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Introduction

The upcoming new era of automobile-electric vehicle (EV), hybrid electric vehicle (HEV) and plug-in hybrid electric vehicle (PHEV), demands a rapid development of battery technology to meet their high energy density and high power density requirements.¹⁻³ Among all the types of batteries, the lithium ion battery is one of the most likely candidates to fulfil the high energy demands because of its several advantages such as high voltage, large specific capacity and excellent cycling performance.4-6 However, because of its intrinsic low ionic conductivity of organic electrolytes, compared with its aqueous counterparts, its power capability is sluggish. To improve its power performance, many efforts have been made, e.g. to reduce the particle size of electrode materials to the nanometer scale.⁷⁻¹³ Physically, the smaller the particle size is and the shorter the lithium ion diffusion distance and the electron transfer distance are, the better the rate capability is. On the other hand, the employment of nanomaterials in cell manufacture has some disadvantages, such as high viscosity of slurry and low solid percentage, both of which lead to low active materials coated and low energy density. To achieve both



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Porous LiNi_{0.5}Mn_{1.5}O₄ sphere as 5 V cathode material for lithium ion batteries†

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A new type of microsized porous spherical LiNi_{0.5}Mn_{1.5}O₄ (LNMO-Air) cathode material for a lithium ion secondary battery has been synthesized by an impregnation method using highly reactive nanocupule MnO₂ spheres as the manganese source. These LNMO-Air spheres are aggregates of nanosized polyhedron particles with well-defined cubic spinel structure. They showed excellent rate capability and cycle stability, compared with other microspheres of LNMO. We also investigated the effect of the trace amounts of Mn³⁺ in the crystal structure on its specific capacity and cycle stability. Compared with the sample (LNMO-O₂) calcined in an oxygen atmosphere, which is considered to be Mn³⁺ free, LNMO-Air exhibits superior specific capacity, cycling ability and rate capability. Because of the presence of trace amounts of Mn³⁺, the LNMO-Air sample presents a discharge specific capacity of 108 mA h g⁻¹ at 5 C rate at 55 °C after 80 cycles without significant reduction. These improvements can be explained by better ion conductivity as the metal oxide layer spacing is enlarged to facilitate faster ion transfer and significantly improved electrical conductivity; both are attributed to the presence of Mn³⁺.

excellent rate capability and high energy density, it is desired that the micrometer particles are composed of aggregated nanosized particles. In electrode processing, this kind of particle also leads to high loading and can better accommodate the volume change and can reduce electrode tension upon cycling.¹⁴

Because of its low cost, low toxicity and good safety performance,¹⁵ spinel LiMn₂O₄ is considered to be an ideal cathode material for lithium ion batteries. Moreover, by doping the spinel LiMn₂O₄ materials with a certain amount of transition metal elements M (M = Fe, Co, Ni, Cr, *etc.*), the Fermi energies of the materials can be adjusted and their electrode potentials can be increased as desired.16,17 Among the doped spinel cathode materials, LiNi_{0.5}Mn_{1.5}O₄ (LNMO) has been shown to have an acceptable performance and stable discharge capacity.¹⁶ This cathode shows a large charge-discharge platform at 4.7 V and a small platform around 4 V.18 The platform around 4.7 V is assigned to the oxidation-reduction process of Ni^{2+}/Ni^{4+} , whereas the 4.0 V platform is attributed to the Mn^{3+}/Ni^{4+} Mn⁴⁺ oxidation-reduction process. In real practice, the stoichiometry of LNMO is not perfect because when it is sintered above 600 °C to obtain good crystallinity, side reactions of generating oxygen voids and more Mn³⁺ cation is unavoidable:

$$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \rightleftharpoons \text{aLi}_x\text{Ni}_{1-x}\text{O(NiO)} + \\ \text{LiNi}_{0.5-\nu}\text{Mn}_{1.5+\nu}\text{O}_4 + \text{cO}_2$$
(1)

However, the effects of more Mn^{3+} in the LNMO cathode are controversial. Some believe that the presence of Mn^{3+} is helpful to stabilize the cycling performance and to improve the

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stability.¹⁹ The Mn^{3+} induces more Ni and Mn disordering with a higher proportion of Fd3m lattice, which thus improves Li ion transport coefficiency and the electrical conductivity of LNMO. Others argue that Mn^{3+} ions have a higher tendency to disproportionate:²⁰

$$Mn^{3+} \rightleftharpoons Mn^{2+} + Mn^{4+}$$
 (2)

The Mn²⁺ ion can easily dissolve in electrolyte and is capable of electrochemically depositing at the anode surface after passing through a membrane;²¹ therefore it brings an adverse influence for the cycling performance.

In our present work, we synthesized microsized spherical LNMO (LNMO-Air) comprised aggregated nanopolyhedrons by an impregnation method and investigated its electrochemical properties as cathode materials. In our two-step synthesis, we first prepared nanometer chestnut-cupule-like MnO_2 spheres and then impregnated them with an ethanol solution of LiNO₃ and Ni(NO₃)₂·6H₂O, followed by solvent evaporation and high temperature calcination. The uniquely structured LNMO^{20,21} exhibits better rate capacity and cycle performance compared with the LNMO materials synthesized by using commercial MnO_2 as the original material in impregnation and ball-milling methods. We also prepared LNMO-O₂ in an oxygen gas atmosphere with similar morphology but fewer oxygen voids to explore the influence of Mn^{3+} to its electrochemical performance.

Experimental section

Material preparation

The nanoscale chestnut-cupule-like MnO₂ spheres (MnO₂-S) were prepared by a modified solvothermal method.²² An aqueous solution of 20 mmol MnSO4 was mixed with 8 mL concentrated sulfuric acid, and then K2S2O8 solution was quickly poured into the solution under rapid stirring. The solution was kept in a water bath at 65 °C undisturbed for 18 h. After filtration and washing with deionized water and ethanol, the product was dried in an oven at 100 °C. To synthesize LNMO-Air, 24 mmol of MnO₂-S, 8 mmol of Ni(NO₃)₂·6H₂O, and 17.28 mmol of LiNO3 was dispersed into 20 ml ethanol. After being ground in a mortar for 30 min, the solution was evaporated slowly at 80 °C under constant stirring. Finally, the obtained mixture was sintered in air at 800 °C for 20 h, and then slowly cooled to room temperature. The LNMO-O2 sample was prepared in the exact same manner except that the final calcination was carried out in O2 atmosphere. A similar procedure was employed to synthesize LiNi_{0.5}Mn_{1.5}O₄ (LNMO-C) using commercially available MnO₂ as the manganese source. The commonly used ball-milling method (FRITSCH-Pulverisette 14) was also tested to prepare LiNi_{0.5}Mn_{1.5}O₄ (LNMO-B) from a mixture of Li₂CO₃, NiO and MnO₂ in stoichiometric amounts. The mixture of the solids was milled for 2 h at 200 rpm and treated at 800 °C for 20 h in air.

Material characterization

The XRD patterns were collected on a Rigaku miniflex 600 instrument equipped with Cu K α radiation operated at 40 kV

and 15 mA from 10° to 80° at 5° min⁻¹ with a recording interval of 0.02° , while in XRD refinement, the scanning speed is 1° min⁻¹. Field emission scanning electron microscopy (SEM, HITACHI S-4800) was used to characterize the morphologies of the samples, and energy dispersive X-ray spectroscopy (EDS, OXFORD 7426) was carried out to analyze the element composition on particle surface with 20 kV acceleration voltage. Nitrogen adsorption and desorption data was collected on a Tristar 3000 system. The specific surface area analysis was calculated using multipoint BET (Brunauer-Emmett-Teller) method, whereas the pore volume was performed by the BJH (Barrett-Joyner-Halenda) model. Fourier-transform infrared spectra (FTIR) were determined with a Nicolet 330 infrared spectrometer in transmittance mode (KBr pellet) over the range of 400–1000 cm⁻¹. Raman spectra (JOBIN Yvon Horiba Raman Spectrometer model HR800) were collected with a 10 mW helium/neon laser at 632.8 nm excitation.

Electrochemical measurements

Electrochemical performances of these materials were evaluated in CR2016-type coin-cell configuration. The cathode electrode film was obtained by spreading a slurry (70 wt% active material, 20 wt% acetyleneblack and 10 wt% polyvinylidene difluoride [PVDF] binder were dispersed in *N*-methyl pyrrolidione [NMP] solvent) onto an aluminum foil using a doctor blade. After drying in a vacuum oven at 100 °C overnight, the electrode was punched out and roll pressed. The coin cells were assembled by sandwiching a porous polyethylene separator between the electrode and Li metal foil in an Ar-filled glove box. The electrolyte used was 1 mol L^{-1} LiPF₆ salt dissolved in a mixed solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a weight ratio of 1 : 1 (#301 electrolyte, Guotai-Huarong New Chemical Materials Co., China).

The cells were galvanostatically charged and discharged on a battery test system (LAND CT-2001A instrument, Wuhan, China, or NEWARE BTS type battery charger, Shenzhen, China) between 3.5-4.9 V at room temperature. When the rates were higher than 1 C (including 1 C), to overcome the polarization of the battery at high rates, a two-step charge process (constant current and constant voltage charge) was employed.²³ Cyclic voltammogram (CV) measurements were performed on a CHI 660D potentiostat at a scan rate of 0.1 mV s⁻¹ with voltage ranging from 3.4 to 5.0 V. Electrochemical impedance spectra (EIS) were carried out on Solartron SI 1287 electrochemical workstation with frequencies from 0.1 Hz to 100 kHz. All the tests were conducted at 25 °C except the high-temperature tests specified. The mass loading for all the cells was controlled at about 3 mg cm⁻².

Results and discussion

Fig. 1 shows the SEM images of precursor compounds before impregnation reactions. Fig. 1(a) and (c) are the SEM images of the synthesized MnO₂-S spheres and commercial MnO₂, respectively. The high-magnification SEM image of a synthesized MnO₂-S sphere is presented in Fig. 1(b). The microstructures of these two materials are quite different. MnO₂-S spheres



Fig. 1 SEM images of the precursors (a) MnO_2 -S spheres, (b) magnified image of a single MnO_2 -S sphere, (c) commercial MnO_2 particles, (d) commercial NiO.

are quite uniform in a size ranging from 2 μ m to 4 μ m. Each of these MnO₂-S spheres is composed of several MnO₂ nanoneedles radiating from its center, rendering the entire structure look like a chestnut cupule. The nanoneedles are well separated, generating a large space between adjacent nanorods, resulting in a significantly larger surface area (shown below). The commercial MnO₂ particles are an aggregation of small granules with a low surface area. As shown in Fig. 1(d), commercial NiO particles are nanoparticles of hundreds of nanometers in diameter randomly stacked together.

The N₂ adsorption–desorption analysis of chestnut-cupulelike MnO₂-S spheres and the commercial MnO₂ are shown in Fig. 2. The BET total surface area and pore volume of the chestnut-like MnO₂-S are 67 m² g⁻¹ and 0.116 cm³ g⁻¹, respectively, which are considerably larger that of the commercial MnO₂, which are only 1.3 m² g⁻¹ and 0.002 cm³ g⁻¹, respectively. The MnO₂-S material exhibits an absorption– desorption hysteresis, whereas the commercial MnO₂ material shows essentially a flat line. These features of the MnO₂-S larger



Fig. 2 Nitrogen adsorption–desorption isotherms of porous MnO_2 -S and commercial MnO_2 .

surface area, bigger pore volume, and smaller nanostructures make it a better candidate for the impregnation process to form a more homogeneous material; therefore, the metal ions are more uniformly distributed in the structure.

The SEM images of the morphologies and microstructures of the three synthesized LNMO materials are shown in Fig. 3. The low-magnification SEM image (Fig. 3(a)) indicates that the LNMO-Air spheres are uniformly micron-sized spheres with the diameters of 2-4 µm, which are similar to its MnO₂-S precursor. Under high-magnification (Fig. 3(b) and (c)), it can be seen that these microspheres are made up of nanopolyhedrons with welldefined edges and planes, and these polyhedrons are fused together by vertex and/or plane. The LNMO-C (Fig. 3(d)), however, is constituted of diversely micron-sized particles with agglomeration to some extent. More details are shown in Fig. S1.[†] The LNMO-B (Fig. 3(e)) is large granular aggregate with some unreacted NiO nanoparticles (Fig. S2[†]) resulting in the inhomogeneous distribution of metal ions. Results obtained from nitrogen adsorption and desorption curves are shown in Table S1 in ESI.[†] For the samples, LNMO-Air, LNMO-C and LNMO-B, their average surface area calculated using the multipoint BET (Brunauer-Emmett-Teller) method are 4.6, 3.7 and 1.4 m² g⁻¹, the average pore radius obtained by use of BET model are 1.03, 0.26, and 0.19 nm, and the average pore volume observed by the BJH method are 0.025, 0.0082 and 0.0024 cm³ g^{-1} , respectively. It can be found that LNMO-Air is bigger than the other samples in the average surface area, pore radius and average pore volume, which is consistent with their structure of the precursors and SEM results.



Fig. 3 SEM images of (a) spherical LNMO-Air, (b) highly magnified image of a single LNMO-Air, (c) highly magnified image of a single LNMO-Air sphere surface, (d) LNMO-C, (e and f) LNMO-B.

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The TEM characterization of the LNMO-Air is displayed in Fig. 4. As shown in Fig. 4(a), the LNMO-Air hollow, which is consistent with the BET results. SAED pattern (Fig. 4(a) inset) of the entire micron-sized LNMO-Air sphere at the bottom of Fig. 4(a) shows unordered diffraction spots, implying the polycrystalline structure of the entire LNMO-Air sphere. After complete grinding, a single nano-sized polyhedron as shown in Fig. 4(b) is obtained from the micron-sized LNMO-Air sphere. SAED pattern (Fig. 4(c)) with the electron beam in the [110] direction corresponding to Fig. 4(b) presents a well-organized array of diffraction spots that index a typical spinel lattice structure. This implies that the polycrystalline LNMO-Air micron-sized sphere is composed of monocrystalline nanosized polyhedrons. A high-resolution TEM (HRTEM) image of the nano-sized polyhedron of Fig. 4(b) appears as clear lattice fringes (Fig. 4(d)). The interplanar spacing lattice is 0.48 nm, which is in accordance with the *d*-spacing of the (111) crystal planes of the LiNi_{0.5}Mn_{1.5}O₄. The ordered lattices in long-range order result in the intercalation and deintercalation of the Li ion easily occurring, which is favourable for the rate property.

The LNMO structures are further proved by XRD patterns, as shown in Fig. 5. In Fig. 5, the XRD patterns of three samples are plotted. From these patterns, all three can be indexed to cubic spinel structure (JCPDS card no.: 80-2162) with impurity (peaks of $2\theta = 37.335^\circ$, 43.381° and 63.024° (ref. 24)), which is indexed as rock salt phase (Li_xNi_{1-x}O/NiO). However, the relative diffraction intensities of the rock salt phase in LNMO-C and LNMO-B are considerably stronger than that of LNMO-Air. The presence of less rock salt phase impurity in LNMO-Air is attributed to the more porous structure and smaller particle size of the MnO₂-S precursor. The more open structure renders

b

50nm

0.485666

d

Fig. 4 TEM images of (a) the as-prepared LNMO-Air and (b) a nanosized polyhedron obtained from LNMO-Air sphere by fully grinding. (c) SAED pattern in the [110] zone of the nano-sized polyhedron corresponding to (b); (d) HRTEM image of the nano-sized polyhedron.

2um

[110]

10 1/nm

С



Fig. 5 XRD patterns of spherical LNMO-Air, LNMO-C and LNMO-B.

better impregnation, and the smaller particle size facilitates kinetically more homogeneous ion ordering.

Fig. 6 presents the charge-discharge profiles of the samples at a rate of 0.5 C (74 mA g^{-1}) between 3.5 and 4.9 V at 25 °C. All three samples show very slow specific discharge capacity decay (Fig. 5(a)), and their specific discharge capacities are very different. For example, in the fifth cycle, the LNMO-Air shows the highest specific discharge capacity at 118 mA h g^{-1} , whereas LNMO-C and LNMO-B cathode materials only deliver specific capacities of 76 mA h g^{-1} and 87 mA h g^{-1} , respectively. In addition to the smaller particle size and the better morphology of LNMO-Air, the better ion ordering in LNMO-Air is considered to have a more profound effect on its higher specific discharge capacity. The columbic efficiencies for the sample test were shown as Fig. S3 in ESI.[†] The columbic efficiencies of the initial few cycles is low, especially for the first cycle, which is attributed to the decomposition of #301 electrolyte and catalysis action of Ni and Mn ion in the spinel material. After 10 cycles, its columbic efficiencies are maintained at 98.2%. The decomposition of electrolyte actually occurred but was maintained at an acceptable level after several cycles, which guarantees our cell a long life. In general, the irreversible capacity loss in the first cycle corresponds to the formation of a solid surface layer by the oxidation of the electrolyte.25 The irreversible capacity loss on each cycle is attributable to the oxidation of the electrolyte and the formation of an unstable solid surface film in the following



Fig. 6 Electrochemical properties of the as-prepared samples at 25 °C. (a) Cycle performance at 0.5 C; (b) the 20th discharge curve at 0.5 C.

cycles.²⁵ A cyclic voltammogram experiment of commercial electrolyte was carried out by the use of the coin cell with a blank cathode and lithium film as anode on a CHI 660D potentiostat at a scan rate of 0.1 mV s^{-1} during a voltage range from 3.4 to 5.0 V (Fig. S4 in ESI†). After the first cycle, the oxidation currents became lower, so the decomposition of electrolyte is relieved. The discharge capacity–voltage profile in Fig. 6(b) can shed light on the origin of the difference. All three materials show two flat voltage plateaus; one is around 4.7 V and the other is around 4 V, but the magnitudes are drastically different. LNMO-Air has the largest 4.7 V plateau but the smallest 4.0 V plateau, whereas LNMO-B has the smallest 4.7 V one and, largest 4.0 V one. The 4.7 V plateau corresponds to the reaction:

$$LiNi_{0.5}Mn_{1.5}O_4 + 0.5e^- \rightleftharpoons Li_{0.5}Ni_{0.5}Mn_{1.5}O_4 + 0.5Li,$$
 (3)

$$Li_{0.5}Ni_{0.5}Mn_{1.5}O_4 + 0.5e^- \rightleftharpoons Ni_{0.5}Mn_{1.5}O_4 + 0.5Li,$$
 (4)

However, the plateau around 4.0 V is from the side reaction of Mn^{4+}/Mn^{3+} . The more homogeneous metal ion ordering results in a larger 4.7 V plateau, the more the nonuniform distribution of Ni and Mn, the larger the 4 V is, even though the instability of LNMO at high-temperature calcination makes a small contribution to it. Thus, it is clear that LNMO-Air has the best metal ion ordering among these samples, which indicates that MnO_2 -S is a much better precursor for LNMO material. Cyclic voltammogram curves of these samples are shown in Fig. S5.† The LNMO-Air exhibits two major redox peaks in the region of 4.7–4.9 V and a very small peak at around 4.0 V, whereas for LNMO-C and LNMO-B, two major redox ranges 3.8– 4.4V and 4.5–4.9 V emerge, which are in accordance with the discharge curve (Fig. 6(b)).

Fig. 7 shows the comparison of electrochemical performance of these LNMO at different rates. All the three samples show that their specific capacities at 1.0 C are slightly higher than those at 0.5 C, which is also reported by Zhou²³ and Lazarraga²⁶ without a clear conclusion. This is possibly caused by the



Fig. 7 Rate cycling performance of samples.

different charging process between 0.5 C and 1 C. In our experiment, the cells were galvanostatically charged and discharged on a battery test system between 3.5-4.9 V at room temperature at low rates. When the rates were higher than 1 C (including 1 C), a two-step charge process (constant current and constant voltage charge) was employed to overcome the polarization of the battery at high rates. In the latter case, following the constant current charge step, the constant voltage charge process was carried out till the current decreased to one tenth of its initial constant value. Among these samples, the LNMO-Air not only exhibits the considerably higher capacity than the other two (about 50% more) but also a better rate capability. At a low rate of 0.2 C (29 mA g⁻¹), LNMO-Air delivers a discharge capacity of 123 mA h g^{-1} , which is 83.6% of the theoretical capacity of LNMO (147 mA h g^{-1}). It delivers 86% and 82% of 0.2 C discharge capacity at 5 C (735 mA g^{-1}), and at 10 C (1470 mA g^{-1}), respectively, which are all considerably higher than that of commonly reported submicron LNMO, or nano-LNMO. On the other hand, LNMO-C and LNMO-B can only deliver a discharge capacity of 82 mA h g^{-1} and 86 mA h g^{-1} at 0.2 C, respectively. At 5 C rates, they show specific discharge capacities of 73 mA h g^{-1} and 71 mA h g^{-1} , with comparable retention percentage to LNMO-Air. Once the current is increased to 10 C, the discharge capacity of LNMO-C and LNMO-B is only 59 mA h g^{-1} (72%) and 57 mA h g^{-1} (66%) respectively, both at a much lower retention percentage than LNMO-Air. After 50 cycles with successive charge-discharge rate variation, all the materials can recover to their original specific discharge capacities when chargedischarge rate returns to 0.2 C. The excellent rate capability of the LNMO-Air is due to its unique porous structure.¹⁴ In this particular structure, both micropores between the micro-sized particles and nanopores between the nanoparticles are present, generating a high active surface area for better wetting the electrode by the electrolyte and shortening the Li⁺ ions' diffusion distance. Thus a better rate capability is attained.

The rule of Mn³⁺ in LNMO materials is controversial and still under debate. Ma²⁷ has proposed that the presence of Mn³⁺ is adverse for the reversible Li ion extraction/insertion reaction, especially at a higher cycle rate and high temperature. By the attack of trace amounts of HF, Mn³⁺ ions are known to undergo a disproportionation reaction²⁰ to form Mn^{2+} and Mn^{4+} ions. Mn²⁺ ions are readily dissolved into electrolyte and can be reduced to Mn metal on the anode surface.21 The resulting Mn film prevents Li ion transportation, causing significant capacity decline during the cycling. However, Zhang¹⁸ argued that the presence of Mn³⁺ promoted more disorder among the metal sites that facilitated the Li⁺ transport, especially for the high rate. To further explore the influence of Mn³⁺, we synthesized LNMO materials without Mn³⁺ ions present, by calcining the impregnated MnO₂-S particles in O₂ atmosphere.²⁸ This Mn³⁺ ion free LNMO material is denoted as LNMO-O₂.

To capture the fine-structure difference, XRD refinements on LNMO-Air and LNMO-O₂ with a slow scan speed of 1° min⁻¹ were conducted, and the data are shown in Fig. 8. As expected, both the samples show strong spinel structure peaks at $2\theta = 18.75^{\circ}$, 36.40° , 44.32° and 64.44° , and the peak intensity ratio of NiO at 63.42° and LNMO at 18.95° for LNMO-Air is bigger than





that of LNMO-O₂, suggesting that the NiO content in LNMO-Air is bigger than that in LNMO-O2. It is understood that the electrochemical properties are not necessarily decided by the optimized crystallographic structure; they indeed require an appropriate concentration of oxygen vacancies and Fd3m configuration.²⁹ The lattice parameters, d_{111} and size of subgrain calculated by the Scherrer Equation along the (111) surface are obtained from the least-square refinement based on a cubic structure using PDXL2 software (Rigaku, Japan), and the results are summarized in Table 1. The crystal lattice parameter and interlayer space of (111) lattice plane for the LNMO-Air are 8.1740 Å and 4.7266 Å, and for LNMO-O₂ are 8.1656 Å and 4.7175 Å; both are shorter in LNMO-O₂. This is because calcination in air atmosphere leads to more oxygen vacancies than in O₂ atmosphere. To keep charge neutrality, more Mn³⁺ was thus generated in LNMO-Air. The ionic radius of Mn^{3+} (0.645 Å) is larger than Mn⁴⁺ (0.530 Å). As a result, the crystal lattice parameter and interlayer space of the (111) lattice plane for the LNMO-Air are slightly larger than that of LNMO-O₂.

There are no visible differences in the LNMO-O₂ and LNMO-Air by SEM characterization (Fig. S7†). IR spectroscopy is an effective technique in identifying the subtle difference between $P4_332$ and Fd3m spinels of LNMO.³⁰ The IR spectra of these samples are shown in Fig. 9. The vibration bands at 650 and 428 cm⁻¹, which are present in LNMO-O₂ but absent in LNMO-Air, are indicative of a $P4_332$ crystallographic structure.⁶ On the other hand, the Fd3m crystal lattice exhibits a peak at 587 cm⁻¹.

Table 1 The summary of the as-synthesized samples of lattice parameters for all samples (*a*, *b*, *c*, *a* = *b* = *c*), *d*₁₁₁, size of subgrain calculated by the Scherrer Equation along the (111) surface and the integrated intensity ratios of the (400)/(311)

	Lattice	D ₍₁₁₁₎	Subgrain
	parameter (Å)	(Å)	size (Å)
LNMO-O ₂	8.1656	4.7175	359.22
LNMO-Air	8.1740	4.7266	365.36



Fig. 9 FT-IR spectra of LNMO-Air and LNMO-O₂ samples.

The characteristic of Fd3m crystallographic structure lies in the fact that the band intensity of 622 cm⁻¹ is higher than that of 587 cm⁻¹,³¹ which is clearly seen in LNMO-Air spectrum. Thus, we can conclude that LNMO-O₂ calcined in O₂ atmosphere exhibits a cation ordered $P4_332$ phase, and LNMO-Air calcined in air presents cation ordered Fd3m spinel.

The difference between LNMO-Air and LNMO-O₂ can also be examined by Raman spectroscopy, as shown in Fig. 10. According to previous reports,^{32,33} the strong band that appeared at 649 cm⁻¹ is attributed to the symmetrical Mn–O stretching vibration (A_{1g}) in MnO₆ octahedra. Peaks around 416 and 510 are related to the Ni²⁺–O stretching mode in spinel. The $T_{2g}^{(3)}$ band of the spinel is at around 600–625 cm⁻¹. The split of this $T_{2g}^{(3)}$ band is the fingerprint of the *P*4₃32 space group. The splitting of $T_{2g}^{(3)}$ can be clearly seen for LNMO-O₂ because a doublet at 621 and 604 cm⁻¹ is observed. The other characteristic peaks of *P*4₃32 structure are around 249, 228 and 170 cm⁻¹, which are all present in the LNMO-O₂ spectrum.^{6,33,34} In the LNMO-Air Raman spectrum, all these features referring to *Fd3m*



Fig. 10 Raman spectra of LNMO-Air and LNMO-O₂ samples.

structure are absent. Thus, we are confident that LNMO-O₂ is $P4_332$ spinel.

Fig. 11 shows the cyclic voltammograms of the LNMO-O₂ and LNMO-Air in button cells. The two curves are similar to two redox peaks in the region of 4.7–4.9 V and a very small peak around 4.0 V. The two redox peaks in the region of 4.7–4.9 V are assigned to the Ni²⁺/Ni³⁺ and Ni³⁺/Ni⁴⁺ redox couples at 4.7 V and 4.75 V. However, the tiny current peak near 4.0 V, corresponding to the Mn³⁺/Mn⁴⁺ redox couple, for LNMO-Air cannot be neglected, although for LNMO-O₂ it is very small to have significant effect on its discharge capacity. This is in accordance with XRD refinement, IR spectra and Raman results that there is a small amount of Mn³⁺ in LNMO-Air, whereas it is almost absent in LNMO-O₂.

Typical discharge curves and cycle performances of the two samples at room temperature are shown in Fig. 12. Both the LNMO-Air and LNMO-O₂ have a dominant plateau around 4.7 V (Fig. 12(a)). The difference is that there is a small plateau at about 4.0 V for LNMO-Air (Fig. 12(a) inset), whereas for LNMO-O₂, this plateau is unobservable. The discharge cycling performance of these materials at 1 C are shown in Fig. 12(b). The first discharge capacities of LNMO-Air and LNMO-O₂ are comparable, 122 and 120.5 mA h g⁻¹, respectively. Their discharge capacity retentions are also comparable, 94.6% and 94.1% after



Fig. 11 Cyclic voltammogram curves (0.1 m V s⁻¹) of (a) spherical LNMO-O₂ sample, (b) spherical LNMO-Air sample.



Fig. 12 Electrochemical properties of the as-prepared samples at 25 °C (a) cycle performance at 1 C; (b) the 20th discharge curve at 1 C; (c) rate cycling performance. (d) EIS spectra of the LNMO-O₂ and LNMO-Air in the frequency range between 0.1 Hz and 100 kHz.

200 cycles, respectively. The rate capabilities of these two materials have apparent differences, as shown in Fig. 12(c): at low rate (0.2 C-1 C), LNMO-O₂ exhibits slightly higher discharge capacity than LNMO-Air; at an intermediate rate (2 C) their specific capacities are the same; at high rates (5 C-10 C), however, the specific capacity of LNMO-Air becomes larger than that of LNMO-O₂. We believe that the presence of Mn³⁺ ions causes this difference. In Fd3m lattice,¹⁹ the presence of Mn³⁺ ions generates more disordering among the Ni sites and Mn sites, which is beneficial to Li ion transportation³⁵ as well to electron conductivity. There are two additional electron hopping pathways that are absent in $P4_332: Ni^{2+/3+} \rightarrow Mn^{4+} \rightarrow$ $Ni^{3+/4+}$ and $Ni^{2+/3+} \rightarrow Mn^{4+} \leftrightarrow Mn^{3+} \rightarrow Ni^{3+/4+}$.³⁰ With these additional electron hopping pathways, charges can be transferred faster, which helps to relieve the ohmic polarization and electrochemical polarization in the materials,36 and thus a better cycling LNMO material especially at higher rates.

To verify our assumption, EIS was measured in the range from 100 kHz to 0.1 Hz after 30 cycles at 1 C rate, as shown in Fig. 12(d). The Nyquist plots of both the materials display a similar profile, exhibiting a semicircle in the high-frequency region and a linear slope in the low-frequency region. Both the equivalent circuits are the same as insets shown in Fig. 12(d). The R_s is assigned to electrolyte resistance, whereas the R_{ct} is attributed to the direct charge transfer resistance of electrode materials. The EIS results clearly show that the charge transfer resistance of the LNMO-Air (21.2 Ω) is much smaller than that of the LNMO-O₂ (52.2 Ω), which agrees well with our hypothesis that the small amount of Mn³⁺ in LNMO-Air, generated by calcination in air atmosphere, lowers the barriers for Li⁺ ion transportation and electron conducting and thus improves its rate capacity at high rates.

The presence of Mn^{3+} ions in LNMO-Air also greatly improves its electrochemical performance at high temperature (55 °C), as shown in Fig. 13. The discharge capacity (Fig. 13(a)) of LNMO-Air does not deteriorate; however, the cycle life of



Fig. 13 Electrochemical properties of the LNMO-O₂ and LNMO-Air as-prepared samples at 55 °C (a) cycle performance at 5 C (735 mA g^{-1}); (b) the 20th and 40th discharge curve at 5 C; (c and d) EIS spectra in the frequency range between 0.1 Hz and 100 kHz.

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LNMO- O_2 shows a sudden death after 30 cycles, implying the latter is not a suitable electrode material for high temperature application. By examining the relationships between discharge capacity and voltage, we can see the obvious differences: the LNMO-Air material can retain its 4.7 V plateau throughout 40 cycles but the LNMO-O2 material drops its plateau from 4.58 V to 4.12 V as cycled, and the magnitude of the plateau is also constantly shrinking. This dramatically different behaviour likely results because the LNMO-O2 cathode is more highly polarized than the LNMO-Air cathode due to their quite different ion and electronic conductivities, as discussed above. EIS studies unambiguously demonstrate their R_{ct} different behaviours, as shown in Fig. 13(c) and (d). It can be seen that the $R_{\rm ct}$ of all samples at 55 °C is higher than that at 25 °C. According to Seung M. Oh's research,³⁷ the surface film became enriched by inorganic fluorinated species and became thicker with cycling at elevated temperature, resulting in a continued electrode polarization and even cell invalidation. This similar phenomenon was also reported by the Markovsky's study.³⁸ LiF, C-F and P-F_x species were formed at the surface of aged LiNi_{0.5}Mn_{1.5}O₄ electrodes operating at high temperature.³⁸ These oxidative products acted as an electrically insulating layer that could decrease the electronic conductivity and impede the transportation of ions.²⁹ The R_{ct} of the LNMO-O₂ cathode increases from 172 Ω to 469 Ω , whereas that of LNMO-Air only changes from 79 Ω to 103 Ω . As the resistance of the LNMO-O₂ electrode keeps increasing as the cycling goes on, its performance gets worse and worse; on the other hand, with Mn³⁺ ions present in LNMO-Air, its ion and electron conductivities are much improved, its electrode polarization is greatly reduced, and its performance is perfectly preserved. The electrical performance and the capacity retention of the LNMO-Air sphere are comparable to other reported LNMO.39,40 The electrical performance at high rate⁴¹ and elevated temperature⁴² are even better.

Conclusions

In summary, the porous micron-sized sphere LiNi_{0.5}Mn_{1.5}O₄ particles were synthesized via an impregnation method based on highly prominent nanothorn MnO₂ spheres as the manganese sources. The obtained materials were of good crystalline with a particle size of approximately 2-4 µm composed of nanosize polyhedrons. In comparison to the conventional ballmilling method, the method presented here can be easily operated and is energy efficient. The electrochemical properties of the sphere LiNi_{0.5}Mn_{1.5}O₄ cathode material was superior to those made from commercial manganese sources and conventional approaches, because of its more porous structure for the enhanced immersion of electrolyte and better structure for insertion/desertion of Li ions. We also investigated the effects of the trace amount of Mn³⁺ ions in the structure on its specific capacity and cycle stability. We proposed that these trace Mn³⁺ ions are beneficial to its rate capability and cycle life, especially at high rates and increased temperature, by improving the conductivities of Li ions and electrons of the LNMO material.

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