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Insight into the improved cycling stability of sphere-nanorod-like micro-nanostructured high voltage spinel cathode for lithium-ion batteries

Abstract

Currently, developing cathode material with high energy density and good cycling performance is one of the key challenges for lithium-ion batteries. $\text{LiNi}_{0.5-x}\text{Mn}_{1.5+x}\text{O}_4$ (LNMO) spinel cathode has attracted great attention as the most promising cathode candidate due to its extraordinarily high operating voltage, but its inferior long-term cycling stability has limited its further development. In this work, we successfully designed LNMOs with specific facets and different morphologies, among which the hybrid sphere-nanorod-like micro-nanostructured LNMO possesses excellent cycling performance, with capacity of over 107.8 mAh g^{-1} after 1000 cycles at 10 C and superior rate capability up to 10 C. Its superior rate capability is found to originate from the large Li-O bond length by Rietveld refinement, which contributes to decreased charge transfer resistance and ease of Li insertion/extraction at tetrahedral sites. On the other hand, the excellent cycling stability comes from its having the least structural deformation from mechanistic reactions, which involve the longest solid-solution reaction, the highest spinel structural tolerance/stability up to $\Delta = \sim 0.69 \text{ Li}$, and a highly reversible two-phase reaction during charge and discharge in the hybrid LNMO, as revealed by the in operando synchrotron X-ray powder diffraction results. Moreover, the hybrid LNMO exhibits surface planes (210) with the highest Mn defect formation energy, prohibiting Mn^{3+} disproportionation and further stabilizing its cycling stability. This work not only demonstrates the importance of crystallographic and morphological controls on the high-voltage spinel performance, but also opens a window for battery engineers and researchers to develop battery technology for high-power applications.

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Insight into the improved cycling stability of sphere-nanorod-like micro-nanostructured high voltage spinel cathode for lithium-ion batteries

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Keywords: lithium-ion batteries; high-voltage spinel; hybrid morphology; high rate performance; superior cycling stability

Abstract

Currently, developing cathode material with high energy density and good cycling performance is one of the key challenges for lithium-ion batteries. $\text{LiNi}_{0.5-x}\text{Mn}_{1.5+x}\text{O}_4$ (LNMO) spinel cathode has attracted great attention as the most promising cathode candidate due to its extraordinarily high operating voltage, but its inferior long-term cycling stability has limited its further development. In this work, we successfully designed LNMOs with specific facets and different morphologies, among which the

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hybrid sphere-nanorod-like micro-nanostructured LNMO possesses excellent cycling performance, with capacity of over 107.8 mAh g⁻¹ after 1000 cycles at 10 C and superior rate capability up to 10 C. Its superior rate capability is found to originate from the large Li-O bond length by Rietveld refinement, which contributes to decreased charge transfer resistance and ease of Li insertion/extraction at tetrahedral sites. On the other hand, the excellent cycling stability comes from its having the least structural deformation from mechanistic reactions, which involve the longest solid-solution reaction, the highest spinel structural tolerance/stability up to $\Delta = \sim 0.69$ Li, and a highly reversible two-phase reaction during charge and discharge in the hybrid LNMO, as revealed by the *in operando* synchrotron X-ray powder diffraction results. Moreover, the hybrid LNMO exhibits surface planes (210) with the highest Mn defect formation energy, prohibiting Mn³⁺ disproportionation and further stabilizing its cycling stability. This work not only demonstrates the importance of crystallographic and morphological controls on the high-voltage spinel performance, but also opens a window for battery engineers and researchers to develop battery technology for high-power applications.

1. Introduction

Recently, Li-ion batteries have been proposed as a potential energy source for the electric vehicle and hybrid electric vehicle because of its high energy density and good superior cyclability [1-4]. As one of the most promising high-voltage cathode materials, spinel LiNi_{0.5-x}Mn_{1.5+x}O₄ (LNMO) has gained intensive attention due to its high working voltage of 4.7 V (vs. Li/Li⁺), its high energy density of 650 Wh kg⁻¹, and its rapid transportation of lithium ions via three-dimensional (3D) diffusion tunnels in the spinel structure [5-9]. Nevertheless, its inferior cycle capability, especially its severe capacity decay when working at high temperature or high voltage because of disastrous side reactions, such as Mn³⁺ disproportionation and dissolution, etc., is the main obstacle for the commercialization of LNMO. Generally speaking, the structural stability and the surface states of LNMO are the two most important factors for excellent electrochemical performance [5, 10, 11]. On the

one hand, spinel LNMO can be classified into two groups, namely ordered spinel with
 a simple cubic structure and space group of $P4_332$, and disordered spinel with a face-
 centered cubic structure with $Fd-3m$ symmetries[12, 13]. Ni and Mn ions occupy the
 octahedral sites, connecting with O atoms to form a 3D octahedral network in both
 spinels. Note that Ni and Mn occupy the $4b$ and $12d$ sites, respectively, in the $P4_332$
 structure and Ni shares the $16d$ sites with Mn in disordered structure (Fig. S1 in the
 Supporting Information). The structural differences result in different mechanistic
 behavior of the ordered and disordered phases. Apparently, the working plateaus for the
 $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox couples are separated in the disordered phase, but are not
 distinguishable in the ordered phase. Mechanistically, the ordered phase undergoes
 multiple two-phase reactions during $\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$ redox reactions, whereas the
 disordered spinel exhibits a solid-solution reaction and a two-phase reaction during the
 corresponding $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox couples, respectively. In addition, in the
 ordered phase, Mn only exists in the form of Mn^{4+} , while in the disordered phase, Mn
 has 3^+ and 4^+ valences, giving rise to the 4 V plateau of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox reactions
 [12, 14]. Electrochemically, the disordered spinel shows better electrochemical
 performance due to its higher stability. The degree of Ni/Mn disorder and the
 concentration of Mn^{3+} ions also play important roles in mandating the electrochemical
 performance of the disordered phase [11, 15]. Aside from the intrinsic mechanistic
 reactions, the Mn^{3+} dissolution is the key impediment to the cycling performance of
 Mn-based electrodes, including LNMOs.

On the other hand, the crystallographic facets of LNMO particles could result in
 different electrochemical properties, through mitigating the Mn^{3+} dissolution and
 promoting the Li diffusion during cycling [10, 16, 17]. For example, some researchers
 suggested that the densest (111) planes have the lowest surface energy and the lowest
 Mn dissolution, which could contribute to a stable solid electrolyte interphase (SEI) and
 a resultant excellent cycle life [10]. On the other hand, the dissolution of Mn^{2+} into the
 electrolyte is proposed to be more likely to occur at the (110) planes [16]. There is still

1 debate about this issue, however, and other researchers reported that the (100) planes
2 are more stable and favorable to long-term cycling stability [17].

3 To prepare LNMO materials with good cycling performance, the synthesis method is
4 one of the key factors and needs to be optimized. Until now, the solid-state method [18,
5 19], co-precipitation method [20], hydrothermal method [21], sol-gel method [22],
6 molten salt method [23], etc. have been used to prepare the LNMO materials. Recent
7 studies also show that different synthesis methods can result in different microstructures
8 and different surface states of the LNMOs, which have a non-negligible influence on
9 the electrochemical performance, via shortening the Li diffusion paths for the lithium
10 ions [24-26] and limiting the Mn^{3+} dissolution [27]. Surface coating [28-30] cation or
11 anion doping [31-33], and morphology control [34, 35] have also been applied to
12 improve the cycling performance of LNMO to a certain extent. Despite these earlier
13 studies, the enhancement mechanisms that act on the cycling properties of LNMO due
14 to this surface morphology and microstructure are not yet clear and need to be further
15 investigated, which is crucial, extendable, and desirable for the design and development
16 of novel cathode materials.

17 In our previous work, we found that the LNMO/graphene composites with nanorod
18 morphology featured better electrochemical performances, but the long-term cycling
19 stability of the nanorod LNMO material is still far from satisfactory [36]. As the
20 structure and the surface states are very important for the cycling performance of
21 LNMO, in this work, we designed LNMOs with different microstructures and different
22 morphologies via the one-pot hydrothermal-calcination method. We further enhanced
23 the disordered LNMOs with morphological control and design of the surface
24 orientation using a one-pot hydrothermal method and subsequent solid-state method.
25 The spherical, nanorod, and hybrid sphere-nanorod LNMOs exhibit excellent, but
26 slightly different, electrochemical performances. Comprehensive and comparative
27 investigations have been performed to illustrate the origins of the structural and
28 electrochemical properties of these three microstructured LNMO materials by means

of electrochemical evaluation, electron imaging, *in operando* synchrotron-based X-ray diffraction (XRD), and *ab initio* calculations.

2. Experimental

2.1 Material preparation

Three LNMO materials with different morphologies were synthesized separately by the hydrothermal-calcination method, and the synthetic process is graphically illustrated in Fig. S2. For the nanorod LNMO, the MnOOH nanorods precursor was first prepared through a template method, with KMnO₄ (97%, Sigma Aldrich) as one of the raw materials and polyethylene glycol (PEG-400, Sigma Aldrich) as the template. The detailed preparation process is described in our previous studies [36].

For the spherical LNMO, the spherical Ni_{0.25}Mn_{0.75}CO₃ precursor was firstly prepared by a co-precipitation method, using NiSO₄ (99.99%, Sigma Aldrich) and MnSO₄ (99.99%, Sigma Aldrich) as the raw materials, and NH₄HCO₃ (99.5%, Sigma Aldrich) as the precipitator. The obtained precursor was then heated at 160 °C for 3 hours in a Teflon-lined hydrothermal reactor. After that, the obtained materials were filtered with deionized water and then washed with ethanol (99.8%, Sigma Aldrich), followed by drying in an oven at 90 °C for 12 hours to obtain the hollow sphere-like precursors. Then, the obtained precursors were dispersed in deionized water with the appropriate amount of LiOH·H₂O (99.99%, Sigma Aldrich) (5% excess), stirred for 3 hours, and dried in an oven at 80 °C for 24 hours. Then, the mixture was moved to a furnace and air-annealed at 800 °C for 10 h to obtain the sphere-like LNMO material.

The hybrid sphere-nanorod micro-nanostructured LNMO was also synthesized by a one-pot hydrothermal-calcination method. In this synthesis process, the spherical Ni_{0.25}Mn_{0.75}CO₃ precursor and the MnOOH nanorods precursor were firstly prepared by a hydrothermal process, corresponding to part 1 in Fig. S2. Then, the spherical Ni_{0.25}Mn_{0.75}CO₃ precursor and the MnOOH precursor were mixed in a 1:1 ratio (by weight), transferred into Teflon-lined hydrothermal reactor, and heated at 160 °C for 3 hours. After that, the obtained materials were filtered and washed with deionized water

and ethanol for many times. After mixing with a Li source, the mixture was moved to a furnace and annealed at 800 °C for 10 h to obtain the sphere-nanorod-like micro-nanostructured LNMO material, corresponding to part 2 in Fig. S2.

2.2 Material characterization

The morphology of the prepared samples was characterized by field-emission scanning electron microscopy (FESEM, NERLIN Compact, Zeiss, Germany), equipped with a Quanta-450 SEM instrument, and transmission electron microscopy (TEM, JEOL2100). In addition to X-ray diffraction (XRD), neutron powder diffraction (NPD) was carried out to characterize the structure and composition of the active materials on the high-resolution neutron powder diffractometer ECHIDNA [37] at the Open Pool Australian Light Water (OPAL) research reactor at the Australian Nuclear Science and Technology Organization (ANSTO). The NPD data were collected over the 2-theta range of 4-164° with a step-size of 0.125°. The wavelength of the neutron beam was determined to be 1.62157(5) Å using LaB₆ standard reference material 660b. Rietveld refinement was carried out using GSAS-II software [38], where the refining parameters include background coefficients, zero shift, peak shape parameters, lattice parameter, oxygen positional parameter, site occupancy factors, and isotropic atomic displacement parameters. The three LNMOs were also characterized using Raman spectroscopy (Renishaw in Via, Britain using 532 nm excited laser) for structural analysis in the spectral range from 200 to 800 cm⁻¹.

The electrochemical properties of the obtained LNMO materials were studied using CR2025 coin-type cells. The CR2025 cells were assembled in a glove box filled with argon (Universal 2440/750, Mikrouna), and the content of oxygen and moisture was less than 0.1 ppm. The cathode electrode was fabricated by mingling the obtained LNMO material, polyvinylidene difluoride (PVDF) binder, and conductive carbon black in the mass ratio of 8: 1: 1 with an adequate amount of N-methyl-2-pyrrolidone (NMP), and then coating the mixture on an aluminum current collector to form the electrode; the cathode material loading was 2-3 mg cm⁻². The electrode was dried at

1 90 °C for 3 hours in an air oven and then diverted to a vacuum oven and dried at 90 °C
2 for 8 hours to evaporate the excessive solvent, then pressed into circles of diameter 15
3 mm. Lithium foil and polypropylene membrane (Celgard® 2400) were used as the
4 counter electrode and separator, respectively. 1 mol L⁻¹ LiPF₆ dissolved in a 1: 1 mixture
5 of dimethyl carbonate (DMC) and ethylene carbonate (EC) was prepared and used as
6 the electrolyte in the batteries. Galvanostatic charge/discharge performance was tested
7 on a Land 2000T auto-cycler (China) at several current densities in the voltage range
8 of 3.5-4.9 V vs. Li/Li⁺ at room temperature. The electrochemical impedance
9 spectroscopy (EIS) tests were performed using a CHI electrochemical workstation (CHI
10 660E) in the frequency range from 0.01 to 10⁵ Hz.

11 The *in operando* synchrotron-based XRD experiment was carried out in Australian
12 Synchrotron, Australia. The preparation method for the customized coin cell can be
13 found elsewhere [39, 40]. The wavelength of the synchrotron beam was 0.688800(1) Å,
14 determined by using the LaB₆ standard reference material 660b. The diffraction pattern
15 was continuously recorded with the acquisition time of 180 s per pattern using a
16 MYTHEN microstrip detector. The time gap between each pattern was around 828
17 seconds during discharging and charging processes. The coin cell for the *in operando*
18 experiment was tested at 0.1 C (1 C = 147 mA g⁻¹) in the voltage range from 3.5 to 4.9
19 V.

20 The density functional theory (DFT) calculations were performed by using the Vienna
21 Ab initio Simulation Package (VASP) [41-44]. For all calculations, the Perdew-Burke-
22 Ernzerhof (PBE) functional [45] and the projector augmented-wave (PAW) technique
23 [46] were applied. Geometry optimization was converged until the energy change was
24 less than 10⁻⁵ eV and the force less than -0.03 eV/Å. Furthermore, the energy cut-off
25 was set to 400 eV, and the sampling over the Brillouin zone was treated by a 2×2×1
26 grid for the surfaces. To avoid the pseudo interactions of periodic images along the z-
27 axis, a vacuum slab with a thickness of 15 Å was introduced.

28

3. Results and discussion

Fig. 1a and 1b present the hollow spherical material and the nanorod material, respectively. It can be seen that the diameter of the spherical particles is about 1-2 μm and the wall thickness of the hollow spheres is about 200-300 nm, whereas the length of the LNMO nanorods is about 1~2 μm , with diameters of around 300-500 nm. Fig. 1c shows the LNMO with hybrid sphere-nanorod-like micro-nanostructured morphology. Compared with Figure. 1a and 1b, the spheres and the nanorod-like particles in the sphere-nanorod-like materials are similar in size and shape. It is noteworthy that the nanorod-like and spherical hollow particles are connected to each other in the hybrid sample, reducing the barrier energy and easing the lithium migration, which makes its electrochemical performance significantly different from the physical mixture of the nanorod and spherical samples.

The microstructure and surface morphology of the three LNMO samples were further characterized by TEM and high-resolution TEM (HRTEM), as shown in Fig. 1d, 1e and 1f. In Fig. 1d, the structure of the sphere-like sample was examined. It showed lattice spacing of 0.29 nm, corresponding to the (220) lattice planes. Fig. 1e displays an overview of the structure of the nanocrystals of the nanorod-like LNMO material, and the internal HRTEM image shows clear lattice fringes with the lattice spacing of 0.47 nm, corresponding to the interplanar spacing for the (111) planes. As for the hybrid LNMO material, an overview of the structure and an HRTEM image of the lattice fringe patterns of the selected sphere-like and nanorod-like particles are displayed in Fig. 1f. The lattice spacing of the circled sphere particle is 0.29 nm, indicating that the sphere particles grow along the [220] direction, whereas the nanorod-like particles show the lattice spacings of 0.37 nm and 0.47 nm, indexed to the (210) and (111) planes respectively. Accordingly, the three LNMO samples with different surface morphologies show different preferred orientations, and a new (210) plane was detected in the sphere-nanorod sample, which may have different effects on the electrochemical properties of LNMO materials.

1 The XRD patterns of the three LNMOs are similar, as shown in Fig. S3. In order to
 2 further identify the structural and crystallographic details of the three samples, neutron
 3 powder diffraction (NPD) was adopted because of the better elemental contrast between
 4 Ni and Mn, and the higher sensitivity towards Li and O of the neutrons [47]. This
 5 superiority derives from the unique coherent scattering lengths of different elements.
 6 For instance, in the LNMO system, Li, Ni, Mn, and O have the values of -1.9, 10.3, -
 7 3.7 and -5.8 fm ($1\text{fm} = 10^{-13}\text{ cm}$), respectively [48]. The Rietveld refinement results are
 8 shown in Fig. 1g-1i and Tables S1-S3, respectively. All three samples were refined to
 9 be cubic with the $Fd-3m$ group symmetry. Among them, the nanorod sample features
 10 the largest lattice parameter of 8.1801(7) Å and cell volume of 547.3(1) Å³, followed
 11 by hybrid sphere-nanorod sample and the sphere sample. Interestingly, it is found that
 12 the ratio of Ni ions to Mn ions in the unit cells of the three samples are all refined to be
 13 around 1:4, which may lead to an increased concentration of Mn³⁺ as a result of less
 14 Ni²⁺ content. Considering that Mn³⁺ has a larger ionic radius (0.645 Å) than Mn⁴⁺ (0.53
 15 Å), the increased Mn³⁺ content probably accounts for the larger lattice parameter than
 16 that in our previous report [49]. It should be noted that the degree of Ni/Mn disorder
 17 and the concentration of Mn³⁺ ions are critical for mandating the electrochemical
 18 performance of the disordered phase [11, 15]. In addition, the Ni: Mn ratio (1:4) makes
 19 it different from the typical LiNi_{0.5}Mn_{1.5}O₄ (1:3) material. Our refinement profiles also
 20 show that LNMO in the three samples exists in both ordered and disordered phases,
 21 where the disordered content accounts for the majority. Meanwhile, minor impurities
 22 are refined to include the rock-salt Li_xNi_{2-*x*}O₂ phase (space group $Fm-3m$, ICSD#71422)
 23 and spinel Li_xMn₂O₄ phase (space group $Fd-3m$, ICSD#50415), which were probably
 24 introduced during the sintering process. We note that the sample with hybrid
 25 morphology contains the least impurities compared to the other two samples, with
 26 LNMO accounting for 91.6(2) wt% of the composite. Although the impurity phases
 27 inevitably decrease the capacity of the electrode, their influence on the battery
 28 electrochemical performance will be ignored in the following discussion due to the

1 minor nature of their content. Last but not least, the lengths of the Li-O bonds and
2 Mn(Ni)-O bonds were also investigated. It is shown that the hybrid LNMO has the
3 longest Li-O bond length of 1.9552(4) Å, implying easy Li insertion into/extraction
4 from the tetrahedral sites during the cycling process, and the longest Mn-O bond is in
5 the nanorod LNMO, also implying instability of the octahedra in the structure.
6 Furthermore, Raman spectroscopy was also used to further analyze the LNMO
7 materials, and the results are shown in Fig. S4. Similarly, as per the results in the
8 literature [13, 50], the two main Raman bands peaking at about 487-489 and 623-624
9 cm⁻¹ can be assigned to the Ni²⁺-O stretching mode and the Mn-O stretching vibration
10 of MnO₆ groups, respectively, consistent with the features of the *Fd-3m* space group of
11 LNMO.

12 The electrochemical performances of these three LNMO materials at room temperature
13 were evaluated. The first discharge curves of these samples at 1 C in the voltage range
14 between 3.5 and 4.9 V (vs. Li/Li⁺) are presented in Fig. 2a. All the curves at 1 C show
15 similar features in their discharge behavior with two long plateaus at around 4.7 V and
16 a short plateau at or near 4.0 V. The plateaus at ~4.7 V are attributed to the
17 Ni⁴⁺/Ni³⁺/Ni²⁺ redox couple, while the plateau at ~4.0 V is ascribed to the Mn³⁺/Mn⁴⁺
18 redox couple, which confirms the conclusion drawn in the Rietveld refinements that
19 Mn³⁺ exists in the LNMO [13]. At 1 C, the total discharge capacities of the sphere
20 LNMO, nanorod LNMO, and hybrid LNMO are 117.1, 96.9, and 124.2 mAh g⁻¹,
21 respectively. In order to clarify the importance of the one-pot synthesis for hybrid
22 LNMO, a mechanical mixture of sphere-like and nanorod-like LNMO (in a mass ratio
23 of 1:1) was also prepared and evaluated for comparison purposes. The three
24 microstructured LNMOs and the mechanical mixture of LNMOs were tested for 100
25 cycles at 1 C (Fig. 2b). After the 100 cycles at 1 C, the hybrid LNMO delivered the
26 highest discharge capacity (122 mAh g⁻¹), significantly higher than those of the sphere-
27 like, nanorod, and mixed LNMOs (115.4, 97.7, 106.2 mAh g⁻¹, respectively).
28 Furthermore, Fig. 2c displays the rate capabilities of these three samples at various

1 current densities between 0.1 C and 10 C, each sustained for 8 cycles. With the current
 2 density increased from 0.1 C to 10 C sequentially, the capacities of the hybrid and
 3 sphere LNMOs were much higher than that of the nanorod sample, especially at the
 4 high rates of 5 C and 10 C. For example, the hybrid LNMO material delivered a capacity
 5 of 108 mAh g⁻¹, while the sphere LNMO delivered 105 mAh g⁻¹ and the nanorod
 6 LNMO only exhibited 72 mAh g⁻¹ at 10 C. More importantly, when the current density
 7 was returned to 0.1 C, the capacities for all these three materials were higher than the
 8 initial values, which may be related to wetting and electrochemical activation processes.
 9 It is believed that this is the reason for the increasing trend in the capacities at the initial
 10 stage for these three samples. In addition, as shown in Fig. S5, the hybrid LNMO also
 11 shows larger capacities at 1 C and 5 C than samples in previous reports. Fig. 2d shows
 12 the EIS plots of the three samples, and the inset is the equivalent circuit, with the
 13 corresponding fitting parameters shown in Table S4. All the EIS plots contain a
 14 semicircle in a high-frequency region corresponding to the charge transfer resistance
 15 (R_{ct}), and a straight line in the low-frequency region related to the Warburg impedance
 16 (Z_w), which is associated with the solid phase diffusion of Li-ion in the electrodes [51,
 17 52]. In addition, in the equivalent circuit, C_{d2} is placed to represent the double-layer
 18 capacitance, while C_{d1} and R_I are the insertion capacitance and resistance at the applied
 19 potential. We found that the hybrid LNMO had lower charge transfer resistance (R_{ct})
 20 than the other samples, which is beneficial to the kinetic behavior during
 21 charge/discharge processes, and thus favorable to enhance the electronic conductivity.
 22 It also had the longest Li-O bond lengths, as determined in NPD, explaining its having
 23 the best rate performance obtained in the cycle tests. At 10 C, the first discharge
 24 capacities of the hybrid sphere-nanorod-like LNMO, the single sphere LNMO, the
 25 mechanical mixture, and the single nanorod LNMO were 95.9, 86.6, 81.7, and 58.8
 26 mAh g⁻¹, respectively. After 1000 cycles at 10 C, however, the sphere-nanorod
 27 microstructured LNMO material could still deliver a capacity of 107.4 mAh g⁻¹,
 28 demonstrating the excellent cycling performance of the hybrid LNMO, even at high C

1 rates (Fig. 2e). To conclude, at 1 C discharge, all these three samples showed good
2 cycling performance, whereas at 10 C, the hybrid LNMO material displayed the best
3 cycling stability with the highest discharge capacity. There was no obvious capacity
4 decay at high current density even after the 1000 cycles. It should be noted that the
5 hybrid LNMO not only shows a higher capacity, but also better cycling performance
6 than the mixed LNMO, demonstrating the necessity of the one-pot synthesis and the
7 bridging features between the nanorod-like and spherical hollow particles, as observed
8 in the hybrid LNMO.

9 In short, the LNMO materials with various microstructures exhibited excellent but
10 different electrochemical performances, especially at high current density. In order to
11 further reveal the underlying mechanism of enhanced electrochemical performance in
12 the hybrid morphology LNMO, *in operando* synchrotron-based XRD was used to
13 illustrate the differences in the structural changes and phase evolution of the three
14 samples during the charging and discharging processes (shown in Fig. 3). As mentioned
15 above, ordered and disordered LNMOs show different electrochemical behavior during
16 the lithiation and delithiation processes [53]. It was reported that the typical ordered
17 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ undergoes two cubic/cubic two-phase reactions during the charging
18 process, from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($a = 8.17 \text{ \AA}$) to $\text{Li}_{0.5}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($a = 8.09 \text{ \AA}$) and finally
19 to $\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($a = 8.00 \text{ \AA}$) [54]. On the other hand, the typical disordered
20 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phase undergoes the combination of a solid-solution reaction at the
21 $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox couple at the voltage of around 4.6 V (vs. Li/Li^+ , from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$
22 to $\text{Li}_{0.5}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$) and a two-phase reaction during the $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox couple stage
23 at approximately 4.7 V (vs. Li/Li^+ , from $\text{Li}_{0.5}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ to $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_2$) [49].
24 Generally speaking, the two-phase reactions usually involve phase segregation and
25 grain boundary movement, inevitably leading to the problems of active material
26 pulverization and electrical contact loss from the current collectors [47]. It should be
27 noted that, in our work, the major phase in LNMOs is $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ with a Ni: Mn =
28 1:4 ratio, considering that 20% of Ni^{2+} is replaced by Mn^{3+} . The phase evolutions of

1 these LNMOs are expected to be similar, but also come with slight differences. The
2 solid-solution reaction (one-phase reaction) is generally preferable due to its having
3 fewer structural changes and higher transformation reversibility.

4 In order to show the peak shift and new peak occurrence in more detail, a selected
5 region of 2-theta has been exhibited, and the 111 reflections of LNMO phase were
6 chosen to illustrate the structural response of disordered LNMO. Meanwhile, the peak
7 position evolution of the (511) reflection is also shown in Fig. S6. From Fig. 3, it can
8 be obtained that all LNMOs suffer a solid-solution reaction and a subsequent two-phase
9 reaction, corresponding to the redox couples of $\text{Mn}^{3+}/\text{Mn}^{4+}$, $\text{Ni}^{2+}/\text{Ni}^{3+}$, and $\text{Ni}^{3+}/\text{Ni}^{4+}$,
10 respectively, in the charging process, similar to those of typical $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ reported
11 in the previous literature [49]. In the case of the charge behavior, we can see that the
12 solid-solution reaction contributes 68.9% (~0.69 Li), 63.6%, and 56.8% to the
13 capacities of the hybrid, sphere-like, and nanorod-like LNMOs, demonstrating that the
14 hybrid LNMO exhibits the best structural stability and tolerance, so that it allows more
15 Li to be extracted. This observation explains why the hybrid LNMO has the best cycling
16 performance at 1 and 10 C rates. Although the two-phase reaction at the high charge
17 stage constitutes of less than 50% of the capacity and is not avoidable, its reasonable
18 reversibility on discharge does not harm the cycling performance of the LNMOs to any
19 significant degree. When extra attention is paid to the discharge behavior, during the
20 solid-solution stage, the peak location of the (111) reflection continuously shifts to
21 lower angles, corresponding to a lattice deformation with an increasing lattice
22 parameter and cell volume upon the insertion of Li. The existence of a rapid structure
23 breakdown, which is highlighted by the red boxes in the contour plots and inevitably
24 leads to structural instability, in both the sphere-like and the nanorod-like LNMOs, may
25 be the culprit in the poorer cycling performance. In comparison, the hybrid LNMO
26 features a smooth structural deformation during discharge, and its peak returns to
27 almost its initial position at the end of discharging, which indicates the excellent
28 structural stability of the hybrid LNMO sample.

For high-voltage and Mn-based cathodes, the dissolution of Mn^{3+} ions, under the effects of electrolyte decomposition, HF attack, high current, and high voltage is another major concern for the cycle performance [55, 56]. From Fig. 1, it can be obtained that the three LNMO samples with different surface morphologies show different preferred orientations, which may result in different degrees of side reactions in the LNMO materials. Therefore, to evaluate the influence of the morphology and resultant surface facets on the issue of Mn^{3+} dissolution, density functional theory (DFT) calculations were performed using the Vienna *ab initio* Simulation Package (VASP) [41-44]. It is worth mentioning that the model of LNMO was designed as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in order to simplify the calculation issues.

According to above experimental observations in HRTEM (Fig. 1), several representative surfaces were constructed, and VASP was employed to perform DFT calculations on the formation energies of Mn defects on different surface facets (as depicted in Fig. S7), according to the following equation,

The calculation results listed in Table S5 clearly show that the Mn species on (100), (110), (210), and their equivalent (i.e. (010) or (101) ones) surfaces are stable, although the dissolution of Mn ions from (111) and equivalent surfaces is easy. As a result, it can be expected that LNMO materials with exposed (111) and equivalent facets will be unstable and suffer from capacity reduction during repeated charging/discharging cycles, while the LNMO with exposed (100), (110), (210), and equivalent facets will exhibit excellent stabilities. The corresponding equivalent surfaces of these three LNMO samples and the formation energies of Mn ion dissolution from the corresponding surfaces are summarized in Fig. 4. Although a very recent investigation suggested that the dissolution energy of Mn follows the order of (111) > (100) > (110) [57], our calculations have clearly shown that the stability of Mn ions on the surface is strongly correlated with the Mn-O coordination. For the (100) clean surface, Mn is 5-fold coordinated with oxygen, whereas the coordination number of Mn ions on the

outermost layer of the (111) clean surface is reduced to 3, which leads to a lower dissolution energy and is responsible for their lower stability on the surface. Therefore, as shown in the TEM images (Fig. 1), the hybrid LNMO with dominant (111) and (210) facets should exhibit less Mn dissolution compared with the sphere-like (with (220) facets) and nanorod-like (with (111) facets) LNMOs.

In short, the hybrid LNMO exhibits the best electrochemical performance for the following reasons:

- 1) The longest Li-O bond of 1.9552(4) Å exists in the hybrid LNMO, as confirmed by Rietveld refinement, which is coupled with the lowest charge transfer resistance from the EIS results, confirming the ease of Li insertion into/extraction from the tetrahedral sites.
- 2) Most of the capacity is contributed by the solid-solution behavior (up to 0.69 Li) in hybrid LNMO, unlike the other two samples, ensuring the structural stability of its LNMO material during the cycling process. Moreover, the absence of rapid structural deformation on discharge and the relatively short Mn-O bond length in hybrid LNMO also helps to stabilize the spinel structure.
- 3) The dominant surface plane (210) in the hybrid sample shows the least Mn dissolution, as indicated by the *ab initio* calculations, as further confirmed by its cycling stability under long-term testing at 1 and 10 C.

4. Conclusion

In this paper, LNMO materials with a Ni/Mn ratio of 1:4 and various morphologies have been successfully prepared by a one-pot hydrothermal-calcination process. Notably, the hybrid sphere-nanorod-like micro-nanostructured LNMO material reveals outstanding high rate performance and excellent cycling stability. Through chemical and morphological controls, we introduced a large Li-O bond length and low charge transfer resistance into the hybrid LNMO, leading to superior rate capability. Meanwhile, the *in operando* synchrotron XRD results show that the hybrid LNMO

1 delivered up to 69% charging capacity through a solid-solution reaction and
2 experienced smooth structural deformation during discharge, which accounts for its
3 excellent structural stability during the cycling process. Moreover, theoretical
4 calculations also indicate that the existence of (210) planes in the hybrid LNMO could
5 help to alleviate the side reactions leading to Mn dissolution, further ensuring its cycling
6 stability. This work not only demonstrates the successful preparation of a high-
7 performance, high-voltage spinel through chemical and morphological modifications,
8 but also provides insight into the origins of its electrochemical behavior and its
9 enhancement mechanisms.

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27

1

2

3 **Fig. 1** SEM images of LNMO materials with different microstructures: a) spheres, b)
 4 nanorods, c) the hybrid material; TEM images of LNMO materials with different
 5 surface microstructures: d) spheres, e) nanorods, and f) the hybrid material. Insets of
 6 the panels are HRTEM images of the corresponding selected area (marked by green
 7 lines); Rietveld refinement profiles for the NPD data for (g) spheres, (h) nanorods, and
 8 (i) the hybrid LNMO (weighted profile R-factor, $R_{wp} = 5.38, 5.17,$ and 4.90% ;
 9 goodness-of-fit (GOF) = 2.32, 2.35, and 2.01, respectively).

10

Fig. 2 Electrochemical behavior of the LNMO samples at room temperature. (a) Initial discharge curves at 1 C, (b) cycling performance at 1 C, (c) rate capabilities at various current densities, (d) Nyquist plots, with the inset showing the equivalent circuit used to fit the EIS, and (e) long-term cycling performances of the four samples at 10 C.

Fig. 3 *In operando* synchrotron-based XRD profiles of (a) sphere, (b) nanorod, and (c) hybrid LNMOs with i) stacking and ii) contour plots of synchrotron XRD in the selected 2-theta region, showing the evolution of (111) reflections of LNMO, iii) variation of d spacing of LNMO during charge and discharge, and iv) the corresponding charge-discharge curves at 0.1 C.

1 Mn-O coordination: 4 Mn-O coordination: 3 Mn-O coordination: 5 Mn-O coordination: 4 & 5
2 **Fig. 4** Corresponding equivalent surfaces of (a) sphere, (b) nanorod, and (c) hybrid
3 LNMO samples, and the Mn ion dissolution from the corresponding surfaces (see Fig.
4 S7 and Table S5 for more details).

5

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Supporting information for

Insight into the improved cycling stability of sphere-nanorod-like micro-nanostructured high voltage spinel cathode for lithium-ion batteries

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Fig. S1 Schematic structures of ordered LNMO ($P4_332$) and disordered LNMO ($Fd-3m$)

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Fig. S2 Synthesis process of the sphere-rod-like micro-nanostructure LNMO materials.

Fig. S3 XRD pattern of sphere, nanorod and hybrid sphere-nanorod LNMO, respectively

Table S1 Phase fraction in three LNMO samples obtained from Rietveld refinements

Weight fraction	LNMO ($Fd-3m$)	LNMO ($P4_332$)	$\text{Li}_{0.208}\text{Ni}_{1.792}\text{O}_2$	$\text{Li}_{0.3}\text{Mn}_2\text{O}_4$
Sphere LNMO	81.8 wt%	2.7(2) wt%	5.2(2) wt%	4.3(2) wt%
Nanorod LNMO	77.6 wt%	8.1(3) wt%	6.6(1) wt%	7.7(2) wt%
Hybrid sphere-nanorod LNMO	89.1 wt%	2.5(2) wt%	5.5(2) wt%	2.9(1) wt%

Table S2 Crystallographic details in three LNMO samples

Sphere LNMO Space group = $Fd-3m$						
$a = 8.1705(4) \text{ \AA}$, volume = $545.44(8) \text{ \AA}^3$						
Atom	Wyckoff site	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$	Site occupancy factor
Li	$8a$	0.125	0.125	0.125	0.015(2)	1
Ni	$16d$	0.5	0.5	0.5	0.010(2)	0.195(3)
Mn	$16d$	0.5	0.5	0.5	0.010(2)	0.805(3)
O	$32e$	0.26311(8)	0.26311(8)	0.26311(8)	0.0100(4)	1

Nanorod LNMO Space group = $Fd-3m$						
$a = 8.1801(7) \text{ \AA}$, volume = $547.3(1) \text{ \AA}^3$						
Atom	Wyckoff site	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$	Site occupancy factor
Li	$8a$	0.125	0.125	0.125	0.010(2)	1
Ni	$16d$	0.5	0.5	0.5	0.016(3)	0.181(4)
Mn	$16d$	0.5	0.5	0.5	0.016(3)	0.819(4)
O	$32e$	0.2627(1)	0.2627(1)	0.2627(1)	0.0084(4)	1

Hybrid sphere-nanorod LNMO Space group = $Fd-3m$						
$a = 8.1746(1) \text{ \AA}$, volume = $546.27(3) \text{ \AA}^3$						
Atom	Wyckoff site	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$	Site occupancy factor
Li	$8a$	0.125	0.125	0.125	0.012(1)	1
Ni	$16d$	0.5	0.5	0.5	0.006(2)	0.202(3)
Mn	$16d$	0.5	0.5	0.5	0.006(2)	0.798(3)
O	$32e$	0.26309(8)	0.26309(8)	0.26309(8)	0.0096(2)	1

Table S3 Bond length obtained from Rietveld refinements in three samples

Bond length ($\text{\AA}$)	Sphere LNMO	Nanorod LNMO	Hybrid sphere-nanorod LNMO
Li-O bond	1.9545(4)	1.9516(5)	1.9552(4)
Mn-O bond	1.9414(7)	1.9464(9)	1.9426(6)

Fig. S4 Raman spectra of obtained LNMO materials with different microstructure.

Fig. S5 rate capability comparison between our work and previous literatures ¹⁻⁵ at 1C and 5C.

Fig. S6 *Operando* synchrotron XRD data of (a) sphere LNMO, (b) nanorod LNMO, and (c) hybrid sphere-nanorod LNMO.

Table S4 the corresponding parameters of the hybrid sphere-nanorod-like LNMO material, single sphere LNMO and nanorod LNMO material.

Samples	R_s/Ω	R_{ct}/Ω	R_l/Ω	$C_{dl}/10^{-5}\text{F}$	$C_{d2}/10^{-6}\text{F}$
Hybrid sphere-nanorod	6.021	224.4	25.71	1.441	1.439
Nanorod	5.569	346.5	54.14	5.322	6.374
Sphere	5.422	235.5	34.65	2.245	6.155

Fig. S7 Theoretical models for (a) (001), (b) (110), (c) (111), and (d) (210) surfaces of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material.

Table S5 Formation energies (FE, in eV) of Mn defects on different surfaces and relevant Bader charges (BC, in e)^a.

	(100)	(110)	(111)	(210)
FE	10.627	7.831	5.0471	9.112
BC	1.513	1.390	0.994	1.440

^a Due to the symmetry, many surfaces are equivalent, i.e. (100), (100), and (010) ones.

Figure S8 (a) Relationship between Bader charge and defect formation energy and (b) The Gibbs free energy of formation (ΔG_f) for MnOx compounds

According to our calculated Bader charges and defect formation energies, a well-defined quadratic fit curve was obtained. A very similar trend was also observed in the relationship between the Gibbs free energy of formation (ΔG_f) for MnOx compounds and the oxidation states of Mn ions). The data suggested that the stabilities of Mn ions in bulk and on surface are related to their oxidation states and the Mn-O coordination.

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