

Short communication

Synthesis by molten salt and cathodic properties of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$

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Abstract

The mixed oxide, $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$, with the layer structure has been prepared by a one-pot method using the molten-salt mixture, $\text{LiNO}_3\text{--LiCl}$ at temperatures 750, 850 and 950 °C in air. The compounds were characterized by a variety of techniques. As per Rietveld data, only 4.0 and 2.5% of ‘cation-mixing’ was observed in the compounds prepared at 850 and 950 °C, respectively. Cyclic voltammetry with Li metal as counter electrode showed a clear indication of $\text{Ni}^{2+/4+}$ redox couple at $\sim 3.6\text{--}3.9$ V in all compounds. Charge–discharge cycling was carried out in the range 2.5–4.3, 2.5–4.4 and 2.5–4.5 V versus Li at a current rate of 20 or 30 mA g^{-1} . The fifth cycle discharge capacities varied from 125 to 145 (± 5) mA h g^{-1} for the compounds prepared at 850 and 950 °C. They exhibited excellent capacity-retention without noticeable capacity-fade till 50 cycles irrespective of the voltage cut-off.

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1. Introduction

The mixed oxide $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$, has been extensively studied as an alternative 4 V-cathode material to replace LiCoO_2 for rechargeable lithium ion batteries (LIB) [1–14]. The electrochemical performance of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ depends on various factors, like the preparation conditions, e.g., temperature and time of heating, starting raw materials as well as their morphology (mixed hydroxides, carbonates, nitrates with or without glycine) and voltage range and current rate of cycling. Various methods have been employed on optimizing morphology, structure and electrochemical performance of this compound. It was realized that atomic scale-mixing of Ni, Co and Mn ions in the starting materials is necessary to obtain the precursors, preferably as spherical particles which are then mixed with LiOH/LiNO_3 followed by heat-treatment at $T \geq 750$ °C.

Recently, molten salt synthesis has been proven to be simple one-pot method to obtain homogenous single phases of LiCoO_2 and other cathode materials [15–17]. Presently, we report the synthesis of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ at various temperatures by using the molten salt of eutectic, $0.88\text{LiNO}_3\text{--}0.12\text{LiCl}$ and its cathodic performance at ambient temperature.

2. Experimental

The compound was prepared at temperatures of 750–950 °C using high purity $\text{LiNO}_3\text{--LiCl}$ (Alfar Aesar or Merck) salts in the mole ratio 0.88:0.12 (eutectic mixture) and Ni- and Co-nitrate hexahydrates and Mn-nitrate tetrahydrate (Merck). The mole ratio of eutectic and transition metal nitrates was fixed at 4:1. After proper mixing, the reactants were placed in a recrystallized high density alumina crucible and heated to desired temperature (750, 850 or 950 °C) in air in a box furnace (Carbolite, UK) at a heating rate of 3 °C min^{-1} , soaked for 8 h and then cooled to ambient temperature ($RT = 25$ °C). The products were washed with distilled water several times, filtered and the powder dried in air oven at 150 °C for 24 h. Batches of ~ 5 g were thus prepared.

The powder X-ray diffraction (XRD) patterns were taken using Bruker axis D8 diffractometer with $\text{Cu K}\alpha$ radiation. Rietveld refinement of XRD data was carried out using TOPAS-R (Version 2.1) software. The scanning electron microscope (SEM) (JEOL JSM-67500F), Micromeritics Tristar 3000, USA, and AccuPyc 1330 pycnometer (Micromeritics, USA) were used to study the morphology, Brunauer, Emmett and Teller (BET) surface area and density, respectively, of the compounds. Composite cathodes were fabricated with the active material, super P carbon black and binder (Kynar 2801) in the 80:12:8 (w/w/w) by using *N*-methyl pyrrolidone (NMP) as solvent and an etched aluminum foil as current collector. Lithium metal foil (Kyokuto Metal Co., Japan), 1 M LiPF_6 in

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ethylene carbonate (EC) + diethyl carbonate (DEC) (1:1, v/v) (Merck) and Celgard 2502 membrane were used as counter electrode, electrolyte and separator, respectively, to assemble coin-type cells (size 2016) in Ar-filled glove-box (MBraun, Germany). Details of cell fabrication have been described elsewhere [17]. The cells were aged for 24 h before measurement. Cyclic voltammetry and charge–discharge cycling at a constant current were carried out at RT by using computer controlled Mac-pile II system (Bio-logic, France) and Bitrode multiple battery tester (Model SCN, Bitrode, USA), respectively. Differential scanning calorimetry (DSC) was carried out using DSC 204 HP (Netzsch, USA) instrument, with a heating rate of $5^{\circ}\text{C min}^{-1}$.

3. Results and discussion

3.1. Structural aspects

The compound, $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$, was prepared at 750, 850 and 950°C (here after LNCMO-750, LNCMO-850 and LNCMO-950) using the eutectic salt mixture, $0.88\text{LiNO}_3\text{--}0.12\text{LiCl}$ (melting point, 280°C). The metal-nitrates decompose to the respective oxides during heat-treatment and then react with the Li ions from the eutectic to form LNCMO. The LiNO_3 and LiCl act as oxidizing and ‘mineralizing’ agents, respectively, and ensure the formation of Mn^{4+} and Co^{3+} ions and a well-crystalline product. The large concentration of Li ions in the melt aid in suppressing, to a large extent, ‘cation-mixing’ in LNCMO leading to better electrochemical performance. Cation-mixing refers to anti-site disorder wherein Li and Ni ions exchange sites in the respective layers in the lattice. Beneficial effect of addition of excess LiOH during ceramic synthesis on the cathodic performance of LNCMO has been recently shown [6,10]. We have not yet optimized the synthesis conditions of LNCMO by varying the salt:metal mole ratio nor the soaking time. These factors are known to control the morphology as well as crystallinity of cathode materials prepared by the molten salt method [15–17].

The LNCMO are crystalline black powders and all the peaks in the XRD patterns could be indexed on the basis of layer structure. The Rietveld refinement of the XRD data was carried out assuming the space group $R\bar{3}m$ with $\alpha\text{-NaFeO}_2$ -type structure

Table 1

Crystal parameters of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (LNCMO) synthesized at various temperatures and of LNCMO-850 in the charged-state (first-cycle)

Compound	a (Å)	c (Å)	c/a
LNCMO-750 R (I_{003}/I_{104}) = 1.8	2.8418 (4)	14.2038 (5)	5.0
LNCMO-850 R (I_{003}/I_{104}) = 1.6	2.8467 (4)	14.1967 (5)	4.99
LNCMO-950 R (I_{003}/I_{104}) = 3.4	2.8465 (4)	14.1654 (5)	4.98
LNCMO-850; virgin electrode	2.851 (5)	14.16 (2)	4.96
Charged to 3.9 V	2.827 (5)	14.26 (2)	5.04
4.1 V	2.831 (5)	14.38 (2)	5.08
4.3 V	2.832 (5)	14.45 (2)	5.10
4.4 V	2.828 (5)	14.49 (2)	5.12
4.5 V	2.824 (5)	14.42 (2)	5.10
Discharged to 2.5 V	2.845 (5)	14.20 (2)	4.99

with Li at the 3b site (0, 0, $\frac{1}{2}$), transition metal ions at 3a site (0, 0, 0) and O at the 6c site (0, 0, 0.25). The lattice parameters are given in Table 1 and XRD pattern of LNCMO-850 is shown in Fig. 1. The R-Bragg, Rwp and GOF are in the range 0.9–2.8, 2.0–3.0 and 0.7–3.0, respectively, for the LNCMO-750, LNCMO-850 and LNCMO-950. The hexagonal c lattice parameters of the molten salt synthesized LNCMO are slightly smaller compared to those reported in the literature $c \cong 14.24 \text{ \AA}$ [5–14]. This might be due to smaller cation-mixing and better ordering of the transition metal ions in the metal-layer with increasing synthesis temperature (Table 1). Indeed, the Rietveld refinement of data on LNCMO-750 showed $\sim 6.5\%$ cation-mixing (Ni ions in Li-layer at the 3b site and vice versa) and only 4.0 and 2.5% in case of LNCMO-850 and LNCMO-950, respectively. The relative intensity ratio (R) of XRD peaks I_{003}/I_{104} is ≥ 1.5 for our LNCMO and well-defined splitting of the lines due to (006, 102) and (108, 110) in the XRD pattern (2θ ranges $37\text{--}40^{\circ}$ and $64\text{--}67^{\circ}$, respectively, in Fig. 1) are indication of well-ordered layer structure. The measured density of LNCMO-850 is $4.461(\pm 0.003) \text{ g cm}^{-3}$ and compares well with the calculated X-ray density of 4.823 g cm^{-3} . The SEM photographs showed agglomerations of submicron particles with platelet morphology in the case of LNCMO-750, whereas the particle sizes are in the range of $2\text{--}8 \mu\text{m}$ for LNCMO-850 and LNCMO-950 (Fig. 2). The measured BET surface area of LNCMO-850 is $4.2(\pm 0.2) \text{ m}^2 \text{ g}^{-1}$.

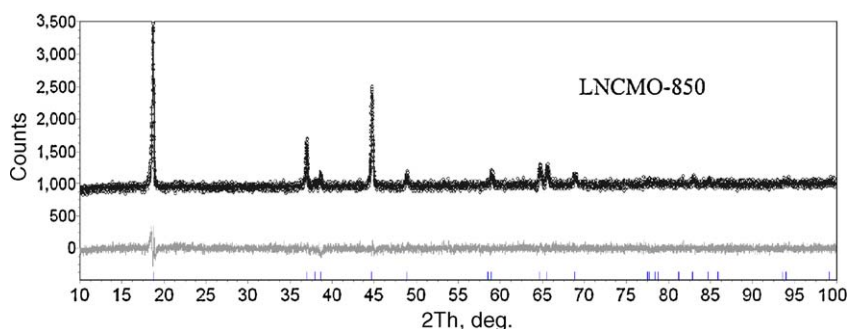


Fig. 1. Observed (circles) and calculated (lines) X-ray diffraction pattern of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ prepared at 850°C (LNCMO-850). Rietveld fitted difference pattern is also shown. Vertical bars represent the positions of allowed hkl reflections.

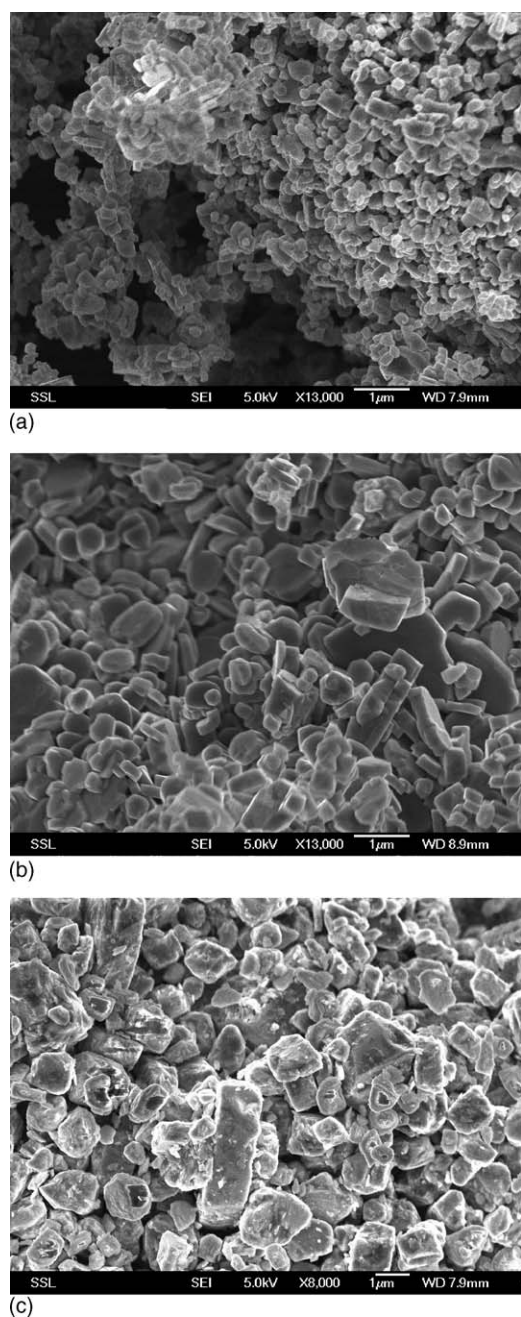


Fig. 2. SEM photographs of LNCMO powders prepared at: (a) 750 °C, (b) 850 °C and (c) 950 °C.

3.2. Electrochemical properties

3.2.1. Cyclic voltammetry

Cyclic voltammograms (CV) of LNCMO as cathodes were recorded with Li metal as the counter and reference electrode in the range 2.5–4.5 V at RT at the scan rate 0.058 mV s⁻¹ up to 25 cycles and are shown in Fig. 3(a–c). Selected cycles are shown for clarity. All the compounds show the first cycle anodic peak at 3.9–4.1 V (versus Li) whereas the corresponding cathodic peak is at 3.5–3.7 V. In the second cycle, the anodic peak shifts to a lower voltage (~0.1–0.25 V), but the corresponding cathodic peak shifts only by ~0.02 V, to a higher voltage.

The shift in the peak voltages is an indication of the ‘formation’ of the electrode in the first cycle, whereby the active material makes good electrical contact with the conducting carbon particles in the composite electrode, the current-collector and the liquid electrolyte. The shifts in the main peak voltages is complete by fifth cycle. The hysteresis (ΔV = the difference between the 8th or 12th anodic and cathodic peak voltages) is in the range 0.11–0.24 V in all cases indicating good reversibility. Fig. 3d shows the CV in the range 2.5–4.7 V at the 26th cycle which is a continuation of Fig. 3b to a higher cut-off voltage. Indication of a minor anodic peak at ~4.5–4.6 V and corresponding cathodic peak at ~4.4–4.5 V are seen but it is not clear whether these represent a reversible phase transition. Similar behaviour of CV of LNCMO have been reported in literature [1,7,9,11]. The major anodic/cathodic peaks just below 3.9 V are assigned to the Ni^{2+/3+/4+} redox couple [1–6].

3.2.2. Galvanostatic cycling and thermal stability

Charge–discharge cycling of the cells containing LNCMO as cathodes was carried out up to 50 or 90 cycles at RT at a current density of 20 or 30 mA g⁻¹ in the voltage ranges 2.5–4.3, 2.5–4.4 and 2.5–4.5 V versus Li. The voltage versus capacity profiles of selected cycles for the LNCMO-850 in the 2.5–4.4 V range are shown in Fig. 4a. During the first-charge (Li-deintercalation) process, the voltage suddenly increased to ~3.75 V from the open circuit voltage (OCV = 3.0 V) followed by a small plateau till about 10–15 mA h g⁻¹ and then gradually increased to the cut-off voltage value. The discharge curve did not show any plateau region. During the subsequent charge cycles, the initial voltage shifted to ~3.65 V without any noticeable plateau indicating that the ‘formation’ of the electrode is complete (Fig. 4a). The discharge capacity versus cycle number plots are shown in Fig. 4b. There was an irreversible capacity loss (ICL) between the first-charge and first-discharge reaction, ranging from 30–75 mA h g⁻¹ for all LNCMO compounds depending on the upper cut-off voltage and synthesis temperature. However, the Coulombic efficiency (difference between the charge and discharge capacity for a given cycle) increased to >97% after 4–8 cycles. As expected, the fifth cycle reversible capacities increased with the upper cut-off voltage: 4.3 V, 115; 4.4 V, 135; 4.5 V, 145 (±5) mA h g⁻¹ at 30 mA g⁻¹ with LNCMO-850 and LNCMO-950 exhibiting consistently higher values. The capacity values for the latter two compounds remained stable up to 50 cycles, showing excellent capacity-retention without noticeable capacity-fade (Fig. 4b). Cycling of LNCMO-850 was continued up to 90 cycles (4.4 V cut-off; 20 mA g⁻¹; 0.14 C rate) and it showed slight capacity-fading after 60 cycles. The presently observed capacity values upto 4.5 V cut-off are slightly smaller than those reported on some of the optimized LNCMO prepared by the ceramic precursor techniques but the cycling performance is better [1,5–7,11].

Ex situ XRD patterns of LNCMO-850 in the charged-state (cut-off voltage 4.3–4.5 V) and in the discharged-state (2.5 V) during the first cycle have been recorded after dismantling several duplicate cells and recovering the composite electrodes (along with the Al-foil) in the glove-box. The patterns were indexed and the lattice parameters calculated by the least square

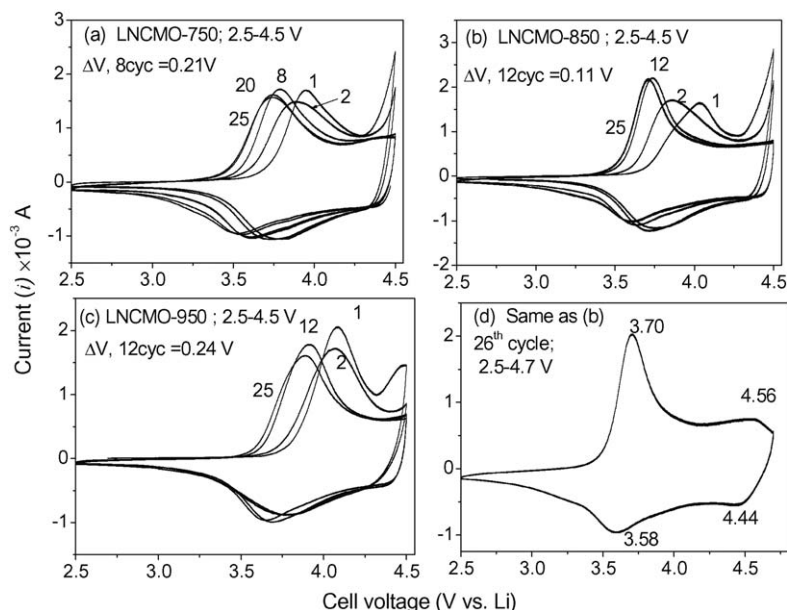


Fig. 3. Cyclic voltammograms of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (LNCMO) prepared at various temperatures: (a) LNCMO-750, (b) LNCMO-850, (c) LNCMO-950 and (d) same as (b) for the 26th cycle in the range 2.5–4.7 V. Scan rate is 0.058 mV s^{-1} , between 2.5 and 4.5 (4.7) V vs. Li at ambient temperature. The numbers refer to the cycle numbers in (a–c) and to voltages in (d).

fitting. Data are given in Table 1. The a and c parameters of the cycled electrode after the first cycle agree with those of the original compound. In the charged-state, as can be expected [6,8,9] the a parameter decreased, c and c/a increased depending on the cut-off voltage, in the range 3.9–4.4 V. This is due to the electrostatic repulsion of the oxide ion layers caused by the removal of Li ions from the Li-layer and formation of the $\text{Ni}^{3+/4+}$ ions in

the (NiCoMn)-layer having a smaller ionic radius than that of Ni^{2+} ion. Thermal stability of LNCMO-850 in the charged-state (4.3 V cut-off) after dismantling the electrode in the glove-box has been studied by DSC. It showed the characteristic decomposition temperature (T_d) at $305(\pm 3)^\circ\text{C}$. This value compares well with the reported results on LNCMO charged to 4.1–4.6 V [14,18].

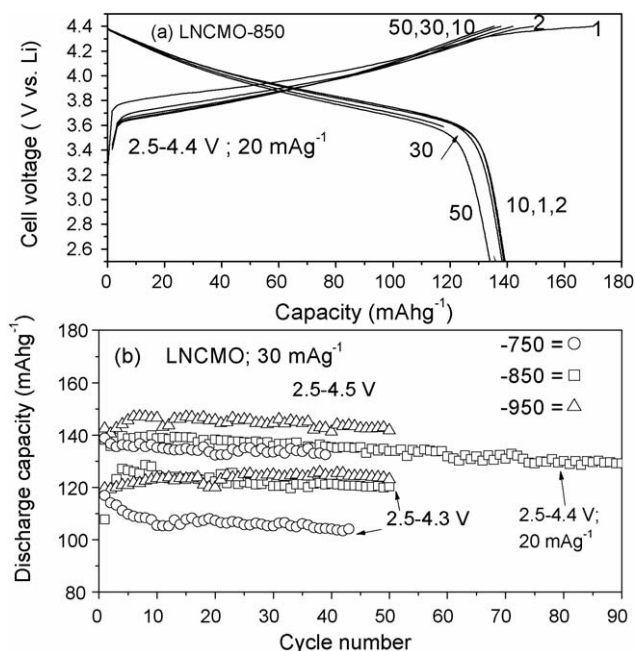


Fig. 4. (a) Voltage vs. capacity profiles of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ prepared at 850°C (LNCMO-850). Voltage range 2.5–4.4 V vs. Li-metal at the specific current 20 mA g^{-1} . The numbers refer to cycle numbers. (b) Discharge capacity vs. cycle number of LNCMO-750, LNCMO-850 and LNCMO-950 at the specific current of 20 or 30 mA g^{-1} . Voltage ranges are indicated.

4. Conclusions

Layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (LNCMO) compounds were prepared at various temperatures (750 , 850 and 950°C) by one-pot method using the molten-salt ($\text{LiNO}_3\text{--LiCl}$) in air. The compounds were characterized by X-ray diffraction, Rietveld refinement, SEM, surface area and density techniques. Cyclic voltammetry results show a clear indication of $\text{Ni}^{2+/4+}$ redox couple at $\sim 3.6\text{--}3.9 \text{ V}$. Charge–discharge cycling tests carried out in the range 2.5–4.3, 2.5–4.4 and 2.5–4.5 V versus Li at a current rate of 30 or 20 mA g^{-1} showed that LNCMO-850 and LNCMO-950 perform well with a fifth cycle reversible capacity of $125\text{--}145 (\pm 5) \text{ mA h g}^{-1}$ and without any noticeable capacity-fade up to 50 cycles.

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