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Comparison of corn starch-assisted sol–gel and combustion methods to prepare LiMn$_x$Co$_y$Ni$_z$O$_2$ compounds

Gangulibabu · D. Bhuvaneswari · N. Kalaiselvi

Abstract In a novel attempt to exploit corn starch as gelling agent (in sol–gel method) and combustible fuel (in solution-assisted combustion method), high-capacity LiMn$_{0.4}$Ni$_{0.4}$Co$_{0.2}$O$_2$ and LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ cathode materials have been prepared and a comparison of electrochemical performance of the same has been made. Among the two compounds chosen for the study, LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ exhibits better physical and electrochemical properties. Particularly, LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ cathode synthesized using corn starch-assisted combustion method exhibits an appreciable capacity of 176 mAh g^{-1}, excellent capacity retention of 93 % up to 100 cycles and susceptible to rate capability test up to 1 C rate, thus qualifying the same for high-capacity and high-rate lithium battery applications. The study demonstrates the possibility of exploiting corn starch as gelling agent and as a combustible fuel in synthesizing lithium intercalating oxide compounds with improved electrochemical behaviour.

Keywords Layered compounds · Sol–gel method · Combustion method · Electrochemical measurements · Rechargeable lithium battery

Introduction

Layered oxides with a general formula of LiMO$_2$ (M=Mn, Co, and Ni) arguably represent themselves as one of the most successful cathode materials for rechargeable lithium batteries. Unlike geometric stabilization, wherein the structure of the native oxide is stabilized using non-'ccp' structure or pillars [1–3], the electronic stabilization of pristine

Gangulibabu · D. Bhuvaneswari · N. Kalaiselvi (✉)
CSIR—Central Electrochemical Research Institute,
Karaikudi 630 006, India
e-mail: kalaiselvicecri@gmail.com

LiMO$_2$ oxide to arrive at LiM$_x$Ni$_y$Co$_z$O$_2$ solid solutions {$x=y=z=0.33$(333) and $x=y=0.4$; $z=0.2$ (442)} with improved electrochemical performance has been chosen for the present study. Particularly, LiMn$_{0.4}$Ni$_{0.4}$Co$_{0.2}$O$_2$ (442) and LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ (333) compositions assume importance as they exhibit intriguing electrochemical behaviour, especially when Ni, Co and Mn adopt valence states of +2, +3 and +4, respectively [1, 4–9]. These compounds encompass advantages like high ordering of lithium and transition metals due to the presence of cobalt, and the appreciable capacity of 160–180 mAh g^{-1} results from that of Ni^{2+}/Ni^{4+} red–ox couple. Similarly, the cost and toxicity are reduced due to the presence of manganese, which in turn addresses the issues related to structural stability upon cycling [1, 10]. In addition, LiMn$_{0.4}$Ni$_{0.4}$Co$_{0.2}$O$_2$ and LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ solid solutions are known to exhibit an admissible volume change in the range of $0<x\geq0.7$ [1], thus rendering enhanced electrochemical performance. Several synthesis approaches such as ceramic or acetate decomposition [11, 12], hydroxide precipitation [13], carbonate co-precipitation [14], solution combustion [15], microwave [15], inverse micro emulsion [6] and modified sol–gel [5] methods are reported for the preparation of LiMn$_{0.4}$Ni$_{0.4}$Co$_{0.2}$O$_2$ and LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ compounds.

It is well known that synthesis procedure has an impeccable impact on cation ordering, on particle size and ultimately on the electrochemical properties [5, 16, 17] of synthesized electrode materials. Particularly, adoption of a simple and easier synthesis approach bestowed with time- and energy-saving prospects is preferred for known reasons. Towards this direction, solution-assisted sol–gel and combustion methods are preferred as they ensure uniform distribution and atomic-level mixing of reactants with the gelling agent/combustible fuel and to produce phase pure final product in the form of ultra-fine powder with reduced particle size. Again, the role of gelling agent and combustible fuel is very

important as the same is responsible for the formation of transparent gel in sol–gel method and the liberation of energy to produce fluffy mass in combustion method, respectively.

Quite different from conventional approaches, a first-ever attempt to exploit corn starch that could play dual role as gelling agent in sol–gel approach and as combustible fuel in combustion method has been made due to the following reasons: Corn starch, a polysaccharide of glucose that consists of two types of polymeric chains of amylose (linear) and amylo-pectin (branched), is commonly used as a gelling agent in soap and food industries [18, 19] based on the fact that the molecular chains of corn starch unravel upon heating and colloid with each other and with precursor ions to form a gel. Considering such an advantageous segmental motion of polymeric chains in forming a gel, a novel attempt to exploit corn starch as a gelling agent in sol–gel method with acetate precursor has been made to prepare the compounds of interest, viz. $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$. Similarly, literature is replete with reports on solution-assisted combustion synthesis, wherein (rice) starch has so far been used to synthesize $LiCoO_2$, $LiMn_2O_4$ and $LiNiVO_4$ [20, 21] cathodes and not the compounds of interest of the present study. More interestingly, corn starch has never been exploited as a combustible component to synthesize either simple $LiMO_2$ cathodes or $LiMO_2$-based solid solutions to date. Hence, a novel attempt on the exploitation of corn starch as a combustible carbonaceous fuel has been made to prepare $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compounds, respectively.

It is believed that the amylo-pectin branched chain dominates in forming a gel with the acetate precursor in sol–gel method and the linear amylose chain reacts predominantly with the nitrate precursor of the combustion process to liberate NO_x and CO_x gases to form a fluffy mass with desired porosity besides the liberation of energy resulting from the breaking of N–O bonds of nitrate precursor to cook the precursor mix effectively. As a result, phase pure and nano-crystalline $LiMn_xNi_yCo_zO_2$ solid solutions are obtained from corn starch-assisted gelling and combustion techniques, which are subjected to physical and electrochemical characterization studies for comparison of results and to gain better understanding of properties as a function of corn starch-assisted synthesis methods. Further, the versatile nature of corn starch in aiding sol–gel and combustion methods to prepare $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compounds, known for their high capacity, reversibility and structural stability, has been demonstrated in the present study.

Experimental section

All of the chemicals (analytical grade) used in the experiments were purchased from Sigma Aldrich and used as received without further purification. In all the experiments, 15 % of excess lithium (Li/M=1.15:1) has been used to avoid lithium loss during calcination at high temperature.

In sol–gel method, a precursor mix consisting of an appropriate amount of lithium acetate, cobalt acetate, nickel acetate and manganese acetate was dissolved in water with stirring for 1 h to get a homogeneous solution. To the solution, 3 g of corn starch was added and the process of stirring and heating (~80 °C) was continued for 2 h to get a thick gel. Similarly, in combustion method (nitrate precursor-based), a precursor mix consisting of an appropriate amount of lithium nitrate, cobalt nitrate, nickel nitrate and manganese nitrate was dissolved in water with stirring for 1 h to get a homogeneous solution. To the solution, 3 g of corn starch was added and the process of stirring and heating (~80 °C) was continued for 2–3 h to get a foamy mass. The obtained gel (sol–gel method) and foamy mass (combustion method) were dried for 12 h at 120 °C and furnace-heated to 300 °C for about 12 h followed by calcination at 850 °C for about 12 h in air using alumina crucibles. The ultra-fine powders thus obtained were ground and subjected to characterization studies.

The electrodes were prepared from a combination of 80 wt.% active material with 10 wt.% super P carbon and 10 wt.% polytetrafluoroethylene binder. The chosen powders were mixed thoroughly and rolled into thin sheet on a glass plate using isopropanol. Such a thin sheet was cut in a circular shape (14 mm) and pressed over an Al mesh (3 ton of pressure). The electrodes typically had an active material content of 8–10 mg and were dried under vacuum at 80 °C for 12 h prior to assembling the cells in an argon-filled glove box [22]. Electrochemical characterizations were carried out on freshly fabricated 2032 coin cells consisting of lithium anode, $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ or $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathode and a non-aqueous electrolyte containing 1 M $LiPF_6$ (dissolved in 1:1 v/v EC/DMC) with a celgard separator.

Thermal analysis of acetate- and nitrate-based metal precursors with corn starch was studied by thermogravimetry and differential thermal analysis (TG/DTA) with a thermobalance model STA 409 PC in the temperature range of 30–800 °C using alumina crucibles under air with a heating rate of 20 °C min^{-1}. Phase characterization was done by a powder X-ray diffraction technique on a PANalytical X'pert PRO X-ray diffractometer using Ni-filtered Cu Kα radiation (λ=1.5406 Å) in the 2θ range of 10–90° and at a scan rate of 0.04° s^{-1}. Surface morphology of synthesized active materials was investigated using Jeol S-3000 H scanning electron microscopy (SEM), and particle size analysis was carried out on Malvern particle size analyser. Charge–discharge study at C/10 rate (for 100 cycles) and rate capability test at different current rates (C/10, C/5, C/2 and 1 C rate) were carried out in the potential range of 2.5–4.6 V using ARBIN charge–discharge cycle life tester.

Results and discussion

Thermal analysis—TG/DTA

Figure 1 shows the results obtained from TG/DTA of the gels (acetate precursors) and foamy masses (nitrate precursors) corresponding to the respective precursors of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compounds with corn starch. It is quite interesting to note that the thermal behaviour of sol–gel precursors corresponding to the formation of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compounds is found to be identical. Likewise, the thermal behaviour of combustion precursors of 442 and 333 compounds also exhibits similarity with respect to each other, thus evidencing the fact that the thermal behaviour of each method has a major dependence on the type of precursors chosen and the same is irrespective of the type of compound being synthesized. Further, the formation temperature of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compounds is found to be significantly lower for combustion method compared to sol–gel method.

Details pertinent to the thermal behaviour of acetate and nitrate precursors in sol–gel and combustion methods could be understood as follows: the acetate precursors of sol–gel method exhibit several weight loss steps corresponding to the loss of physically absorbed water (25–120 °C), decomposition of acetate precursor and corn starch (125–250 °C), and formation and dissociation of meta-stable chelating complex (380 and 450 °C, respectively) with an indication of formation of desired product viz. $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ at 432 °C and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ at 467 °C as evident from Fig. 1. Similarly, nitrate precursors of combustion process exhibit weight loss steps corresponding to the evaporation of physically absorbed water (25–120 °C), decomposition of corn starch (200–250 °C), removal of NO_x and CO_x gases (250–328 °C) and completion of corn starch–nitrate combustion process (250–335 °C) to produce the final products viz. $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ at 328 °C and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ at 335 °C, respectively.

More interestingly, the thermal behaviour of corn starch in producing mixed metal oxides such as $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ of the present study is exhibiting similarity with that of starch-assisted nitrate combustion method in preparing $LiCoO_2$ and $LiMn_2O_4$ [20]. Hence, it is understood from TG/DTA studies that corn starch could also be exploited as an exothermic combustible fuel and as gelling agent to prepare a wide variety of lithium intercalating electrode materials with a special reference to combustion and sol–gel methods.

Fig. 1 Thermal behaviour of corn starch with acetate- and nitrate-based metal precursors of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compounds
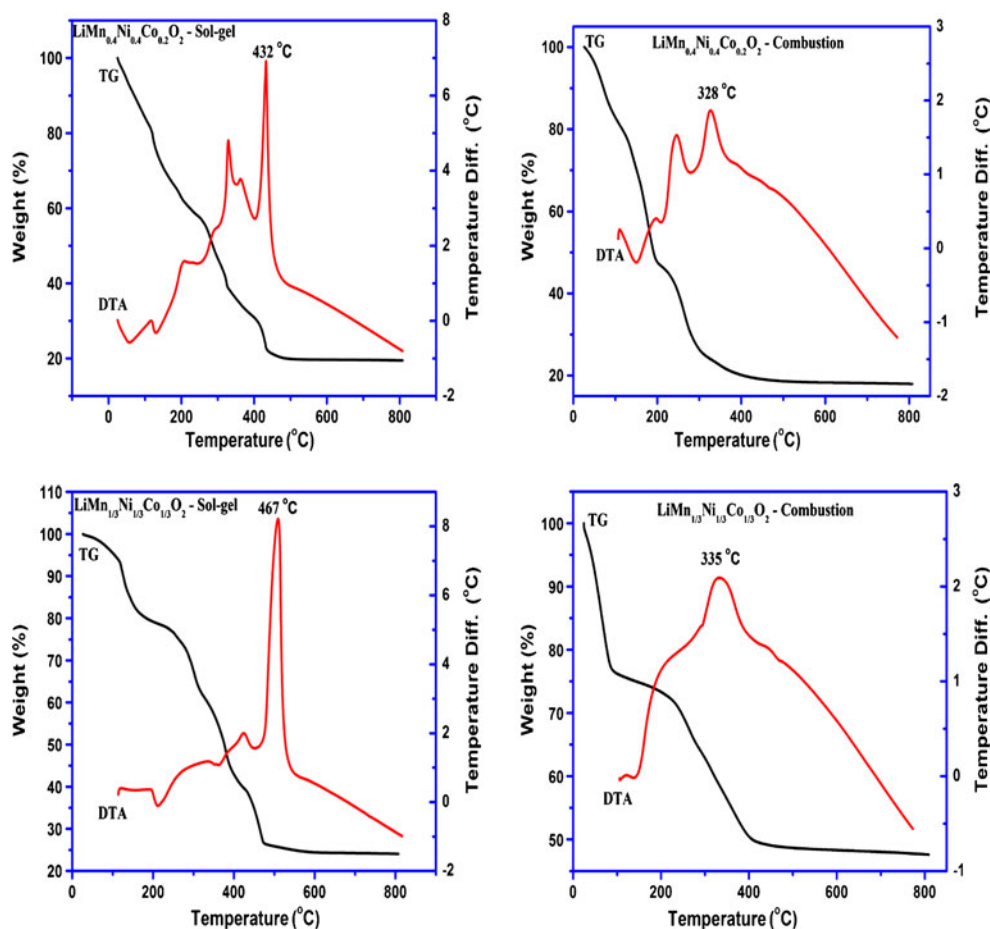
Phase analysis—XRD

Figure 2 shows the XRD pattern of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compounds synthesized using corn starch as gelling agent (sol–gel method) and combustible fuel (combustion method), wherein all the Bragg peaks can be indexed on the α-$NaFeO_2$ type of layered structure with R-3 m space group. Both of the compounds are found to be phase pure with the absence of cubic NiO phase at 2θ=44°, which would impede lithium ion movement due to its incompatibility with the layered structure [23]. As it is well known that the separation of $(006)/(102)$ and $(108)/(110)$ peaks of the hexagonal structure indicates the formation of an ordered layered structure [24], $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compounds of the present study are found to possess an ordered and crystalline layered structure. Also, the effect of precursors and increased cobalt content in producing an ordered layered structure could be understood from the significant splitting of peaks observed with $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compound compared to that of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$, especially when synthesized using combustion method.

The lattice parameters a and c of the synthesized materials were calculated using unit cell software and the values are summarized in Table 1. As reported, the lattice parameter a is found to be pro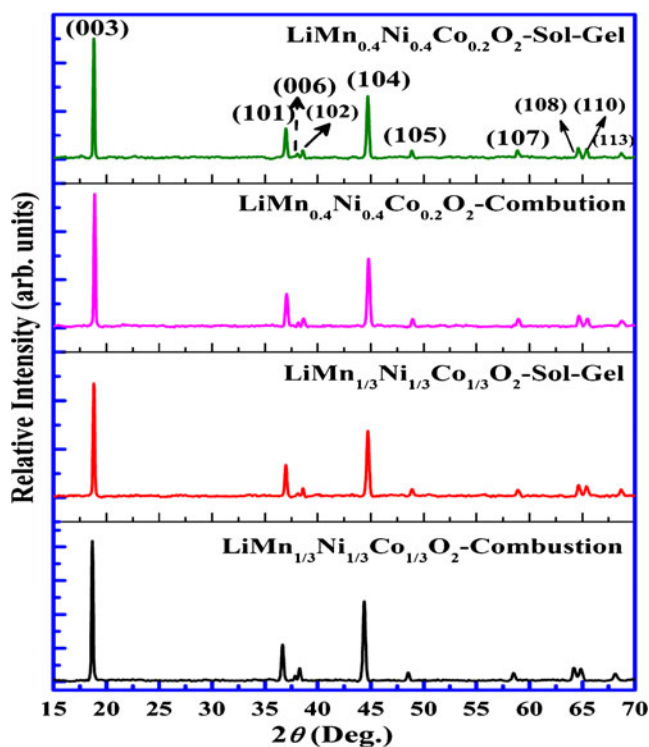portional to Ni content and inversely proportional to Co content, with a constant Mn content [1, 25]. In other words, the calculated a value of $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ is slightly lower than that of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ due to the excess concentration of cobalt in the former sample. Since the lattice parameter c is the average metal–metal interslab distance and c/a is related to trigonal distortion, a c/a value greater than 4.9 is generally preferred for a well-defined hexagonal layered structure [26, 27]. From Table 1, it is evident that the c/a ratio increases linearly with the concentration of cobalt, which in turn increases the hexagonal layeredness of $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compound in a better manner than that of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$.

It is reported that cation mixing in layered oxides deteriorates the electrochemical performance [28, 29]. Accordingly, the intensity ratios of $I_{(003)}/I_{(104)}$ (R) and $(I_{(102)}+I_{(006)})/I_{(101)}$ (R'), which are sensitive to the degree of cation mixing in lattice, have been calculated (Table 1). Basically, a higher R value (1.2) and a lower R' value are desirable for a lower degree of cation mixing [16]. From Table 1, it is understood that an R value greater than 1.2 has been obtained for all the four compounds, which is in favour of low cation mixing [30–32]. Similarly, a lower R' value has been obtained for combustion-derived samples, thus indicating the possibilities of better hexagonal ordering of combustion-derived products than the sol–gel-derived ones. In the light of the cited observations, it is clear that the compounds synthesized using a combination of nitrate precursor and corn starch provide the desirable layered structure than those obtained from acetate precursor and corn starch. By considering the highest R and the lowest R' values, a combustion-synthesized $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compound with increased cobalt content is expected to possess better hexagonal ordering amongst the compounds chosen for the study.

Morphology analysis—SEM

The surface morphology of 442 and 333 compounds prepared by corn starch as gelling agent (sol–gel method) and as combustible fuel (combustion method) has been investigated by scanning electron microscopy (Fig. 3). The presence of ultra-fine particles with definite grain boundaries is evident in the SEM images. In particular, closely arranged spherical grains of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compounds with a particle size of ~0.6 μm have been synthesized by combustion method (as evident from Fig. 3b, d). On the other hand, aggregates consisting of slightly bigger particles of >0.8 μm are seen from the images of sol–gel-synthesized 442 and 333 compounds (Fig. 3a, c). Thus, the fluffy mass resulting from the combination of nitrate precursor and corn starch is found to possess reduced particle size which is desirable for improved electrochemical behaviour, which is in line with the results derived from XRD studies.

Fig. 2 XRD pattern of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compounds prepared using corn starch as chelating agent (sol–gel method) and as combustible fuel (combustion method), respectively

Table 1 Lattice parameters, c/a ratio and $I_{(003)}/I_{(104)}$ (R) and $(I_{(102)}+I_{(006)})/I_{(101)}$ (R') intensity ratios for the synthesized samples

| Compound	a (Å)	c (Å)	c/a	R	R'
LiMn$_{0.4}$Ni$_{0.4}$Co$_{0.2}$O$_2$ sol–gel method	2.871(7)	14.257(5)	4.966	1.68	0.45
LiMn$_{0.4}$Ni$_{0.4}$Co$_{0.2}$O$_2$ combustion method	2.868(6)	14.256(4)	4.971	1.76	0.42
LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ sol–gel method	2.853(8)	14.201(6)	4.977	1.87	0.40
LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ combustion method	2.849(6)	14.185(4)	4.979	1.91	0.38

Particle size analysis

The particle size analysis results of mixed metal oxides synthesized using sol–gel and combustion methods are shown in Fig. 4. It is evident that the compounds derived from combustion method exhibit narrow distribution of particles corresponding to 0.7–0.9 μm (Fig. 4b, d). On the other hand, compounds synthesized using sol–gel method display a wide distribution of particles in the 0.7–1.4 μm range (Fig. 4a, c). Hence, it is understood from particle size analysis that the combination of nitrate-based metal precursors with corn starch as combustible fuel yields size-reduced particles, which are desired to facilitate facile intercalation and de-intercalation of lithium ions.

Electrochemical characterizations

In order to investigate the influence of corn starch-assisted solution synthesis methods on the electrochemical behaviour of currently prepared high-capacity cathode materials, 2032 coin cells containing synthesized LiMn$_{0.4}$Ni$_{0.4}$Co$_{0.2}$O$_2$ or LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ materials as cathode and lithium as anode were tested at 0.1 C rate between 2.5 and 4.6 V limit.

From Fig. 5a, b, it is evident that the initial capacity of combustion-derived LiMn$_{0.4}$Ni$_{0.4}$Co$_{0.2}$O$_2$ and LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ cathodes is found to be 182 and 176 mAh g^{-1}, respectively. On the other hand, sol–gel-derived 442 and 333 cathodes suffer from sluggish lithium diffusion kinetics resulting from the slightly bigger particles and, due to the same reason, slightly reduced initial discharge capacity values of 176 and 171 mAh g^{-1} have been exhibited by them, respectively. Similarly, the irreversible capacity measured during the initial cycle (excluding the formation cycle) is found to be lower for combustion-synthesized LiMn$_{0.4}$Ni$_{0.4}$Co$_{0.2}$O$_2$ (1.8 %) and LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ (1.7 %) cathodes compared to those of sol–gel-synthesized 442 (3.5 %) and 333 (2.0 %) cathodes. Further, maintenance of discharge plateau at 3.8 V and the absence of plateau around 4.0 V exhibited up to 100 cycles confirm the absence of possible structural changes of layered 442 and 333 cathodes into spinel-related phases [23, 24]. Such an improved structural stabilization is attributed to the presence of Mn^{4+} that

Fig. 3 **a**–**d** SEM images of LiMn$_{0.4}$Ni$_{0.4}$Co$_{0.2}$O$_2$ and LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ compounds

a

b

c

d
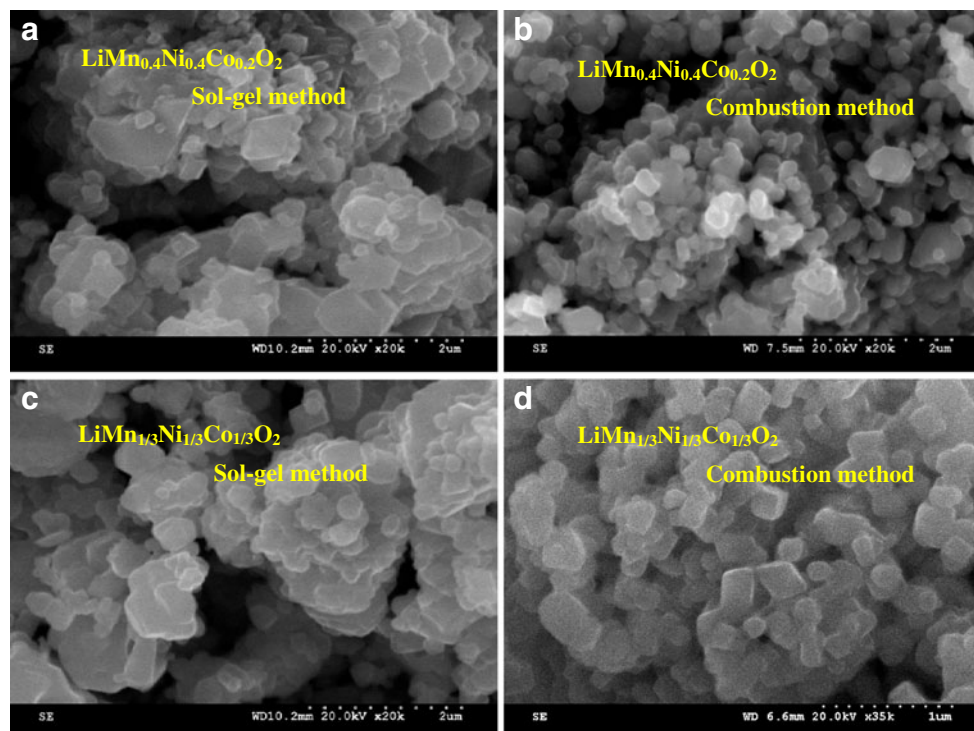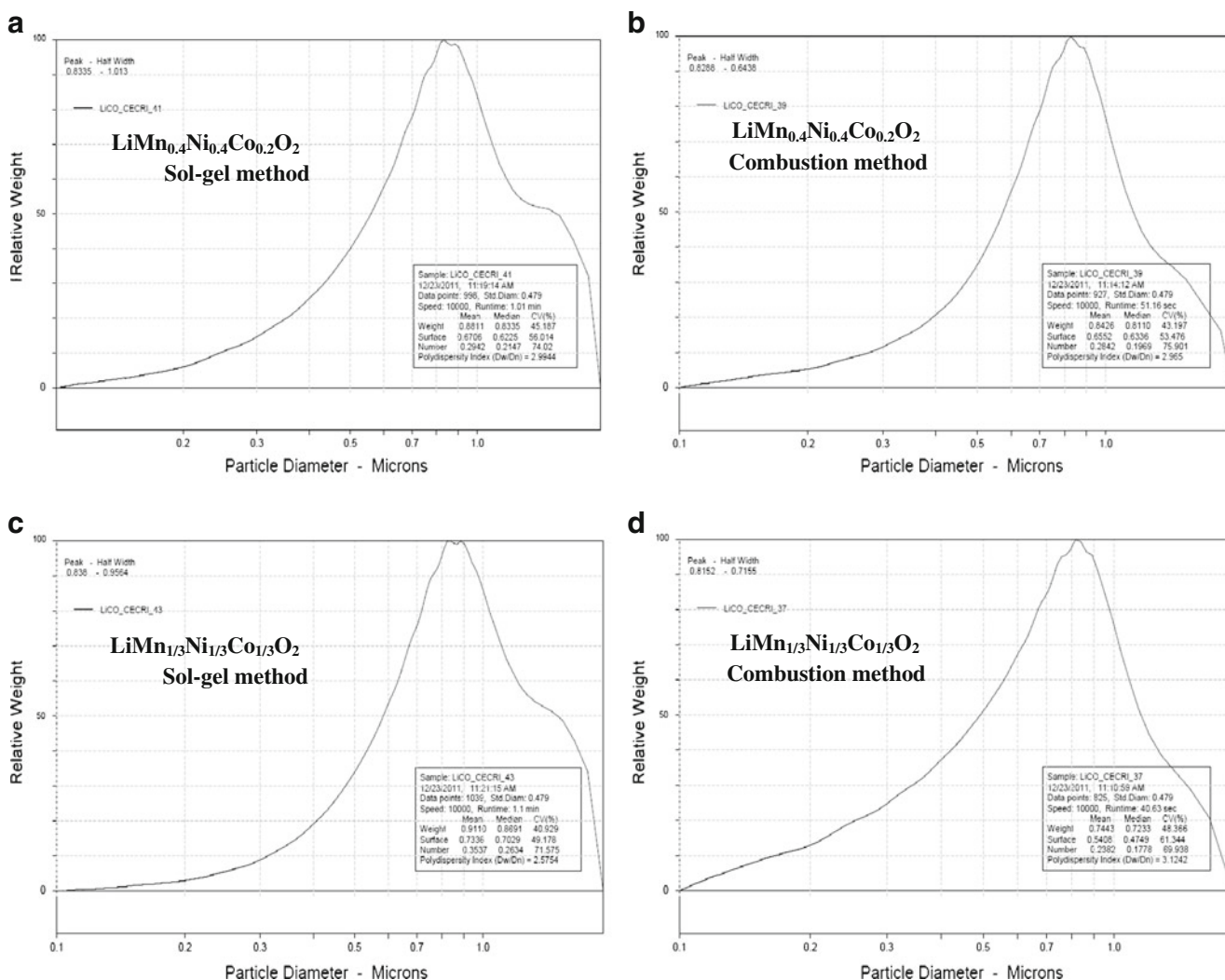
Fig. 4 **a**–**d** Particle size analysis of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compounds synthesized using sol–gel and combustion methods

maintains the oxide network favourable for facile lithium intercalation/de-intercalation upon extended cycling.

A comparison of the cycling behaviour of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathodes up to 100 cycles (0.1 C rate) and coulombic efficiency details are furnished in Fig. 6a. The observed discharge capacity value (Q_{dc}) of initial, 50th and 100th cycle and the corresponding capacity fade behaviour of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathodes are summarized in Table 2. It is evident from Fig. 6a and Table 2 that corn starch-assisted combustion-synthesized $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode has delivered a capacity as high as 176 mAh g^{-1} with an appreciable capacity retention and a negligible capacity fade of 3 and 7 % corresponding to 50 and 100 cycles, which is either comparable with or superior than the recent reports [2, 12, 15]. However, the same cathode, when synthesized using corn starch-assisted sol–gel method, exhibits a reduced capacity of 171 mAh g^{-1} with a capacity fade of 9 and 17 %

after the completion of 50 and 100 cycles, respectively. On the other hand, combustion-derived $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathodes are found to suffer from significant capacity fade to the extent of 14–26 %, especially upon extended cycling. Further, the cycling efficiency of combustion-synthesized $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathode subjected to 100 cycles is found to be ~98 % (Fig. 6a), which is noteworthy. Based on these observations, combustion-synthesized $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathode is regarded as a superior cathode material and combustion as the better synthesis method. Such an improved electrochemical performance could be endorsed to the synergistic effect of an increased concentration of cobalt present in $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode and the presence of ultra-fine particles (~0.6 μm) obtained from combustion method. Hence, the role of synthesis method and the selection of compound in realizing better electrochemical behaviour could be understood.
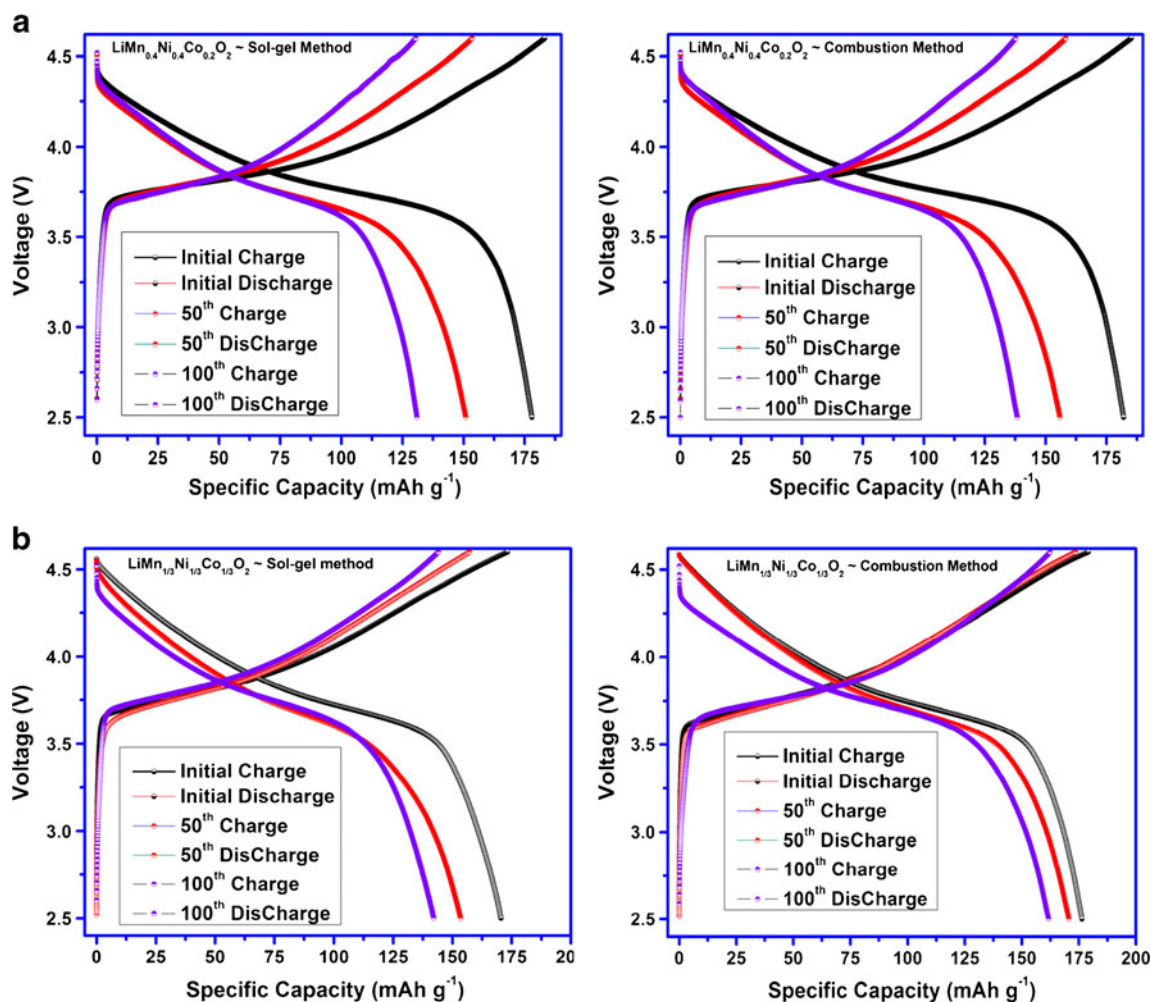
Fig. 5 **a**, **b** Voltage profile of initial, 50th and 100th cycle recorded for sol–gel- and combustion-synthesized $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathodes (C/10 rate) in the potential range of 2.5–4.6 V
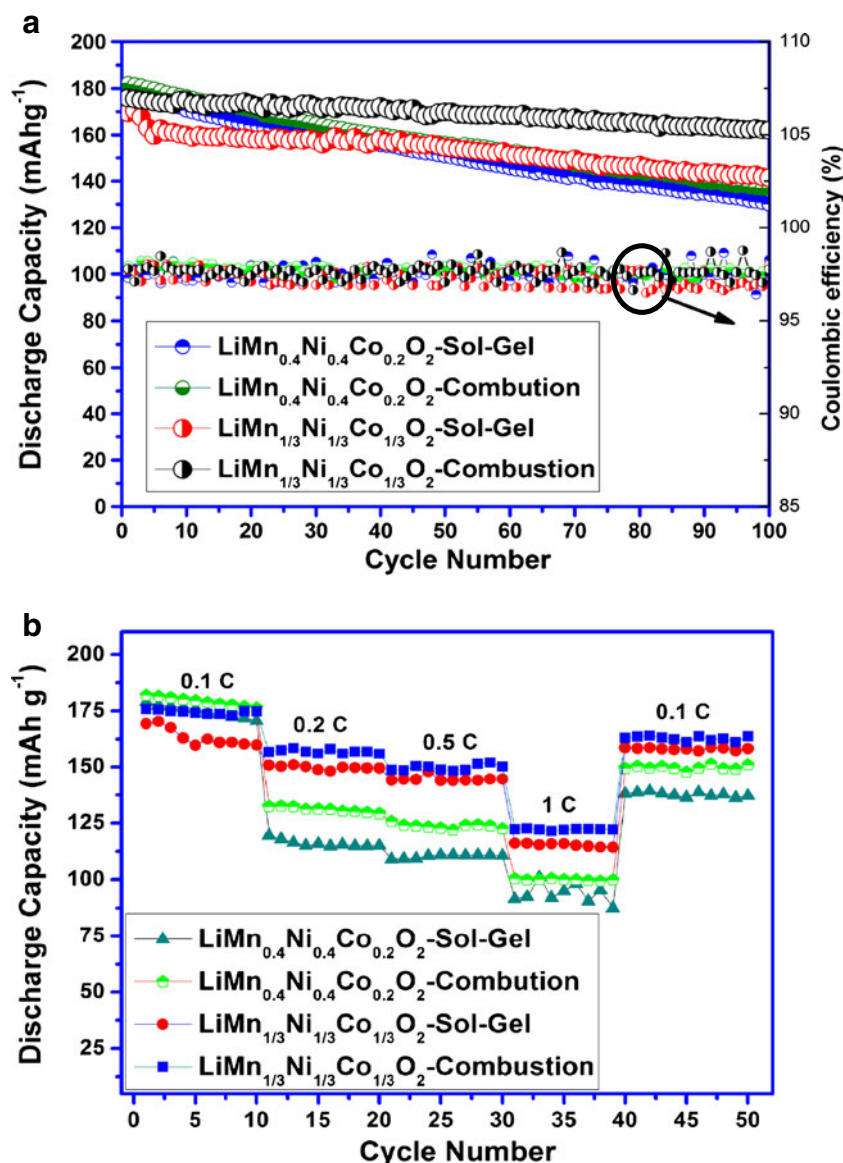
In order to investigate the suitability of corn starch-assisted sol–gel- and combustion-synthesized cathodes for high-rate lithium intercalation and de-intercalation applications, a rate capability test was performed and a comparison of the results has been made (Fig. 6b). The chosen cathodes were subjected to 0.1, 0.2, 0.5 and 1 C rate discharge conditions, wherein the effect of each rate has been studied for ten subsequent cycles. Prior to the end of the rate capability test, the cells were discharged at C/10 rate with a view to examine the extent of regaining the initial capacity, which is a measure of capacity retention behaviour, too. As expected, the rate capability and capacity retention behaviour of combustion-synthesized $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathode is found to be superior to the rest of the cathodes under the influence of varied discharge current values. Interestingly, specific capacity values of 175, 156, 148 and 122 mAh g^{-1} have been observed for combustion-synthesized $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathode after 10, 20, 30 and 40 cycles corresponding to 0.1, 0.2, 0.5 and 1 C rate. In other words, the discharge capacity (122 mAh g^{-1}) exhibited by the compound at 1 C rate (or after completing 40 cycles) is found to be more than 80 % of the initial capacity of 176 mAh g^{-1}. Further, excellent capacity retention of 93 % has been exhibited by combustion-synthesized $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathode even after the completion of 1 C rate discharge conditions, which is also superior than the rest of the cathodes considered for rate capability test. Thus, the suitability of combustion-synthesized $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathode for high-rate lithium intercalation and de-intercalation applications has been demonstrated through the current study.

Conclusion

Layered $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ compounds have been synthesized using a novel corn starch-assisted sol–gel and combustion methods, wherein the gelling and combustible nature of corn starch with

acetate and nitrate precursors, respectively, has been exploited for the formation of phase pure and crystalline products with desired physical as well as electrochemical properties. From the series of compounds synthesized in the current study, $LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$ obtained from corn starch-assisted combustion method with a narrow distribution of particles (~0.6 μm) has delivered an appreciable discharge capacity of 176 mAh g^{-1}, better capacity retention (93 %) up to 100 cycles and an appreciable rate capability behaviour at 1 C rate, which is superior compared to the rest of the cathodes. This study demonstrates the feasibility of deploying corn starch as a gelling agent and

Table 2 Observed discharge capacity values and the corresponding capacity fade after 50 and 100 cycles exhibited by $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathodes

Compound	Discharge capacity (mAh g^{-1})			Capacity fade (%)	
	Initial	50th cycle	100th cycle	50th cycle	100th cycle
$LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ sol–gel method	176	152	130	16	26
$LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ combustion method	182	157	136	14	25
$LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ sol–gel method	171	155	141	9	17
$LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ combustion method	176	170	163	3	7

as combustible fuel in sol–gel and combustion methods to prepare high-capacity mixed oxide cathode materials such as $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$. Further, this study recommends that corn starch-assisted combustion-synthesized $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathode with improved electrochemical behaviour could be considered favourably for high-capacity and high-rate lithium battery applications.

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