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The application process of nanomaterials development in Lithium-ion batteries (LIBs) cathode materials of electrochemicals performance

Shishir kumar[1], Priyanka Singh[1], Vipin Kumar Singh[2], R B Singh[3]
[1] Department of Chemistry, Maharishi University of Information Technology, Sitapur Road, IIM Byepass, Bhitauli Tiraha, Lucknow, Utter Pradesh, India
[2] Department of Chemistry, Agra College, Agra, Utter Pradesh, India
[3] Scientist 'C' UGC, School of Life Sciences, Dr. Bhimrao Ambedkar University, Khandari Campus, Agra, Utter Pradesh, India

Abstract

Environmental pollution and energy scarcity are getting worse as science and technology advance, which has a significant influence on people's living conditions. Therefore, in light of the present sustainable development plan, the discovery and implementation of new energy sources are crucial for sustainable development. Lithium-ion batteries (LIBs) have been playing an increasingly significant role in the field of smart grids, electric vehicles, and personal electronic devices due to the fact that solar, wind, hydropower and nuclear energy are new renewable energy sources in this context, but these energy sources are seasonal, regional and discontinuous. There are currently more demanding specifications for lithium-ion batteries (LIBs), including high energy density and high power density, due to the growth of electric vehicles and other energy storage technologies. In order to enhance the electrochemical performance of lithium-ion batteries, this manuscript focuses on the incorporation of nanomaterials into the cathode materials. It is discovered that there is still much opportunity for nanomaterial development in the cathode materials of batteries.

Keywords: Nanomaterial's, lithium-ion battery, cathode materials, transition metals performance, electrochemical

Introduction

New energy batteries, known as green energy, have been widely used in various fields of life and have stronger environmental sustainability compared with other batteries. Lithium-ion battery has become an important new energy battery because of its large storage capacity, no memory, can be charged and discharged many times and recyclable advantages. Lithium-ion batteries (LIBs) are a very important secondary electrochemical energy storage device, which works through the round-trip movement of lithium ions between positive and negative electrodes. With the advantages of high energy density, lightweight and environmental protection, lithium-ion batteries have been widely used in electric vehicles, portable electronic devices, energy storage systems and other fields. As the main component of lithium-ion batteries, the cathode material has an important impact on the battery performance. At present, the commonly used cathode materials for lithium-ion batteries mainly include lithium cobaltite, lithium tetanize, lithium iron phosphate, ternary materials [1]. At present, this type of cathode material still faces problems such as high energy density and long cycle life that cannot be achieved at the same time which has become a bottleneck limiting its development.

In the past few years, nanomaterial's have presented new ideas for the modification of cathode materials for lithium batteries; Nanomaterial's have higher specific surface area and better ion diffusion properties than conventional materials, which can improve the reaction rate and cycle life of electrode materials, thus increasing the energy density and power density of Lithium-ion batteries[2]. This paper aims to study the preparation methods of nanomaterials in depth and provide the application of nanomaterial's in various fields of industries. Currently, the field of lithium-ion click cathode material preparation has developed diverse preparation techniques such as chemical precipitation, sol-gel, micro emulsion hydrothermal, etc., and synthetic raw materials include metal oxides, carbides [3]. Therefore, the use of nanomaterials in lithium-ion battery cathode materials is one of the hot spots in the study of lithium-ion batteries(LIBs).

In this manuscript, the research progress of nanomaterials in lithium-ion battery cathodes is presented. It focuses on the application of Nano-transition metal-embedded lithium compounds and explores nanomaterial modification's effect on the electrochemical properties of these materials. The applications of several different types of metal oxide nanomaterials are presented afterwards.

Materials And Methods

Transition metal lithium intercalation compounds

Lithium iron phosphate ($LiFePO_4$) nanomaterial's: Lithium iron Phosphate ($LiFePO_4$), is a crucial component of the cathode for lithium-ion batteries(LIBs), has received a lot of interest due to its large capacity, long cycle time, and excellent safety However, due to its relatively poor ionic and electronic conductivity, Lithium iron phosphate will exhibit performance degradation during high-rate charging and discharging. Therefore, nanoparticle modification can significantly improve its electrochemical properties.

In recent years, researchers have developed a variety of synthesis methods to prepare Lithium iron phosphate nanomaterials. The commonly used methods include hydrothermal method, solvothermal method, solid-phase method, hydrogen thermal method[4]. The solvothermal synthesis method can achieve the formation of nanoparticles by heating the reaction mixture in organic solvents, controlling the reaction conditions and precursor ratio. The hydrothermal method utilizes high-temperature and high-pressure hydrothermal conditions to prepare nanoparticles at appropriate reaction times and temperatures. The solid-state method involves mixing and grinding appropriate proportions of raw materials, and then sintering them under high-temperature conditions to obtain nanoparticles. The sol-gel rule is to obtain nano Lithium iron phosphate. Material through the formation of sol and the heat treatment of gel. These methods can control the morphology, size, and structure of nanoparticles, thereby regulating their electrochemical performance. In addition, Lithium iron phosphate's electrochemical characteristics can also be improved by means of carbon coating, ion doping, morphology control, and other modification methods[5].

Carbon coating: Carbon coating is the process of wrapping carbon-based materials such as graphene, carbon nanotubes and carbon black with iron phosphate particles on the surface of lithium to create a thin layer of carbon. By hydrothermal method, Ni and other researchers prepared LiFePO$_4$ nanoparticles with sizes ranging from 50 to 100 nanometers using citric acid and ascorbic acid as raw materials and treated them with carbon coating at 600 °C for 1 hour to finally obtain the positive electrode material of LiFePO$_4$/C[6]. According to the data in Table-1, the electrochemical characteristics of LiFePO$_4$/C have been significantly improved through the improvement of ascorbic acid, which has a maximum 122 mAh/g discharge specific capacity at a SC rate. The data of LiFePO$_4$/C in Table-I shows that as the discharge rate increases, the capacity also changes.

Table 1: Specific discharge capacities of LiFePO$_4$/C samples at different magnification

Spiked Sample	0.1 C/mAh·g^{-1}	1C/mAh.g^{-1}	5 C/mAh.g^{-1}
Citric Acid	153	139	95
Ascorbic acid	162	154	122

After 100 cycles, the LiFePO4/C material's discharge specific capacity, which was created by coating carbon with 7% ascorbic acid, dropped to 152.2 mAh/g, and the capacity retention rate was close to 97.1%[7].

Ion doping: Ion doping modification is a commonly used strategy aimed at further improving its electrochemical performance. Ion doping is achieved by introducing other metal ions into the Lithium iron phosphate lattice, which can replace some Fe/Fe positions to form doped materials. Common ion-doped elements include manganese (Mn), cobalt (Co), nickel (Ni), etc. One of the advantages of ion doping modification is the optimization of lattice structure and electronic structure. Taking manganese doping as an example, the smaller Ionic radius of manganese ion can replace the Fe/Fe" position, and the +3 valence state of manganese ion helps to improve the electronic conductivity. In this way, the manganese-doped LiFePO$_4$ nanomaterial has better conductivity and a quicker ion diffusion rate, enhancing the battery's rate performance and cycling stability, By using wet and Nano grinding techniques, the ZHANG team prepared LiMnFoneyMgyPO$_4$/C (-0, 0.5%, 1%, 1.5%) as a material [8]. This material has excellent electrochemical properties, having an up to 159.6 mAh/g discharge specific capacity, and its capacity can be kept at 96.2% even at IC. This is because the appropriate amount of Mg doping changes the lattice parameters of the material expands the Lit transport channel, and thus improves the Li transport efficiency.

Morphology control: By controlling the morphology and structure of nanoparticles, their surface area, ion diffusion path and electron transport ability can be regulated, enhancing battery cycle life, rate performance and capacity retention. The morphology control methods include crystal growth regulation, template method, and post-treatment modification. The crystal growth regulation method can control the size, shape, and crystallinity of nanoparticles by adjusting the synthesis conditions and reactant ratio. The advantage of morphology control is that it can achieve size consistency and shape controllability of nanoparticles, thereby improving the durability of materials electrochemical properties and structural stability Shi *et al.* added P123(polyethylene oxide polypropylene oxide polyethylene oxide) during the synthesis of FePO$_4$ precursors, introducing a mesoporous structure and increasing the specific surface area, resulting in improved electrochemical performance of the synthesized LiFePO$_4$ cathode material[9].

Lithium cobaltate (LiCoO$_2$) nanomaterials: Lithium cobaltate material has been studied as the anode material for lithium-ion batteries for nearly 40 years, but there are still many properties waiting to be explored. It belongs to the battery cathode material that is the earliest studied and most widely used. Due to the different temperatures in its production process, lithium cobaltate. forms two types of crystals: layered structure and spinel structure. High-temperature sintering generates lithium. cobaltate material with a laminar structure crystalline. type, while low-temperature generates cubic spinel structure, but the structure is not conducive to the deem bedding of lithium ions which are released during the discharge process, however, the electrochemical performance is insufficient to fulfil the criteria, hence it is not currently applicable. The layered structure of lithium cobaltate is a hexagonal crystal system, similar to a-NaFeO, structure, with a space group of R-3m, and the atoms are connected with the nearest Co and Li atoms through covalent or ionie bonds to form CoO$_6$ octahedra and Lio$_6$ octahedra, thus showing an overall alternating arrangement of three kinds of atoms, which is equivalent to Li ions embedded in the whole structure so it does not affect the de-embedding [10].

The two primary types of modification actions for lithium cobalt oxide cathode materials are surface coating and doping modification. Theoretically, aluminium atoms have a stabilizing effect on the layered structure of lithium cobalt oxide, which can prevent the irreversible phase change of its structure in the high-voltage operating environment usage of aluminium trioxide to coat lithium cobalt oxide. Their team then significantly improved the cycle life and developed a material with a discharge specific capacity of 174 mAh/g at an operating voltage of 2.75-4.4 V[11]. Additionally discovered that the aluminium trioxide-coated lithium. Cobalt oxide material can adapt to the high voltage. Cycling of 4.7 V[12]. In addition to the aforementioned methods, the ion transport rate can also be increased by doping trivalent metal ions with divalent metal ions that have better modification capabilities.

The lithium cobalt-acid material is used as the positive electrode of the battery to get electrons. When charging the lithium ions in the Free State in the charging process move from the negative electrode to the positive electrode and form lithium atoms with electrons. It can be connected to an external appliance such as a cell phone, the principle of action and process is just the opposite of charging. Between the positive and negative electrodes, lithium ions are embedded and de-embedded during the whole charging and discharging operation [13].

For a more visual study of the morphology and properties of lithium cobaltate cathode material as affected by its surface fusion cladding layer. The image of the material obtained under SEM analysis. It can be seen that there is a coating layer on the surface of lithium cobaltate particles and between the lithium cobaltate particles after White ford. During the charging and discharging process, the exposed lithium cobaltate is in direct contact with the electrolyte so some side reactions may occur on the surface, which is not conducive to the stability of the battery. The existence of this coating film is conducive to the occurrence of these side reactions, reducing the dissolution of the electrode and the oxidative decomposition of the electrolyte, enhancing its electrochemical performance[14].

Ternary cathode compound materials: LiNiCo $\mathrm{MnyO_2}$ ternary materials were proposed by Liu *et al.* of the National University of Singapore in 1999, 1. iN i 1 y Co z $\mathrm{MnyO_2}$ materials gather the high capacity of nickel-based materials, the long cycle life of cobalt-based materials, and the high safety and low-cost characteristics of manganese-based materials[15]. Ternary $\mathrm{LiNi_{1-x-y}Co_x}$, $\mathrm{MnyO_2}$ materials belong to the hexagonal crystal system, R-3m space group, with lattice constants of a=b=2.862 Å and c=14.227 Å After two decades of development, ternary cathode materials have been widely used in new energy vehicles, medical devices, mobile communications, smart wearable devices, ete. Although the ternary compounds have solved the problem to a certain extent, the ternary materials have been widely used in new energy vehicles, medical devices, mobile communications, and smart wearable devices. Although ternary compounds have solved some of the drawbacks of binary compounds to some extent, they still have limitations such as cation mixing, unstable surface structure, strain and micro cracks inside the particles or excessive surface alkali content.

In NCM ternary cathode materials, Ni is involved in the redox reaction and determines the capacity of the material, Co can increase the ionic conductivity, improve the multiplicity performance, and also reduce the Li/Ni mixing to a certain extent; Mn is not involved in the redox reaction, but can improve the structural stability. Compared with conventional cathode materials such as $\mathrm{LiCoO_2}$ (≈ 120mAh / g). $\mathrm{LiMn_2O_4}$ (≈ 140mAh /z), $\mathrm{LiFePO_4}$ (≈ 160mAh / g) $\mathrm{LiNiCoMnO_2}$ (≈160 mAh/g), lithium nickel cobalt aluminum acid (NCA) cathode materials have high reversible ratio (≈200 mAh/g). Capacity (≈200 mAh/g), low cobalt content and lower cost [16]. Cyclic voltammetry tests on the assembled button cells were performed at room temperature at the electrochemical workstation of C.H. Shanghai in the voltage range of 2.5 4.3 V with a scan rate of 0.1 mV/sec. It was concluded that the electrochemical properties of the NCA materials were gradually optimized and the specific capacity gradually increased with increasing ball milling time.

Results And Discussion

Metal oxide nanomaterials

Manganese oxide ($\mathrm{MnO_2}$): Free-standing layer-by-layer hybrid thin film of the graphene-$\mathrm{MnO_2}$ nanotube (NT) was shown to be an effective anode for lithium ion batteries [17]. The reversible capacity was demonstrated by the transition metal oxide. Conversion process between $\mathrm{Mn_2ONT}$ and Li ions at 0.35 to 0.40 volts. The conversion reaction may have an impact on 2.15 V whereas graphene is credited with a reversible capacity over 2.15 V. At current rates of 100 mA per gram and 80 mA per gram, respectively, the initial irreversible capacities of the LBL-alone graphene-$\mathrm{MnO_2}$, NT film and the LBL graphene-free- Mn manganese dioxide NT electrode were 581 and 873 mA h/g. These results imply that the graphene matrix increases the reversibility of the redox reaction involving the transition metal oxide.

According to electrochemical impedance spectra (EIS) studies, it has a special LBL. Structure that allows for quick lithium ion movement in the film and plays a significant role in enhancing rate capacity. According to the EIS findings, the charge transfer resistance of the LBL graphene-$\mathrm{MnO_2}$ film (36 Ohms) is significantly lower than that of the NT electrode made of grapheme-free manganese dioxide. In other words, it demonstrates that the charge transfer process is more rapid in the LBL graphene-Mao: films, improving the rate performance as a whole.

The preparation of an ultrathin, standalone LBL-constructed graphene-$\mathrm{MnO_2}$ NT thin film with distinctive nanostructures for use as a lithium-ion battery anode is discussed above. Related scientists think that the unusual film structure of this material improves the migration of lithium ions to the film's active site as well as the conductivity of the vast surface area graphene layer. As a result, the composite film exhibits 208 mAh/g at a high current rate of 1600 mA/g in addition to a reversible capacity of 686 mAh/g at a current rate of 100mA/g, which is higher than the realized value of traditional graphite. After cycling at various current rates, the capacity was stabilized at a value of 500 mAh/g. With great rate and cycling ability, the independent LBL thin graphene-MnO, films have emerged as some of the most promising lithium-ion battery anodes

Cobalt oxide (Co_3O_4): The high capacity and rate capabilities of mesoporous Co_2O_4, nanowire (NW) arrays as anodes in lithium-ion batteries, the necessary technicians created non-self-supporting NWs as well as commercial powder samples combined with carbon black and polymer adhesives[18]. The non-self-supported NWs only had a reasonable capacity of 350 mAh/g after 20 cycles. compared to the commercial powder's poor capacity of 80 mAh/g under the same circumstances bottom and middle curves, respectively. Carbon can be utilized as a reference anode material because it is the anode substance used in industrial lithium-ion batteries. The graphite has a 372 mAh/g theoretical capacity. As a result, the Co_3O_4 NW array described here has a capacity that is over two times more than graphite's. Fe_3O_4/Cu composite NW 800 mAh/g, and carbon nanotube membrane (490 mAh/g) are examples of earlier literature. Additionally, there are studies on anodes made of tin oxide (400 mAh/g), multi-walled carbon nanotubes (320 mAh/g), and titanium dioxide (305 mAh/g). In contrast, among the known NW anode materials, Co_3O_4 array has one of the best capacities They also examined how well NW arrays performed at larger currents, ranging from 2 to 50 C as quick discharge and/or charging rates are necessary for many battery applications, including electric automobiles and portable power tools. If the concerned expert compares the second cycle's discharge capacity at various currents. it will be 50% at 50 C, 85% at 1 C. 69% at 20 C, and 69% at 8 C. In contrast, as the current was increased, the capacity of non-self-supported NWs or powders degraded more quickly. The NW array continued to have a capacity of 450 mAh/g at 20 C and 240 mAh/g at 50 C after 20 cycles. The rate capacity of the NW array outperforms the majority of Co_3O_4 measurements. In conclusion, lithium-ion battery anodes made of self-supporting Co_3O_4 NW arrays grown on titanium foil have been evaluated.

The application of lithium-ion battery nanomaterials improves the electrochemical performance of the battery, and the nano ionization of electrode materials will be a more promising development direction for lithium-ion battery electrode materials. However, according to some reports in this area in recent years, it is found that the factors affecting the performance of the full play are quite complex, and there still a gap in the practical requirements, and many problems to be explored. The main problems are that the synthesis of nanoparticles is difficult and the particle size is difficult to control, the cost is high, and the transition from the laboratory research and development stage to the industrial production stage is very challenging.

Further research on nano anode materials, and improvement of traditional synthesis methods using optimization design according to the emerged problems, in addition to the development of new methods for synthesizing nano anode materials, have practical significance and broad development prospects. It is possible to try to explore new methods to synthesize nano scale particles as well as to apply the optimal methods to new materials, thus improving the electrochemical activity of electrode materials and helping to advance the industrialization of nano anode materials for practical use.

Conclusion

This manuscript introduces the current development status and characteristics of lithium-ion batteries (LIBs) from two main categories of materials, namely, lithium metal. Embedded compounds and metal oxide materials, introduces and elaborates on the structure and performance of each material, and finally compares and summarizes the shortcomings and improvement directions. In addition to the above issues, it needs further research on the microstructure of lithium-ion battery cathode nanomaterials such as particle size, morphology and the impact of the spatial location of the embedded lithium on the capacity and electrode process. To achieve a significant improvement in the performance of new lithium-ion batteries, it is necessary to further enhance the chemical stability of the surface interface of nanomaterials, such as by controlling the synthesis conditions to optimize the design of the crystal growth direction, grain size and stacking mode, which can improve the energy density, cycle life and charge/discharge rate of the battery. So in summary, Nano sizing cathode materials becomes an important step in the development of electrode materials for lithium-ion batteries and opens the door to the diversification of lithium-ion batteries (LIBs).

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