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Advancements in Layered Cathode Materials for Lithium ion Batteries

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ABSTRACT

Improvements in the capacity of modern lithium batteries continue to be made possible by enhanced electronic conductivities and ionic diffusivities in anode and cathode materials. Lithium ion battery technology has been applied to both thin, light and flexible portable electronic devices and more recently, to batteries for transportation systems including hybrid and electric vehicles. $LiCoO_2$ has been commercially used as a cathode material for lithium-ion batteries due to its high capacity and excellent cycling stability. Layered $LiNiO_2$, $LiMnO_2$ and their derivatives are promising cathode materials for lithium-ion batteries due to their high theoretical capacity and low cost. Lithium-excess layered oxides, $Li[Li, Mn, Ni, Co]O_2$, such as $(Li_2MnO_3)x(LiMO_2(M=Ni, Co, Mn))_{1-x}$, offer a working voltage much higher capacity values than those of $LiCoO_2$ and $LiMn_{1.5}Ni_{0.5}O_4$ and $LiNi_{1-x}Co_xO_2$, where $x \leq 0.4$, is considered as a promising material based on its lower price, higher specific capacity and better cycleability.

Keywords: Lithium-ion Batteries, Cathode Materials, Advancements, Properties, Applications.

INTRODUCTION

The world energy consumption, along with CO_2 emission, has been increasing exponentially during the past 50 years or so. As we become more aware of greenhouse gas emissions (GHG, such as CO₂ and CH₄) and their detrimental effects on our planet, it has become more important than ever to develop clean and renewable energy systems, such as solar cells, fuel cells, batteries and wind power generators. Being powered largely by burning fossil fuels, transportation vehicles, including automobiles, ships, airplanes and spacecrafts, are among the primarily sources for the GHG [1]. The inevitably increasing fuel shortage, along with the public awareness of greenhouse effects, has made it highly desirable to develop electric vehicles and/or plug-in hybrid electric vehicles, instead of fossil fuel vehicles, with a low GHG emission. However, commercial applications of electric vehicles will not be realized if advanced energy storage systems with an efficient energy saving and emission reduction cannot be successfully developed [2]. Improvements in the capacity of modern lithium (Li) batteries continue to be made possible by enhanced electronic conductivities and ionic diffusivities in anode and cathode materials. Fundamentally, such improvements present a materials science and manufacturing challenge: cathodes in these battery cells are normally comprised of metal oxides of relatively low electronic conductivity, and separator/electrolyte compositions must be tuned to readily admit ions, while simultaneously forming safe, impenetrable and electronically insulating barriers. The challenges faced by researchers in this field include the relatively low electrical and ionic conductivity values in cells, an unclear relationship between electrical conduction and ionic conductivity in cathode materials, constantly changing conduction properties in anode materials dependent upon phase transformations and the inherent difficulty in identifying and measuring the microstructure and conductivity of the solid-electrolyte interphase (SEI) film.

IMPORTANCE OF LITHIUM BATTERIES

Lithium ion battery technology has been applied to both thin, light and flexible portable electronic devices and more recently, to batteries for transportation systems [3] including hybrid and electric vehicles. Though these markets present different challenges in battery cell design, the former requiring in general higher power density and the latter requiring higher energy density for greater degrees of vehicle electrification, the technical requirements of improved conductivity and diffusivity are common to both. Models of battery cells and materials [4–6] critically require the best available estimates for conductivity and diffusivity, in order to both predict response and design improved materials. One of the problems associated with the performance of Lithium ion batteries is the capacity decay in the cell with cycling. This capacity fade is caused by various mechanisms, which depend on the electrode materials and also on the protocol adopted to charge the cell. Capacity fade in Lithium ion cells can be attributed to unwanted side reactions that occur during overcharge or discharge, which causes electrolyte decomposition, passive film formation, active material dissolution and other phenomena. Overcharging the Lithium ion cells causes deposition of metallic Lithium on the negative electrode surface, which is a primary side reaction. Lithium deposition will take place in cells with excess cyclable Lithium due to either higher than desired initial mass ratio or lower than expected Lithium losses during the formation period.

Lithium ion batteries are light weight as compared to the other rechargeable batteries of the same weight. Lithium ion batteries have a very high energy density hence lot of energy can be stored in it and this is due to the fact that electrodes of lithium ion batteries are made of light weight lithium and carbon and lithium is highly reactive element. Batteries made by lead-acid which weighs 6 kilograms can store the same amount of energy which a 1 kilogram lithium ion battery can store. Charge lost by lithium ion batteries is as low as 5 percent per month as compared to NIMH batteries which has 20 percent charge loss per month. Lithium ion batteries do not need to be discharged completely, i.e. they do not have any memory effect which some other batteries have. Hundreds of charge and discharge cycle can be handled by lithium ion batteries. Lithium iron phosphate has the wide range of characteristics due to which variety of different sizes of batteries can be produced and they found major areas of application: big electric vehicles, light electric vehicles, power tools, remote control toys, wind energy storage and solar equipment, small medical equipment and portable instruments. Lithium ion batteries are made up of one or more generating compartments called cells. Each cell is composed of three components: a positive electrode, negative electrode and a chemical called an electrolyte in between them. The positive electrode is made from chemical compound named lithium cobalt oxide (LiCoO₂) or lithium iron phosphate (LiFePO₄). The negative electrode is made up of carbon (graphite) and the electrolyte varies from one type of battery to another. During charging the battery, lithium based positive electrode withdraws some of its lithium ions, which move through the electrolyte to reach to the negative electrode and remain there. The battery stores energy during this process. When the battery is discharging, the lithium ions move back across the electrolyte to the positive electrode, producing the energy that powers the battery.

CATHODE MATERIALS

In the past two decades, the layered oxide $LiCoO_2$ cathode has been widely used in portable electronics [7]. The high cost, toxicity, chemical instability in the deep charged state, safety concern and limited capacity associated with LiCoO₂, however, have prevented its large-scale applications in transportation and stationary storage. Having a similar capacity as that of LiCoO₂, but a relatively high working voltage LiMn_{1.5}Ni_{0.5}O₄ is becoming an attractive candidate for high energy applications. Furthermore, the cycle life and rate capability of doped $LiMn_1 SNi_0 SO_4$ (spinel structure) could be enhanced significantly by cationic substitutions (Co, Cr, Fe, Ga or Zn) [8] and surface modification (AIPO₄, ZnO, Al₂O₃ and Bi₂O₃) [9]. In order to obtain a uniform surface modification and/or strong cationic coating, however, a complicated and high- cost post-chemical process is necessary [10]. To make the matter even worse, the currently used standard electrolytes (LiFP₆ in EC/DEC/DMC) are not appropriate for LiMn_{1.5}Ni_{0.5}O₄ cathode, which requires the high working voltage. Lithium-excess layered oxides, Li[Li, Mn, Ni, Co]O₂, such as $(Li_2MnO_3)_x(LiMO_2(M=Ni, Co, Mn))_{1-x}$, offer a working voltage much higher capacity values than those of LiCoO₂ and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ [11]. However, there is often a huge irreversible capacity loss associated with the oxygen and lithium loss from the host structure of the lithium-excess layered oxides (Li[Li, Mn, Ni, Co]O₂) at the end of the first charging process. Although the irreversible capacity loss can be significantly reduced by coating with insulating materials (e.g., Al₂O₃, AlPO₄, MgO, RuO₃), the high surface area associated with the nanostructured lithium excess layered oxides (Li[Li, Mn, Ni, Co]O₂) could have a high surface reactivity to induce side reactions between the electrodes and the electrolyte. This could lead to destabilization of the active materials and an increase in impeding passivation. Therefore, the electrolyte safety, together with the relatively high cost of the electrode materials, is the major concern for lithium excess layered oxides to be used as the cathode in LIBs.

Since 1980 when the $LiCoO_2$ was demonstrated firstly as a possible cathode material for rechargeable lithium battery, the transition metal intercalation oxides have caught the major research interests as the LIB cathodes [12, 13]. Categorized by structure, the conventional cathode materials include layered compounds $LiMO_2$ (M = Co, Ni, Mn, etc.), spinel compounds LiM_2O_4 (M = Mn, etc.), and olivine compounds $LiMPO_4$ (M = Fe, Mn, Ni, Co, etc.). Most of the researches are performed on these materials and their derivatives. New structure intercalation materials such as silicates, borates and tavorites are also gaining increasing attentions in recent years. During the materials optimization and development, following designing criterions are often considered: energy density; rate capability; cycling performance; safety; cost. The energy density is determined by the material's reversible capacity and operating voltage, which is mostly determined by the material intrinsic chemistry such as the effective redox couples and maximum lithium concentration in active materials. For rate capability and cycling performances, electronic and ionic motilities are key determining factors, though particle morphologies are also important factors due to the anisotropic nature of the structures and are even playing a crucial role in some cases. Therefore materials optimizations are usually made from two important aspects, to change the intrinsic chemistry and to modify the morphology (surface property, particle size, etc.) of the materials. The materials with promising theoretical properties have high potentials as the candidates of future generation LIB cathode, therefore are under intensive studies. For certain materials such as the LiFePO₄ olivine, significant property improvements have been achieved during the past decade with assistance of newly developed technologies. The ideal structure of layered compound LiMO₂ is demonstrated in Figure 1. The oxygen anions form a close-packed fcc lattice with cations located in the 6coordinated octahedral crystal site. The MO₂ slabs and Li layers are stacked alternatively. Although the conventional layered oxide LiCoO₂ has been commercialized as the LIB cathode for twenty years; it can only deliver about 140 mAh/g capacity which is half of its theoretical capacity.

LAYERED CATHODES FOR LITHIUM BATTERIES

LiCoO₂ has been commercially used as a cathode material for lithium-ion batteries due to its high capacity and excellent cycling stability. Nonetheless, cobalt has economic and environmental problems that leave the door open to exploit alternative cathode materials. For example, layered LiNiO₂, LiMnO₂ and their derivatives are promising cathode materials for lithium-ion batteries due to their high theoretical capacity and low cost. Unfortunately, these materials still have significant drawbacks. The major problems associated with LiNiO₂ include the difficulty in preparing stoichiometric LiNiO₂ powders without cation mixing, the structure degradation caused by irreversible phase transition during electrochemical cycling and thermal safety problems caused by oxygen release in the charged state. The main shortcoming of layered LiMnO2 is the crystallographic transformation to spinel structure during electrochemical cycling [14]. Although layered LiMnO₂ materials that do not convert to spinel during cycling were reported by Paulsen et al. [15], the preparation of the materials involved a cost-adding, multistep process of ion exchange of Na⁺ with Li⁺. Various approaches such as partial replacement of nickel and manganese by transition metals and optimizing preparation methods and conditions were adopted to improve their performance. For example, $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$, where $x \leq 0.4$, is considered as a promising material based on its lower price, higher specific capacity and better cycleability. However, its thermal safety still cannot satisfy the requirements for practical applications. The most appropriate and successful approach is to introduce Ni, Co, and Mn ions simultaneously in the layer structure. A solution of $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ may possess improved performances, such as thermal stability, due to the synergistic effect of the three ions. Therefore, recently, intensive effort has been directed towards the development of LiNi_xCo_yMn_{1-x-y}O₂ as a possible replacement for LiCoO₂. Similar to LiCoO₂, $\text{LiNi}_{x}\text{Co}_{v}\text{Mn}_{1-x-v}O_{2}$ generally exhibits a well defined α -NaFeO₂ layered structure (Figure 2), which is hexagonal crystalline and indexed as R-3m space group. This structure has Li^+ at the 3a sites, the transition metal ions M (M = Mn, Co and Ni) at the 3b sites, and O_2^- at the 6c sites in a MO₆ octahedron. X-ray diffraction is an effective methodology to investigate the crystalline structure since it gives one a good picture of the long-range structural changes in the materials. The value of I $_{(003)}$ I $_{(104)}$ is used as a standard to measure the degree of the cation mixing in the layered compounds. The smaller the I $_{(003)}$ I $_{(104)}$ value, the higher the disordering. Generally, the undesirable cation mixing takes place when I $_{(003)/}$ I $_{(104)} < 1.2$. Moreover, distinct splitting of the (108), (110), and (006), (102) peaks were also taken as the standard of a well-ordered α -NaFeO₂ structure.



Figure 2: Layered structure of LiTiS₂, LiVSe₂, LiCoO₂, LiNiO₂ and LiNi_yMn_yCo_{1-2y}O₂, showing the lithium ions between the transitionmetal oxide/sulfide sheets

The structure of LiMn₂O₄ belongs to the face center cubic lattice and each lattice is made up of 2 lithium atoms, 4 manganese atoms and 8 oxygen atoms [16-22]. In contrast to the layered oxides (Li_xCoO₂ or Li_xM_yCo_yO₂, M = Ni, Mg, Ti) presently used in commercial Lithium ion cells LiMn₂O₄ adopts a (3D) structure that can simply be threedimensional described as a cubic close packing (ccp) of oxygen atoms with Mn occupying half of the octahedral and Li an eighth of the tetrahedral sites referring to the 16d and 8a sites ([Li]_{tet} [Mn₂]_{Oct}O₄), respectively (Figure 3).



Figure 3: The spinel structure showing the MnO₆ octahedra and the Li 8a tetrahedral positions

However, this structure is complicated by possible cations mixing between the two types of sites. It is well documented that, within the spinel family, the degree of cations mixing and extent of cationic or anionic non stoichiometry affecting the spinel magnetic or optical properties is strongly dependent on the thermal story of the sample. Thus, it was important to first determine whether or not the Li intercalation/deintercalation process within LiMn₂O₄ was sensitive to the sample history (precursors, heat-treatments) and subsequent cation mixing as the early electrochemical data suggested. In the LiMn₂O₄ spinel structure (space-group: Fd3m), a ccp array of oxygen ions occupy the 32e position, Mn ions are located in the 16d site and Li in the 8a site. The Mn ions have an octahedral coordination to the oxygens, and the MnO₆ octahedra share edges in a three-dimensional host for the Li guest ions. The 8a tetrahedral site is situated furthest away from the 16d site of all the interstitial tetrahedra (8a, 8b and 48f) and octahedra (16c). Each of the 8a-tetrahedron faces is shared with an adjacent, vacant 16c site. This combination of structural features in the stoichiometric spinel compound constitutes a very stable structure.

The growth of LiCoO₂ thin films with preferred orientation is known to be crucial. Several thin film deposition techniques such as RF sputtering [23], pulsed laser deposition [24- 33], electrostatic spray deposition [34] and chemical vapour deposition [35] were employed for the growth of LiCoO₂ thin films. PLD has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films [36]. In particular, it has been successfully employed for the deposition of simple and complex metal oxide materials with desired composition, structure, physical and chemical properties. When PLD is carried out in the atmosphere of a chemically reactive gas (a process known as Reactive Pulsed Laser Deposition (RPLD)), the flux of the laser ablated material interacts with the gas molecules all along the transit from the target to the collector surface. The resulting deposited layer was found to have a chemical composition substantially the same as the base or starting material. LiCoO₂, LiMn₂O₄ and LiNi_xCo_{1-x}O₂ thin films were grown by pulsed laser deposition technique and the systematic characterization like structure, surface morphology, vibrational studies, optical properties, electrical properties, thermodynamic properties, gas sensing properties and electrochemical properties were studied [37-47] which are different from many transition metal oxides which have been exploited in many challenging fields of information science, nano and microelectronics, computer science, energy, transportation, safety engineering, military technologies, optoelectronic, electrochromic devices etc. These transition metal oxides are most interesting materials exhibiting a wide variety of novel properties particularly in thin film form useful for advanced technological applications. Sometimes they exhibit structural transformations and sub-stoichiometric phase transitions, which attracted the attention of researchers over the past few years to explore their potential scientific and technological applications in the fields of display systems and microelectronics [48-51]. Besides these battery materials we have studied other materials like CdTe, ZnSe and CdSe nanopolymers and glassy materials are of great industrial interest for developing photoluminescence based biomedical labeling reagents [52-70]. Quantum dots have applications in both organic and inorganic light emitter devices such as electroluminescence devices. They are dispersed within or between phosphor layers and emit a specific color of light [71-82].

CONCLUSION

Lithium ion batteries are light weight as compared to the other rechargeable batteries of the same weight. Lithium ion batteries have a very high energy density hence lot of energy can be stored in it and this is due to the fact that electrodes of lithium ion batteries are made of light weight lithium and carbon and lithium is highly reactive element. $LiMn_{1.5}Ni_{0.5}O_4$ is becoming an attractive candidate for high energy applications. Furthermore, the cycle life and rate capability of doped $LiMn_{1.5}Ni_{0.5}O_4$ (spinel structure) could be enhanced significantly by cationic substitutions (Co, Cr, Fe, Ga or Zn) and surface modification (AlPO₄, ZnO, Al₂O₃ and Bi₂O₃). LiCoO₂ has been commercially used as a cathode material for lithium-ion batteries due to its high capacity and excellent cycling stability. Layered LiNiO₂, LiMnO₂ and their derivatives are promising cathode materials for lithium-ion batteries due to their high theoretical capacity and low cost.

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