential for LRMO to increase LIB's energy density.

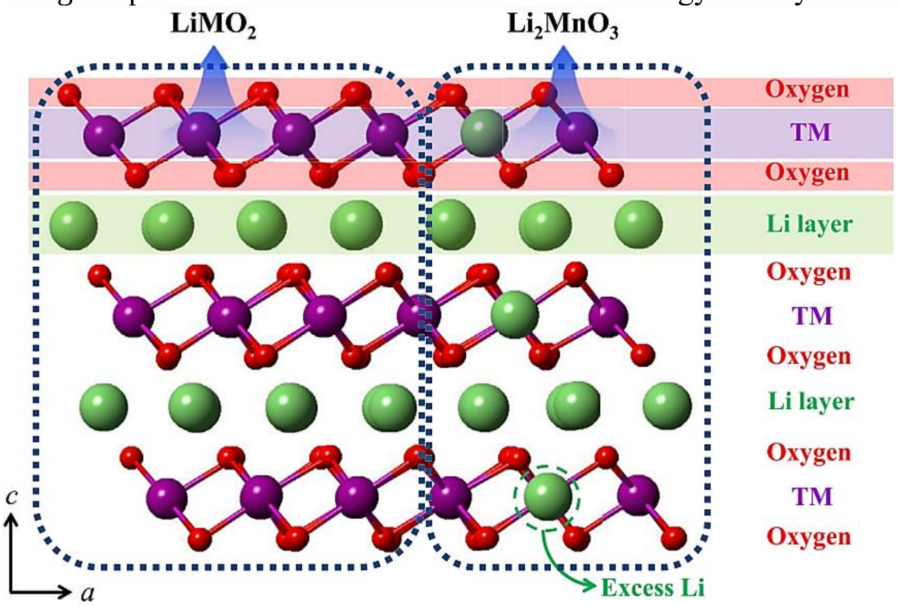

Fig. 1 Structural presentation of $xLi_2MnO_3 \cdot (1-x) LiMO_2$ [9].

2.3. Chromium oxide anode materials

Chromium oxide materials have attracted much attention by virtue of their high energy density and high capacity. Chromium oxide can not only be used as anode materials, but also as anode materials applied to LIBs. Chromium oxides have also gained considerable market competitiveness by virtue of their lower cost. In this part, three kinds of chromium oxide materials will be introduced from both the principle as well as the application performance.

Norby et al. used neutron diffraction to pinpoint the stoichiometric ratio of Cr_3O_8 as Cr_8O_{21} [11], where the [CrO_6] octahedron is a Cr_2O_3 unit layer and the [CrO_4] tetrahedron is a CrO_3 unit layer, with a distance of 1.17 nm between the (001) planes. Such a structural layer provides a lot of suitable storage space for the lithium ions, substantially increasing the Cr_8O_{21} the lithium storage capacity of this material. Chromium can make the transition between n-trivalent and n-hexavalent in the structure, which facilitates the flow of electrons in the structure. The combined effect of the two factors makes this material have a high theoretical lithium storage capacity. Teng et al. explained the discharge mechanism of Cr_8O_{21} [12], and the complete discharge curve of Cr_8O_{21} has two discharge platforms, so there are two reactions in its discharge process. The first platform ends near 3.0 V and the second platform starts at around 3.0 V. Lithium ions entered during the discharge process and destroyed the original structure, and new $LiCrO_2$ products were generated in both phases.

2.4. Nanostructured CuO anode materials

Copper oxide-based materials have become a preferred material for LIBs anode due to its low cost, stable effect and high safety. CuO is used to achieve lithium storage by redox reaction with Li-ions at the anode of LIBs. During the discharge process, CuO is reduced, and the products are nanoscale monomeric copper and stable Li_2O crystalline colloid [13]. The nano-copper in the product has high electrochemical activity, and the nano-copper monomers are oxidized to CuO and CuO_2 during charging. However, CuO suffers from low electrical conductivity, which restricts the charge transfer of the LIBs during operation, resulting in unsatisfactory electrochemical performance [14]. CuO nanoparticles have become an emerging anode material in the field of LIBs research due to their excellent physical and chemical properties. The nanostructure of CuO has significant advantages in practical applications, such as shorter ion and electron transfer distances, larger electrolyte-electrode contact area and the ability to regulate the structural changes induced by lithium-ion insertion. The introduction of nanostructured CuO has a positive effect on improving the electrode reaction rate and prolonging the battery service life. Different types of nanostructured CuO have different application effects in LIBs. This part will focus on the one-dimensional and two-dimensional nanostructures of CuO.

2.4.1 One-dimensional nanostructures

One-dimensional nanostructures of CuO often refer to CuO nanowires, nanorods, or nanotubes arrays. CuO nanowires arrays (CuO NWAs) possess large gaps between them, which allow lithium ions to diffuse rapidly into the electrodes. At the same time, the gaps between the nanowires allow them to effectively adapt to volume changes caused by lithium ions, thus maintaining the stability of the electrode structure. The Cu and LiO_2, generated during the discharge process, produced a stable solid electrolyte interfacial phase (SEI), which is good for the flow of Li-ions. The SEI also forms a layer of insulator for the electrons, which is helpful to keep the stability of the electrode material.

2.4.2 Two-dimensional nanostructures

CuO 2D nanostructures have similar size advantages as 1D nanostructures, but 2D nanostructures are superior to thought nanostructures in terms of stability. Apart from direct application in battery anodes, CuO can be employed as a substrate for the growth of other nanostructures and has the potential to become a composite electrode. Pu et al. reported a new synthetic route to synthesize copper oxide/reduced graphene oxide (CuO/RGO) materials [14]. CuO was dispersed homogeneously on RGO flakes, which effectively avoided agglomeration phenomenon, and increased the conductive efficiency and service life of the lithium battery anode materials.

2.5. Carbon/metal oxide composite anode materials

The research on anode materials for LIBs mainly focuses on the field of new carbon materials. Materials such as graphene and carbon nanotubes are widely applicated in the anode materials of LIBs because of good electrochemical properties, but there is a problem of low theoretical capacity of simple new carbon materials. Pure metal oxide electrode materials can suffer from phenomena such as structural collapse during multiple charging and discharging processes, leading to shortened battery life. The disadvantages of purely new carbon electrodes are improved with the advantage of metal oxides possessing higher theoretical capacity. The introduction of carbon atoms will also reduce the agglomeration and crystalline growth of some classes of metal oxides, so that the composite material has a more stable structure. Therefore, the carbon/metal oxide composite negative electrode material can have good stability and long service life while maintaining high capacity.

For carbon/metal oxide materials, scientists have made a lot of researches. Dong et al. used graphene aerogel compressed as a growth substrate for nano-CoO to prepare graphene aerogel/CoO composites [15], which still maintain good battery performance after more than 100 charge/discharge cycles, showing good battery life. Wu et al. prepared graphite/Fe_2O_3 composites using carbon wrapped with nano-Fe_2O_3 after graphitizing [16], which showed more excellent properties. Wang et al. prepared a $BaTiO_3$/graphene oxide/carbon nanotube ($BaTiO_3$/GO/CNT) composite [17], in which graphene oxide and carbon nanotubes both play a role in keeping the structure of $BaTiO_3$, which combines the advantages of the three materials, and the material exhibits good electrochemical performance. material exhibits good electrochemical properties.

3. Conclusion

This research describes the mechanism of LIBs, introduces the current problems faced by LIBs, and takes the problems faced as the departure point, states the research focus on improving the electrode materials of LIBs, where improves the structural stability of electrode materials to increase the lifespan of LIBs and the lithium storage capacity of the electrode materials to improve the energy density of LIBs. This research focuses on four types of metal oxide materials and introduces four kinds of metal oxide materials from three aspects of their mechanism, effect and research status. It can be shown that metal oxide materials have great advantages in increasing the lifespan and performance of LIBs. The research on metal oxide materials to improve the performance of LIBs is in a hot stage, and a variety of new materials continue to emerge. With the continuous development of nanotechnology and composite material technology, metal oxide materials will also be applied to the modification of lithium battery electrode materials in the form of nanostructures and composite materials.

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