
**LITERATURE SURVEY & SCOPE OF
THE PRESENT WORK**

LITERATURE SURVEY AND SCOPE OF THE PRESENT INVESTIGATION

In this chapter, earlier work on the preparation of LiMn_2O_4 based thin film cathode materials have been focused, along with a scope of the present investigation.

2.1. INTRODUCTION

In the late 1980s carbon anodes become a break through in realizing the lithium-ion batteries [1] and have solved the safety problem of lithium metal anode [2]. Since the first commercialization by Sony [3] in the early 1990s, the lithium-ion rechargeable battery has become a major product to dominate the market for small rechargeable batteries [4]. Though commercialized Li-ion batteries are using various types of cathode materials such as layered LiCoO_2 [5], LiNiO_2 [6] and LiMn_2O_4 spinel phase [7-10], low cost materials based on manganese are being developed [11-15]. Wakihara et al [16] reported that lithium diffusion is easier in three dimensional frame works than in two-dimensional structure, as in the former structure the number of contact points of the diffusion paths for lithium ions is larger than that in the later. They suggested that the intercalated cathode materials for lithium-ion batteries with three-dimensional frame work are more stable than two-dimensional materials. A three-dimensional frame work with spinel phase LiMn_2O_4 based thin film active materials has been focused here.

2.2. LITERATURE SURVEY

The spinel LiMn_2O_4 has attracted wide attention as an intercalation cathode material for rocking chair batteries due to its several advantages, eventhough the commercial exploitation of LiMn_2O_4 has been hampered by capacity loss upon prolonged cycling [17,18]. The capacity fade has been attributed to Jahn-teller distortion [19,20], lattice instability [21,22], manganese dissolution [19,20,23,24], oxidation of the electrolyte [23,25], formation of oxygen-rich spinel [26] and lattice site exchange between lithium and manganese ions [27]. This deficiency was overcome by introducing extra lithium in the spinel with a limited success [19,27]. Substitution of the manganese with another metal may increase the stability of the spinel structure or may enhance the operating voltage of the system at the expense of deliverable capacity [28-30].

Hee-Soo Moon et al [31] synthesized LiMn_2O_4 thin films by a co-sputtering method to improve its structural and electrochemical properties. They also prepared LiMn_2O_4 thin films by radio frequency magnetron sputtering to know the effect of film stress on the electrochemical properties [32].

Cheng - Lung Liao et al [33] prepared LiCoO_2 thin film by rf sputtering on Pt coated silicon. The as-deposited film had a nano-crystalline structure with (104) preferred orientation. After annealing at 500-700°C, single phase LiCoO_2 was obtained when the film was originally deposited under an oxygen partial pressure from 5 to 10 mTorr. The degree of crystallization of the LiCoO_2 films was strongly affected by the annealing temperature; a higher temperature enhanced the crystallization of the deposited LiCoO_2 film. LiCoO_2 films deposited by rf sputtering

were economically active. The first discharge capacity of LiCoO_2 thin film annealed at 500°C was about 41.77 which increased with annealing temperature.

Seung-Joo Lee et al [34] prepared thin film $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode for rechargeable microbattery by electron beam evaporation method. The deposited film showed almost amorphous characteristics with some crystalline phases. Hexagonal phase of $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ formed in the films was annealed between $500\text{-}700^\circ\text{C}$. The crystallinity of the film was improved as the annealing temperature increased to 700°C . The film annealed at 700°C for 10 min. showed a similar OCV curve to that of bulk powder cathode. It was suggested that $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ thin film was suitable cathode for Li-rechargeable microbattery.

F.K. Shokoohi et al [35] fabricated thin film cathodes of $\text{Li}_x\text{Mn}_2\text{O}_4$ ($x \leq 1$) which can reversibly intercalate nearly one Li atom per unit formula at a steady potential of 4.1V. This resulted in a theoretical energy density of about 600 Wh/Kg. The polycrystalline films showed an electrochemical performance exceeding that of bulk materials. This was attributed to the small grain size and to the porosity with these $\text{Li}_x\text{Mn}_2\text{O}_4$ three dimensional spinel films, which reduced the diffusion path length for Li^+ ions. The films were tested as the cathodes at about 70 charging/discharging cycles in a secondary lithium cell, at current rates of $10\text{-}100 \mu\text{Acm}^{-2}$. No measurable self discharge over 12h periods was observed.

S.B. Tang et al [36] prepared LiMn_2O_4 thin films on Si substrates at 575°C and 100 mTorr of oxygen by pulse laser deposition. The film was flat and dense with an average size of crystals of about 260 nm and showed mainly (111) out of plane

preferred texture. The initial specific capacity is about 111 mAhg^{-1} with a current density of $50 \mu\text{Acm}^{-2}$.

S.B. Tang et al [37] prepared LiMn_2O_4 thin films with nano-crystals less than 100 nm were successfully grown on polished stainless steel substrates at 400°C and 200 mTorr of oxygen by pulse laser deposition. A maximum discharge capacity of $62.4 \mu\text{Ah cm}^{-2}\mu\text{m}^{-1}$ when cycled between 3.0 and 4.5V with a current density of $20 \mu\text{Ahcm}^{-2}$ was achieved.

Th. Dumont et al [38] deposited LiMn_2O_4 by pulse laser method and the influence of the Li-content in LiMn_2O_4 was studied. The films deposited at different background pressures and different substrate / target distances showed very different behaviour in the electrochemical measurements.

Hui Xia et al [39] grew LiCoO_2 thin films by pulse laser deposition on stainless steel and SiO_2/Si (SOS) substrates. The structural properties of LiCoO_2 on both substrates were investigated. The electrochemical properties of LiCoO_2 thin films on both substrates were investigated by cyclic voltammetry and charge / discharge against lithium anode. Thin films on stainless steel substrates showed on rough surfaces random orientations, while those on SOS substrates showed relatively smooth surfaces and preferred (003) out of plane orientation. Charge/discharge measurements indicated that the thin films on SOS substrates had higher utilizations with better capacity retentions. It revealed that the thin film with random orientation had faster mass transport of lithium ions and the thin film with preferred (003) orientation had better structural stability.

Chuying ouyang et al [40] grew LiMn_2O_4 films on different substrate from pulse laser deposition techniques. Substrate determined the film quality. The laser energy and the pulse frequency were very important to the surface morphology. The films grown on the SrTiO_3 (100) surface showed (400) and (111) orientations, while the films grown on the stainless steel had no preferred orientations.

K.A. Striebel et al [41] prepared thin films of LiMn_2O_4 and Li_xCoO_2 by pulse laser deposition on heated stainless steel substrates. These films had thickness from 0.2 to 1.5 μm and were crystalline without post deposition annealing. Film capacity densities as high as 56 and 62 $\mu\text{Ahcm}^{-2}\text{-}\mu\text{m}^{-1}$ were measured for $\text{Li}_x\text{Mn}_2\text{O}_4$ and Li_xCoO_2 respectively and its suitability for the production of cathode films for microbatteries were explained.

A. Rughier et al [42] prepared $\text{Li}_x\text{Mn}_2\text{O}_4$ spinel by pulse laser deposition method using constant current cycling and cyclic voltammetry. Films had been cycled more than 220 times with no significant capacity loss. Films were subjected to over charge and over discharge. Over charges did not significantly affect the structure of the film. But it led to changes in the shape of the cyclic voltammogram.

C. Julien et al [43] grew LiMn_2O_4 thin film by pulse laser deposition (PLD) and their electrochemical properties were tested for lithium microbatteries. Electrochemical measurements showed a good cycleability of PLD films when cells were charged-discharged at current densities of 5-25 μAhcm^{-2} .

P. Frangnaud et al [44] prepared LiCo_2O_4 and LiMn_2O_4 by low pressure chemical vapour deposition at 450 - 650°C. The use of spray pyrolysis technique was

successful in preparing both LiCoO_2 and LiMn_2O_4 at substrates heated to temperatures as low as 400°C .

Hee-soo Moon et al [45] also deposited LiMn_2O_4 by CVD method and a diamond like carbon (DLC) coated LiMn_2O_4 film. Among them, DLC coated LiMn_2O_4 film was more stable during the charge / discharge reaction and showed higher discharge capacity and a wide voltage window than the uncoated LiMn_2O_4 film.

Y. Iriyama et al [46] fabricated highly crystalline nanosized lithium manganese oxide particles by spray pyrolysis. The resultant particles had well-developed face planes in a transition electron microscopy image and electron diffraction pattern from a single particle showed clear diffraction spots, suggesting the prepared particles were highly crystalline. The mean crystalline size increased with in annealing temperature and influenced the electrochemical lithium insertion-extraction properties of the particles. Samples annealed at 773K showed different kinds of lithium insertion extraction properties in the cyclic voltammogram and only a couple of broad redox peaks were observed at around 0.8V between 0.4 and 1.0V . It was suggested that the sample annealed at 773K sample of grain boundaries, affected in different kinds of phase transition reactions.

Izumi Taniguchi et al [47] prepared LiMn_2O_4 microparticles by a combination of spray pyrolysis and drying method from the precursor solution LiNO_3 , $\text{Mn}(\text{NO}_3)_2$ in distilled water. The tap density of LiMn_2O_4 microparticles prepared by a combination of spray pyrolysis and drying method was larger than that by a conventional spray pyrolysis method. The LiMn_2O_4 obtained by the combination of

spray pyrolysis and drying method was studied for electrochemical characteristics and tap density.

Do youp Kim et al [48] prepared fine sized LiCoO_2 particles by spray pyrolysis from polymeric precursor solution using citric acid and ethylene glycol. The mean size and aggregation degree of the primary particles are affected by the concentrations of polymeric precursors added into spray solutions. LiCoO_2 particles obtained from the spray solution without polymeric precursors had irregular and aggregated morphology. The discharge capacities of LiCoO_2 particles changed from 132 to 151 mAhg^{-1} when the concentration of citric acid and ethylene glycol changed from 0 to 1M. The particles prepared from the spray solution containing 0.3M each of citric acid and ethylene glycol had the maximum discharge intensity.

J.L. Shui et al [49] fabricated LiMn_2O_4 thin film electrodes with three different morphologies sponge like porous, fractal - like porous and dense structures. It was found that the cells with LiMn_2O_4 electrodes of porous (especially the sponge like porous) morphology had better rate capacity than those with dense LiMn_2O_4 electrodes. Electrochemical impedance spectroscopy study indicated that the large surface area of the porous electrodes should be attributed to the smaller interfacial resistance and better rate capability.

Shinji Koike et al [50] prepared LiMn_2O_4 films with vertically aligned holes by electrostatic spray deposition (ESD) and subsequent annealing. Different surface morphologies such as dense grains, $1\mu\text{m}$ - diameter pores with $1\mu\text{m}$ thickness walls, and $5\mu\text{m}$ pores with $3\mu\text{m}$ walls were formed by varying the lithium sources in the precursor solution. The randomly oriented pores in the films prepared using ESD

were rearranged in vertical stacks after annealing to produce crystalline LiMn_2O_4 . This process would be suitable for constructing three-dimensional interfaces between active materials and solid state electrolytes.

Jun Ma et al [51] fabricated LiMPO_4 ($M=\text{Mn, Fe}$) and $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ thin films by electrostatic spray deposition combined with sol-gel method, in which P_2O_5 was used as a phosphorous resource in Li-M-P-O alcohol precursor solution. Analysis of LiMnPO_4 solid films using X-ray diffractometry and scanning electron microscopy demonstrated the formation of olivine phase of space group $Pmn2_1$ with nanocrystalline morphology. The prepared LiMPO_4 films were evaluated electrochemically by cyclic voltammetry and charge / discharge measurements. $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ exhibited better electrochemical performance than that of pure LiFePO_4 and LiMnPO_4 .

I. Taniguchi et al [52] synthesized LiMn_2O_4 powder with submicron size particles by ultrasonic spray pyrolysis method. The powder was synthesised successfully at a constant temperature distribution (1073K) at various gas flow rates ranging from 0.5 to 4.0 dm^3/min . The as-prepared samples were used as cathode materials for lithium ion battery and their charge/discharge properties had been investigated.

K. Matsuda et al [53] successfully synthesised LiMn_2O_4 particles by ultrasonic spray pyrolysis method and the product characteristics were examined. All the samples exhibited the spinel structure with out determined lattice parameter and chemical composition of all the samples showed any impurities in the XRD patterns. The as-prepared samples were then used as cathode active materials for lithium-ion

battery, and electrochemical studies were carried out on the charge/discharge characteristics of the Li/LiMn₂O₄ cells. The effects of LiMn₂O₄ particle properties such as crystallite size, specific surface area and particle morphology on the electrochemical properties were studied.

S.-H. Park et al [54] prepared LiMn₂O₄ by ultrasonic spray pyrolysis method which was characterized using X-ray diffraction, SEM, TEM and electrical cycling at 3V regions. The LiMn₂O₄ powders were of about 10 nm-sized primary particles. The delivery discharge capacity of the synthesized nano-materials was 125 mAh/g between 2.5V and 3.5V and its retention was about 96% upon 50 cycling. Here, the structural transition of the parent material did not occur even after the 50th electrochemical cycling on the 3V region. It seems that the reversible structural change was possible for nanocrystalline LiMn₂O₄ as observed by the X-ray diffraction and transition electronic microscopic observations.

S.-H. Park et al [55] synthesised LiNi_{1/2}Mn_{3/2}O₄ powder via ultrasonic spray pyrolysis method with different pH condition. After pyrolysis the as-prepared particles with pH 7 condition had a dense spherical morphology without aggregation. High crystalline powder synthesized over 900°C showing well developed octahedron particle shape. The discharge capacity of the synthesised materials was delivered over 135 mAh/g between 3.5 and 5.0V with high capacity retention during 40 cycles.

Z. Bakenov et al [56] nanostructured powders were successfully synthesized LiM_xMn_{2-x}O₄ (M=Co,Al) by ultrasonic spray pyrolysis method. The resulting powders were spherical nanostructured particles with few tens of nanometers on

size. The nanostructured $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ ($M=\text{Co}, \text{Al}$) powder were sintered at 750°C for 4 hrs in air. However its particle morphology and pure spinel phase did not change after sintering. The nanostructured $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ ($M=\text{Co}, \text{Al}$) obtained by ultrasonic spray pyrolysis technique showed excellent high charge-discharge rate capability.

2.3. SCOPE OF THE PRESENT INVESTIGATION

Fabrication of all solid state microbatteries has received much attention in the recent years, to use as a power source for microelectronic devices. Among these batteries, lithium-ion microbattery made from thin film electrode materials and polymer electrolytes plays an important role. Several metal oxides have been reported to be used as cathode material for Li-microbatteries. Among them, cubic spinel lithium manganese oxide has attracted much attention because of its high voltage, low cost and non-toxicity [57, 54]. However, the cubic spinel cathode material suffers from Jahn-Teller instability on prolonged cycling [21]. So thin film electrodes are prepared as an useful alternative in order to avoid the cycling stability problem, kinetics of Li^+ ion transport, conductivity and high interfacial resistance with porous electrode etc.

The present investigation, aims in preparing LiMn_2O_4 thin film cathode materials by conventional spray pyrolysis method and polymer spray pyrolysis method using poly (ethylene glycol). In these methods, the best method has to be selected for the preparation of $\text{LiY}_y\text{Mn}_{2-y}\text{O}_4$, $\text{LiGd}_y\text{Mn}_{2-y}\text{O}_4$ and $\text{LiNd}_y\text{Mn}_{2-y}\text{O}_4$ ($y = 0.01, 0.03, 0.05$) thin films. Physical and electrochemical characterization studies are to be carried out on these materials. They are

- ❖ Thermal analysis to find out the phase formation and/or complete crystallization temperature of the precursor solutions.
- ❖ The measurement thicknesses of the prepared thin films by Stylus surface profilometer.
- ❖ The prepared thin film cathode materials are to be characterized by X-ray diffraction studies.
- ❖ The surface morphology and particle size of the prepared thin film cathode materials are to be studied by scanning electron microscopy (SEM) studies.
- ❖ The surface analysis of prepared thin film cathode materials is to be carried out by atomic force microscopy (AFM).
- ❖ Electrochemical cells in the configuration of $\text{Li} // \text{LiM}_y\text{Mn}_{2-y}\text{O}_4$ ($M = \text{Y, Gd, Nd}$) employing Li^+ ion conducting PVdF-HFP based micro-porous polymer electrolyte would be fabricated using these thin film cathodes. The charge and discharge studies would be carried out galvanostatically at the current density of $0.2\text{mA}/\text{cm}^2$ in the voltage range of 3.0 - 4.5 V.

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