Combustion synthesis and characterization of Ni-doped LiMn$_2$O$_4$ cathode nanoparticles for lithium ion battery applications

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ABSTRACT

In this research work, fine powders of spinel-type LiMn$_{2-x}$Ni$_x$O$_{4-\delta}$ (where x = 0.1, 0.2, 0.3, 0.4 and 0.5) as cathode materials for lithium ion batteries were synthesized by combustion synthesis using urea as fuel and metal nitrates as oxidizers at a temperature of 600°C. The physiochemical properties of the prepared cathode materials were investigated by X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), particle size analysis, energy dispersive analysis (EDAX) and scanning electron microscopy (SEM). The electrochemical characteristics were studied by impedance spectroscopy. It was found that the physical charactetertistics were moderately influenced because of different dopant (Ni) concentration. Among the samples studied, LiMn$_{1.9}$Ni$_{0.1}$O$_{4-\delta}$ resulted in better electrical conductivity (6.49 x 10^{-5} Scm^{-1}) at room temperature and hence it may be suitable for lithium ion battery applications.
Keywords: Ni doped LiMn$_2$O$_4$, physical characterization, lithium ion battery application

INTRODUCTION

Electrochemical devices, i.e, batteries can convert chemical energy into electrical energy. With increase in the consumption of electronic energy storages in our daily life usage such as portable electronic toys such as laptops, digital cameras, cellular phones and other usages like electric vehicles, hybrid vehicles, military and aerospace which have been developed and explored. The lithium-ion batteries have received much attention as the most viable and eco-friendly power source [1-5]. Furthermore it is an extreme challenging for renewable energy sources like wind and solar energy. The world market has valued billions of dollars for lithium-ion batteries in large scale storage [6-9]. The three dimensional crystal structure of LiMn$_2$O$_4$ is one of the most promising cathode materials for its high abundance, low toxicity, high energy density and high excellent voltage characteristics [10-12]. The main usage of Li-ion battery technology reveals that itnot only possess high energy density also it is the most electropositive metal [13]. However, LiMn$_2$O$_4$ faces some disadvantages by fading in capacity on storage and charge-discharge cycling at certain temperature [14]. Researchers noticed the drawback in loss of capacity of LiMn$_2$O$_4$ is because of LiMn$_2$O$_4$ include dissolution of a disproportionation of Mn^{3+} into the electrolyte [15], 2Mn^{3+}→ Mn^{2+} + Mn^{4+} at high electrode potential, electrolyte decomposition [16]. In order to improve the performance of LiMn$_2$O$_4$ needs a further improvement by doping divalent or trivalent LiM$_x$Mn$_{2-x}$O$_4$ spinel phase (m = Co, Ni, Fe, Cr) including by various synthesis such as sol-gel method [17], one-step precipitation method [18], solid-state reaction method [19] and combustion method [20]. Among the above methods, combustion method is a promising technique, which is based on a highly exothermic, self-sustaining reaction generated by heating solution mixture of aqueous metal salts with fuels, such as, urea, glucose, glycine and citric acid. This method has been used efficiently to prepare a variety of oxide materials for the application of energy storage devices such as fuel cells, super capacitors and batteries. It not only yields nanomaterials with very high surface areas but also enables uni-

form (homogenous) doping of trace amounts of various elements in a single step [21-23].

Yu and Zhou have studied the effect of sintering temperature on structure and electrochemical properties of $LiMn_2O_4$ [24]. It was reported that $LiMn_2O_4$ suffers from the surface dissolution of manganese in the electrolyte at elevated temperature, especially above 60 °C, which leads to a severe capacity fading. To overcome this barrier, LEE *et al.* [25] have developed an imaginative material design; a novel heterostructure. $LiMn_2O_4$ with epitaxially grown layered ($R\overline{3}m$) surface phase. Mg^{2+} and Ti^{4+} co-doped spinel $LiMn_2O_4$ lithium-ion cathode material was prepared via a simple high-temperature solid-state route, presenting the high specific capacity, upgraded cyclability, and enhanced rate capability contemporaneously [26]. Among the various dopants reported literature, Ni doping in $LiMn_2O_4$ is regarded as a typical method to enhance the structural stability and increase in the electrochemical performance of the $LiMn_2O_4$ material [27]. The importance of doping Ni and also other metals in the $LiMn_2O_4$ was to weaken the Jahn-Teller effect which results in the improvement of stability of the material and also in the cyclic performance even after 500 cycles [28].

In this research paper, we describe the urea-nitrate based combustion synthesis of Ni doped $LiMn_2O_4$ fine particles, $LiMn_{2-x}Ni_xO_{4-\delta}$ (where x = 0.1, 0.2, 0.3, 0.4 and 0.5) and their physio-chemical / electrochemical characterization for use as cathode material in lithium-ion batteries.

2. MATERIALS AND METHODS

2.1 Materials

Nickel nitrate (98%, Loba Chemie, India), lithium nitrate (98%, Merck, India), manganese nitrate (98%, Merck, India) and urea (99.5%, Merck, India) were used in the preparation of Ni doped / undoped $LiMn_2O_4$ nanoparticles without further purification. Deionized water was used throughout.

2.2 Methods

2.2.1 Synthesis of $LiMn_{2-x}Ni_xO_{4-\delta}$ nanoparticles

In the typical experiment, stoichiometric amounts of lithium nitrate, manganese nitrate, nickel nitrate were calculated based on propellant chemistry calculations [29] and dissolved in a minimum quantity of distilled water (approximately, 20 ml) along with appropriate quantity of urea as organic fuel. The mixed solution was heated in a mantle at 50 – 70°C and the volume was reduced to half. Afterwards, the solution was introduced into a muffle furnace maintained at 600° C where it boiled, frothed, ignited and caught fire (temperature rise up to 1100 ± 100° C). At these high temperatures, the metal nitrates decomposed to metal oxides of nitrogen and hence acted as oxidizer for further combustion which led to voluminous foamy combustion residue within 5 – 10 minutes.The flame persisted for about 1 minute. The foam was them lightly ground in glass mortar with pestle to obtain fine nanoparticles. The stoichiometric proportion of precursor materials used for the synthesis of Ni doped $LiMn_2O_4$ oxide nanoparticles is indicated in Table 1.

Table 1: Stoichiometric proportion of the precursor materials used for the synthesis of $LiMn_{2-x}Ni_xO_{4-\delta}$ nanoparticles.

SAMPLES	WEIGHT OF $LiNO_3$ (g)	WEIGHT OF $Mn(NO_3)_2.4H_2O$(g)	WEIGHT OF $Ni(NO_3)_2.6H_2O$(g)	WEIGHT OF Urea (g)
$LiMn_2O_4$	0.689	--	5.02	2.498
$LiMn_{1.9}Ni_{0.1}O_{4-\delta}$	0.689	0.290	4.769	2.503
$LiMn_{1.8}Ni_{0.2}O_{4-\delta}$	0.689	0.581	4.518	2.506
$LiMn_{1.7}Ni_{0.3}O_{4-\delta}$	0.689	0.872	4.267	2.506
$LiMn_{1.6}Ni_{0.4}O_{4-\delta}$	0.689	1.163	4.016	2.505
$LiMn_{1.5}Ni_{0.5}O_{4-\delta}$	0.689	1.453	3.765	2.505

The stoichiometric redox reactions between nitrate salt precursors and urea fuel to produce $LiMn_{2-x}Ni_xO_{4-\delta}$ (where x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) nanoparticles can be represented by a common theoretical equation - 1.

$LiNO_3 + (2-x) Mn(NO_3)_2 + x Ni(NO_3)_2 + 4.165 NH_2CONH_2 \rightarrow$

$LiMn_{2-x}Ni_xO_{4-\delta} + 6.665 N_2 + 4.165 CO_2 + 8.33 H_2O$ (1)

The mechanism for the above reaction is reported as follows in the literature [30]. The metal nitrate – fuel mixture reaction involve dehydration, decomposition, swelling and burn. When urea $(CO(NH_2)_2)$ is used as a fuel, the probable mechanism involves melting and dehydration in the first few minutes, then the mixture decomposes, with frothing that may be due to the formation of metal-$(OH)(NO_3)_2$ gel alongwith other products urea nitrate $(CH_5N_3O_4)$, $(H_2N-CO-NH-CO-NH_2)$ (biuret), HNCO, and NH_3. It then foams, due to the gaseous decomposition products of the intermediates, causing enormous swelling of the reaction product. The gaseous decomposition product is a mixture of N_2, NH_3 and HNCO, which are combustible. Finally, the accumulation of the combustible mixture of gases causes the foam to burst into flame and burn into incandescence, with further swelling, producing a doped oxide powder.

2.3 Physical characterization

The powder XRD study was carried out using a Shimadzu XRD6000 X-ray diffractometer at a scan speed of 5 deg/min using CuKα radiation. The crystallite sizes of the ceramic powders were calculated by Scherrer's formula. FTIR spectra of all the samples were studied by Shimadzu IR Prestige – 21 model FTIR spectrometer. The particle size of the powder was measured using Malvern particle size analyzer (Malvern Instruments, Worcestershire, UK) using triple distilled water as medium. The morphology of the particles and percentage of elements present in the samples (EDAX) was studied by means of JEOL Model JSM-6360 scanning electron microscope (JEOL Ltd., Tokyo, Japan).

2.4 Electrochemical characterization

The resultant Ni doped $LiMn_2O_4$ materials was ground into a fine powder with addition of PVA binder solution, mixed well, dried and placed in a die. A pressure of around 4000 kg/cm^2 was been applied to form the pellet with a thickness in the range of 1.4-1.5 cm and a diameter of 1 cm. After this process, the pellets were sintered at 600°C for 6 hrs before subjecting them for conductivity studies. The electrochemical impedance studies were conducted using an electrochemical work station with two electrode system under aluminium foil substrate in the frequency range of 40 Hz – 1 MHz at room temperature.

3. RESULTS AND DISCUSSIONS

3.1 XRD Studies

Figure 1 shows the XRD pattern obtained on the pure $LiMn_2O_4$ and Ni doped $LiMn_2O_4$ nanoparticles prepared by combustion technique using urea as organic fuel.
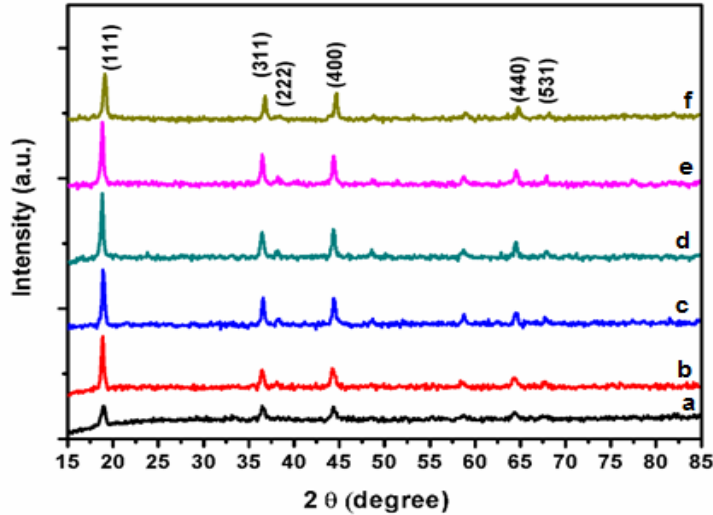
Figure 1: XRD patterns obtained on parent $LiMn_2O_4$ and Ni doped $LiMn_2O_4$ such as a) pure $LiMn_2O_4$; b)$LiMn_{1.9}Ni_{0.1}O_{4-\delta}$; c) $LiMn_{1.8}Ni_{0.2}O_{4-\delta}$; d) $LiMn_{1.7}Ni_{0.3}O_{4-\delta}$; e) $LiMn_{1.6}Ni_{0.4}O_{4-\delta}$; f) $LiMn_{1.5}Ni_{0.5}O_{4-\delta}$ nanoparticles prepared by combustion technique.

The existence of well-defined and highly intense Bragg peaks demonstrated that the synthesized products are phase pure and highly crystalline in nature. The obtained diffraction peaks of both $LiMn_2O_4$ and Ni doped $LiMn_2O_4$ are well in agreement with standard diffraction data (JCPDS no: 89-8325) for $LiMn_2O_4$ and confirmed the existence of spinel cubic type crystalline structure with Fd3m space group in the samples. No other secondary or impurity peaks observed in the samples. The crystallite sizes have been calculated by Scherrer's equation (2).

$$D = \frac{K\,\lambda}{\beta\cos\theta} \qquad\qquad (2)$$

where 'D' is the crystalllite size, 'k' is the numerical constant (~0.9), 'λ' is the wavelength of x-rays (for CuKα radiation, λ = 1.5418 Å), 'β' is the effective broadening taken as a full width at half maximum (FWHM) (in radians), 'θ' is the diffraction angle for the peak. The calculated average crystallite size is found to be 10.6 to 24.7 nm respectively. Crystallography parameters obtained on Ni doped $LiMn_2O_4$ nanoparticles are given in Table.2. The XRD data of $LiMn_{2-x}Ni_xO_{4-\delta}$ is in line with the reported data [31]. From this, we could understand that when high concentration of dopants is added the intensity of peaks gets increased, however, pure $LiMn_2O_4$ resulted with low intensity peaks. Therefore, the crystalline behavior of the materials is highly dependent on dopant concentration. $LiMn_2O_4$ with high dopant concentration will have high crystalline characteristics than others.

Table 2: Crystallographic parameters obtained on $LiMn_{2-x}Ni_xO_{4-\delta}$ nanoparticles.

SAMPLES	CRYSTAL STRUCTURE	UNIT CELL PARAMETER 'a' (Å)	UNIT CELL VOLUME (Å³)	CRYSTALLITE SIZE (nm)
$LiMn_2O_4$	Cubic spinel	8.119	535.18	10.6
$LiMn_{1.9}Ni_{0.1}O_{4-\delta}$	Cubic spinel	8.149	541.14	23
$LiMn_{1.8}Ni_{0.2}O_{4-\delta}$	Cubic spinel	8.117	534.79	23.6

$LiMn_{1.7}Ni_{0.3}O_{4-\delta}$	Cubic spinel	8.169	545.13	24.2
$LiMn_{1.6}Ni_{0.4}O_{4-\delta}$	Cubic spinel	8.163	543.93	24.7
$LiMn_{1.5}Ni_{0.5}O_{4-\delta}$	Cubic spinel	8.047	521.07	21.2

3.2 FTIR Studies

Figure 2 shows the FTIR spectra obtained on the pure $LiMn_2O_4$ and Ni doped $LiMn_2O_4$ nanoparticles prepared by combustion technique using urea as organic fuel in the range of 4000 to 400 cm^{-1}. The broader peak appeared at 498.58 cm^{-1} in the prepared samples can be ascribed to the metal oxygen vibrations, i.e., Li-O / Ni-O and the peaks appeared between 615 to 624 cm^{-1} can be due to Li-Mn-O. The peaks found near 1506.47 cm^{-1} are due to Li-O bending vibration modes in the samples. The intensity of the IR spectra increases while increasing Ni dopant level. This means that the stability of the $LiMn_2O_4$ structure is enhanced and which may result in better electrochemical performance. Appearance of broad band near 2900 cm^{-1} corresponds to O-H stretching frequency of the water or moisture [32, 33].

3.3 Particle size measurements

The particle size patterns of the Ni doped $LiMn_2O_4$ nanoparticles prepared by combustion technique are shown in Figure 3. For all the measurements, 0.01g of sample was sonicated in 30 ml triple distilled water for about 10 minutes and after that the sample was subjected for particle size analysis. The particle size distribution data is indicated in Table.3. The particle are present in the range of 234 – 329 nm. The presence of bigger particles (> 200 nm) in the sample may be due to high temperature treatment.
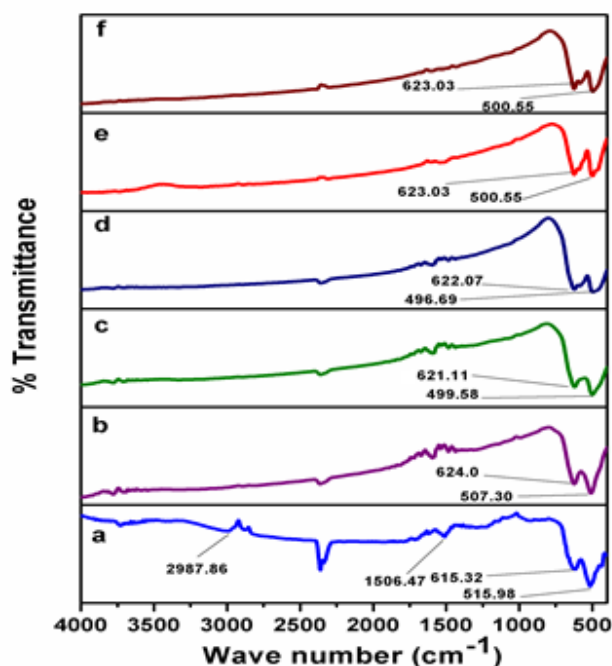

Figure 2: FTIR spectra obtained on parent $LiMn_2O_4$ and Ni doped $LiMn_2O_4$ such as a) pure $LiMn_2O_4$; b) $LiMn_{1.9}Ni_{0.1}O_{4-\delta}$; c) $LiMn_{1.8}Ni_{0.2}O_{4-\delta}$; d) $LiMn_{1.7}Ni_{0.3}O_{4-\delta}$; e) $LiMn_{1.6}Ni_{0.4}O_{4-\delta}$; f) $LiMn_{1.5}Ni_{0.5}O_{4-\delta}$ nanoparticles prepared by combustion technique.

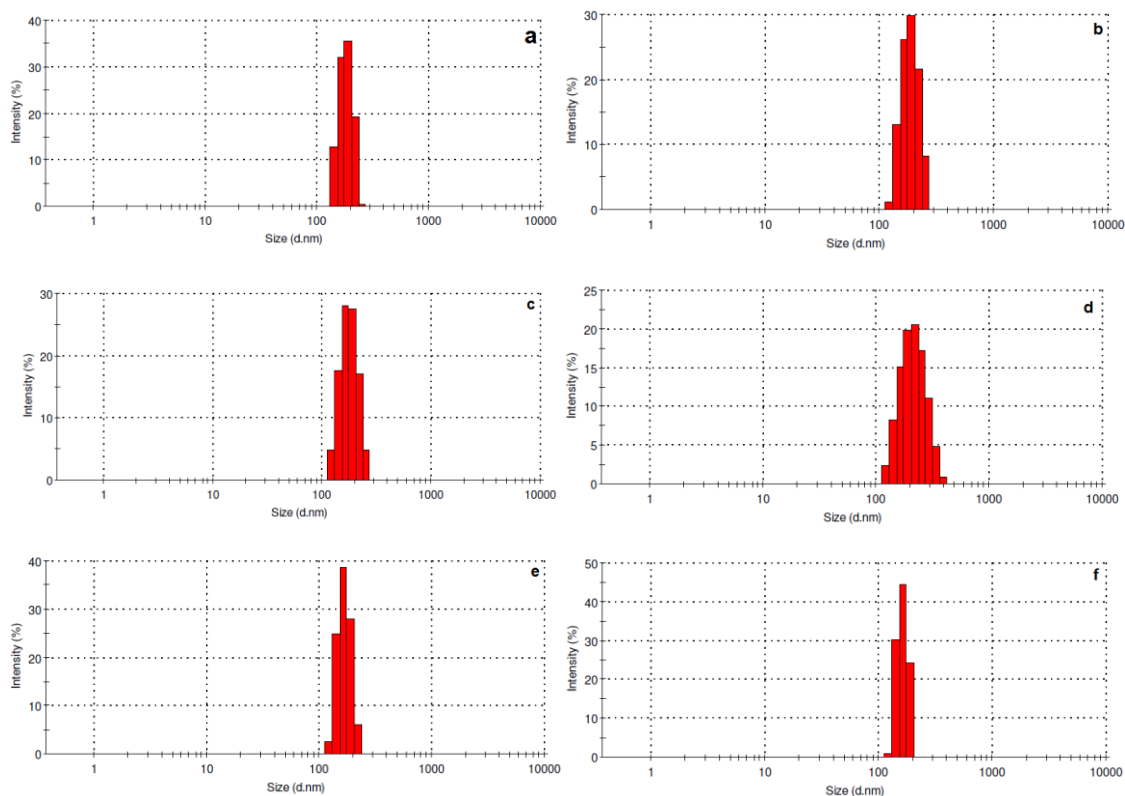**Figure 3:** Particle size patterns obtained on parent $LiMn_2O_4$ and Ni doped $LiMn_2O_4$ such as a) pure $LiMn_2O_4$; b) $LiMn_{1.9}Ni_{0.1}O_{4-\delta}$; c) $LiMn_{1.8}Ni_{0.2}O_{4-\delta}$; d) $LiMn_{1.7}Ni_{0.3}O_{4-\delta}$; e) $LiMn_{1.6}Ni_{0.4}O_{4-\delta}$; f) $LiMn_{1.5}Ni_{0.5}O_{4-\delta}$ nanoparticles prepared by combustion technique.

Table 3: Particle characteristics data obtained on $LiMn_{2-x}Ni_xO_{4-\delta}$ nanoparticles.

SAMPLES	PEAK 1		AVERAGE PARTICLE SIZE (nm)
	% INTENSITY	DIAMETER (nm)	
$LiMn_2O_4$	100	181.7	294.9
$LiMn_{1.9}Ni_{0.1}O_{4-\delta}$	100	188.1	242.9
$LiMn_{1.8}Ni_{0.2}O_{4-\delta}$	100	179.4	234.9
$LiMn_{1.7}Ni_{0.3}O_{4-\delta}$	100	218.7	236.7
$LiMn_{1.6}Ni_{0.4}O_{4-\delta}$	100	168.2	327.6
$LiMn_{1.5}Ni_{0.5}O_{4-\delta}$	100	163.4	329.9

3.4 SEM studies

The SEM photographs of the Ni doped $LiMn_2O_4$ nanoparticles prepared by combustion technique are displayed in Figure 4. From the SEM photographs, it was noticed that compared to the parent $LiMn_2O_4$ compound, Ni doped $LiMn_2O_4$ nanomaterials are homogenous along with the presence of few larger particles. The presence of bigger particles in the samples such as $LiMn_{1.9}Ni_{0.1}O_{4-\delta}$, $LiMn_{1.8}Ni_{0.2}O_{4-\delta}$, $LiMn1_{.7}Ni_{0.3}O_{4-\delta}$, $LiMn_{1.6}Ni_{0.4}O_{4-\delta}$ and$LiMn_{1.5}Ni_{0.5}O_{4-\delta}$ may due to the agglomeration of few nanoparticles together at high temperature.

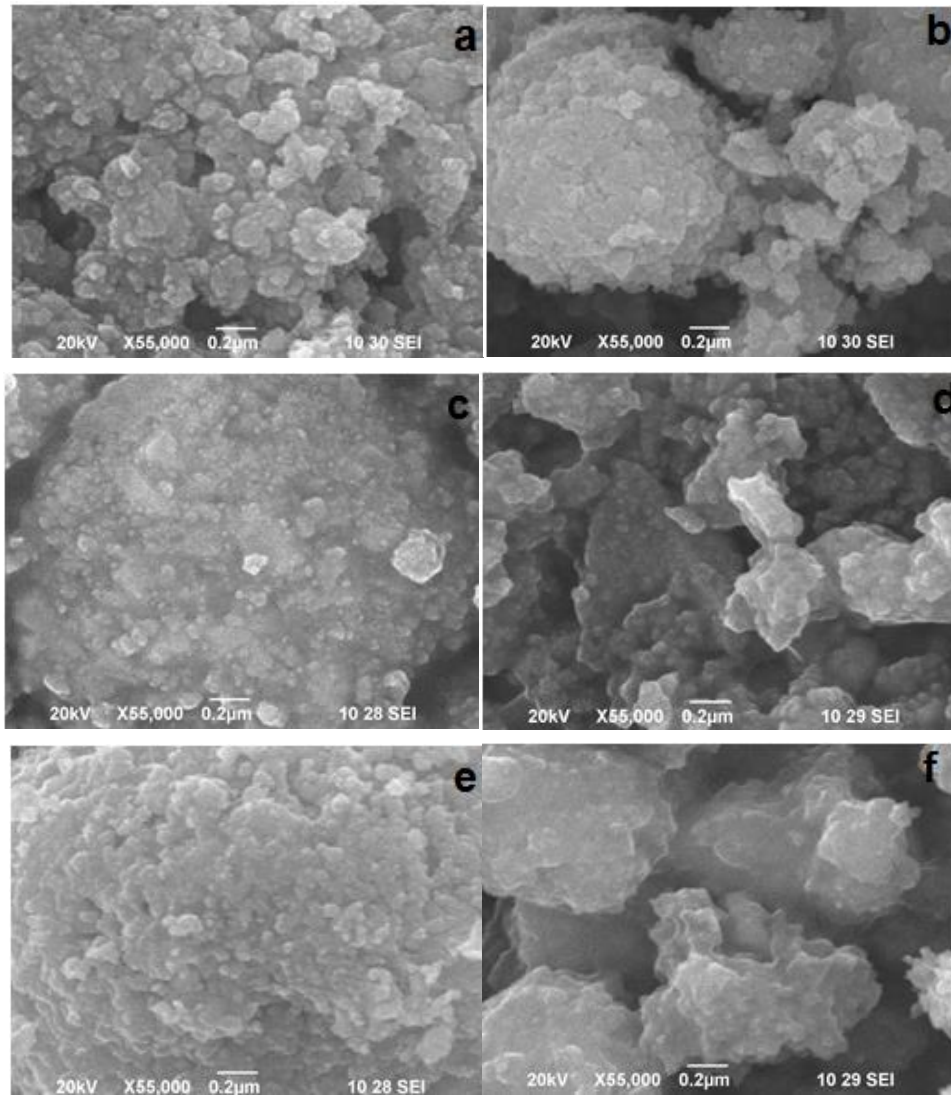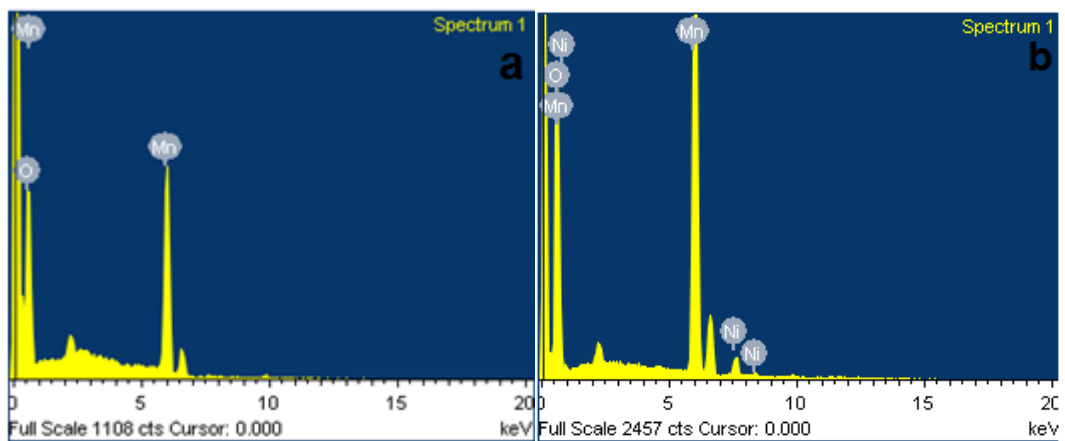**Figure 4:** SEM photographs obtained on parent $LiMn_2O_4$ and Ni doped $LiMn_2O_4$ such as a) pure $LiMn_2O_4$; b) $LiMn_{1.9}Ni_{0.1}O_{4-\delta}$; c) $LiMn_{1.8}Ni_{0.2}O_{4-\delta}$; d) $LiMn_{1.7}Ni_{0.3}O_{4-\delta}$; e) $LiMn_{1.6}Ni_{0.4}O_{4-\delta}$; f) $LiMn_{1.5}Ni_{0.5}O_{4-\delta}$ nanoparticles prepared by combustion technique.

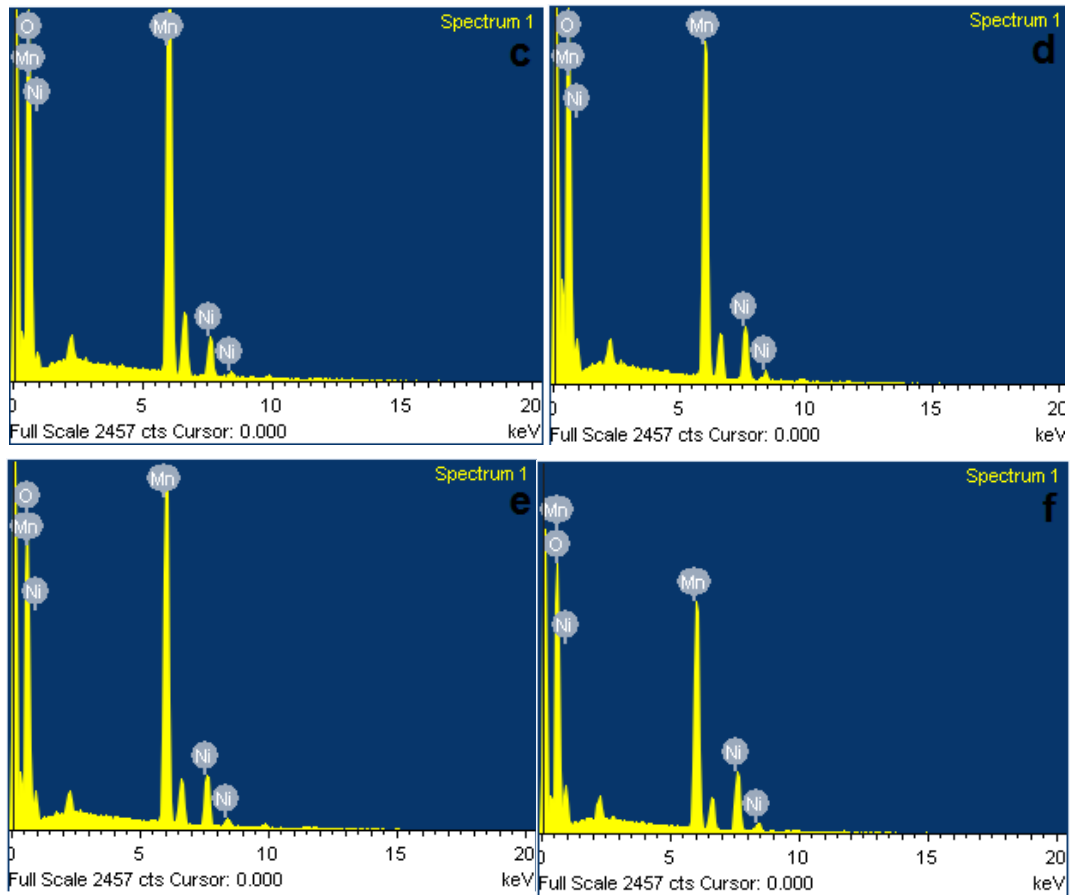**Figure 5:** EDAX obtained on nanocrystalline materials such as a) pure $LiMn_2O_4$; b) $LiMn_{1.9}Ni_{0.1}O_{4-\delta}$; c) $LiMn_{1.8}Ni_{0.2}O_{4-\delta}$; d) $LiMn_{1.7}Ni_{0.3}O_{4-\delta}$; e) $LiMn_{1.6}Ni_{0.4}O_{4-\delta}$; f) $LiMn_{1.5}Ni_{0.5}O_{4-\delta}$ nanoparticles prepared by combustion technique.

3.5 Electrochemical impedance studies

Figure 6 displays the typical Nyquist ac impedance plots obtained on the Ni doped $LiMn_2O_4$ cathode materials in the frequency range of 40 Hz to 1 MHz in the amplitude of 0.05 V at room temperature in the two electrode system. The electrochemical impedance measurements were carried out for all the sintered pellets. The pellets were kept in between the conducting aluminium foils like a sandwich and the measurements were made in air. From the impedance data conductivity values were calculated by using Equation.

$$\sigma = d/R_b\, S \tag{3}$$

σ = ionic conductivity

Table 4: Chemical composition data obtained on $LiMn_{2-x}Ni_xO_{4-\delta}$ nanoparticles by EDAX analysis.

SAMPLES	ATOMIC % OF ELEMENTS		
	Mn	Ni	O
$LiMn_2O_4$	31.61	--	68.39
$LiMn_{1.9}Ni_{0.1}O_{4-\delta}$	27.94	1.32	70.74
$LiMn_{1.8}Ni_{0.2}O_{4-\delta}$	24.29	2.76	72.75
$LiMn_{1.7}Ni_{0.3}O_{4-\delta}$	18.42	3.55	78.02
$LiMn_{1.6}Ni_{0.4}O_{4-\delta}$	22.14	3.94	73.92

|			
$LiMn_{1.5}Ni_{0.5}O_{4-\delta}$	17.36	5.75	76.89

d = thickness of the sample

S= area of the sample

R_b = bulk resistance

Fitting of the measurement data was performed with the software Zview software. The impedance data of the $LiMn_2O_4$ and Ni doped $LiMn_2O_4$ oxide pellets fitted with an equivalent circuit as indicated in Figure 7.

The impedance spectra was fitted to the conventional equivalent electronic circuit containing three Resistance-Constant Phase Element (R-CPE) sub circuits in series, which generates two semicircles on the Nyquist plots at the room temperature. The electrical conduction of Ni doped $LiMn_2O_4$ based materials results from impurity and intrinsic factors. At room temperatures, its conduction is dominated by the dissociated electron concentration from the energy gap of the impurity, whose activation energy of electrical conduction is much lower than that of the intrinsic conduction [34-36]. The conductivity decreases is predominantly due to the addition of nickel. The electrons from the energy gap of the impurity are all dissociated and activated.
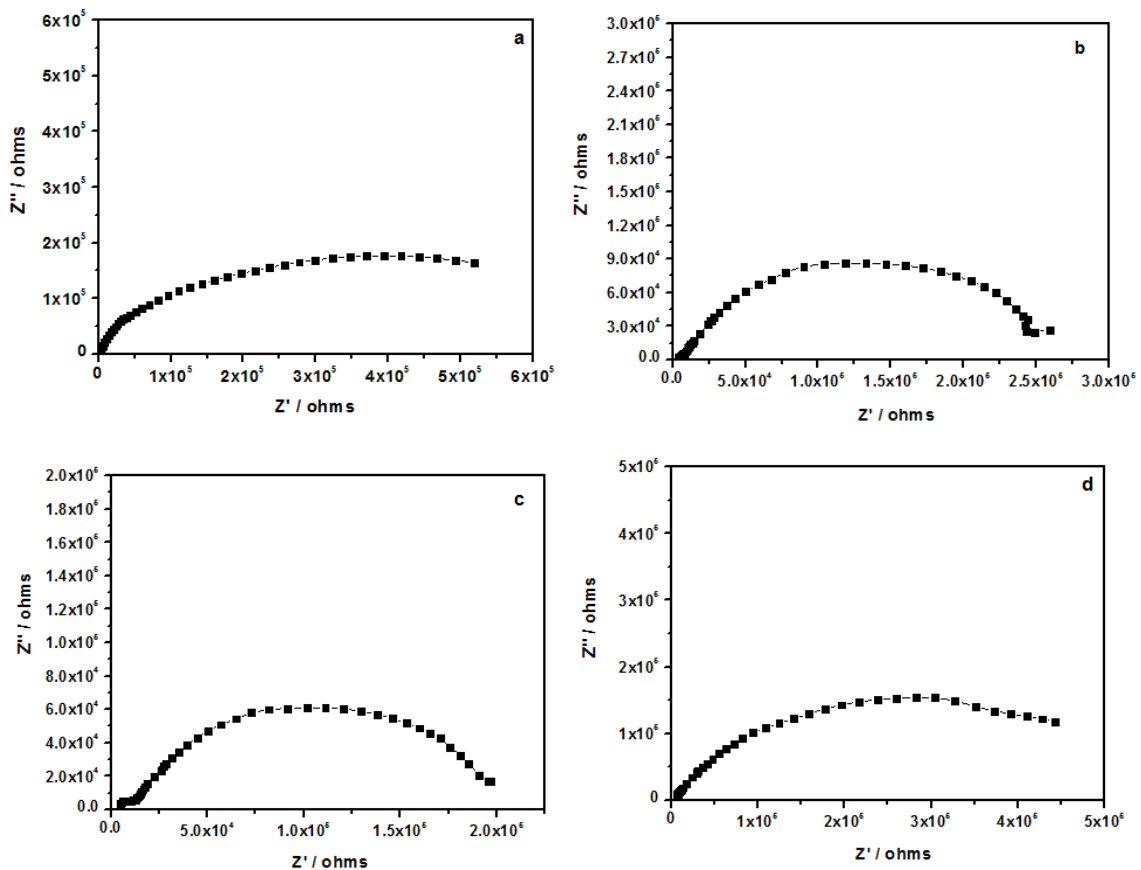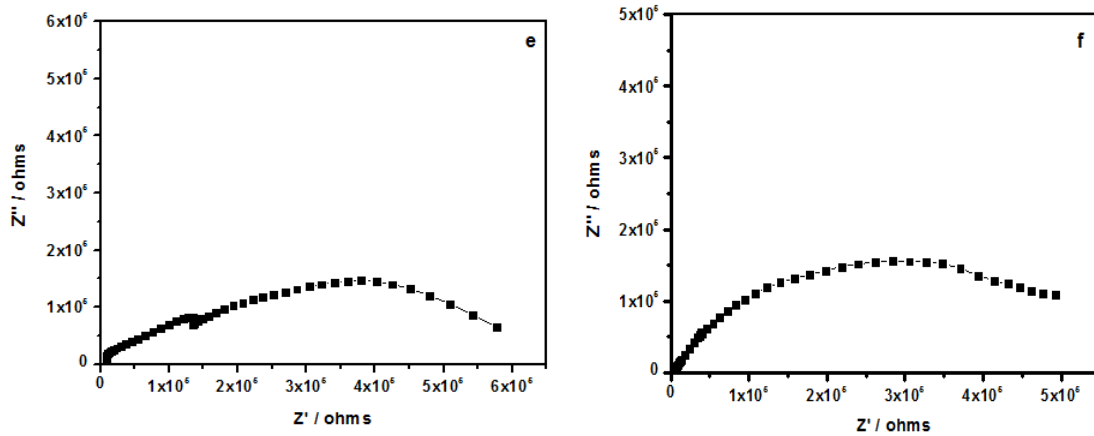
Figure 6: Electrochemical impedance spectra obtained on sintered cathode specimens a) pure $LiMn_2O_4$; b) $LiMn_{1.9}Ni_{0.1}O_{4-\delta}$; c) $LiMn_{1.8}Ni_{0.2}O_{4-\delta}$; d) $LiMn_{1.7}Ni_{0.3}O_{4-\delta}$; e) $LiMn_{1.6}Ni_{0.4}O_{4-\delta}$; f) $LiMn_{1.5}Ni_{0.5}O_{4-\delta}$ at room temperature.

Table 5: Conductivity values calculated for sintered $LiMn_2O_4$ and Ni doped $LiMn_2O_4$ compacts using electrochemical impedance spectroscopy at room temperature.

SAMPLES	ELECTRICAL CONDUCTIVITY (Scm^{-1})
$LiMn_2O_4$	1.58×10^{-6}
$LiMn_{1.9}Ni_{0.1}O_{4-\delta}$	6.49×10^{-5}
$LiMn_{1.8}Ni_{0.2}O_{4-\delta}$	1.6×10^{-6}
$LiMn_{1.7}Ni_{0.3}O_{4-\delta}$	1.95×10^{-6}
$LiMn_{1.6}Ni_{0.4}O_{4-\delta}$	1.32×10^{-6}
$LiMn_{1.5}Ni_{0.5}O_{4-\delta}$	1.67×10^{-6}

Figure 7: Equivalent circuit, used to fit measurement data obtained $LiMn_2O_4$ and Ni doped $LiMn_2O_4$ oxide pellets.

(Where, the symbol ⊣⊢ referred as capacitor (constant phase element, CPE) and the symbol ⌇⌇ referred as resistor)

The bulk conductivity was calculated from the impedance plot and reported in the Table 5. Among the samples studied, $LiMn_{1.9}Ni_{0.1}O_{4-\delta}$shown better conductivity (6.49×10^{-5} S/cm). However, all other samples have shown moderate conductivity values which may be useful for Li-ion battery application.

4. CONCLUSIONS

In the present work, a set of $LiMn_2O_4$ and Ni doped $LiMn_2O_4$ such as$LiMn_{1.9}Ni_{0.1}O_{4-\delta}$, $LiMn_{1.8}Ni_{0.2}O_{4-\delta}$, $LiMn_{1.7}Ni_{0.3}O_{4-\delta}$, $LiMn_{1.6}Ni_{0.4}O_{4-\delta}$ and$LiMn_{1.5}Ni_{0.5}O_{4-\delta}$ based cathode materials were prepared by combustion route using urea as an organic fuel. The physico-chemical studies, such as, effect of Ni doping on the phase structure of $LiMn_2O_4$, structural, particle and morphological performances were studied for all the prepared materials and results found good in comparison with the reported data. The electrochemical characteristics

for Ni doped $LiMn_2O_4$ by impedance spectroscopy were also measured. Among the samples studied, $LiMn_{1.9}Ni_{0.1}O_{4-\delta}$ cathode has resulted in better conductivity of 6.49×10^{-5} Scm^{-1}. Hence, it may be suitable as cathode for Li-ion battery applications.

5. ACKNOWLEDGEMENTS

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