

Novel synthesis of layered $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ as cathode material for lithium rechargeable cells

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Abstract

A new solution combustion synthesis of layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ involving the reactions of LiNO_3 , $\text{Mn}(\text{NO}_3)_2$, NiNO_3 , and glycine as starting materials is reported. TG/DTA studies were performed on the gel-precursor and suggest the formation of the layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ at low temperatures. The synthesized material was annealed at various temperatures, viz., 250, 400, 600, and 850 °C, characterized by means of X-ray diffraction (XRD) and reveals the formation of single phase crystalline $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ at 850 °C. The morphology of the synthesized material has been investigated by means of scanning electron microscopy (SEM) and suggests the formation of sub-micron particles. X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV) studies on the synthesized $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ powders indicate that the oxidation states of nickel and manganese are +2 and +4, respectively. Electrochemical galvanostatic charge–discharge cycling behavior of $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cell using 1 M LiPF_6 in EC/DMC as electrolyte exhibited stable capacities of ~125 mAh/g in the voltage ranges 2.8–4.3 V and 3.0–4.6 V and is comparable to literature reports using high temperature synthesis route. The capacity remains stable even after 20 cycles. The layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ powders synthesized by this novel route have several advantages as compared to its conventional synthesis techniques.

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1. Introduction

Recently, lithium rechargeable batteries are gaining much importance in view of the various advantages like high voltage, good low temperature performance, easy handling [1,2], etc., and involving applications ranging from cell-phones, toys to electric vehicles, etc. The system basically involves the use of lithiated transition metal oxides as cathode materials, viz., LiCoO_2 , LiMn_2O_4 , and LiNiO_2 . Among these investigated cathode materials, LiCoO_2 is the most preferred in majority of commercial lithium ion cells due to its high reversibility and ease of synthesis [3]. However, considering the toxicity of cobalt coupled with its high cost and low practical capacity output of ~137 mAh/g (~50% of theoretical capacity of 273.8 mAh/g) has stim-

ulated researchers to search for alternative more safer and cheaper cathode materials with either comparable or better electrochemical performance than LiCoO_2 . In a very recent article, Amundsen and Paulsen [4] highlighted the efforts of various researchers in stabilizing the layered manganese oxides and the need for developing novel complex solid solutions based on layered manganese oxides with improved capacity, cycling stability and safety. Layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ has very recently attracted [5–9] much attention of researchers in view of its comparable performance with LiCoO_2 , high thermal stability and more so eliminating toxic cobalt. Ohzuku and Makimura [5] successfully demonstrated the synthesis of 1:1 solid solution of LiNiO_2 and LiMnO_2 namely $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ employing solid state synthesis technique by heating at 1000 °C for 15 h, thus eliminating the drawbacks of the end members like capacity fading, structural stability, difficult synthesis procedures, etc. Simultaneously, Lu et al. [6,7] also reported the synthesis of a series of layered $\text{Li}[\text{Ni}_x\text{Li}_{(1/3-2x/3)}\text{Mn}_{(2/3-x/3)}]\text{O}_2$ using mixed hydroxide method. However, the layered

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$\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ synthesized by Lu et al. [6,7] was different as compared to that synthesized by Ohzuku and Makimura [5] in terms of the oxidation states of nickel and manganese. Subsequently, few other researchers [8,9], also reported the synthesis of layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ involving high temperature synthesis and confirming the observations of Lu et al. Thus, it is clear that either solid state or double hydroxide techniques have been employed for the synthesis of layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ either involving high temperatures of 900 °C and above or requiring longer processing time or multi-step cumbersome processes. Glycine nitrate pyrolysis route has been found to be very useful for the synthesis of other functional or ceramic materials especially for solid oxide fuel cell (SOFC) applications [10,11]. Hence, we found it timely to explore the possibility of preparing the layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ using this novel solution combustion technique hitherto not reported. The advantages of the present technique over the reported methods of synthesis for layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ involve low temperature of synthesis, lesser processing time in addition to being a simple process. Further, the novelty of the present technique has recently been demonstrated by us for synthesizing CoV_2O_5 [12] for use in lithium rechargeable cells. Thus, we report in this communication, investigations involving physical (X-ray diffraction (XRD), TG/DTA, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM)) and electrochemical (cyclic voltammetry (CV) and galvanostatic cycling) properties of layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ synthesized by a new glycine assisted sol–gel combustion technique for use in lithium rechargeable cells.

2. Experimental

Stoichiometric amounts of high purity LiNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, glycine (Aldrich), and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka) were dissolved in distilled water and the solution was initially heated to 80 °C followed by heating to 135 °C. The glycine to metal ratio was fixed at 1:1. Inductively cou-

pled plasma (ICP)–AES analysis was performed on the synthesized powders for confirming the stoichiometry of nickel and manganese. The ratio of Ni:Mn is found to be 1:1. The sample synthesized at 135 °C is classified as gel-precursor. TG/DTA studies were performed on a portion of the gel-precursor with TA Instruments (Texas, USA) at a scan rate of 10 °C/min in the temperature range 15–700 °C. Portions of gel-precursor were annealed at 240, 400, 600, and 850 °C for 8 h in flowing oxygen and slowly cooled to room temperature.

The structure of the prepared powders at different temperatures were recorded with an automated Rigaku powder X-ray diffractometer using $\text{Cu K}\alpha$ radiation by measuring the diffraction angle (2θ) between 10 and 80° with an increment of 0.02°/min. The XRD patterns were indexed and lattice parameters a and c were determined using least squares hexagonal fitting of all the diffraction lines for the samples annealed at 850 °C with d -spacing and Miller indices (hkl).

Scanning electron microscope (SEM, HITACHI S2700) was used for observing the morphology of the synthesized powder. X-ray photoelectron microscopy of the synthesized powder was investigated using VG electron spectroscopy. The powder sample was spread over a polymeric adhesive tape and affixed to the sample holder. All spectra were recorded using an X-ray source ($\text{Al K}\alpha$ radiation) with a scan range of 1200–0 eV binding energy. The collected high-resolution XPS spectra were analyzed using XPS peak software fitting program. The energy scale was adjusted on the carbon peak in C1s spectra at 284.9 eV.

Electrochemical measurements were carried out using a two-electrode coin cell 2016 type with metallic lithium as counter and reference electrodes while the working electrode consisted of the synthesized layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ mixed powder coated on an aluminum current collector. The powder mix in the working electrode consisted of 85% of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, 10% acetylene black and 5% PVDF binder blended with NMP solvent. Cyclic voltammetric measurements were carried out at a sweep rate of 25 $\mu\text{V/s}$ using the above cell with 1 M LiPF_6 in EC/DMC

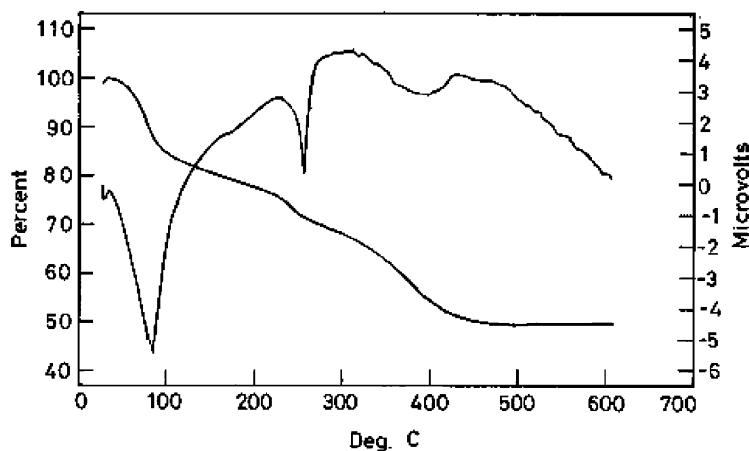


Fig. 1. TG/DTA pattern of the gel-precursor at 135 °C.

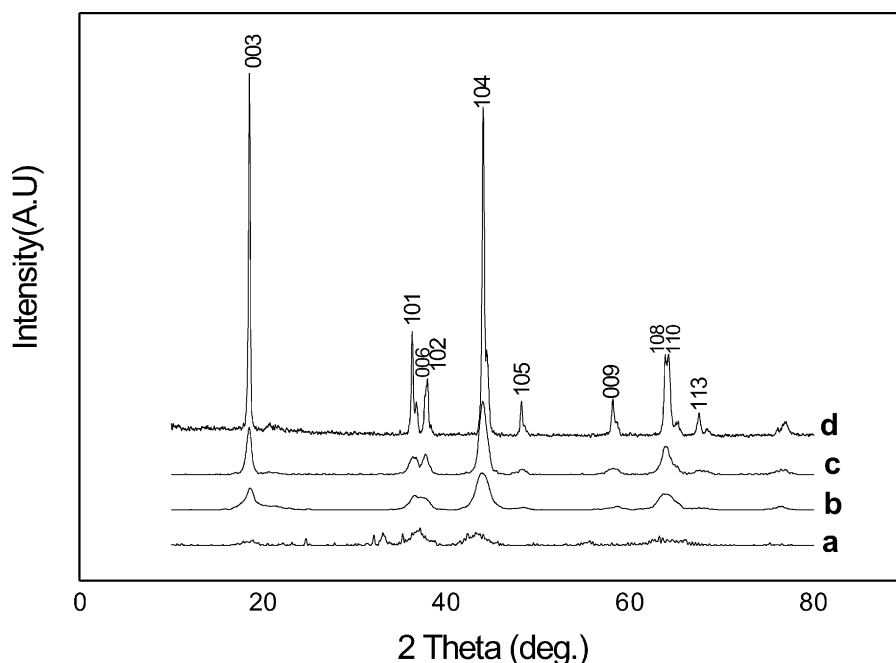


Fig. 2. XRD pattern of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ at (a) 250°C, (b) 400°C, (c) 600°C, and (d) 850°C.

as electrolyte solution in the potential range 2.5–4.6 V. Galvanostatic charge/discharge cycling experiments were performed using the assembled cells and at different voltage ranges, viz., 2.8–4.3 V and 3.0–4.6 V at a current density of 0.1 mA/cm² using an automatic battery cycle life tester.

3. Results and discussion

TG/DTA curves obtained for the precursor using glycine assisted sol–gel combustion technique are depicted in Fig. 1. It can be clearly seen from the curve that the formation of layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ takes place around 480°C. Fur-

ther, a close look at the curve suggests that the formation of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ from the precursor stage can be divided into two main regions. The weight loss observed between the temperatures 30 and 120°C could be ascribed due to the departure of water molecules and adsorbed gasses during the formation of gel-precursor. Thereafter, a slight decrease in weight at around 230°C is due to the initiation of the glycine combustion reaction followed by a vigorous reaction accompanied by about 50% weight loss ascribed to the combustible organic materials up to 480°C. The above observations are supported by DTA studies, viz., the presence of two endothermic peaks in the DTA curves located at around 95 and 250°C can be assigned to the departure



Fig. 3. SEM photograph of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ synthesized at 850°C.

of water molecules and gasses like ammonia, etc., respectively. A broad exothermic peak initiating at $\sim 270^\circ\text{C}$ and ending at around 480°C corresponds to the 50% weight loss in TGA for the combustion reaction. However, beyond this temperature there is no weight loss or reactions involved indicating the completion of the combustion or in other words the formation of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ in the amorphous state as revealed by XRD.

Fig. 2 presents the X-ray diffraction patterns of all the synthesized powders obtained by heating the gel-precursor

at 250, 400, 600, and 850°C . The XRD of the gel-precursor was found to be amorphous. Further, it can be seen from Fig. 2 that the characteristic peaks start growing up with increase in annealing temperature indicating the formation of the layered material as evidenced from TGA studies. However, with increase in annealing temperature to 850°C the peaks become sharper and also increase in intensities. It is interesting to note that the intensity of 104 peak is more than that of 003 peaks for samples annealed below 850°C suggesting slight cation mixing. A comparison of the present

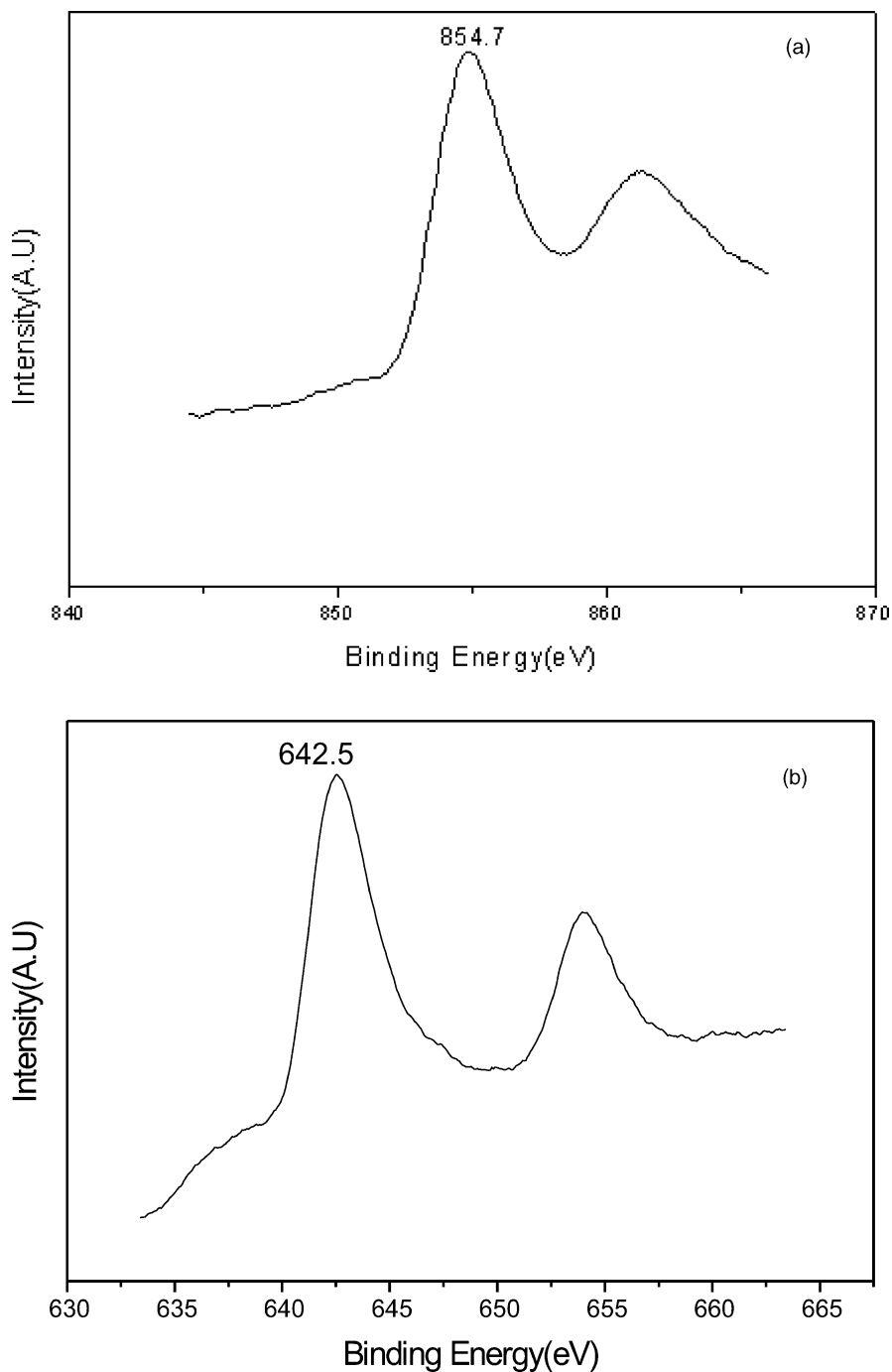


Fig. 4. XPS of (a) Ni 2p_{3/2} and (b) Mn 2p_{3/2} in the synthesized $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$.

XRD patterns with that of Lu et al. [6] suggests similar patterns and has been ascribed to the adoption of spinel-type structure with mixing of Li and Ni atoms. However, they also found that the intensities of 104 and 003 become same at higher temperatures ($>900^{\circ}\text{C}$). Indeed, in the present case, the intensity ratio of 003:104 peak at 850°C is more than unity indicating no cation mixing. This can be understood as the samples were annealed in flowing oxygen in contrast to Lu et al., where the samples were annealed in air. It is easily observed from the X-ray patterns that the entire fingerprint peaks, viz., 003, 101, 006, 102, 104, 108, 110, and 113 are clearly identifiable in the samples annealed at 850°C thereby suggesting the formation of the $\alpha\text{-NaFeO}_2$ structure. Further, looking at the intensity ratio of 003/104 as also the existence of doublets at 006, 102 and 108, 110 clearly confirms the structure of the synthesized $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ to be layered with $R\text{-}3m$ space group. The diffraction peaks of the synthesized pristine $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ are in excellent agreement with those reported in literature [6–9]. Therefore, we can confirm the formation of solid solution for this composition, i.e., $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$. The hexagonal parameters namely a and c and c/a ratio of the synthesized $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ were calculated from the least square fits and are found to be 2.89 \AA , 14.32 \AA , and 4.946 , respectively. As is well known the lattice parameter a represents the intralayer metal–metal distance while c is ascribed to inter slab distances. It can be seen that our values of a and c for synthesized pristine $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ are in close agreement to that reported in literature [6,7,9], viz., 2.894 and 14.301 \AA , respectively. Furthermore, c/a ratio is an indicator of the metal–metal layering distance or in other words hexagonal setting and is also found to be in close agreement with the reported values, i.e., 4.947 [7]. It should be emphasized here that a new solution

and lower annealing temperature method for synthesizing $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ has resulted in layered material with agreeable lattice parameters.

Rietveld analyses were not done in the present case but to a very good approximation the intensities of the XRD fingerprint peaks can predict cation mixing. It can be noted that the ratio of the intensities of 003 and 104 (I_{003}/I_{104}) peaks are greater than unity thereby suggesting no cation disorder which is supplemented by the values of c/a , i.e., >4.947 . As can be seen in the present case, the c/a ratios are in the range of 4.947 , thereby indicating no cation mixing. According to Ohzuku and Makimura [5], that a low value of I_{003}/I_{104} is an indicator of poor electrochemical reactivity due to high concentration of inactive rock-salt domains in a layered solid matrix. Interestingly, it is seen that the ratio of the intensities of 003 and 104 peaks for pristine $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ synthesized by this novel solution combustion technique is around 1.09 and seems to be the highest as compared to literature reports [5–9]. This result suggests no cation mixing and should have good electrochemical activity as will be discussed later.

The morphology of the synthesized $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was observed using scanning electron microscopy and reveals that the individual particles are of sub micron size ($100\text{--}200\text{ nm}$) and forms agglomerates (Fig. 3). We believe that this kind of morphology could enhance the diffusion of lithium ions and subsequently the electrochemical performance.

XPS studies are useful in gaining information on the oxidation states of the metal species present in the synthesized lithiated transition metal oxides. There has been lot of debate on the oxidation state of Mn and Ni in these materials [7,9]. Hence, we also found it necessary to record the

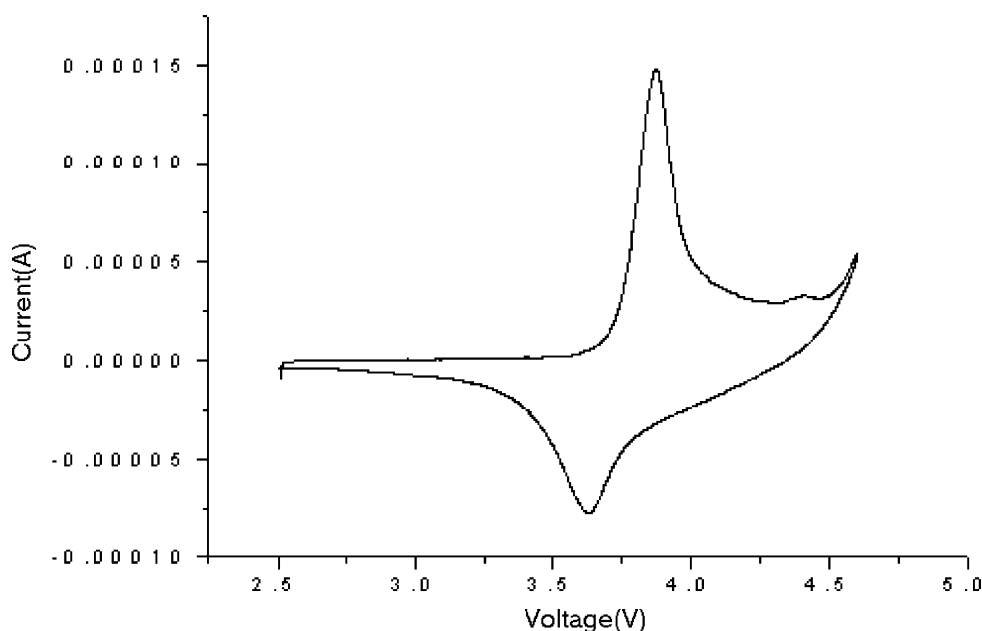


Fig. 5. Cyclic voltammety of the synthesized $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ in the voltage range $2.5\text{--}4.6\text{ V}$ at 0.1 mA/cm^2 .

patterns for ascertaining the oxidation state of Ni and manganese in the present study. The Ni XPS spectrum (Fig. 4a) reveals the characteristic binding energy located at around 854.7 eV with a satellite peak at 860 eV and hence could be assigned to Ni²⁺. The presence of the satellite peak has also been observed by other researchers and has been ascribed to the multiple splitting of nickel oxide energy levels [13,14]. Fig. 4b presents the XPS spectra of Mn 2p_{3/2} with a major peak located at a binding energy of around 642.5 eV and can be indexed to the Mn⁴⁺ while the satellite peak is observed around 654 eV in the synthesized LiNi_{0.5}Mn_{0.5}O₂.

The above observations are in agreement with the values reported by Kang et al. [9]. Thus, we could say that the binding energies located at 854.7 and 642.5 eV are due to the presence of Ni in +2 and Mn in +4 states, respectively. A small difference of 0.4 eV observed uniformly is due to the difference in charge referencing using carbon, i.e., C 1s binding energy of 285 eV in the present XPS measurements. The O 1s is located around 529.8 eV originating from oxygen linked to Mn–O and Ni–O in the synthesized material.

CV is an useful electrochemical tool wherein the changes taking place in an electrochemical reaction is monitored by

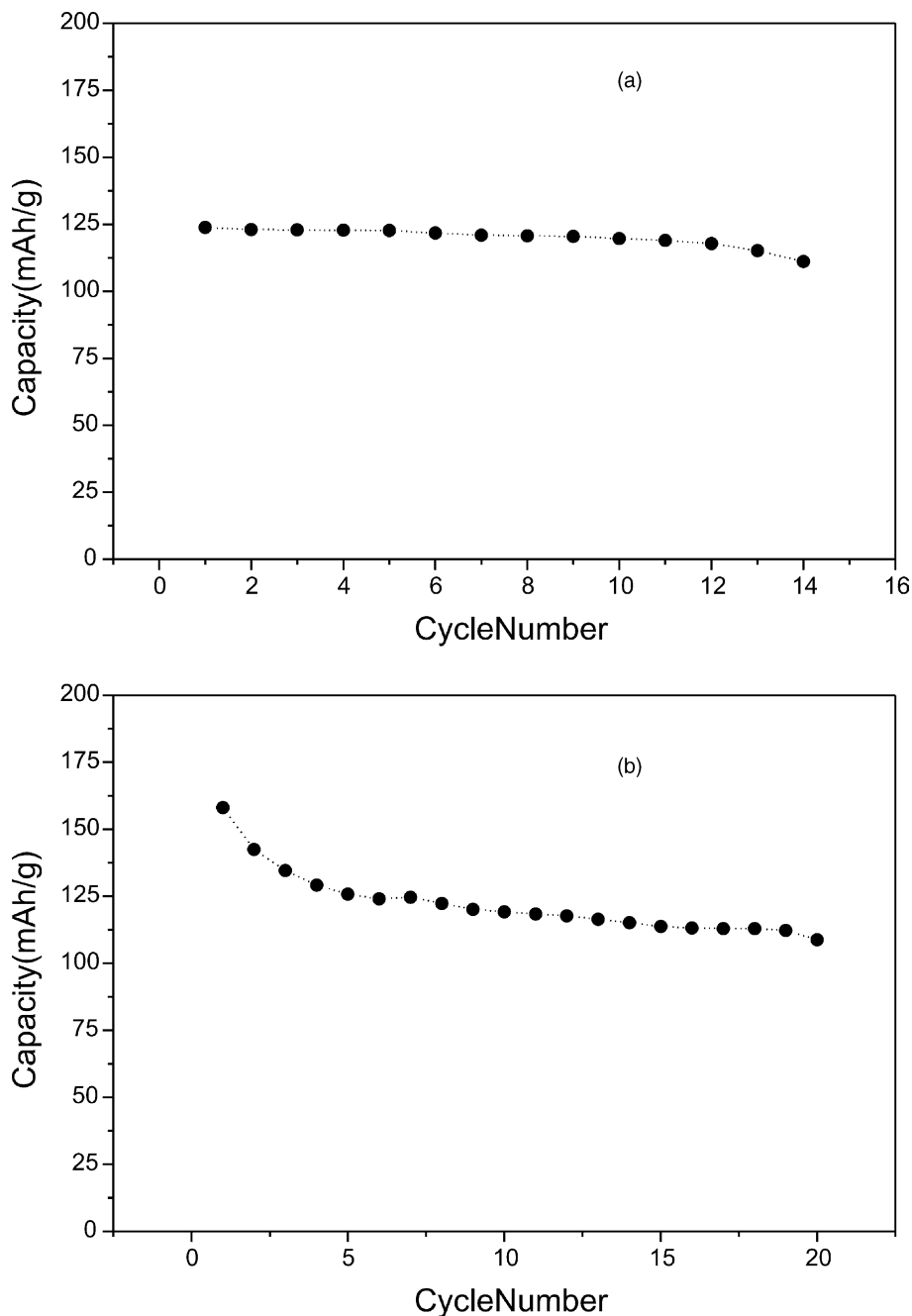


Fig. 6. Galvanostatic cycling of the synthesized LiNi_{0.5}Mn_{0.5}O₂ in the voltage range (a) 2.8–4.3 V and (b) 3–4.6 V.

measuring the current–potential responses. Typical CV obtained in the present case for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ is depicted in Fig. 5. As we observe no peak around 3 V it can be said that no manganese is present in the +3 state [15] in the synthesized material. It is clear from the figures that the major oxidation and reduction peaks are observed at around 3.95 and 3.75 V, respectively and is representative of lithium deintercalation and intercalation processes, respectively. These peaks are also signature of hexagonal phase in these types of layered compounds and indicating perfect reversibility. These observed peaks could be assigned to $\text{Ni}^{2+}/\text{Ni}^{4+}$ electrochemical process. Further, a very low intensity small high voltage broad peak is also noticed in the oxidation process only at around 4.41 V depicting the presence of Mn^{4+} state in the investigated materials. The absence of the peak at around 4.41 V in the reintercalation process suggests to the inactive nature of manganese present. It should be emphasized here that these high voltage peaks in pristine $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ in the present case is detectable and is similar to the observations of Kang et al. [9]. However, we find that the major hexagonal peak is centered at a lower voltage (~ 3.95 V) as compared to 4.03 V in the case of Kang et al. [9] but is similar in position to Lu et al. [7]. Further, the high voltage peak is clearly detectable in the present case as compared to Kang et al. [9] and could be ascribed to the smaller particle size. Such an observation has already been observed in the case of LiCoO_2 wherein the high voltage peaks are very prominent with decrease in particle size as reported by Uchida et al. [16] on their study of thin films and also in the case of sol–gel [17] synthesized LiCoO_2 . Our results of CV of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ are in agreement with Lu et al [7] and Kang et al. [9].

Fig. 6a and b depicts the capacities of the synthesized pristine $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ investigated in the voltage ranges

2.8–4.3 V and 3–4.6 V for 15 and 20 cycles, respectively. As can be seen from Fig. 6a that the capacities are in the range of 125 mAh/g over the 15 investigated cycles and showing negligible capacity loss on cycling at a current rate of 0.1 mA/cm^2 in the voltage range of 2.8–4.3 V. Interestingly, the obtained capacities are in good agreement with the literature reports [8,9,18], i.e., 130 mAh/g for the material in spite of being synthesized at a lower temperature. The very low irreversible capacity of 3 mAh/g confirms the purity of our sample and from second cycle onwards there is hardly any difference in the charge and discharge capacities. The loss of capacity (3 mAh/g) in the first cycle can be assigned to the formation stage. Furthermore, as observed in XRD patterns, the well-defined doublets of 006,102 as well as that of 108 and 110 coupled with the lattice parameters 'a' and 'c' are agreeable to $R\text{-}3m$ structure thereby endorsing the high electrochemical performance of the synthesized material. Having encouraged by the cycling in this voltage range and with excellent results as compared to literature reports, we decided to deep discharge the material up to 4.6 V at 0.1 mA/cm^2 . It is seen from Fig. 6b that a capacity of $\sim 160 \text{ mAh/g}$ is obtained in the first cycle which could be ascribed to the high cut off voltage, i.e., 4.6 V but however slowly fades and becomes almost stable after fifth cycle. The capacities are in the range of 125 mAh/g over the 20 investigated cycles with negligible capacity loss on cycling at a current rate of 0.1 mA/cm^2 in the voltage range of 3–4.6 V from the fifth cycle. A comparison of the present results with the literature shows good agreement [8,9,18], i.e., $\sim 120\text{--}130 \text{ mAh/g}$ for the synthesized material in spite of being synthesized at a lower temperature. Finally, the voltage profiles of initial 10 charge–discharge cycles are presented in Fig. 7 and indicate a two step process in the first charge with a shoulder around 4.4 V for Mn^{4+} . However, this shoulder is

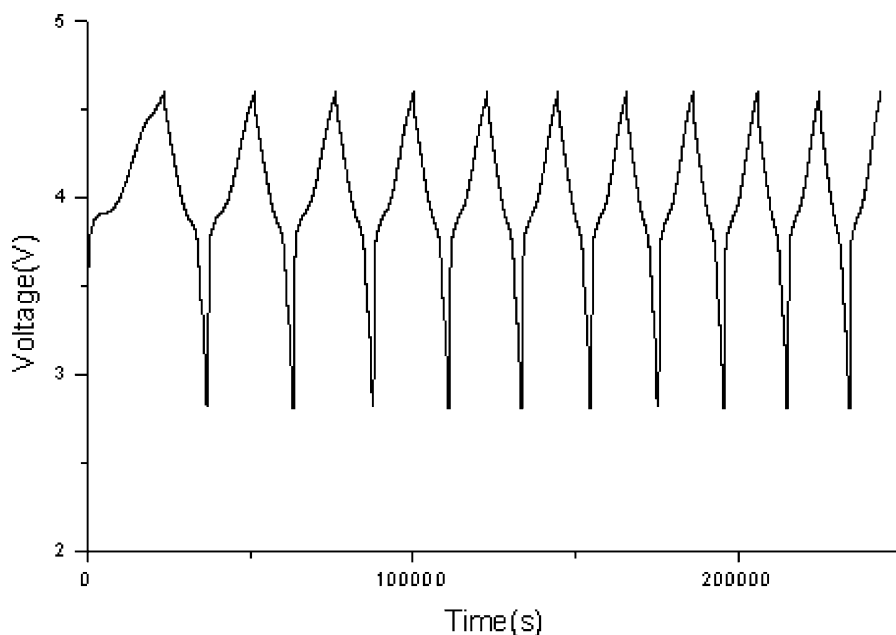


Fig. 7. Voltage profiles of charge–discharge cycles (first 10 cycles) of the synthesized $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$.

not observed from the first discharge onwards thereby suggesting the single step electrochemical nickel oxidation and reduction in the deintercalation and intercalation processes, respectively. We can therefore say that the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ material synthesized by this novel technique can be cycled up to 4.6 V with good capacity retention.

4. Conclusion

We have demonstrated a new route for synthesizing $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ at a lower temperature (850 °C) involving sol–gel combustion technique. XRD analysis confirms to a layered structure. XPS and CV studies suggest that Ni and Mn are present in +2 and +4 oxidation states, respectively. The synthesized material exhibits good cycleability in the voltage range 2.8–4.6 V with good capacity retention of ~125 mAh/g.

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