The effect of particle size on performance of cathode materials of Li-ion batteries

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Abstract | Beginning with the 'frog-leg experiment' by Galvani (1786), followed by the demonstrations of Volta pile by Volta (1792) and lead-acid accumulator by Planté (1859), several battery chemistries have been developed and realized commercially. The development of lithium-ion rechargeable battery in the early 1990s is a breakthrough in the science and technology of batteries. Owing to its high energy density and high operating voltage, the Li-ion battery has become the battery of choice for various portable applications such as note-book computers, cellular telephones, camcorders, etc. Huge efforts are underway in succeeding the development of large size batteries for electric vehicle applications.

The origin of lithium-ion battery lies in the discovery that Li^+-ions can reversibly be intercalated into/de-intercalated from the Van der Walls gap between graphene sheets of carbon materials at a potential close to the Li/Li^+ electrode. By employing carbon as the negative electrode material in rechargeable lithium-ion batteries, the problems associated with metallic lithium in rechargeable lithium batteries have been mitigated. Complimentary investigations on intercalation compounds based on transition metals have resulted in establishing $LiCoO_2$ as the promising cathode material. By employing carbon and $LiCoO_2$, respectively, as the negative and positive electrodes in a non-aqueous lithium-salt electrolyte, a Li-ion cell with a voltage value of about 3.5 V has resulted.

Subsequent to commercialization of Li-ion batteries, a number of research activities concerning various aspects of the battery components began in several laboratories across the globe. Regarding the positive electrode materials, research priorities have been to develop different kinds of active materials concerning various aspects such as safety, high capacity, low cost, high stability with long cycle-life, environmental compatibility, understanding relationships between crystallographic and electrochemical properties. The present review discusses the published literature on different positive electrode materials of Li-ion batteries, with a focus on the effect of particle size on electrochemical performance.

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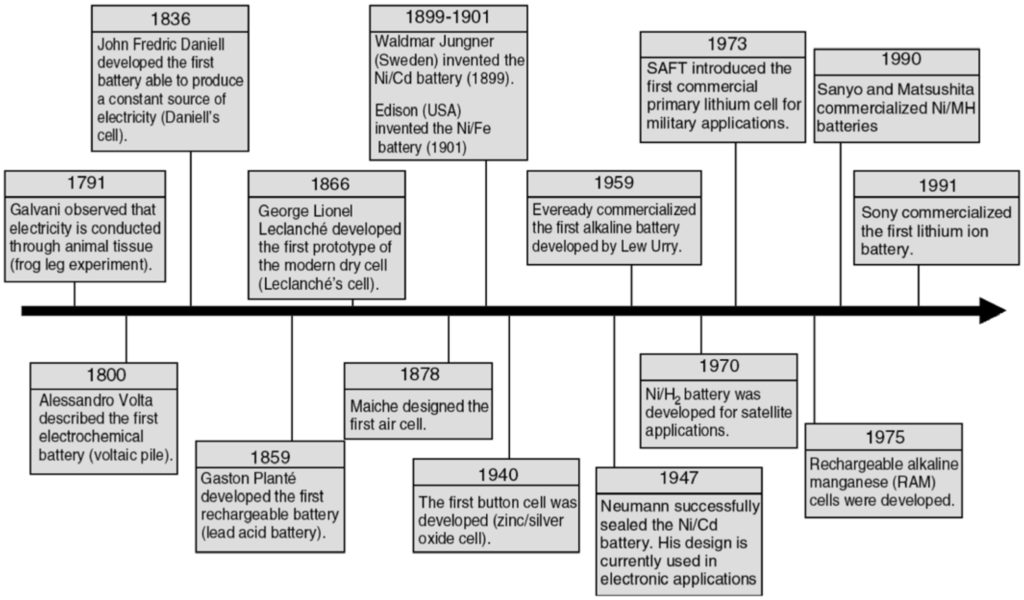
Introduction

In response to the needs of today's mobile society and the emergence of ecological concerns such as global warming, one of the major challenges in the new century is undoubtedly energy generation and storage. Electrochemical energy conversion is one

Figure 1: Timeline for the major events in the history of batteries.[5]



of the clean and green processes. Electrochemical energy conversion and storage were probably used more than 4000 years ago by Parthian and Egyptian to electroplate silver and antimony on copper. However, the written evidence on battery history began in the late 1700s and the early 1800s.[1] Galvani (1791) demonstrated the existence of bioelectric current in animal tissue. This demonstration led to the landmark discovery by Volta (1800) and development of the voltaic pile.[2] In 1836, Daniell[3] invented a battery capable of working for long periods and the battery was named as Daniell cell. Later on Planté demonstrated the lead acid battery in 1859 in front of French Academy of Science.[4] Since then a wide variety of electrochemical systems, which include primary, secondary, reverse, thermal, etc., batteries, have been developed. Fig. 1 represents the schematic of the major events during the evolution of batteries starting with Galvani's frog leg experiment and finishing with the most recent Li-ion batteries (1991).[5]

The importance of secondary or rechargeable batteries is the transformation of electric energy to chemical energy and vice versa by reversible charge-discharge steps. Furthermore, they are cost effective because they can be recharged several times. There had been interest in the development of Li-based batteries since 1950s. The motivation for developing a battery technology based on Li metal as the anode was due to the fact that, Li has low atomic mass (6.94), high specific capacity (3.86 Ah g^{-1}) and it is the most electropositive (−3.04 V vs. SHE) alkali metal, which facilitate designing of high energy density batteries.[6] Research on lithium batteries started in the late 1950s and Li metal was found to be stable in a series of electrolyte systems due to surface passivation.[7] Li metal-based primary batteries were successfully developed. However, this was not so in the case of rechargeable batteries. In 1973, SAFT introduced the first commercial rechargeable lithium cell for military application. However, it encountered several difficulties in terms of cycle-life and safety.[8,9] The problems included dendritic growth of the lithium metal upon cycling and the dendrites pierce through the separator towards the cathode leading to an internal short, and thermal runaway resulting in cell explosion.[10,11] In 1989, incidents of fire due to failures of Li/MoS_2 cells annulled general enthusiasm in using Li metal as the anode in secondary batteries. As a consequence, several alternative approaches were studied to circumvent the safety issues. Substituting Li metal by an alloy of Li and Al reduced the dendrite problem,[12] but it suffered from large volume changes which essentially lead to poor cycle-life. Numerous inorganic compounds were shown to intercalate and de-intercalate Li in a reversible way. Most of the host materials were transition metal oxides or sulfides with stable crystal lattices and their layer or tunnel structures provided the pathways for the guest ion to diffuse.[13–18] In late 1980s, Murphy et al.,[19] and Scrosati et al.,[20] introduced the concept of Li-ion or rocking chair technology by incorporating $Li_6Fe_2O_3$ or $LiWO_2$ as an intercalation anode and another oxide WO_3, TiS_2 or V_2O_5 as a cathode in non aqueous electrolytes.[21] However, the enhanced safety and extended cycle-life were not sufficient to offset the penalty in energy density caused by the replacement of Li metal; hence these systems were never commercialized.

A breakthrough was made when Japanese researchers exploited an old concept of using carbonaceous materials as anode intercalation hosts.[22–24] The term "lithium-ion battery" that was introduced by those researchers eventually prevailed and replaced the other aliases such as "rocking-chair",[25] "shuttle-cock"[26] or "swing" batteries.[27] In 1990, both Sony[28] and Moli[29] commercialized Li-ion cells based on petroleum coke and $LiCoO_2$. Since then these cells are found in most of today's high performance electronic devices. The performance of Li-ion batteries depends intimately on the properties of the materials used for the electrodes. So, innovative material chemistry lies at the heart of advances that have been taking place in energy conversion and storage by introducing rechargeable Li-ion battery.

Several reviews on different aspects of Li-ion batteries have appeared in the literature.[30–38,38A] The present review focuses on the effect of particle size of cathode materials for Li-ion batteries on electrochemical properties.

History of the cathode materials

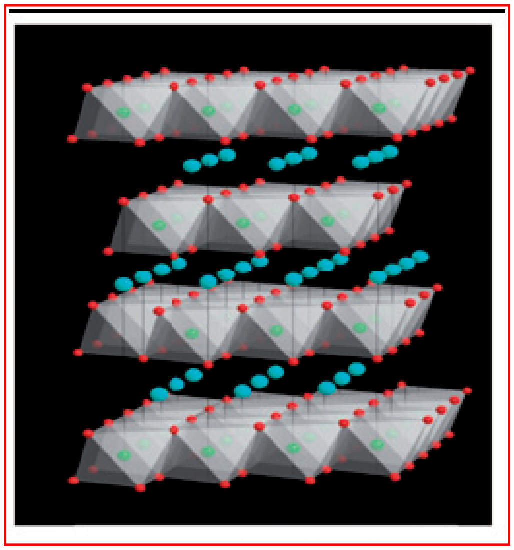
Initial research efforts were focused on transition metal chalcogenides (sulfides and selenides) as cathodes for rechargeable Li cells, and TiS_2 was the first material to undergo commercialization.[39] However, it turned out that it was difficult to stabilize the higher oxidation state of the transition metal ions in chalcogenides to achieve a high cell voltage (> 2.5 V vs. Li^+/Li). Research in Goodenough's group in 1980 led to exploration of oxides as cathode materials.[40,41] Since then a lot of fundamental and technological contributions in search of various positive electrode materials have been devoted to transition metal oxides with different crystal systems. They include oxides with general formula $LiMO_2$ (M = Co, Ni, Mn, etc.) having a two dimensional layered structure, $LiMn_2O_4$ [42] having the three dimensional spinel structure and so on. The concept of 3D insertion/extraction of Li^+ in positive electrode was then extended to new families of 3D framework structure by Goodenough et al.,[43,44] and Delmas et al.[45,46]The framework unit is polyanions such as tetrahedral XO_4^- groups (X = P, Mo, W and S). In 1997 Padhi et al.,[47] discovered the electrochemical properties of olivine phase ($LiMPO_4$, where M = Fe, Mn, Co and Ni), in particular $LiFePO_4$.

Importance of particle size

In recent years, there has been an explosive growth of nanoscience and nanotechnology because of interesting properties of nanomaterials, which are different from the properties of both bulk materials and the corresponding atoms.[48] By confining to nanodimensions, these materials possess combined properties of bulk and surface thereby exhibit unusual mechanical, electrical, optical, biological, chemical, etc., properties. The applications include microelectronics,[49] chemical and biological sensors,[50] catalysis,[51] nanoprobes,[52] nanocables,[53] drug delivery,[54] superconductivity and magnetism,[55,55A] nanodevices,[50,52,53] etc. The performance of battery cathode materials is influenced by several factors such as crysatllinity,[56] composition,[57] particle size,[58] etc. Nanostructured materials have become increasingly important for electrochemical energy storage in Li-ion batteries. However, there are several disadvantages associated with nanomaterials in addition to the advantages for Li-ion battery application.[59–65] The advantages are (i) they offers new reactions which cannot take place in micrometer size particles (for example, the reaction of transition metal compounds with Li leads to the *in situ* formation of metal nanoparticles embedded in a Li_2X matrix, $MX + ZLi^+ + Ze^- \leftrightarrow Li_ZX +$ M, where $X = O$, S, F or N); (ii) nanostructured materials provide short path lengths for both Li^+-ion diffusion and electron transport in comparison with micron-sized particles and therefore can enhance the charge/discharge rate; (iii) short path length for electronic transport can allow utilizing materials having low electronic conductivity; (iv) an increased electrode/electrolyte contact area can also lead to enhanced charge/discharge rates; and (v) nanomaterials can accommodate large volume expansion/contraction associated with Li^+-ion transport and preserve the integrity of the electrode leading to longer cycle-life. The disadvantages include (i) a high surface area can increase undesirable electrode/electrolyte reactions resulting in the formation of solid electrolyte interface (SEI) leading to self-discharge, poor cycling, low calendar life and poor safety of the cell; and (ii) inferior packing of particles.

In view of the above advantages and disadvantages associated with nanoparticles for Li-ion batteries, literature on important cathode compounds are reviewed below. The compounds include $LiCoO_2$, $LiNiO_2$, $LiMnO_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiMn_2O_4$ and $LiMPO_4$ (where M = Fe and Mn). They fall into three broad categories, namely, layered ($LiCoO_2$, $LiNiO_2$, $LiMnO_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$), spinel ($LiMn_2O_4$) and olivine's ($LiMPO_4$), which are basic for development of several other compounds of the parents' structures. Essentially, a review of parent compounds is discussed below.

Figure 2: Crystal structure of $LiCoO_2$



Lithium cobalt oxide ($LiCoO_2$)

$LiCoO_2$ has served as an archetype cathode material for secondary Li-ion batteries ever since the discovery by Goodenough's group[40] in 1980. It has a perfectly ordered α-$NaFeO_2$[66] rock salt structure with R3¯m space group[67] in which Li^+ and Co^{3+} ions occupy the alternate (111) planes of rock salt structure to give a layer sequence of O-Li-O-Co-O along the c-axis as shown in the Fig. 2.

The stacking sequence of the oxygen sub-lattice is ABCABCABC along the c-axis. This structure is designated as the O3 layer structure and it provides an ideal two dimensional pathway for Li^+-ion diffusion in and out of the lattice during charge-discharge cycling. The deintercalation of Li^+-ion from the lattice involves a change in the stacking sequence of CoO_2 slabs, which results in the formation of two phases and one phase regions.[67] In situ XRD studies confirmed the presence of two hexagonal phases in Li_xCoO_2 with a two phase region between $x = 0.94$ and 0.75. Around $x = 0.5$ a monoclinic phase was observed.[67] Amatucci et al.,[68] and Yang et al.,[69] showed that all the lithium can be removed from $LiCoO_2$ forming CoO_2 with O1 structure. However, according to Venkataraman and Manthiram[70] the fully delithiated phase has P3 structure which coexists with O3 phase in the range of $0.2 \leqslant x \leqslant 0.45$ in Li_xCoO_2. For structural stability, however, the Li content is cycled between 0.5 and 1.0 in commercial application corresponding to the voltage range 2.9–4.2 V.

In general, $LiCoO_2$ is synthesized by heating a palletized mixture of lithium carbonate and cobalt carbonate in air at 900°C for 60 h with repeated intermittent, grinding and heating.[40] However, the evaporation loss of lithium is a serious problem. Therefore, many inorganic and organic lithium precursors were utilized in order to reduce both the calcination temperature and time. Conventionally $LiCoO_2$ electrodes are fabricated based on powder processing using micron sized particles. Micrometer size particles of $LiCoO_2$ were synthesized by a variety of procedures, which include LiCl flux,[71] hydrothermal,[72] solution combustion,[73,74,74A,74B]molten salt synthesis,[75] microwave heating,[75A,75B] spray drying,[76] etc. Tang et al.,[71] synthesized the $LiCoO_2$ by LiCl flux method at 650°C with particle size distribution between 1 and 5 μm. A discharge capacity of about 156 mAh g^{-1} was obtained with about 98% of columbic efficiency. In another study, uniform particle size of 3 μm was obtained by the hydrothermal method[72] using Co_3O_4 and Li_2CO_3 as starting materials. The reported discharge capacity was 138 mAh g^{-1}. Shalini et al.,[73] reported the synthesis of $LiCoO_2$ particles 2–5 μm by solution combustion method and the discharge capacity measured was 120 mAh g^{-1} with good faradaic efficiency. $LiCoO_2$ powder prepared by molten salt synthesis[75] using the eutectic mixture of 0.6 $LiCO_3$ and 0.4 LiCl in the temperature range from 700 to 900°C yielded an average particle size of 8 μm with a discharge capacity of 140 mAh g^{-1}. Konstantinov et al.,[76] prepared 10 μm size particles of $LiCoO_2$ by spray drying method followed by heating at 900 °C. A discharge capacity of 160 mAh g^{-1} was obtained at a current density of 0.3 mA g^{-1} in the potential range 3.0–4.4 V.

Nanocrystalline $LiCoO_2$ has been synthesized by several methods such as, sol-gel,[77–79] spray drying,[80] co-precipitation,[81] evaporation,[82] and freeze drying,[83] etc. Peng et al.,[77] synthesized $LiCoO_2$ by sol-gel method followed by heat treatment at 750 °C for a few hours. The particle size was in the range from 30 to 50 nm and a discharge capacity of 154 mAh $g^{-1}$was reported. In another study, Wu et al.,[79] synthesized nanosize $LiCoO_2$ by a modified sol-gel method using P123 as a template. They controlled the particle size by controlling the temperature and obtained particles in the range of 50–120 nm. The sample synthesized at 850°C (120 nm) provided higher discharge capacity of 150 mAh g^{-1} with good cyclability compared to the samples heated at lower temperatures with particles less than 100 nm. $LiCoO_2$ synthesized by co-precipitation method[81] composed of particles in the range of 20–100 nm. Discharge capacity values of 100 and 130 mAh g^{-1} were obtained at 50 C and 10 C rates, respectively. However, the capacity retention was poor. Kumta et al.,[82] prepared low temperature $LiCoO_2$ particles of about 70 nm. However, the electrochemical performance was poor. Nanocrystalline $LiCoO_2$ powder with particle size 50–70 nm was prepared by freeze drying method[83] followed by annealing at 550°C. A discharge capacity of about 125 mAh g^{-1} was obtained in the first cycle and it decreased to 115 mAh g^{-1} after 10 cycles. On the other hand, the bulk material provided 135 mAh g^{-1} discharge capacities with out fading on cycling. Smaller discharge capacity of the nanomaterial was accounted for the lattice distortion in $LiCoO_2$.

The nanosized $LiCoO_2$ was reported to possess a poor cyclabilty due to the reactivity of the large surface area and high oxygen thermodynamics.[83–88] The high surface area resulted in an increased side reaction with the electrolyte leading to the formation of SEI layer, which was responsible for the capacity fade and poor cycle-life. Zhang et al.,[84] reported that the formation of SEI layer was responsible for the irreversible capacity loss of the layered $LiNiO_2$. Choi and Manthiram[85] correlated the irreversible capacity loss with surface area and pointed out that high surface area of the oxide resulted in poor electrochemical performance. Liu et al.,[86] reported that SEI layer thickness on the $LiCoO_2$ nanaoparticle was about 2–5 nm and it increased with an increasing surface area of the particles. Accordingly, large irreversible capacity losses with the nanosize particles essentially lead to poor cycle-life. Okuba et al.,[87]attributed that the poor performance of the nanoparticles synthesized by sol-gel method assisted by a triblock copolymer surfactant to the cation mixing between Li^+ and Co^{3+} within the layered structure of $LiCoO_2$. In another study, Choi et al.,[88] reported poor performance of nano-$LiCoO_2$ compared to micron size $LiCoO_2$ in the temperature range from -15 to 60°C. From review of the above literature, it is observed that, nanoparticles are used for enhancing the rate capability. However the high reactivity of these particles with the electrolyte leads to poor cycling performance. On the other hand, micron-sized particles lead to poor rate capability but a long cycle-life.

Several procedures for synthesis of sub-micron size $LiCoO_2$ are reported in literature.[89–92] Myung et al.,[89] prepared sub-micron size particle of $LiCoO_2$ by emulsion drying method followed by post heating in the temperature range from 600 to 900°C. The discharge capacity obtained for 900°C sample was 156 mAh g^{-1}. $LiCoO_2$ was synthesized by combustion method[90] followed by heat treatment at different temperatures in the range from 400 to 700°C. The highest discharge capacity of 136 mAh g^{-1} was obtained from 700°C heated sample with the particle size of 150 nm. However, the low temperature provided spinel $LiCoO_2$ with reduced diameter, which was electrochemically less active. Han et al.,[91] prepared sub-micron size particle of $LiCoO_2$ by a single step eutectic self mixing methods. The prepared sub-micron size particle of $LiCoO_2$ provided discharge capacity of 137 mAh g^{-1} at 0.1 C rate and 132 mAh g^{-1} at 5 C rate, whereas micron size particle provided discharge capacity of 135 mAh g^{-1} at 0.1 C rate and 119 mAh g^{-1} at 5.0 C rate. Thus, the higher rate capability of sub-micron size particles of $LiCoO_2$ than micron size particles was demonstrated. $LiCoO_2$ consisting of well crystallized, particles of diameter 200 nm were prepared by polymer pyrolysis.[92] The sample prepared at 800°C delivered capacities of 146 mAh g^{-1} and 178 mAh g^{-1} in the potential ranges 3.4–4.25 and 3.4–4.5 V, respectively. These values were greater than the commercial 8–12 μm size particles. Cho et al.,[93] reported the performance of $LiCoO_2$ cathode with a systematic variation of particle size by hydrothermal route using oleylamine as a capping agent. The prepared sample had particle size of 50 nm and on annealing the particle size increased to 100 nm, 300 nm and 1μm at 500, 600 and 700°C, respectively. Sub-micron size particles with diameter 300 nm demonstrated the best discharge capacity as well as rate capability with good cycle-life.

Lithium nickel oxide ($LiNiO_2$)

$LiNiO_2$ is iso-structural to $LiCoO_2$, and provides higher specific capacity (275 mAh g^{-1}).[94] However, it is difficult to prepare stoichiometric $LiNiO_2$ by conventional solid state reaction at higher temperatures, owing to the instability of trivalent nickel species and disordering of cationic distribution.[95,96] In the past, several attempts were made to synthesize electrochemically active $LiNiO_2$ by low temperature ion exchange reaction, [97,98] sol-gel process,[99–102] etc. Palacin et al.,[97] prepared $LiNiO_2$ by ion exchange method using NiOOH and LiOH as the starting materials. The sample prepared at 400 °C exhibited a discharge capacity in the range of 120–140 mAh g^{-1}. Sun et al.,[98] reported the synthesis of $LiNiO_2$ with particle size in the range 10–20 μm by ion exchange method at 550°C for 20 h in air. The product sample exhibited a discharge capacity of 169 mAh g^{-1} at a c.d. of 0.5 mA cm^{-2} with good cycle-life. $LiNiO_2$ synthesized by sol-gel process[99] possessed smooth edged polyhedra particles of size in the range of 3–5μm. The compound provided the first discharge capacity of 166 mAh g^{-1} and it decreased to 155 mAh g^{-1} after 20 cycles at c.d. of 7.5 mA g^{-1} in the voltage range 3.0–4.2 V. Kumta et al.,[100] reported the influence particle size on the performance of $LiNiO_2$

prepared by sol-gel method. The pristine phase was prepared at 750°C and crystallite size varied from 0.3 to 0.8 μm due to the variation of calcination time from 5 to 30 h. The maximum discharge capacity obtained was 250 mAh g^{-1} at a c.d. of 10 μA cm^{-2} for the sample with a particle size 300 nm prepared at 750°C for 5 h. There was about 10% decrease in the electrochemical performance by varying the particle size from 0.3 to 0.8 μm. A discharge capacity of 163 mAh g^{-1} was reported by Kalyani et al.,[101] at a c.d. of 0.1 mA cm^{-2} with particle size distribution in the range of 2–5μm.

Lithium manganese oxide ($LiMnO_2$)

$LiMnO_2$ has attracted considerable attention as an economical and low toxicity positive electrode material for rechargeable lithium batteries.[102] The complete removal of lithium from $LiMnO_2$ corresponds to a charge storage capacity of 285 mAh g^{-1}. $LiMnO_2$ crystallized in two polymorphs, namely, monoclinic and orthorhombic[103] (hereafter referred to as m-$LiMnO_2$ and O-$LiMnO_2$). In m-$LiMnO_2$, Li ans Mn ions have the α-$NaFeO_2$ type of cation ordering in which each ion occupies alternate octahedral sites parallel to the (111) plane of the cubic oxygen sub lattice. In O-$LiMnO_2$, a view along the (010) direction shows alternate zig-zag (corrugated) layers of Li and Mn ions.[99] The O-$LiMnO_2$ polymorph is generally considered to be more stable than m-$LiMnO_2$.[104] Initially, only medium and low temperature synthesized O-$LiMnO_2$ samples were reported to exhibit electrochemical activity.[105,106] But later, it was found that high temperature $LiMnO_2$ with structural defects also showed electrochemical activity.[107,108] Different methods of preparation of O-$LiMnO_2$ were reported. Conventional methods included solid state reaction at high temperature,[109,110] decomposition of $LiMn_2O_4$ above 940 °C,[109] calcination of mixture of Li_2CO_3 and $MnCO_3$ above 940°C under an argon atmosphere,[110] etc. Fan et al.,[111] prepared O-$LiMnO_2$ with different microstructures by co-precipitation method. The spherical shaped micron size O-$LiMnO_2$ delivered the highest discharge capacity of 152 mAh g^{-1} at constant c.d. of 15 mA g^{-1}in the voltage range from 2.0 to 4.4 V.

Although, layered $LiMnO_2$ crystal structure is metastable[102] it was possible to synthesize this oxide by soft chemical routes, namely, ion exchange method.[102] However, $LiMnO_2$ does not crystallize in the $R3\bar{m}$ space group akin to $LiCoO_2$ but in a monoclinic symmetry with space group C2/m due to cooperative Jahn-Teller distortion of MnO_6 octahedra.[103] Many attempts were made to prepare layered $LiMnO_2$.[112–114] But the resulting product turned out to be, in different stoichiometries than $LiMnO_2$, which contained protons or water and poorly crystalline in nature. Nevertheless, Bruce et al.,[102] succeeded in preparing layered $LiMnO_2$ by ion-exchange method. The initial discharge capacity was found to be 270 mAh g^{-1}. However, subsequent discharge showed poor and declining cyclability. The stabilization of capacity was achieved by partial replacement of Mn^{3+} by other metal ions such as Co^{3+}, Ni^{2+}, Fe^{2+} etc.[115–117]

Layered $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (LNCMO)

Layered $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (LNCMO) is also iso-structural to $LiCoO_2$ and it integrates the features of $LiCoO_2$, $LiNiO_2$ and $LiMnO_2$. In recent years, LNCMO has drawn much interest because of its favorable features such as high capacity, structural stability and thermal stability.[118–120] Ohzuku et al.,[118] synthesized LNCMO, at 1000°C, and reported a capacity of 150 mAh g^{-1}, when cycled between 2.5 and 4.2 V at 0.17 mA cm^{-2} at 30 °C. Several procedures for synthesis of LNCMO were reported in literature.[121–124] LNCMO was synthesized by co-precipitation method followed by annealing at a high temperature.[121] The average particle size was of about 10 μm in diameter. Electrochemical studies were carried out in different potential ranges by keeping the discharge potential limit at 2.8 V and varying the charge potential limit from 4.3 to 4.5 V. Discharge capacities measured were 159, 168, 177 mAh g^{-1} respectively. Nanoparticles of LNCMO were synthesized by Patoux and Doeff[122] by glycine nitrate combustion method. Precursors were calcined between 600 and 1000°C. The average particle size was in the range 9–70 nm. The 900°C heated sample with particle size 70 nm delivered a capacity of 145 mAh g^{-1}. However, these values are not satisfactory in comparisons to micron size particle. Martha et al.,[125] reported that sub-micron size particles of LNCMO synthesized by self combustion reaction performed better than the nanoparticles of LNCMO synthesized by the same method at low temperature. Several procedures were reported for synthesis of sub-micron size particles of LNCMO.[126–130] LNCMO reported by emulsion method[126] composed of 0.2 μm size particles and delivered a discharge capacity of 156 mAh g^{-1} with good cyclabilty. Sub-micron size particle of LNCMO were prepared by radiated polymer gel method.[128] It was found that the sample annealed at 950°C attained particle size of 320 nm and showed the best electrochemical performance with the first discharge capacity of 178 mAh g^{-1} at C/6 rate and stability on repeated cycling between 2.8 and 1.5 V. The optimized LNCMO exhibited rather good rate capability with

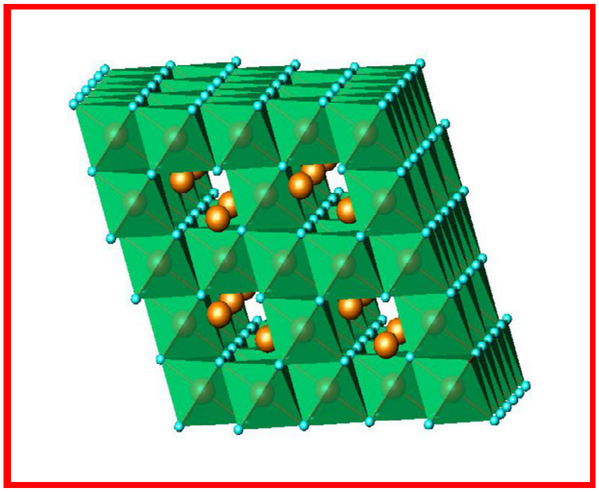


Figure 3: Crystal structure of $LiMn_2O_4$

173 mAh g^{-1} at 0.2 C rate and 116 mAh g^{-1} at 4 C rate. In another study, LNCMO was synthesized by a wet chemical process.[129] The compound annealed at 900°C delivered capacities of 180 and 160 mAh g^{-1} in potential windows 2.5–4.6 and 2.5–4.4 V, respectively. Recently, porous LNCMO was synthesized by our group.[130] The particle size and porosity were varied systematically by annealing the precursors with different temperatures ranging from 600 to 900°C. It was shown that sub-micron size particles of LNCMO with crystallinity prepared at 900°C delivered a discharge capacity of 163 mAh g^{-1} at C/5 rate in potential range between 2.5 and 4.3 V. Additionally, this sample exhibited good rate capability with specific capacity 163 mAh g^{-1} at C/5 rate and 60 mAh g^{-1} at 24 C rate. It was shown recently by Martha et al.,[125] that sub-micron size particles of LNCMO performed better than nano-LNCMO. Our studies further strengthen the importance of sub-micron size particles of LNCMO for Li- ion battery application.

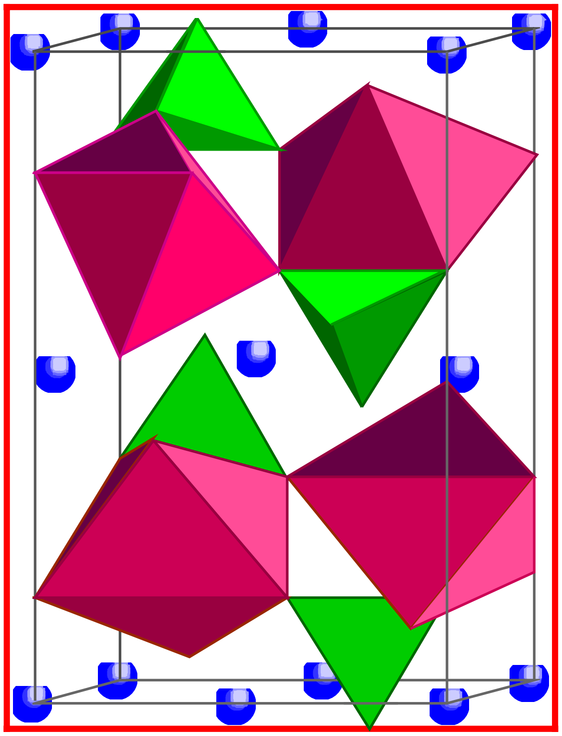
Spinel lithium manganese oxide ($LiMn_2O_4$)

The use of manganese based oxides in rechargeable lithium ion battery has been stimulated due to their low cost and environmental compatibility.[42] The spinel $LiMn_2O_4$ was originally proposed by Thackeray et al.,[42] and it was extensively developed by Belcore.[131–133] The attractive features of $LiMn_2O_4$ led in 1996 to the announcement by Nippon of the first commercial rechargeable Li battery in which they replaced $LiCoO_2$with $LiMn_2O_4$.[134]$LiMn_2O_4$ is quite different from the layered oxide in that it is a three dimensional host. The structure of stoichiometric spinel $LiMn_2O_4$ with space group $Fd\bar{3}m$, can be described as layers of close packed oxygen atoms, in which Li and Mn ions occupy tetrahedral (8a) and octahedral (16a) sites, respectively, as shown in the Fig. 3.

In the framework, MnO_6 octahedra share edges to build a rigid three dimensional network with open interconnected channels in (110) direction where Li^+ ions are present.[135] Li^+ ions are mobile along the 8a–16c–8a path. The spinel $LiMn_2O_4$ possesses 10% less capacity than $LiCoO_2$. Reversible extraction/insertion of Li^+ from the matrix proceeds in predominantly two steps, one around 4 V and the other around 3 V.[132,136,137]However, the insertion/deinsertion at about 3 V leads to poor cycling behavior due to the asymmetric lattice expansion/contraction associated with the Jahn-Teller effect of the Mn^{3+} ion.[138,139] During the 4 V potential range the cubic symmetry was maintained consequently leads to good rechargeability and cycling stability.

Traditionally, spinel $LiMn_2O_4$ was synthesized by conventional solid state methods[140,141] by heating lithium compounds (LiOH, Li_2CO_3, $LiNO_3$ or LiI) with manganese oxide, acetate or hydroxide. Since the annealing process involves at high temperature in air it leads to the formation of large particle size in the range 1–3 μm. Nanoparticles of spinel $LiMn_2O_4$ were synthesized by a variety of procedures, which included sol-gel,[142–144] laser ablation,[145] template synthesis,[146,147] combustion synthesis, [148] spray drying,[149] resorcinol-formaldehyde route,[150] solid state reaction,[151,152] Pechni method,[153,154] and microemulsion, [155,156] etc. Cabana et al.,[139] obtained the $LiMn_2O_4$ by hard template route. Particles of an average size of 15 nm were obtained by firing the reactants at 600°C for 4 h. In comparison to the micron size particles, nanoparticle of $LiMn_2O_4$ offered better performance. A discharge capacity of 113 mAh g^{-1} was obtained by nano- $LiMn_2O_4$ whereas micron size particles of $LiMn_2O_4$ delivered a capacity of 105 mAh g^{-1}. Moreover nano-$LiMn_2O_4$ was found to exhibit better performance at 2C rate with better capacity retention in comparison with the micron size particles. Nanocrystalline $LiMn_2O_4$ particles of size around 42–70 nm were prepared by combustion synthesis.[148] The compound synthesized by using PVA-urea delivered a discharge capacity of 137 mAh g^{-1} with only 10% reduction of the capacity after 50 cycles. In another study, Wu et al.,[149] reported a discharge capacity of 131 mAh g^{-1} at C/5 rate with good capacity retention for $LiMn_2O_4$ of particle size less then 100 nm synthesized by spray drying method. Stoichiometric $LiMn_2O_4$ was synthesized by Shaju et al.,[150] which consisted of particles of

Figure 4: Crystal structure of $LiFePO_4$



50–100 nm fused to form a porous structure. The oxide delivered an initial capacity of about 131 mAh g^{-1} with an excellent cyclability at a discharge rate of C/2. In relation to this value, the oxide retained 90% of its capacity at 40 C and 85% at 60 C. The electrochemical performance of $LiMn_2O_4$ was reported to have a close relationship with its morphology. Cui et al.,[151] synthesized $LiMn_2O_4$ nano rods by a solid state reaction. The prepared $LiMn_2O_4$ had an average diameter of 130 nm and length of 1.2 μm. The performance of the nanorods was better than a commercial sample at high rates, although the discharge capacity was almost the same (100 mAh g^{-1}) at C/10 rate. Single crystalline spinel nanowires were synthesized by a high temperature solid state reaction.[152] However, most of the nanostructured electrode materials were prepared at low temperatures. The discharge capacity values at c. ds. 0.1, 5, 10 and 20 A g^{-1} were 118, 108, 102 and 88 mAh g^{-1}, respectively. However, the commercial samples provided lower capacity values at high rates probably because of their large particle size.

Depending on the synthetic procedure, nanosized $LiMn_2O_4$ with different physical and chemical properties such as crystallinity, specific surface area and different morphologies were obtained. Nanoparticles of $LiMn_2O_4$ synthesized by acetate based solution route[157] exhibited severe capacity fade on cycling. In search for materials with smaller particles in comparison with the existing micron sized particles, recently sub-micron size particles have drawn attention. Several procedures were reported for the synthesis of sub-micron size particle of $LiMn_2O_4$.[158–165] Wu et al.,[158] reported the formation of $LiMn_2O_4$ by Pechni method followed by heating between 600 and 800°C for 6 h. Size of the particles increased from 30 nm to 0.2–0.6 μm on heating from 600–800°C. The sub-micron size particles performed better than the nanosize particles prepared at low temperature. Similar data were reported by Liu et al.,[159] $LiMn_2O_4$ was prepared by sol-gel method[160] using lithium and manganese acetate as precursors. It was reported that the calcined product at 600°C had an average particle size of 119 nm. However, the spinel phase was obtained at 300°C itself. The sample heated at 600°C delivered a discharge capacity of 120 mAh g^{-1} with good cyclability in relation to the nanosize sample prepared at a low temperature. Hydrothermally[161] prepared $LiMn_2O_4$ having particle size distribution in the range of 50–300 nm delivered a discharge capacity of 121 mAh g^{-1} at rate C/10. Synthesis of sub-micron size particles of $LiMn_2O_4$ by microemulsion route is versatile method.[162–163] We have recently synthesized $LiMn_2O_4$ with particle size in the range of 100–200 nm by inverse microemulsion route.[163] $LiMn_2O_4$ obtained at 900 °C provided a discharge capacity of about 100 mAh g^{-1} at C/5 rate and it was shown that there was a moderate decrease in capacity with an increase in rate of cycling.

Olivine compounds (*$LiFePO_4$*)

The importance of $LiFePO_4$ arises from low raw material cost, environmentally compatibility, and high thermal stability at fully charged state, high energy density and high safety in comparison with the other positive electrode materials.[47] Its capacity approaches 170 mAh g^{-1}, higher than that of $LiCoO_2$. $LiFePO_4$ adopts the olivine structure with space group Pmna in which Li, Fe and P atoms occupy octahedral 4a, octahedral 4c and tetrahedral sites, respectively.[47] (Fig. 4)

Lithium iron phosphate was first reported as a cathode material for rechargeable Li-ion batteries in 1997 by Goodenough's group.[47] It can be prepared by several methods including solid state,[47] hydrothermal,[165] sol-gel methods,[166] etc. Depending on the synthetic conditions, the capacity of $LiFePO_4$ can reach high values up to 115 mAh g^{-1}.[167] As this material has very low electronic conductivity (10^{-9} S cm^{-1} at room temperature), it provides poor discharge capacity at high rates. Ravet et al.,[168] showed that carbon coating given on the particles significantly improves the electrochemical performance. An increase in electronic conductivity was studied, in recent years by various group through cationic doping, decreasing the particle size via solution based synthesis, and coating with electronically conducting agents.[169–174] Reduction of the particle size to the nanoscale is reportedly effective for the $LiFePO_4$. The reactivity of the highly oxidized $Co^{3+/4+}$ and $Ni^{3+/4+}$ couples with the electrolyte and Mn dissolution from the spinel lattice restrict the use of nanostructure layered and spinel oxides. On the other hand $LiFePO_4$ is chemically stable, and its reactivity is selective. Only Li moves in and out from the structure, and the phosphate group is totally unreactive. The possibilities for reaction of oxygen with the electrolyte are scarce. Even on reaction with excess lithium the phosphate group remains intact as Li_3PO_4 and Fe metal is formed. Thus, $LiFePO_4$ is suitable for increasing the rate capability by downsizing the particles.

Various synthetic routes, such as sol-gel,[175] hydrothermal,[176] microwave assisted solvothermal and hydrothermal,[177] polyol,[178,179] template method,[180] etc., were reported. $LiFePO_4$ synthesized by sol-gel[175] route in temperature range 450–850°C consisted of 20–30 nm particles. The sample prepared at 850°C delivered better performance with high discharge capacity with good rate capability than the other samples. Nanorods and nanoparticle of $LiFePO_4$ were synthesized by hydrothermal method.[176] The nanorods provided a discharge capacity of 160 mAh g^{-1} and good cycle-life. Manthiram et al.,[177] recently synthesized $LiFePO_4$ with nanostructures by microwave assisted solvothermal and hydrothermal route. It was reported that nanorods with shorter length (ie., 25 nm×100 nm) performed better than 40 nm×1 μm nanorods. The small rods offered capacity of 166 mAh g^{-1}, which was close to the theoretical value of 170 mAh g^{-1}. In another study, nanoparticles of $LiFePO_4$ were synthesized by polyol method.[178,179]discharge capacity of 166 mAh g^{-1} was measured at a current density of 0.1 mA cm^{-2} with good cycle-life. Moreover, it exhibited high rate performance at 30 C and 60 C rates with 58 and 48% of capacity retention, respectively. Sub-micron size particles of $LiFePO_4$ were synthesized by various processes such as sol-gel,[181] precipitation method,[182] and hydrothermal method,[183] etc. Porous $LiFePO_4$ with a size distribution 100–300 nm was prepared by sol-gel route.[181] It delivered discharge capacities of 125 and 157 mAh g^{-1} at 10 C and 1 C rates, respectively with good cylcabilty. Masquelier et al.,[182] prepared $LiFePO_4$ by direct precipitation method followed by soft thermal treatment at 500°C for 3 h under slight reducing atmosphere. Particles of 140 nm were obtained. Electrochemical performance of the sample was attractive in terms of specific capacity, i.e., 147 mAh g^{-1} at 5 C rate, and there was no significant capacity fade after more than 400 cycles. In another study, hydrothermaly prepared $LiFePO_4$ consisting of 100–300 nm size particles yielded an initial discharge capacity of 167 mAh g^{-1} at 0.1 C rate. Zhang et al.,[183] prepared $LiFePO_4$ with particle sizes between 100 nm and 200 nm. The electrochemical performance of the sample synthesized at 500°C delivered a high discharge capacity of 166 mAh g^{-1} at 0.1 C rate and possessed a favorable capacity retention on cycling at different rates from 0.1 to 10 C rate.

Since the pioneering work on $LiFePO_4$ by Padhi et al.,[47] other transition metal phosphates with olivine structure were also studied. Among them, $LiMnPO_4$ is of particular interest due to the potential of Mn^{3+}/Mn^{4+}redox couple located at 4.1 V vs. Li^+/Li. $LiMnPO_4$ therefore is more promising than $LiFePO_4$ due to the higher operational voltage by about 0.6 V.[47]However, Padhi et al.,[47] and Okada et al.,[184] were unable to take any lithium out of $LiMnPO_4$. Later, a reversible capacity of 140 mAh g^{-1} for several cycles was reported by Li et al.,[185] for $LiMnPO_4$/C composite powder synthesized by a solid state route. Improvements in the performance of $LiMnPO_4$ were achieved by reducing the particle size by a different synthetic route.[186–188] Delacourt et al.,[186] synthesized 100 nm diameter particles of $LiMnPO_4$ by precipitation method. A discharge capacity of 70 mAh g^{-1} was obtained at C/10 rate which was higher than micron size particle (1 μm, 38 mAh g^{-1}). $LiMnPO_4$ powder was prepared by polyol method.[187] The particle size was 150 nm, and delivered capacity of about 115 mAh g^{-1}. Exnar et al.,[188] reported the effect of particle size of $LiMnPO_4$ cathode. Particles of different sizes in the range of 140–220 nm were prepared by sol-gel method and followed by post heating at 600°C. Sub-micron size particles of diameter 140 nm delivered discharge capacities of 134 and 156 mAh g^{-1} at C/10 and C/100 rate, respectively.

Conclusions and remarks

Nanotechnology is presently considered as one of the most promising technologies in several fields of applications with significant importance. Electronics has undergone marvelous transformations in recent decade and this field is further expected to experience rapid changes owing to nanotechnology. Miniaturization of electronic devices followed the predictions of Moore. However, there was a lag on the progress of battery technology to compete with miniaturization in electronics. The gap between the technologies of electronics and battery has narrowed down to some extent with the advent of Li-ion battery. However, further rapid developments are required in miniaturization of battery with greater power and energy capabilities than what exists at present. Electric vehicle application is another emerging area for which the society holds expectations on battery technology. High energy density, high power density, long cycle-life, low cost, fast charging and longer mileage are the required features of batteries for electric vehicles. Battery technology employing nanostructured materials may appear to bridge the gap at least partially. However, the reported results as reviewed in this paper appeal for a cautious selection of the particle size of the materials. This aspect essentially arises due to high reactivity of nanoparticles with the electrolyte.

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