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Commonly used commercialized cathode materials in lithium-ion batteries and the corresponding enhancement with the help of nanotechnology

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Abstract. Continuous consumption of non-renewable resources generates a mass of carbon emissions which is blamed for global warming. Consequently, the research of high power and green electric vehicles has brought to the marketing. Therefore, in this paper, four commercialized cathode materials used prevalently in lithium-ion batteries, layered $LiCoO_2$, spinel $LiMn_2O_4$, and olivine $LiFePO_4$, and layered $LiNi_{1-x-y}Co_xMn_yO_2$, and the application of nanotechnology in improving electrode performance are introduced. Due to the different crystal structures of olivine, layered, and spinel, the corresponding lithium-ion diffusion path is 1-dimensional, 2-dimensional, and 3-dimensional, which is closely related to their electrode performance. The utilization of nanotechnology benefits the electrode performance to a large extent because of the shortening of lithium-ion diffusion paths as a result of increasing surface-to-volume ratio. Electrochemical properties including energy density, rate capability, capacity retention, electronic conductivity, and cycling performance are all enhanced through the application of nanorods, carbon nanotubes, reduced graphene oxides, etc.

Keywords: Lithium-Ion Batteries (LIBs), Cathode, Nanotechnology.

1. Introduction

Since petroleum is a continuously consumed and non-renewable resource that will escalate global warming, internal combustion engine vehicles are no longer the best choice for daily transportation. Instead, electric vehicles (EVs) have become a new trend recently because of the propaganda of net-zero greenhouse gas emissions during driving. Also, with the increasing demand for more efficient portable electronics and electric vehicles, many researches have been done for years to conquer the existing problems in the battery industry. Nowadays, lithium-ion batteries (LIBs) have dominated the electronic market due to their higher energy density and longer cycle life compared to other rechargeable batteries. In terms of the components used in LIBs, cathode materials definitely play a crucial role in the manufacturing of lithium-ion batteries, because the cathode takes the majority of the cost in a battery cell and further determines the upper limit of energy density [1]. A desired cathode material for commercialization is considered to meet multiple standards including cost, energy density, capacity retention, cycle life, etc. Since the basis of LIB is the de-/intercalation of lithium ions between the cathode and the anode during charging and discharging, lithium-ion diffusion paths are highly related and extremely important in terms of electrode performance. The dimensionality of the lithium-ion diffusion pathway is determined by various crystal structures, and the electrode performance can be enhanced significantly through nanotechnology by shortening the ion diffusion paths as a result of a larger surface-to-volume ratio. This paper introduces four types of commercialized cathode materials with three different crystal structures (layered $LiCoO_2$, layered $LiNi_{1-x-y}Co_xMn_yO_2$, spinel $LiMn_2O_4$, and olivine $LiFePO_4$) and the development of their electrochemical performance through nanotechnology.

2. Layered $LiCoO_2$

Lithium cobalt oxide ($LiCoO_2$) was initially invented and published by Goodenough in 1980, who won the Nobel Prize in Chemistry 2019 and was first commercialized by Sony in 1991 in their electronic devices [2]. $LiCoO_2$, as the most prevalent used cathode material in portable electronic devices, has high theoretical capacity, high operation voltage, and excellent electric conductivity [2]. Although it seems brilliant as a cathode material, the high price of cobalt and the severe capacity fading under high voltage have become the major reasons why $LiCoO_2$ can only be used as a cathode in portable devices like smartphones and tablets. Due to the limited activity of starting materials, $LiCoO_2$ suffers from lithium composite evaporation and powder coarsening attributed to their synthesis from the solid-state reaction [3]. Moreover, it also encounters irreversible phase transition during the de-/intercalation process, and all these complicated damages result in capacity and retention fading [2]. In order to figure out some solutions, multiple researches have been done on nanosized and nanostructured $LiCoO_2$ that will show a significant enhancement in electrode performance. It has been shown that nanocrystalline particles have a higher crystallinity which allows them to deliver a higher capacity and to maintain structural integrity after cycling [4]. However, capacity fading may also occur for bare nanocrystalline $LiCoO_2$ because of the gradual cobalt dissolution and corresponding phase transition [3]. Scott et al. presented an ultrathin 2 nm Al_2O_3 coating generated through atomic layer deposition (ALD) to the surface of the bulk nano-$LiCoO_2$ which is proved to show better electrode since it can prevent the cathode from hydrofluoric acid corrosion [5]. Al_2O_3 coated nano-$LiCoO_2$ shows a discharge capacity of 133 mAh/g even at a rate of 7.8 C while overcoming the severe capacity fading. Qian et al. also demonstrate the effect of nanoscale ternary lithium, aluminum, and fluorine-modified $LiCoO_2$ (LAF-LCO) in protecting the electrode from the contact of electrolyte to minimize the possible cobalt solution, where the formation of metal oxides is attributed to the existence of aluminum oxide hydrate [6]. With ~7 nm coating layer and metal oxide nanoparticles from 60 to 100 nm scale, the 2% LAF-LCO owns a more efficient Li-ion diffusion path which then improves the rate capability. Unfortunately, one obvious drawback for $LiCoO_2$ to conquer currently is the limited thermal stability which is highly related to the safety and performance retention of the LIB. More approaches are still needed for the portable electronics market.

3. Spinel $LiMn_2O_4$ (4 V) and $LiNi_{0.5}Mn_{1.5}O_4$ (5 V)

The spinel lithium manganese oxide ($LiMn_2O_4$) was first introduced at the University of Oxford as a cathode material [7]. $LiMn_2O_4$ has a relatively low cost and a three-dimensional lithium-ion diffusion path due to its spinel crystal structure which can allow more lithium-ions to de-/intercalate within the structure [8]. Although $LiMn_2O_4$ can tolerate high actual operation voltage, its performance is limited due to its low capacity compared to other cathode materials. Moreover, $LiMn_2O_4$ has been threatened by the structural instability induced by the Jahn-Teller distortion and the manganese dissolution. Because of the presence of active Mn^{3+}, which only has four electrons on the d-orbital and triggers one of the e_g orbital to generate a half-full high spin configuration, Jahn-Teller distortion then occurs to destroy the original structural stability by shrinking or stretching the bond length. Also, $LiMn_2O_4$ also suffers from the dissolution of existing Mn^{2+} which will deposit on the surface of anodes, an increasing amount of Mn dissolution can trigger the irreversible phase transition and can further result in severe capacity fading [3].

Consequently, nanotechnology has been involved as a proper solution to overcome those issues, since it has been revealed that the decrease in particle size of $LiMn_2O_4$ can bring a higher battery capacity [9].

Firstly, other main group elements doping is applied during the manufacturing of nano-$LiMn_2O_4$ as a method to alleviate the effect of Jahn-Teller distortion through decreasing the Mn^{3+} concentration. There are also multiple synthetic methods available in order to manufacture nanosized $LiMn_2O_4$, but the product generated from the resorcinol-formaldehyde (RF) route experiences the highest crystallinity which delivers a higher capacity and longer capacity retention while cycling [10]. Nanowire and nanorod structures are also introduced in the manufacturing of $LiMn_2O_4$ to offer more valid and efficient diffusion pathways for electrons on account of the larger surface-to-volume ratio. Bruce et al. state that nanosized $LiMn_2O_4$ even shows a significantly improved rate capability of 10^4 mAh/g under an extremely high rate of 60 C [11]. Besides, the utilization of electro-conducting nanocarbons, carbon nanotubes (CNTs), and reduced graphene oxide (rGO), can highly enhance the electric conductivity and generate a faster electron transport path while at the same time hinder the nanoparticles from grievous agglomeration [3]. The spinel $LiNi_{0.5}Mn_{1.5}O_4$ shows the ability to deliver capacity at 5 V with the addition of nickel. Unfortunately, 5 V $LiNi_{0.5}Mn_{1.5}O_4$ undergoes potential corrosion between commonly used organic electrolytes under such high voltage. However, Myung et al. proposed that when this 5 V spinel $LiNi_{0.5}Mn_{1.5}O_4$ shields the 4 V spinel $LiMn_2O_4$ to form a core-shell structure, it can make a big progress on the electrode performance [12]. Since the 5 V spinel as a shell compound is no longer exposed to the electrolyte reactions due to its inactivity within the 4 V spinel core range, the advantage of high operation voltage can be fully visualized. This core-shell spinel structure has a capacity retention of 95.2% even beyond 100 cycles [3].

4. Olivine $LiFePO_4$

The olivine lithium iron phosphate ($LiFePO_4$) is one of the most prevalently commercialized cathode materials in electric vehicles today. $LiFePO_4$, due to the abundance of iron, is cheap and environmentally safe. It also possesses an intermediate theoretical capacity of 170 mAh/g and is structurally stable whereas it also shows a detrimentally poor electric conductivity. In addition, the olivine crystal structure has restricted the $LiFePO_4$ to only uni-dimensional lithium-ion diffusion pathways, which results in poor rate capability and high potential polarization.

Issues mentioned previously can be solved to a large extent by reducing the particle size to the nanoscale. As a result of the larger contact surface area and the corresponding reduction in the electron transport path, the electric conductivity of nanosized-$LiFePO_4$ produced through the non-stoichiometric solid solution of lithium-ion supervalent metal cations doping is greatly enhanced approximately to the factor of 10^8. With the explosion of electric conductivity, as a result, nanosized-$LiFePO_4$ shows an improvement in both charging and discharging capacity even cycling under the enormously high current [13]. Khan et al. give another possibility of electrode performance improvement through mesoporous nitrogenous carbon composite with the embedment of nanosized-$LiFePO_4$ [14]. Nitrogen doping to $LiFePO_4$ is tested to exhibit better electrochemical performance such as rate capacity, retention, and cycling stability. The mesoporous nanocarbon structure in this case plays an important role in buffering the given strain and enhancing the lithium-ion diffusion coefficient values to 6-7 times larger. Lu et al. also demonstrate a hollow sphere structure of nano-$LiFePO_4$ along with carbon coating, and this new morphology generated from the Li_3PO_4 nano-spheres template exhibits brilliant electrochemical performance of 92.5% capacity retention after 500 cycles at 1 C [15].

5. Layered $LiNi_{1-x-y}Co_xMn_yO_2$

The layered ternary $LiNi_{1-x-y}Co_xMn_yO_2$ (NCM) has been utilized on a large scale as the commercialized cathode material for LIBs. NCM, as composed of nickel, cobalt, and manganese at the same time, possesses great electrochemical performance in terms of high energy density. Nickel is the most important element in this material since higher nickel content can lead to a significant increase in battery capacity, and Ni-rich ($Ni>0.6$) cathode is a new trend nowadays to explore high-power batteries. Nevertheless, the Ni-rich cathode has encountered a crucial issue of Li/Ni mixing which will destroy its crystal structure, the addition of cobalt is mainly to suppress the cation mixing and enhance the rate capability. The introduction of Mn^{4+} also aims at stabilizing the structure frame. Despite ternary elements, the Ni-rich cathode still suffers from a reduction in both capacity retention and thermal stability. As a result, doping and coating are applied to improve the safety and retention fading.

Chen et al. presented a hierarchical porous nano-/microsphere NCM (PNM-NCM) which is formed by 56.6 nm primary particles with 3 μm secondary particles distributed evenly through the porous fluffy MnO_2 template [16]. This nano-/microscale porous structure effectively shortens the Li-ion diffusion path and lessens the cation mixing while still having high crystallinity. Therefore, the PNM-NCM shows a great reversible specific capacity of 207.7 mAh/g at 0.1 C, a rate capability of 163.6 mAh/g at 1 C while at the same time maintaining a capacity retention of 90.3% after 50 cycles.

Although multiple coatings have been developed to further intensify the properties of NCM, the majority of them are composed of inactive materials which may trigger capacity and retention fading during cycling. Moreover, the Ni^{4+} existing in the NCM cathode experiences irreversible phase change and oxygen evolution during high-voltage charging. Zhong et al. then proposed the nano-$LiFePO_4$ coating on the surface of Ni-rich NCM to achieve a better-performed cathode material [17]. $LiFePO_4$, unlike NCM, has better thermal and structural stability attributes to the strong P-O covalent bond, thus exhibiting great cycling performance as a nanocoating even under high operation voltage. For instance, the nano-$LiFePO_4$ coated Ni-rich NCM is applied as a cathode in the 18650 battery cell, and shows a capacity retention of 91.65% under 1 C rate after 500 cycles whereas the bare NCM has much lower retention, which indicates the efficiency of nano-$LiFePO_4$ coating in improving the electrode performance.

6. Conclusion

This review paper gives an overview of four types of commercialized cathode materials, layered $LiCoO_2$, spinel $LiMn_2O_4$, and olivine $LiFePO_4$, and layered $LiNi_{1-x-y}Co_xMn_yO_2$, and the role of nanotechnology in the enhancement of their electrochemical performance. Their different crystal structures of 1D, 2D, and 3D dimensionalities corresponding to olivine, layered, and spinel structures are directly related to the efficiency of lithium-ion diffusion pathways. $LiCoO_2$ due to its high cost and thermal instability now used solely as a cathode for portable electric devices. $LiMn_2O_4$, although with a 3-dimensional lithium-ion diffusion pathway, is structurally stable along with capacity fading, which can be solved to a certain extent. $LiFePO_4$ and NCM are the two major cathode materials that dominate the commercialized lithium-ion battery markets due to their excellent performance. $LiFePO_4$ has excellent structural stability and high capacity. Its low electric conductivity can be solved by the utilization of nanoscale electro-conducting carbon (eg: carbon nanotubes). Then Ni-rich NCM, although it has high energy density, suffers from cation mixing and thermal instability. Doping of other metals can help stabilize the crystal structure, and nano-coating can prevent the corrosion between the electrolyte and the cathode. In conclusion, nanotechnology has enhanced the overall cathode performance in terms of energy density, electric conductivity, rate capability, capacity retention, etc., through shortening the ion diffusion path of those cathode materials by increasing the surface-to-volume ratio. Despite the tremendous enhancement nanotechnology has brought about, the cost of manufacturing nanosized cathode materials is considerably high. Moreover, the formation of a solid electrolyte interface (SEI) consumes more electrolytes which causes unwanted additional reactions with electrolytes that always occur due to the higher specific contact surface area, and these will result in the reduction of energy density and capacity along with low initial Coulombic efficiency. The introduction of secondary structures and an electrolyte-blocking layer can alleviate the deterioration. Also, low tap density caused by increasing interparticle space of nanomaterials can be mitigated through a structure where microscale secondary particles are agglomerated by nanoscale primary particles. Since many challenges still exist and can be further improved, more researches are desired in the electrochemical field to pursue greater performed cathode materials with lower cost and improved properties.

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