High Energy Mechano-chemical Milling: Convenient Approach to Synthesis of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ High Voltage Cathode for Lithium Ion Batteries

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Abstract:

The high voltage spinel form of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LMNO) with a particle size $\sim 10\text{-}40\text{nm}$ has been synthesized for the first time using high energy mechanical milling (HEMM) followed by low temperature thermal treatments using Li_2O , MnO_2 and NiO as the starting precursors. The nanostructured LMNO cathode, synthesized by the simple, but effective HEMM process followed by thermal treatments to refine the structure in the temperature range $\sim 573\text{K}\text{-}1073\text{K}$, exhibits a reversible capacity $\sim 120\text{-}110\text{mAh/g}$ when cycled at a rate of $\sim 20\text{mA/g}$ in the potential window $\sim 3.6\text{V}\text{-}5.1\text{V}$. The electrochemical results are comparable to reported literature methods suggesting the efficacy of HEMM as an attractive alternative approach for synthesizing battery grade high voltage spinel phase, LMNO.

Keywords: Nanostructured $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, High energy mechanical milling, Li-ion batteries, High voltage Cathode.

1. Introduction:

There is a great demand for low cost high energy density electrochemical energy storage (EES) devices to transition from the hybrid electric vehicle (HEV) technology that is currently in place to enable the realization of plug-in hybrids (PHEV) and the much desired all-electric vehicles (EVs) [1-4]. Chemical energy storage technologies based on rechargeable lithium ion batteries (LIBs) are currently the forerunner among the various EES technologies due to its high

usable specific energy ($\sim 100\text{-}150\text{ Wh/Kg}$) and high voltage operation ($\sim 3\text{V-}4\text{V}$) [2,4]. Furthermore, in recent years LIBs have emerged as the leading battery technologies meeting the much desired expectations of both electric vehicles and stationary power systems [1-6]. The high cost ($400\text{-}800\text{ \$/kWh}$) of the lithium ion battery pack, which directly translates to the materials manufacturing costs juxtaposed with the exorbitantly rising price of materials as well as the cost of labor and the tedious manufacturing steps involved in generating phase pure systems still plague the robust technology. All these factors combined with the low specific energy density ($\sim 100\text{-}150\text{Wh/kg}$) renders the market penetration very tenuous for EV's in comparison to gasoline powered vehicles [1-6]. Therefore, the development of simple and cost effective manufacturing processes of high energy and high power density electrode materials for advanced lithium ion batteries ($<100\text{-}125\text{\$/kWh}$ and $>250\text{Wh/Kg}$) is very much essential in order to enable the realization of practical EV transportation, and efficient distribution of solar- and wind-generated electrical power.

Currently LiCoO_2 , the first system pioneered by Professor Goodenough is still widely used as cathodes in commercial lithium ion batteries for portable electronic devices which exhibit a charge capacity $\sim 140\text{mAh/g}$ [7-9]. However, the high material cost, toxicity, and limited abundance of cobalt is a major deterrent for large scale application of LiCoO_2 , such as for electric vehicle and grid energy storage applications. The next material that received widespread attention in the early 1990s following commercialization of LiCoO_2 is LiMn_2O_4 , the spinel compound with the space group $\text{Fd}\bar{3}\text{m}$ exhibiting a theoretical specific capacity $\sim 148\text{mAh/g}$ and 3D diffusion tunnels for migration of Li^+ for lithiation/delithiation. The system is considered to be most promising due to various advantages, such as elemental abundance, low

materials cost, environmentally benign nature of Mn contributing to the non-toxicity of the system, and the improved safety [7-13]. However, the practical application of LiMn_2O_4 in commercial systems is still rather limited due to the rapid capacity fade which mainly arises due to the cubic to tetragonal phase transition known to occur during the charge/discharge cycle, widely attributed to the well-known Jahn-Teller (JT) distortion of Mn^{3+} , and also the corresponding dissolution of Mn in the LiPF_6 electrolyte [11,14-16].

In order to overcome these obstacles, much research has been conducted to minimize/suppress the JT distortion primarily by the addition of transition metals to substitute for Mn on the Mn site in the lattice of LiMn_2O_4 as an effective way to minimize the JT effect, while also reducing the Mn ion dissolution [16-20]. In addition, it has been reported that $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ (M= Ni, Cr, Cu, Fe, and Co) exhibits a high voltage plateau at $\sim 4.5\text{V}$ - 5V delivering a high specific capacity in the range of 120–150mAh/g with significant improvement in the capacity retention [16-20]. Among the various substituted spinels, $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$, rechargeable lithium ion batteries comprised of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LMNO) as a cathode in recent years has gained tremendous interest due to its high voltage one step discharge curve ($\sim$ above 4.5V) which is expected to deliver high energy density when combined with a high specific capacity anode in the full cell configuration [16,19-23].

Various synthetic strategies combining a combination of different procedures, involving wet chemistry, solid state reaction, sol–gel methods, template synthesis, Pechini method, etc, have been developed to synthesize battery grade LMNO [19-29]. In order to achieve a significant improvement in the electrochemical performance, approaches involving synthesis of novel

microstructures with reduction in the particles sizes of LMNO to yield nanostructured materials as well as surface modification has been proposed as an approach to improve the electrochemical performance of LMNO [16,19-29]. Unfortunately in most of the hitherto popular techniques used to synthesize LMNO, high temperature treatments are required utilizing high cost starting precursors and complicated wet-chemistry techniques adding to the complexity and overall costs for synthesizing the spinel. In addition, the presence of organic impurities particularly, hydrocarbon species arising from the incomplete oxidation of organic precursors commonly used in aqueous and non-aqueous wet chemical processes (e.g. sol-gel) combined with any undesirable species arising from adsorbed organic solvent residues incompletely pyrolyzed is further expected to be detrimental to the electrochemical performance of LMNO synthesized by the low temperature thermal treatment processes. Moreover, the high temperature thermal treatments (above 973K) to synthesize battery grade LMNO is also known to form rock salt $\text{Li}_x\text{Ni}_{1-x}\text{O}$ type impurities, detrimental for the long term cycling performance due to barriers to Li-in diffusion [22,23,25] in addition to contributing to coarsening and exaggerated grain growth further limiting ion transport. In this article, we present a simple and convenient high energy mechanical milling (HEMM) approach utilizing pure metal oxides to synthesize nanometer sized LMNO of nominal composition $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. High energy mechanical milling is a convenient process largely used in the ceramics industry involving room temperature solid state diffusive reaction of the reacting precursors. It is an attractive method for large scale manufacturing of oxide and non-oxide materials by the mechano-chemical reaction (alloying) involving solid state diffusion and comminution leading to the generation of amorphous and nanostructured materials [30-32]. The approach also provides an added advantage of yielding no undesirable byproducts in contrast to other wet-chemical processes although there is the possibility of introduction of

contaminants from the milling media when the reaction is conducted over prolonged periods. Results of the preliminary studies on the synthesis and electrochemical performance of LMNO synthesized by the simple HEMM process is provided in this manuscript.

2. Experimental Details:

Mixture of elemental powders of Li_2O (Alfa Aesar, 99.5%), MnO_2 (Alfa Aesar, 99.5%) and NiO (Alfa Aesar, 99%) of nominal composition corresponding to $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ were subjected to high energy mechanical milling in a high energy shaker mill for 20h in a stainless steel (SS) vial using 20 SS balls of 2 mm diameter (~20g) with a ball to powder weight ratio 10:1. In order to complete the reaction between the unreacted powders, the mechanically milled powders obtained after 20h HEMM were thermally treated at 573K, 673K, 773K, 873K and 973K for 6h at each temperature in air atmosphere using a platinum crucible employing a heating rate of 10K/min.

The milled and heat treated powders were characterized by x-ray diffraction (XRD) using the Philips PW1830 system employing the CuK_α ($\lambda=0.15406\text{nm}$) radiation, in order to perform qualitative phase analysis. The XRD peak profile of LMNO was analyzed using the Pseudo-Voigt function to determine the Lorentzian and Gaussian contribution of the peaks. The integral breadth of the Lorentzian contribution, determined from peak profile analysis using single line approximation method after eliminating the instrumental broadening and lattice strain contribution, is implemented in the Scherrer formula to calculate the effective crystallite size of the LMNO after 20h of milling as well as after thermal treatment [33,34]. The lattice parameter

and molar volume of LMNO after different duration of milling and after thermal treatment has been calculated using the least square refinement techniques. The microstructure of LMNO before and after electrochemical cycling has been carried out using a scanning electron microscope (SEM) equipped with energy dispersive x-ray analysis (EDAX). Philips XL-30FEG equipped with an EDS detector system comprised of an ultrathin beryllium window and Si(Li) detector operating at 25kV was employed for procuring the secondary electron (SE) image. Transmission electron microscopy (TEM) analysis was also conducted to investigate the microstructure and particle size of the HEMM synthesized LMNO. JEOL 4000EX operating at 400kV was employed for conducting the TEM analysis to evaluate the particle size of LMNO.

Electrochemical characteristics were analyzed from electrodes that were prepared by mixing 80 wt.% of the active LMNO powder of -325 mesh and 10wt.% super P conductive carbon. A solution containing 10wt.% polyvinylidene fluoride (PVDF) in N-methylpyrrolidinone was added to the mixture. The as prepared solution was coated onto an Al foil and dried at 110°C under vacuum atmosphere. A 2016 coin cell design was used employing lithium foil as a counter electrode, LMNO on Al foil as working electrode and 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC=1:2 in volume) as the electrolyte. Cyclic voltametry (CV) of 2016 coin cell comprised of LMNO synthesized at ~873K has been performed employing a scan rate of 1mV/sec. All the cells tested in this study were cycled at room temperature (~298K) within the potential range of ~3.6V-5.1V employing the discharge/charge rates of ~20mA/g-160mA/g with a minute rest period between the charge/discharge cycles using a multichannel battery testing system (Arbin BT2000 instrument). Electrochemical impedance spectroscopy (EIS) was also conducted using Versastat 3 over a frequency range of 100 kHz-100 mHz with an A.C. voltage

amplitude of 5mV. For each state of cycling, all the samples were charged to the cutoff voltage of 5.1V and then discharged to the same state of 3V holding for another 4h before EIS measurement was conducted. The Z-View (Scribner Associates, Inc.; version 3.3) was used for modeling of the impedance spectra employing the Randall's equivalent circuit.

3. Results and Discussion:

Fig. 1 shows the XRD patterns of $\text{Li}_2\text{O-MnO}_2\text{-NiO}$ after different periods of mechanical milling. After 5 min of milling, the XRD pattern shows only the presence of pure MnO_2 , NiO and Li_2O without formation of any second phase. This result clearly suggests that Li_2O , MnO_2 and NiO form a homogeneous mixture up to 5 min of milling without any significant diffusive reaction. However, formation of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LMNO) has been observed to be initiated after 1h of milling as shown in Fig. 1. As shown in Fig. 1, the volume fraction of LMNO increases with decrease in the volume fraction of the starting materials upon continued increase in the milling time. Consequently, continuous milling up to 20h appears to result in the formation of a large volume fraction of LMNO with a lattice parameter $a=8.239\text{\AA}$ (molar volume= $42.11\text{cm}^3/\text{mole}$) along with the presence of a small volume fraction of unreacted MnO_2 without any residual x-ray detectable Li_2O or NiO phases. It must be mentioned here however, that the milling time to synthesize LMNO could be significantly reduced to demonstrate the added efficacy of the approach by increasing the milling energy which can be achieved by using higher ball to powder weight ratio, higher density milling media (e.g. WC media), optimizing the filling factor, etc. [30-32]. These aspects were however not explored in the present study since the

primary objective of the present article is to demonstrate the feasibility of formation of LMNO utilizing the high energy mechano-chemical milling process.

The crystallite size of LMNO obtained after 20h of milling has been calculated from the most intense (111) peak ($2\theta = 18.64^\circ$) using the Scherrer formula utilizing the integral breadth of the Lorentzian contribution determined from the peak profile analysis using the single line approximation method after eliminating the instrument broadening and lattice strain contribution [30,31] to be $\sim 8\text{nm}$. In order to complete the reaction, the mechanically milled powder, obtained after 20h of MA, was heat treated at different temperatures in the range of 573K-1073K in an air atmosphere using the platinum crucible. The XRD patterns collected on the heat treated powder obtained after thermal treatment at and above $\sim 673\text{K}$ are shown in Fig. 2. The figure clearly shows no presence of any unreacted MnO_2 suggesting the completion of the solid state reaction between MnO_2 , NiO and Li_2O . The variation of molar volume calculated using the least square refinement technique, and the crystallite size of LMNO with heat treatment temperature is shown in Fig. 3. The molar volume of LMNO decreases with increasing temperature up to $\sim 773\text{K}$ and remains almost constant at $\sim 41.24 \text{ cm}^3/\text{mol}$ ($a = 8.181\text{\AA}$) above $\sim 773\text{K}$ which suggests that the LMNO formed is defect free without the presence of any concentration inhomogeneity. On the other hand, no significant grain growth of LMNO is observed up to $\sim 873\text{K}$ ($\sim 15\text{nm}$ after 773K and $\sim 42\text{nm}$ after 873K), whereas significant grain growth to the microcrystalline domain is observed only above $\sim 973\text{K}$. The TEM bright field image of LMNO synthesized at $\sim 873\text{K}$, shown in Fig. 4, also confirms the formation of LMNO nanoparticles of particle size $\sim 40\text{nm}$. Hence the oxide obtained at this temperature of $\sim 873\text{K}$ which exhibits defect free crystal structure along with nanometer particle size was used for further electrochemical analysis

described below. Furthermore, it is expected that the defect free nanometer sized oxide would exhibit better electrochemical response compared to the oxide derived after heat treatment at 1073K. It has to be mentioned that no detectable XRD peaks corresponding to the rock salt form of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ has been observed in the present study. The results described thus clearly suggest that nano-sized LMNO can be successfully synthesized using the simple and convenient process of mechano-chemical reaction of the individual precursors via high energy mechanical milling (HEMM).

In order to study the electrochemical activity of the synthesized LMNO for potential use as a Li-ion cathode, the electrochemical behavior and performance study of the synthesized LMNO has been carried out. Fig. 5 shows the CV curve of nano-sized LMNO synthesized at ~873K cycled within the potential window of ~2.0V-5.1V employing a scan rate of 1mV/sec. The CV curve shows two distinct reversible reaction regions occurring corresponding to the potential window of ~2V-3.6V and ~3.6V-5.1V respectively, which is indeed a characteristic of the spinel LMNO phase [10,16,17]. In the potential window of ~2V-3.6V, the de-insertion reaction of Li occurs at the peak potential of ~3V and the insertion reaction occurs at ~2.7V which is known to arise due to the $\text{Mn}^{+3}/\text{Mn}^{+4}$ redox reaction attributed to the removal/addition of Li ion from the 16c octahedral sites of the spinel phase [10,16,17]. On the other hand, in the potential window of 3.6V-5.1V, the de-insertion reaction of Li occurs at ~4.72V and ~4.81V, and the corresponding Li insertion reactions occur in the potential of ~4.62V and ~4.69V which is known to arise due to removal of Li ion from the 8a tetrahedral sites of the spinel lattice. The redox pairs corresponding to 4.72V/4.62V and 4.81V/4.69V indicate the characteristic two stages of Li-extraction and insertion occurring from the spinel framework which correspond to

the $\text{Ni}^{+2}/\text{Ni}^{+3}$ and $\text{Ni}^{+3}/\text{Ni}^{+4}$ transitions [16,17]. The small voltage plateau $\sim 3.9\text{V}$ during the de-insertion process is attributed to the Mn^{3+} to Mn^{+4} redox reactions, which may exist due to the charge compensation contribution known to be caused by oxygen loss from LMNO [16,17,23,35,36].

Fig. 6a shows the variation of specific capacity vs. potential of the nano-sized LMNO synthesized at $\sim 873\text{K}$ cycled at a rate of $\sim 20\text{mA/g}$ in the potential window $2\text{V}-5.1\text{V}$. The plot shows a charge (de-alloying) and discharge (alloying) capacity of $\sim 233\text{mAh/g}$ and $\sim 220\text{mA/g}$, respectively, which is in good agreement with previously reported 1st cycle discharge value ($\sim 262\text{mAh/g}$) of LMNO [17]. The specific capacity vs. potential curve (Fig. 6a) and the corresponding differential capacity plot (dQ/dV) (Fig. 6b) of LMNO synthesized at $\sim 873\text{K}$ of the 2nd cycle shows two distinct electrochemical reactions within the potential of $\sim 2-3.6\text{V}$ and $3.6\text{V}-5.1\text{V}$ which are quite similar to the CV plot, shown in Fig. 5 and reported dQ/dV plot in the literature [17]. The distinct plateau (Fig. 6a) and the dQ/dV (Fig. 6b) peak observed at $\sim 2.7\text{V}$ is attributed to the reduction of Mn^{+4} to Mn^{+3} involving Li ion insertion into empty 16c octahedral sites of the spinel structure [17]. It must be mentioned here that a Li-ion insertion plateau corresponding to $\sim 2.1\text{V}$, generally observed in disordered spinel structure [17], is not detected in the present study which suggests the nanostructured LMNO synthesized by HEMM followed by thermal treatment at $\sim 873\text{K}$ is in the ordered state. The associated specific capacity corresponding to the 1st ($2\text{V}-3.6\text{V}$) and 2nd ($3.6\text{V}-5.1\text{V}$) electrochemical reactions are $\sim 105\text{mAh/g}$ and $\sim 128\text{mAh/g}$, respectively as seen in Fig. 6a, which is quite similar with reported value ($\sim 129\text{mAh/g}$ and $\sim 133\text{mAh/g}$) of LMNO cycled in the potential window of $2\text{V}-5\text{V}$ [17]. In order to study this material as a high voltage cathode and also to suppress any Jahn-Teller

distortion and phase transition which is known to arise below ~3V due to the $\text{Mn}^{+3}/\text{Mn}^{+4}$ redox reaction [16-18], the electrochemical performance of LMNO has been studied in the potential window 3.6V-5.1V synthesized at different temperatures. The variation of the charge/discharge capacity with cycle number of LMNO synthesized at ~873K cycled at 20mA/g is plotted in Fig. 7. The LMNO synthesized at ~873K cycled in the potential window 3.6V-5.1V shows a 1st cycle discharge capacity ~120mA/g and a charge capacity ~113mAh/g which is very close to the theoretical (~146mAh/g) and reported value (~110-120mAh/g) [20-27]. The discharge capacity after the 80th cycle is however reduced to ~82mAh/g with a fade in capacity ~0.3% per cycle which is comparable to the materials generated by other high temperature solid-state methods or low temperature wet chemical processes [20-27]. It should be noted that a similar electrochemical behavior also has been noticed for LMNO synthesized at ~773K and ~973K. The SEM micrograph of the cycled samples of LMNO cycled at ~20mA/g (Fig. 8) indicates the excellent structural integrity (devoid of any cracks) even after 80 cycles. The observed fade in capacity with increase in cycle number of the LMNO is expected to arise due to increase in charge transfer resistance (R_{ct}) and the corresponding solid electrolyte resistance (R_{sf}) in the consecutive cycles during cycling [16,17,23,36-38]. The continuous increase in R_{sf} and R_{ct} is known to arise due to the formation of a resistive solid electrolyte interphase (SEI) layer on the electrode surface caused by the electrolyte decomposition and corrosion reaction between the cathode surface and the electrolyte expected to occur at the high operating potential of ~5V [16,17,23,36-38]. The AC impedance spectra (EIS) of LMNO after the 1st cycle, 10th cycle and 50th cycle obtained at the discharged state (3V), shown in Fig. 9, indicates two semicircles at high frequency and medium frequency regions characteristic of R_{sf} and R_{ct} , respectively. In this study, R_{sf} and R_{ct} has only been considered for fitting since they reflect interfacial processes.

From the analysis of the possible equivalent circuit models of cells (inset in Fig. 9), it can be clearly seen that the cell charge transfer resistance (R_{ct}) significantly increases with increase in cycle number (R_{ct} after 1st, 10th and 50th cycle is $\sim 1200\ \Omega$, $1700\ \Omega$ and $\sim 3800\ \Omega$, respectively) which indicates the formation of unwanted resistive layers due to either the electrolyte decomposition or an interfacial side reaction occurring during the consecutive cycles on the LMNO surface during cycling, which results in the consequent degradation of the specific capacity with increase of cycle number depicted in Fig. 7. Improvement of cyclability/stability of LMNO, synthesized by different approaches, has been reported by surface modification (*e.g.* surface coating) which aids in reducing the electrolyte decomposition or any interfacial side reaction, thus minimize the charge transfer resistance [11,16,20,37,38]. It is anticipated that use of similar coating strategies could help to improve the charge transfer characteristics and thus the electrochemical stability.

In order to study the rate capability, the LMNO synthesized at $\sim 873\text{K}$ has been discharged/charged at different current rates (different C rates) varying from 20mA/g-160mA/g. The variation of reversible specific capacity with cycle number of the LMNO for different current rates is shown in Fig. 10a. The variation in discharge capacity of LMNO with discharge/charge rate, plotted in Fig. 10b, shows that the decrease in specific capacity is almost linear with increasing discharge/charge rates, and thus the variation in capacity can be related to a rate equation given by $Y = 117\text{mAh/g} - 0.382 \cdot C\ \text{mAh/g}$, wherein Y and C denote the reversible capacity (mAh/g) and the discharge/charge rate, respectively. From the above equation, the expected first discharge capacity of LMNO at very slow discharge/charge rate ($C \sim 0$) can be extrapolated to be $\sim 117\text{mAh/g}$. The capacity retained at the discharge/charge rate of 80mA/g is

~87mAh/g which is about 75% of this maximum capacity (~117mAh/g) thus indicating that LMNO synthesized by the simple HEMM process is quite promising as a cathode material for lithium battery application even for high charge/discharge rate applications. The present results clearly show that the HEMM is a simple and effective processing route for the synthesis of battery grade LMNO utilizing low cost oxide materials. The simplicity and effectiveness of the approach in generating the material without any secondary phases reflected by the acceptable electrochemical performance comparable to the performance of materials generated by the traditional and hitherto solution, and solid state approaches [20-29] (~90-120mA/g specific capacity with 70-80% capacity retention after 50-100 cycles) demonstrates the potential of the mechano-chemical HEMM approach. In order to improve the cyclability/stability of the nanostructured LMNO synthesized by HEMM, surface modification by utilizing a surface coating comprising a conductive film will be performed in future which is expected to protect the surface and reduce the electrolyte decomposition at high charging potential, and thus minimize the charge transfer resistance [16,20,37,38]. Further optimization of the HEMM synthesis parameters as discussed combined with surface modifications outlined could lead to improved electrochemical performance.

3. Conclusion:

In the present study, a high energy mechano chemical milling (HEMM) process utilizing the respective pure metal oxides Li_2O , MnO_2 and NiO has been employed to synthesize nanometer sized (~8nm) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LMNO). A range of particle size of ~10-40nm has also been synthesized by the controlled thermal treatment of the ~8nm mechanically alloyed powder at different temperatures (~673K-973K) for 6h in an air atmosphere. The cyclic voltammetry plot

of the nanostructured LMNO shows reversible reactions occurring in the potential window ~3.6V-5.1V. The oxide exhibits a specific capacity ~128mAh/g which is corresponding to $\text{Ni}^{+2}/\text{Ni}^{+3}$ and $\text{Ni}^{+3}/\text{Ni}^{+4}$ redox reaction. The nanostructured LMNO synthesized by HEMM followed by thermal treatments shows a reversible capacity ~120-110mAh/g when cycled at a rate of ~20mA/g (~C/6) in the potential window ~3.6V-5.1V. The nanostructured oxide also shows a moderate rate capability with a capacity retention ~87mAh/g when cycled at ~80mA/g rate. The present results thus clearly demonstrate that the HEMM is an attractive alternative approach for synthesizing battery grade LMNO starting from low cost oxide precursors. The AC impedance study also shows that a significant increase in the charge transfer resistance upon cycling is the primary factor contributing to fade in capacity of the HEMM derived LMNO with cycle number. It is also possible that the surface modification could likely minimize the charge transfer resistance arising due to electrolyte decomposition, and as a result improve the cycle life of the HEMM synthesized LMNO. These on-going results will be published in subsequent reports.

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Figures Caption:

Fig. 1: XRD patterns of LMNO after different duration of milling.

Fig. 2: XRD patterns of LMNO after 20h HEMM and after thermal treatment at different temperatures for 6h under UHP-Ar atmosphere.

Fig. 3: Variation of molar volume and crystallite size of LMNO with heat treatment temperatures.

Fig. 4: TEM bright field image of LMNO synthesized at ~873K show the presence of nanoparticles of particle size ~40nm.

Fig. 5: Cyclic voltammetry curve of LMNO synthesized at ~873K scanned employing a scan rate of 1mV/sec.

Fig. 6: (a) Specific capacity vs. cell potential of LMNO cathode cycled at a constant current of ~20mA/g (C/6 rate) in the potential window 2V-5.1V, and (b) Differential capacity vs. cell potential curves of LMNO electrode obtained at the 2nd cycle cycled at ~20mA/g (C/6) rate in the potential window 2V-5.1V.

Fig. 7: Specific capacity vs. cycle number of LMNO electrode cycled at a constant current of ~20mA/g (C/6 rate) in the potential window 3.6V-5.1V.

Fig. 8: SEM micrograph of (a) LMNO electrode before and (b) after 80 cycles.

Fig. 9: EIS spectra of LMNO after the 1st, 10th and 50th cycles at a state of discharge (3V).

Fig. 10: (a) Variation of reversible discharge capacity of LMNO electrode cycled at different current rates, and (b) Plot showing the variation in discharge capacity of LMNO with discharge/charge rates.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6a

Figure 6b

Figure 7

Figure 8

Figure 9

Figure 10a

Figure 10b

Nanostructured high voltage spinel phase of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LMNO) of particle size $\sim 10\text{-}40\text{nm}$ has been synthesized by a cost effective high energy mechanical milling (HEMM) approach followed by low temperature thermal treatments. High energy mechanical milling of lithium and manganese oxide precursors followed by moderate heat treatment results in the formation of single phase of LMNO, the high voltage spinel phase. The nanostructured LMNO has been studied as a high voltage cathode for lithium ion rechargeable batteries. Cyclic voltammetry as well as the differential capacity plots of nanostructured LMNO show the occurrence of two major reversible reactions occurring in the potential window of $\sim 2\text{V}$ - 3.6V and $\sim 3.6\text{V}$ - 5.1V with an associated specific capacity $\sim 105\text{mAh/g}$ and $\sim 128\text{mAh/g}$, respectively. The nanostructured LMNO synthesized by the HEMM process followed by thermal treatments at $\sim 773\text{K}$, $\sim 873\text{K}$ and $\sim 973\text{K}$ shows a reversible capacity $\sim 120\text{-}110\text{mAh/g}$ when cycled at a rate of $\sim 20\text{mA/g}$ ($\sim \text{C}/6$) in the potential window $\sim 3.6\text{V}$ - 5.1V . Furthermore, the nanostructured HEMM derived LMNO shows a moderate rate capability with a capacity retention $\sim 87\text{mAh/g}$ when cycled at $\sim 80\text{mA/g}$ ($\sim \text{C}$) rate.