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Short Communication

Influence of Calcination Temperature on the Electrochemical Behaviour of Novel $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ Cathode Materials for High Energy Density Li-ion Batteries

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Novel, single phase $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ materials are prepared using a sol-gel method without the use of chelating agents. The XRD results showed that the materials are pure and isostructural with α-$NaFeO_2$. The optimization of thermal annealing was done to investigate the best calcination condition for good electrochemical behaviour. The compounds annealed at different temperatures and different annealing times showed variations in discharge profiles and capacities. The compound annealed at 900 °C for 48 h exhibits the highest capacity of 167 $mAhg^{-1}$ over the voltage range of 2.5 to 4.2 V. Other heat-treated samples also exhibit good electrochemical performance approaching that of $LiCoO_2$. XPS studies of the material shows the existence of Co^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Mn^{3+}, Mn^{4+}, Cr^{3+} and Cr^{6+} in the sample material and subsequently, charge-discharge mechanisms are identified.

Keywords: Sol-gel, cathode, XRD, XPS, oxidation states

1. INTRODUCTION

Layered compounds have been extensively studied as a potential replacement for $LiCoO_2$ [1]. The electrochemical performance of a layered cathode material depends, to some extent, on the lattice parameters and structural stability of the crystal framework as well as, to a large extent, on the cation ordering of the compounds [2]. This is because Li in the transition metal site in the crystal lattice will be detrimental to the electrochemical performance of the material.

In the present work, layered novel $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ compounds were prepared *via* a simple sol-gel method without using any chelating agents. The electrochemical performance of the materials are studied with respect to the thermal annealing process done on the materials. Comparisons are made with that of the commercial $LiCoO_2$. Further, X-Ray Photoelectron spectroscopic (XPS) studies are made on sample $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ sample to obtain the oxidation states of the transition metals in the cathode materials.

2. EXPERIMENTAL

In this study, layered $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ compounds were prepared using a simple sol-gel method without the use of any chelating agents [4]. Lithium acetate dihydrate, manganese(II) acetate tetrahydrate, cobalt(II) acetate tetrahydrate, nickel(II) acetate tetrahydrate and chromium(III) nitrate nonahydrate were used as starting materials (assay: 99.9 %). Stoichiometric amounts of the materials were dissolved in deionised water and stirred continuously at 80 ˚C for 4 hours. The homogeneous sol obtained was then heated at 100 ˚C with continued stirring until a viscous gel was produced. To further remove the water, the gel was then heated until dry at 120 ˚C in an oven for about 48 hours. The dry precursors were first precalcined at 500 ˚C for 5 h and subsequently calcined at 800 ˚C and 900 ˚C for 24, 48 and 72 h to obtain black powders of $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ compounds.

The X-ray diffraction patterns were obtained from the PanAnalytical X'pert Pro MPD diffractometer using Cu K_α radiation ($\lambda = 1.5406$) in the 2θ range from 15˚ to 90˚ equipped with a solid-state detector with the capability of fast acquisition of data. Surface morphology of the powders were observed using a Scanning Electron Microscope, the JEOL JSM-7600F.

For the fabrication of the cathode, the electroactive materials were heated at 200 °C for 24 h to get rid of any residual moisture. The positive electrode was fabricated by mixing 80.0 wt.% of active material, 10.0 wt.% of acetylene black as conducting agent and 10.0 wt.% of polytetrafluoroethylene binder in an agate mortar using acetone as solvent. The cathode was then casted onto a metal grid and heated again at 180 °C for 24 hours. The cell was assembled in a high purity argon-filled glove box using lithium foil as anode with porous polypropylene thin film (Celgard 2500) as separator. 1.0 M $LiPF_6$ in 1:1 volume ratio of ethylene carbonate (EC) and dimethylcarbonate (DMC) was used as the electrolyte. The charge-discharge study was done using a battery cycler, the WonAtech WBCS 3000. For the charge-discharge profile studies, the test cells were charged to 4.2 V with 40 mA/g current and discharge to 0.5 V at 20 mA/g current.

XPS studies were made on sample E to see the oxidation states of the samples. The XPS instrument used was the JEOL JPS-9200 using monochromatic Al K_α X-Rays. The pass energy is 10 giving the FWHM value of 0.5 eV.

3. RESULT AND DISCUSSION

The XRD patterns for the $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ compounds annealed at 800 °C and 900 °C for 24, 48 and 72 hours are shown in Fig. 1. The data has high counts and no impurity peaks are observed. The data was indexed using McMaille indexing method and refined using a least squares method in order to obtain the cell parameters. All of the fingerprint peaks, namely (003), (101), (006), (102), (104), (108) and (110) are easily identifiable in all of the diffraction patterns. They are indexed based on the trigonal crystal system with

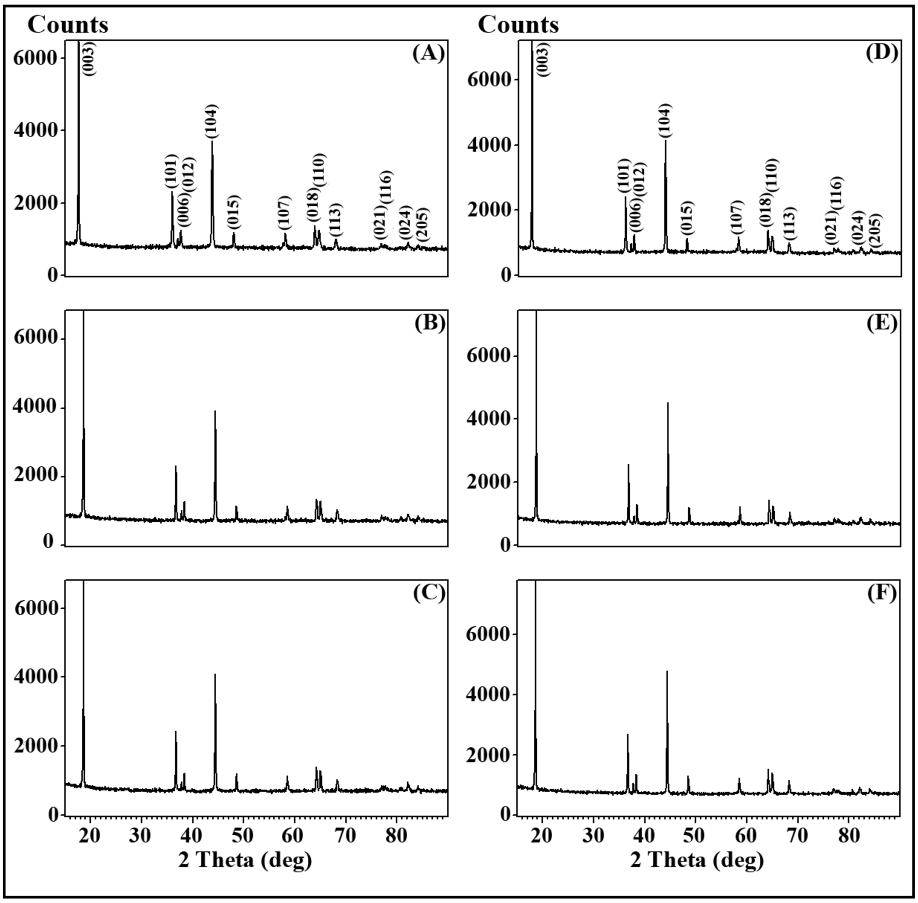

Figure 1. XRD patterns for $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ annealed at: (A) 800 °C; 24h, (B) 800 °C; 48h, (C) 800 °C; 72 h, (D) 900 °C; 24h, (E) 900 °C; 48h and (F) 900 °C; 72 h.

Table 1. The lattice parameters, *RIR* and R-factor values for $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ materials prepared *via* the sol-gel method.

Sample	Heat treatment	*a* (Å)	*c* (Å)	Volume ($Å^3$)	*c/a*	*RIR*	R-factor
A	800 °C, 24 hr	2.870	14.100	101.48	4.913	1.26	0.496
B	800 °C, 48 hr	2.866	14.166	100.56	4.943	1.23	0.407
C	800 °C, 72 hr	2.874	14.160	101.31	4.927	1.22	0.480
D	900 °C, 24 hr	2.869	14.110	100.54	4.918	1.24	0.410
E	900 °C, 48 hr	2.870	14.260	101.67	4.969	1.25	0.382
F	900 °C, 72 hr	2.868	14.170	100.97	4.941	1.24	0.419

$R\bar{3}m$ space group. All the XRD patterns show that the materials are pure and single phase. This illustrates that the layered $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ compounds are obtainable by a simple sol-gel method without the need of chelating agents. The *RIR* values together with the R-factor and the lattice parameters refined using a least square method are shown in Table 1. Low values of R-factor coupled with the values of *RIR* exceeding 1.2 for all samples indicate a highly ordered layered structure with small cation mixing. The sharp peaks observed in all patterns also indicate that the materials possess a high degree of crystallinity. The integrated intensity ratio of (003) and (104) lines, the so called *RIR*, is often used by researchers as a measure of cation mixing, that is, *RIR* < 1.2 indicates undesirable cation mixing [5].

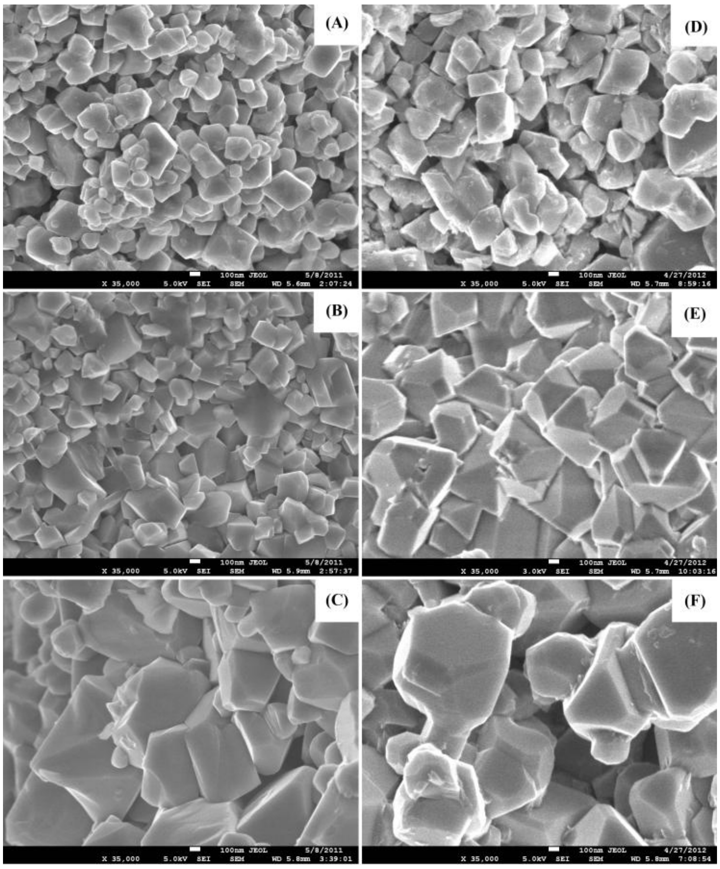

Figure 2. The SEM images of $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ annealed at: (A) 800 ˚C; 24 h, (B) 800 ˚C; 48 h, (C) 800 ˚C; 72 h, (D) 900 ˚C; 24 h, (E) 900 ˚C; 48 h and (F) 900 ˚C; 72 h.

The SEM images of the $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ compounds annealed at six different conditions are displayed in Fig. 2. It is observed that for all of the samples, the grains consist of well-crystallized particles with smooth surfaces and polyhedral shaped crystals. The crystal size seem to be quite uniformly distributed. It is noted that the particle size increases as the heating temperature as well as heating time is increased. Very crystalline samples (sample E and F) with crystal size of about one to a few microns seem to exhibit good electrochemical properties. Smaller crystal sized samples show lower electrochemical discharge (Fig.3).

The discharge profiles of the $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ materials annealed at six different conditions are shown in Fig. 3. The discharge profile for the reference material, $LiCoO_2$ (marked R on the graph in Fig. 3 (a)), is also shown as a comparison. All materials exhibit similar profile with two distinctive plateaus. The first plateau is at about 4.2 to 2.5 V which corresponds to the reduction reaction of the active material and the second plateau is at about 1.0 V region and is believed to be due to the polarization of the electrodes and contribution of the electrolyte reaction.

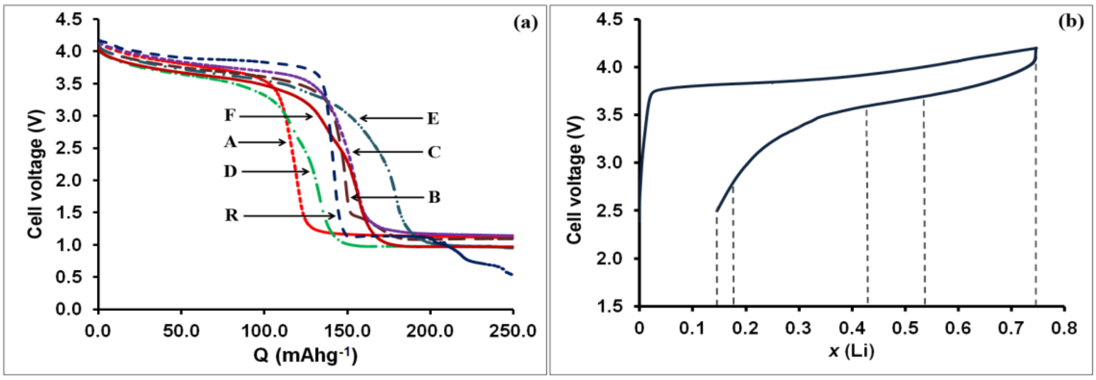

Figure 3. (a) Discharge profiles for: $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$ annealed at 800 ˚C for 24 h (A), 800 ˚C for 48 h (B), 800 ˚C for 72 h (C), 900 ˚C for 24 h (D), 900 ˚C for 48 h (E), 900 ˚C for 72 h (F), $LiCoO_2$ at 800 ^oC for 24 h (R) and **(b)** Charge-discharge state for sample E in the voltage range of 2.5 to 4.2 V.

In the voltage range of 2.0 to 4.2 V, the best performance in terms of discharge capacity is shown by compound E with the discharge capacity of 165 $mAhg^{-1}$, and this value is comparable to those reported by previous researchers for $LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$ [7-11]. Thus, it is believed that the annealing conditions for sample E is the optimum for good crystallinity and cation ordering. This is in agreement with the lattice parameters which show that this sample possesses the best RIR and R-factor values. Although, sample E shows the highest capacity, the voltage plateau is more slopping compared to samples B and C. Their voltage plateau are just slightly lower than the one exhibited by $LiCoO_2$ but their specific capacities are higher than $LiCoO_2$. Material B and C can be said to be comparable to that of the commercial $LiCoO_2$ material.

According to electronic structure studies of Grey et. all [6], Ni, Co and Mn in the $LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$ material exist as Ni^{2+}, Co^{3+} and Mn^{4+} respectively, in which the reversible capacity involves two electron transfer of Ni^{3+}/Ni^{2+} redox couples as well as Ni^{4+}/Ni^{3+} and Co^{4+}/Co^{3+} at the later stage. According to them, Mn does not take part in the redox reaction. In our material, $LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2$, the presence of Cr have changed the oxidation states of the material as is evidenced in the XPS results shown in Fig. 4. The XPS narrow scans clearly reveal that the cations, Co, Mn, Ni and Cr exists in several oxidation states which is listed in Table 2. The binding energies used are compared to those given in the JEOL XPS reference book and NIST database. Our results are different from the XPS results of the $LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$ material done by Cho et. al [8] where the transition metals seem to exist in one oxidation state only. The shift towards the lower oxidation states for Co, Mn and Ni in our material is attributed to the presence of the higher Cr oxidation state of 6+ in the material. Our quantitative analysis gives the total oxidation state of the transition metals as 3.02, which makes the oxidation state of the material about neutral.

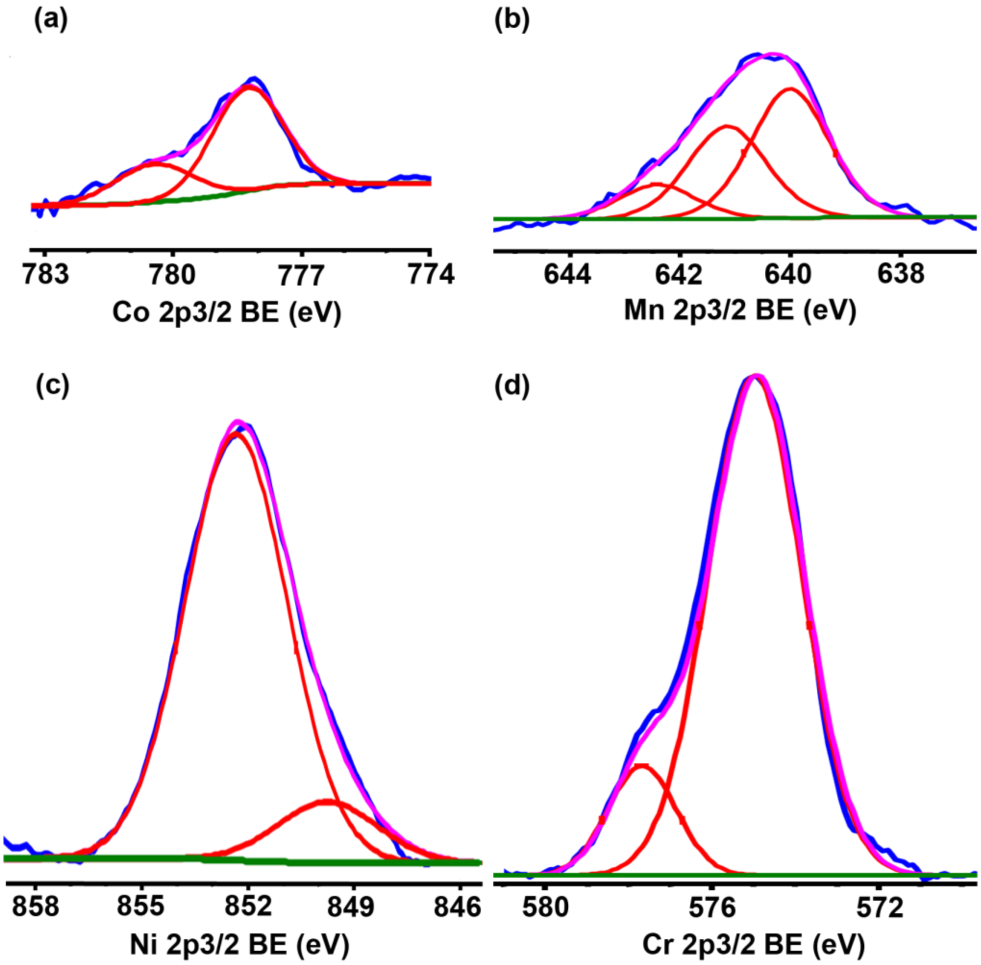

Figure 4. XPS narrow scans of the cations a) C0, b) Mn, c) Ni and d) Cr

Table 2. XPS binding energies and estimated composition from XPS data

Transition metal	Co		Mn			Ni		Cr	
Ion	Co^{3+}	Co^{4+}	Mn^{2+}	Mn^{3+}	Mn^{4+}	Ni^{2+}	Ni^{3+}	Cr^{3+}	Cr^{6+}
FWHM	0.969	1.08	0.828	0.840	0.830	1.68	1.70	1.33	0.967
Binding energy (eV)	778.31	780.46	640.02	641.15	642.43	849.70	852.26	575.03	577.69
Atomic percent	71.0	29.0	42.6	32.6	19.8	12.0	88.0	77.4	22.6

mechanisms of the discharge in Fig. 3(c) is proposed as follows,

for $0.54 \le x \le 0.75$,

$$\mathrm{Li_{0.25}Mn^{4+}_{0.16}Mn^{3+}_{0.13}Ni^{4+}_{0.26}Ni^{3+}_{0.04}Co^{4+}_{0.3}Cr^{3+}_{0.1}O_2} + 0.21\mathrm{Li^+} + 0.21e^- \Leftrightarrow \\ \mathrm{Li_{0.46}Mn^{4+}_{0.16}Mn^{3+}_{0.13}Ni^{4+}_{0.26}Ni^{3+}_{0.04}Co^{4+}_{0.09}Co^{3+}_{0.21}Cr^{3+}_{0.1}O_2}$$

for $0.44 \le x \le 0.53$,

$$\mathrm{Li_{0.46}Mn^{4+}_{0.16}Mn^{3+}_{0.13}Ni^{4+}_{0.26}Ni^{3+}_{0.04}Co^{4+}_{0.09}Co^{3+}_{0.21}Cr^{3+}_{0.1}O_2} + 0.09\mathrm{Li^+} + 0.09e^- \Leftrightarrow \\ \mathrm{Li_{0.56}Mn^{4+}_{0.07}Mn^{3+}_{0.22}Ni^{4+}_{0.26}Ni^{3+}_{0.04}Co^{4+}_{0.09}Co^{3+}_{0.21}Cr^{3+}_{0.1}O_2}$$

for $0.18 \le x \le 0.43$,

$$\mathrm{Li_{0.56}Mn^{4+}_{0.06}Mn^{3+}_{0.23}Ni^{4+}_{0.26}Ni^{3+}_{0.04}Co^{4+}_{0.09}Co^{3+}_{0.21}Cr^{3+}_{0.1}O_2} + 0.25\mathrm{Li^+} + 0.25e^- \Leftrightarrow \\ \mathrm{Li_{0.82}Mn^{4+}_{0.06}Mn^{3+}_{0.23}Ni^{3+}_{0.3}Co^{4+}_{0.09}Co^{3+}_{0.21}Cr^{3+}_{0.1}O_2}$$

for $0.15 \le x \le 0.17$,

$$\mathrm{Li_{0.82}Mn^{4+}_{0.06}Mn^{3+}_{0.23}Ni^{3+}_{0.3}Co^{4+}_{0.09}Co^{3+}_{0.21}Cr^{3+}_{0.1}O_2} + 0.03\mathrm{Li^+} + 0.07e^- \Leftrightarrow \\ \mathrm{Li_{0.85}Mn^{4+}_{0.06}Mn^{3+}_{0.23}Ni^{3+}_{0.27}Ni^{3+}_{0.03}Co^{4+}_{0.09}Co^{3+}_{0.21}Cr^{3+}_{0.1}O_2}$$

The initial discharge is attributed to Co *via* the $\mathrm{Co^{4+}/Co^{3+}}$ redox couples because Co discharges at a high voltage as can be seen by the discharge curve of the reference material, $\mathrm{LiCoO_2}$, shown in Fig. 3(a). The discharge is followed by the redox couples of manganese $\mathrm{Mn^{4+}/Mn^{3+}}$ for the same reason followed by nickel $\mathrm{Ni^{4+}/Ni^{3+}}$. Thus, the chemical environment of the $\mathrm{LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2}$ is different from that of $\mathrm{LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2}$ cathode material.

4. CONCLUSIONS

The present study shows that layered $\mathrm{LiMn_{0.3}Co_{0.3}Ni_{0.3}Cr_{0.1}O_2}$ with good electrochemical behaviour can be prepared *via* a simple sol-gel method without using any chelating agents. It is important to optimize the thermal annealing process for best results. The materials annealed at 800 °C for 72 h and 900 °C for 48 h show performances comparable to $\mathrm{LiCoO_2}$ cathode material. This indicates the possibility of future commercial use. The ease in synthesis and preparation of the materials is another positive factor towards commercialization.

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