

Synthesis and Investigation of Electrochemical properties of $\text{LiBa}_y\text{Mn}_{2-y}\text{O}_4$ Cathode Materials for Lithium-ion Batteries

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Abstract - Many investigations are being carried out to discover a good cathode material for rechargeable lithium ion batteries. In this study, barium doped LiMn_2O_4 ($\text{LiBa}_y\text{Mn}_{2-y}\text{O}_4$ ($y=0.1, 0.2, 0.3, 0.4$)) cathode materials have been synthesized by a new method called citric acid modified microwave assisted sol-gel method. The electrochemical properties were studied through cyclic voltammetric technique. From the cyclic curves, the intercalation and deintercalation of Li^+ over the range of 3-5V are confirmed. The results suggest that Ba doped LiMn_2O_4 cathode materials displayed better cycling stabilities. In general, the doped materials show better electrochemical performance compared with LiMn_2O_4 particularly $y=0.3$ has been observed high capacity retention and less capacity loss. Thus, $\text{LiBa}_y\text{Mn}_{2-y}\text{O}_4$ is found to be the best cathode material for high voltage lithium ion batteries.

Keywords - Lithium ion battery, lithium manganate, doping, barium, high capacity retention

I. INTRODUCTION

Currently, fossil fuels and nuclear power are the major energy sources. However, these sources have some drawbacks such as presence of limited amount of fossil fuels and environmental problems related to nuclear waste disposal. Moreover, the combustion of fossil fuels causes global warming. Hence researchers of interdisciplinary scientific community focus on developing alternative energy sources and storage techniques, for example photo electrochemical cells, fuel cells and batteries in particular, lithium-ion batteries. The commercial lithium ion batteries with high energy density and good life cycle serve as very good power sources for portable electronics. Many researchers have investigated various cathode materials for rechargeable lithium batteries [1]. Lithium batteries can be mainly classified into lithium batteries and lithium-ion batteries. The practical difference between Lithium batteries and Lithium-ion (Li-ion) batteries is that most Lithium batteries are not rechargeable but Li-ion batteries are rechargeable.

In a lithium-ion battery, lithium ions are employed as “energy carriers” and move from the anode across the electrolyte to the cathode during battery discharge and vice versa as the battery is recharged. Insertion is a general term used to describe a reaction involving the transfer of a guest atom or ion into a crystal host, e.g., lithium ion insertion in an electrode material. Electrode materials (lithium insertion

compounds) must combine high lithium-ion conductivity and electronic conductivity, and have a suitable structure to facilitate reversible insertion and extraction of lithium ions. Layered or network structures, in which lithium ions can diffuse and be stored between the layers or in the channels of the material, are commonly used as insertion compounds. Among various insertion compounds used in lithium batteries, the LiMn_2O_4 based spinel phase has been used as an attractive positive electrode material due to its low cost and less toxic nature than layered oxides such as LiCoO_2 and LiNiO_2 [2, 3]. However, LiMn_2O_4 suffers from capacity fade which limits its cycle ability. To overcome these problems, the substitution of some of the manganese with additional lithium ($\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$) or metal cations (Ni, Cr, Co, Ba, Sr) substituted LiMn_2O_4 were widely explored.

In the present work, we have investigated the Ba doped LiMn_2O_4 prepared by a novel method like citric acid modified (CAM) microwave-assisted sol-gel method. Electrochemical studies like Cyclic Voltammetric studies, Charge-discharge studies were done to assess the reversibility of the synthesized cathode materials.

II. EXPERIMENTAL

A. Synthesis of $\text{LiBa}_y\text{Mn}_{2-y}\text{O}_4$

Generally, methodology for synthesis of electrode materials for lithium ion battery can be broadly classified into solid-state, wet-chemical (solution) and vapor phase synthetic routes. Chemical vapor Deposition (CVD) [4], metallo-organic chemical vapor deposition (MOCVD) [5], laser ablation [6] etc., very expensive techniques. In the current research, a new method called CAM microwave assisted sol-gel method was used to synthesize the $\text{LiBa}_y\text{Mn}_{2-y}\text{O}_4$ ($y=0.1, 0.2, 0.3, 0.4$) cathode materials. Microwave processing of materials is fundamentally different from the conventional processing in terms of the heat generation mechanism [7-9].

LiMn_2O_4 cathode material was synthesized through CAM microwave assisted sol-gel method which is schematically represented in Fig. 1. A stoichiometric amount of lithium nitrate, Manganese acetate and barium nitrate was dissolved in triple distilled water. A calculated amount of citric acid was added as a complexing agent followed by the addition of

acryl amide. Here, the acryl amide acts as a gelling agent. The resulting solution was mixed with continuous magnetic stirring at 90°C until a clear viscous gel occurs. The obtained precursor was preserved under vacuum at 100°C for 12 h to eliminate water adequately and then was placed in microwave oven. The microwave power operated at 100% (650W) for 20 min. After the microwave treatment, the samples were calcined at 550°C for 6h, followed by slow cooling to room temperature slowly.

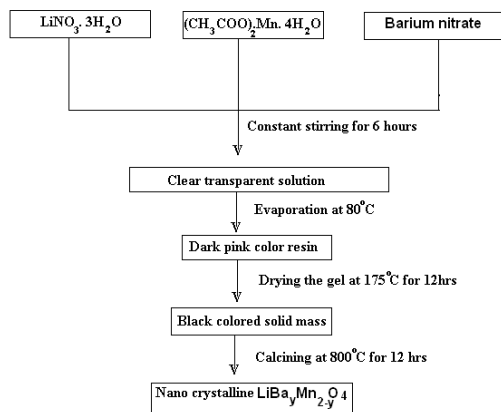


Fig. 1 Flowchart for Preparation of $\text{LiBa}_y\text{Mn}_{2-y}\text{O}_4$

B. Cyclic-voltammograms

Lithium-ion secondary cells were assembled using electrodes such as lithiated Barium based materials as cathodes and graphite pellets as anodes. Polypropylene sheet (celgard separator 2600) was used as a separator, which was soaked in 1M $\text{LiBF}_4/\text{EC}:\text{DMC}$ (1:1) electrolyte. The container for the coin cell (standard 2016 type) is made of stainless steel ASTM 316L. The cells were assembled in argon filled glove box; the humidity and oxygen content inside were maintained at ppm levels. Crimp sealing of the cells was done using a sealing die fitted onto a fly-press. The assembled cells were allowed to set for 24 hrs before they were subjected to study the material. All the works were carried out in argon filled glove box. The cyclic Voltammetric technique was used to assess the top tactical reaction of lithium in the synthesized cathode materials. The working electrode was prepared with the composition of 85% of cathode active material, 10% acetylene black and 5% of polyvinylidene difluoride (PVDF) in N-methyl-2-pyrrolidinone (NMP) with Al foil as the current collector by applying 2 tonnes pressure using a hydraulic press. Active

positive electrode was cycled between 3.0 and 4.5 V with a scan rate of 0.1mV/sec for all the compounds. The cyclic-voltammometric studies were carried out using EG & G instruments, PAR Model 6310. Electrochemical Impedance Analyzer coupled with M270 software.

C. Charge-discharge studies

Charge-discharge cycling tests for positive electrodes were carried out with constant current conditions between 3.0 to 4.5 V. At the end of each charge and discharge cycle a relaxation period of 30minutes was given while the charging was done with constant current of 0.1mA/cm². The positive electrode was made from 85:10:05 wt.% mixtures of positive electrode material, acetylene black and polyvinylidene difluoride (PVDF) binder in N-methyl-2-pyrrolidinone (NMP) solution. This mixture was cast onto pure Al foil with a sq.cm² area (thickness 0.1mm). The electrode was then cured at 140° C in a vacuum condition for 24 hours. The charge-discharge behaviour of the cells was carried out using WPG 100 (Potentiostat/Galvanostat) Won-A-Tech instrument, South Korea. The capacities of the electrodes were calculated as in terms of specific gravity (mAh/g) based on the weight of the sample. All the cathode electrodes were subjected to 25 cycles of intercalation/deintercalation to choose best-suited material for the lithium-ion material.

III.RESULTS AND DISCUSSION

The cyclic voltammetric properties of the cells were examined between the potential window of 3.0 – 5V. The resulting Voltammograms are produced in Fig. 2a-2e. Cyclic Voltammograms of $\text{LiBa}_y\text{Mn}_{2-y}\text{O}_4$ ($y=0.0-0.4$) cells show the existence of reversible structural property by their redox activity. From the cyclic curves, the intercalation and deintercalation of Li^+ over the range of 3.0-5V were confirmed. Among all, the sample prepared at $x=0.3$ has been observed to exhibit relatively narrow peaks with less peak separation compared to the Voltammogram obtained with other compositions. The peak potential separations are presented in Table 1.

A. Charge/discharge studies

$\text{LiBa}_y\text{Mn}_{2-y}\text{O}_4$ cathode materials were examined for their capacity by constant current charge/discharge at potential window 3.0-5.0V at a constant current density of 0.1mA/cm² using the assembled button cells. Figure 3a-3e show the voltage versus capacity profiles of the first charge/discharge curves for all the doped and undoped LiMn_2O_4 materials. Charge and discharge capacities are presented in Table 2

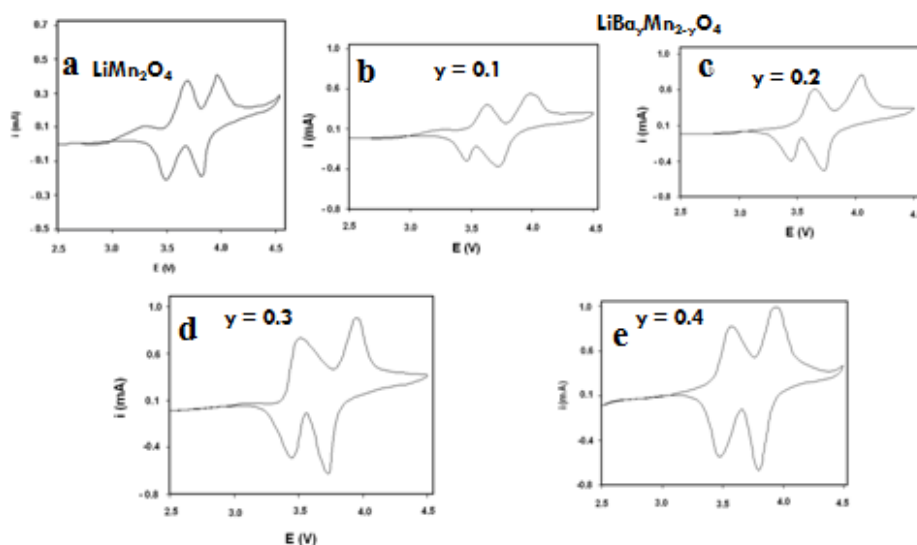


Fig. 2 Cyclovoltammograms of (a) LiMn_2O_4 and $\text{LiBa}_y\text{Mn}_{2-y}\text{O}_4$ with (b) $y=0.1$, (c) $y=0.2$, (d) $y=0.3$ and (e) $y=0.4$

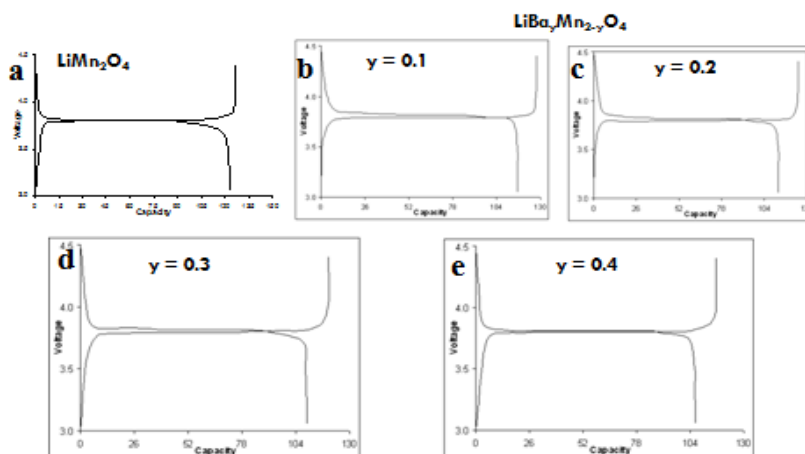


Fig. 3 Voltage versus capacity profiles of (a) LiMn_2O_4 and $\text{LiBa}_y\text{Mn}_{2-y}\text{O}_4$ with (b) $y=0.1$, (c) $y=0.2$, (d) $y=0.3$ and (e) $y=0.4$

TABLE 1 ANODIC AND CATHODIC PEAK POTENTIAL FOR ALL SAMPLES

SAMPLE	ANODIC PEAK POTENTIAL (v)		CATHODIC PEAK POTENTIAL (v)		POTENTIAL DIFFERENCE ΔE_p (V)	
	I	II	I	II	I	II
$\text{LiBa}_{0.1}\text{Mn}_{1.9}\text{O}_4$	4.12	4.5	4.22	3.95	0.17	0.28
$\text{LiBa}_{0.2}\text{Mn}_{1.8}\text{O}_4$	4.14	4.57	4.22	3.94	0.20	0.35
$\text{LiBa}_{0.3}\text{Mn}_{1.7}\text{O}_4$	4.06	4.4	4.20	3.90	0.10	0.20
$\text{LiBa}_{0.4}\text{Mn}_{1.6}\text{O}_4$	4.00	4.42	4.22	3.94	1.94	0.20

TABLE 2 CHARGE AND DISCHARGE CAPACITIES OF ALL SAMPLES

SAMPLE	CHARGE CAPACITY	DISCHARGE CAPACITY
LiMn_2O_4	128	123
$\text{LiBa}_{0.1}\text{Mn}_{1.9}\text{O}_4$	127.5	116.2
$\text{LiBa}_{0.2}\text{Mn}_{1.8}\text{O}_4$	124.8	112.4
$\text{LiBa}_{0.3}\text{Mn}_{1.7}\text{O}_4$	119.9	109.5
$\text{LiBa}_{0.4}\text{Mn}_{1.6}\text{O}_4$	116.6	106.5

B. Cycling behaviour

The capacity retention of assemble coin cells was examined at a constant charge-discharge current density of 0.1mA/cm^2 . The capacity retention in 50 cycles for doped cathode materials is 97% with undoped LiMn_2O_4 giving mainly % capacity retention. In general, the doped materials show better electrochemical performance compared with LiMn_2O_4 particularly $x=0.3$ has been observed high capacity retention and less capacity loss.

IV. CONCLUSIONS

In this study, Barium doped Spinel LiMn_2O_4 cathode materials have been synthesized by citric Acid modified microwave assisted sol-gel method. $\text{LiBa}_y\text{Mn}_{2-y}\text{O}_4$ ($0 \leq x \leq 0.4$) products prepared by calcinating its gel precursor 550°C for 12h had a good crystallinity. The electrochemical experiments results suggest that Ba doped LiMn_2O_4 cathode materials displayed better cycling stabilities. Particularly $\text{LiBa}_{0.3}\text{Mn}_{1.7}\text{O}_4$ is best cathode material for high voltage lithium ion batteries.

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