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Improving Electrochemical Performance of Lithium-Ion Batteries Using $LiMn_2O_4$ Cathodes

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Abstract: The performance of current energy conversion and storage technologies falls short of requirements for the efficient use of electrical energy in transportation, commercial and residential applications.

Materials have always played a critical role in energy production, conversion and storage and today there are even greater challenges to overcome if materials are to meet these higher performance demands. 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.

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.

Lithium ion battery is one of the popular power sources for electronic devices. Although various cathode materials have been studied for lithium ion battery, spinel type $LiMn_2O_4$ is more attractive than any other materials due to its low cost, low toxic and high rate. Recently, researches and developments on spinel type $LiMn_2O_4$ have been carried out to improve its electrochemical performance.

Keywords: Li-ion battery, $LiMn_2O_4$ Cathodes, Safety issues and Applications.

INTRODUCATION

With the worldwide energy shortage being one of the mounting problems in 21st century, efforts have been made to replace the non-renewable fossil fuels by other green energy sources, such as solar, wind, hydroelectric power, etc. Different from the conventional fossil fuels, most of these green energy sources suffer from their uncontrollable and intermittent nature, therefore the difficulty in energy storage and regulation results in larger cost. This brings in enormous amount of research interests in material developments for energy storage.

The Lithium (Li) ion batteries system is regarded as one of the near term solutions because of its high energy density and relatively simple reaction mechanism. Current Li-ion battery technology is well developed for the portable electronic devices and has been widely used in the past twenty years. However, to be implemented in the large-scale high-power system such as the plug-in hybrid electric vehicle (PHEV) or plug-in electric vehicle (PEV), performance requirements are raised especially from the aspects of energy/power density, cycling life and safety issues, therefore further Li-ion battery material and system developments are necessary [1, 2]. It has been reported that the spinel structure $LiMn_2O_4$ exhibits a specific capacity about 120 mAh/g [3, 4], where composite sample electrodes were used.

Recent research demonstrated that the importance of surface structural features of electrode materials for their electrochemical performance so, an effective strategy, coating the spinel $LiMn_2O_4$ with organic and inorganic compounds, has been investigated [5]. Coated $LiMn_2O_4$ spinel with 2wt. % Li–M–PO_4 (M =Co, Ni, Mn) and improved the discharge test showed that the cycling and rate capacities the spinel $LiMn_2O_4$ cathode materials. $LiFePO_4$ due to its potentially low cost, environmental benigness and the belief that it could have a major impact in electrochemical energy storage is the subject of many researches. Also, it can be a good candidate for improving electrochemical properties of conventional cathodes like $LiMn_2O_4$ [6]. Lithium manganese oxide, $LiMn_2O_4$, is an attractive cathode material and has been widely studied because the material has advantages from ecological and economical perspectives as well as easy preparation. However, $LiMn_2O_4$ has a serious drawback. Before cycling, the structure of the $LiMn_2O_4$ is cubic.Then, on cycling, the spinel structure is destroyed due to a cubic-tetragonal phase transition induced by Jahn-Teller distortion. For this reason, batteries with $LiMn_2O_4$ cathodes show capacity loss and poor cyclability. Pure $LiMn_2O_4$ has been improved by doping. If chromium is doped into $LiMn_2O_4$, it can form $Li_{1+x}Mn_{0.5}Cr_{0.5}O_2$ and the doped $Li_{1+x}Mn_{0.5}Cr_{0.5}O_2$ reveals improved capacity and cyclability. It can be assumed that Mn plays an important role to stabilize the structure of the chromium oxide. However, chromium materials are toxic and expensive. Therefore, in order to fabricate successfully stabilized layer structural framework, the doping of other elements into $LiMn_2O_4$ has been studied [7].

IMPORTANCE OF $LiMn_2O_4$ IN LITHIUM ION BATTERIES

A Li-ion battery can work as the energy storage device by converting electric energy into electrochemical energy. The basic working principles of Li-ion battery are shown in **Fig.1.** There are three key components in a Li-ion battery system: cathode, anode and electrolyte. For today's commercialized Li-ion battery system, both cathode and anode materials are intercalation materials. The transition metal oxides in cathode consist of a largely unchangeable host with specific sites for Li ions to be intercalated in. All Li ions are in the cathode sides initially and the battery system is assembled in discharged status. While charging, Li ions are extracted from the cathode host, solvate into and move through the non-aqueous electrolyte and intercalate into the anode host. Meanwhile, electrons also move from cathode to anode through the outside current collectors forming an electric circuit.

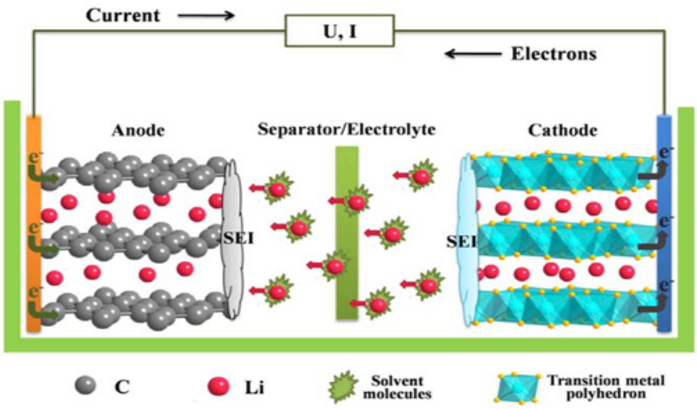

Fig.1: Working principle of Li-ion battery

The chemical potential of Li is much higher in the anode than in the cathode, thus the electric energy is stored in the form of electrochemical energy. Such process is reversed when the battery is discharging where the electrochemical energy is released in the form of electric energy [8]. The cathode region and anode region are separated by the separator, a micro-porous membrane that allows the electrolyte to penetrate and prevent shorting between the two electrodes. The electrolyte should be ionically conducting and electronically insulating in principle, however the actual properties of the electrolyte is much more complicated. During the first cycle, a so-called solid-electrolyte-interphase (SEI) layer will be formed on the surface of electrodes due to the decomposition of organic electrolyte at extreme voltage range. In current Li-ion battery technology, the cell voltage and capacities are mainly determined by the cathode material that is also the limiting factor for Li transportation rate.

The developments of cathode materials therefore become extremely crucial and receive much attention in recent decade [9].Since 1980 when the $LiCoO_2$ was demonstrated firstly as a possible cathode material for rechargeable lithium battery [10]; the transition metal intercalation oxides have caught the major research interests as the Li-ion battery cathodes [11]. Categorized by structure, the conventional cathode materials include layered compounds $LiMO_2$ (M = Co, Ni, Mn etc.), spinel compounds $LiMn_2O_4$ (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: 1) Energy density; 2) Rate capability; 3) Cycling performance; 4) Safety; 5) 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 mobilities 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 [12].

CATHODE MATERIALS OF LITHIUM ION BATTERIES

Conventional cathode materials include layered compounds $LiMO_2$, spinel compounds $LiMn_2O_4$ and olivine compounds $LiMPO_4$. The oxygen anions form a close-packed fcc lattice with cations located in the 6-coordinated octahedral crystal site. The MO_2 slabs and Li layers are stacked alternatively. Although the conventional layered oxide $LiCoO_2$ has been commercialized as the Li-ion battery cathode for twenty years, it can only deliver about 140 mAh/g capacity which is half of its theoretical capacity. Such limitation can be attributed to the intrinsic structural instability of the material when more than half of the Li ions are extracted. On the other hand, the presence of toxic and expensive Co ions in $LiCoO_2$ has introduced the environmental problem as well as raised the cost of the Li-ion battery [13]. For improvement, Co ions in $LiCoO_2$ can be substituted by other transition metal ions such as Ni and Mn. The new substitutions can reduce the cost of the materials and make the materials more environmentally friendly by eliminating the use of Co ions which are expensive and toxic [14]. One of the most promising candidates is so called Li-excess nickel manganese layer oxides. A reversible capacity as high as 250 mAh/g can be obtained routinely 15. The spinel $LiMn_2O_4$ was proposed as the cathode of the lithium ion battery, but the material was found to encounter sever capacity fading problem [16]. Substituting Mn with other metal ions has been used as an important approach to improve cycling performance of spinel materials. Multiple dopants including inactive ions such as Mg, Al, Zn etc., first row transition metal ions such as Ti, Cr, Fe, Co, Ni, Cu, etc [17] and rare earth metal ions such as Nd, La, etc. have been investigated and $LiNi_{0.5}Mn_{1.5}O_4$ shows the best overall electrochemical performances among the above [18]. The voltage of these materials can be raised to more than 4.7 V therefore the energy densities are highly improved. The rate capabilities, on the other hand, are not found to be improved significantly.

SAFETY ISSUES OF LITHIUM ION BATTERIES

Safety issues represent one of the most important drawbacks of Li-ion batteries and have resulted in several battery recall cases in the last years. Li-ion batteries contain flammable organic electrolytes and under certain abuse conditions, flame and smoke may result. The two principal factors that can affect the safety are the insufficient tolerance to overcharging and the poor thermal stability of electrode materials. The overcharge can occur when the cell voltage is incorrectly detected by the charging control system, when the charger breaks down or when a wrong charger is used [19]. When cells are overcharged the number of Li-ions transferred from the cathode to the carbon anode is higher than that it can accommodate and metallic Li deposition may occur. After Li has been removed from the cathode, the electrolyte oxidation occurs and results in a distinct heat output. When the cell temperature increases the anode may simultaneously reduce the organic electrolyte with gas production that increases the internal pressure of the battery [20]. The rapid increase in temperature caused by short circuits, mainly due to Li plating and dendritic growth, may lead to safety-critical conditions. In this case, the cell may smoke, ignite or explode [21]. Battery manufactures attempt to prevent battery overcharge by using a number of safety measures, such as overcharge protection circuits, positive temperature coefficient resistors, pressure sensitive rupture disks, temperature sensitive separators, etc. Recent approaches include the use of various types of electrolyte additives [22].

CONCLUSIONS

Li-ion batteries are one of the most successes of modern electrochemistry. These batteries, which became a commercial reality about a decade ago, are conquering the markets with increasingly wider applications. Li-ion battery systems have a very limited performance at elevated temperatures and their cycle life is also limited, due to surface phenomena on both electrodes that increase their impedance upon cycling. Li-ion batteries are light weight as compared to the other rechargeable batteries of the same weight. They 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 lightweight lithium and carbon and lithium is highly reactive element. $LiMn_2O_4$ is ideal as a high-capacity Li-ion battery cathode material by virtue of its low toxicity, low cost and the high natural abundance of Mn.Unlike V_2O_5 and LiV_3O_8, lithium can be extracted from $LiMn_2O_4$ in the form it is made, qualifying $LiMn_2O_4$ as a positive electrode material for Li-ion batteries. $LiMn_2O_4$ has a spinel or tunnel structure which possesses a three-dimensional space via face sharing octahedral and tetrahedral structures. This provides conducting pathways for the insertion and extraction of lithium ions. $LiMn_2O_4$ powder used in lithium batteries is fabricated at high temperatures. However, most semiconductor devices and micro electro-mechanical systems are fabricated at lower temperatures.

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