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High Rate Micron-Sized Ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

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Ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was synthesized through a solid-state reaction. Even though the material has a particle size of 3–5 μm , it shows very high rate capability and excellent capacity retention. The capacity is as high as ≈ 78 mAh/g at a 167C discharge rate. This high discharge rate performance is consistent with first-principles calculations of the activation barrier for lithium motion, which predict the lithium diffusivity in this material to be around 10^{-9} – 10^{-8} cm^2/s . We also systematically investigated the effect of several cell components and electrode construction on the measured rate performance and conclude that care has to be taken to remove all other rate limitations from the cell to measure the rate performance of an electrode material.
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Developing positive electrode materials with high energy densities is one of the key challenges for lithium-ion batteries. High energy density can be obtained either by high voltage or high capacity. Several compounds have been investigated for their high voltage.^{1–3} $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is one of these, which can work with a conventional carbonate-based electrolyte though some side reaction occurs.^{4–7} With an average voltage around 4.7 V and a comparable capacity (around 140 mAh/g) to LiCoO_2 (~ 620 Wh/kg) and LiFePO_4 (~ 591 Wh/kg), $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (~ 658 Wh/kg) gives a higher specific energy than many commercialized compounds.

Previous work in the literature has distinguished between two types of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ depending on the ordering of Ni/Mn in the octahedral sites.⁸ Most investigators have shown disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ to have better rate capability and cyclability than ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, though the difference in performance between the two phases varies.^{9–11} One explanation put forward is that the disordered phase shows higher electronic conductivity than the ordered one due to the existence of Mn^{3+} in the disordered phase.^{10,11} However, Mn^{3+} is oxidized to 4+ in the beginning of charge and hence would not contribute much to electronic conductivity in most of the charge/discharge regime. Furthermore, this explanation is based on the assumption that electronic conductivity is rate-limiting instead of lithium conductivity, which has not been directly confirmed experimentally or computationally.

Creating nanoparticles, a typical strategy to achieve high rate performance has given mixed results in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. While Shaju and Bruce showed high rate capability and cyclability with 50 nm $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$,¹² some other groups did not achieve comparable rate performance on nanomaterials with a similar size.^{13,14} This indicates that particle size may not be the critical factor affecting the electrochemical performance. For micron-sized materials synthesized by a molten salt method, the ordered phase showed poor rate performance, while the disordered performed better.⁹ Patoux et al. used solid-state reactions to synthesize micron-sized $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ with high rate capability (about 80 mAh/g at 30C) and good cyclability.¹⁵ In their composition, however, 20% of the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple at 4.7 V is replaced by the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple at 4.1 V, which reduces the total energy density.

In this paper, we showed results on micron-sized ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with very high rate performance and good cyclability. First-principles calculations of the lithium diffusion barrier confirm that the intrinsic rate capability of this compound is very high even with micron-sized particles, indicating that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ can be a high rate material with a high tap density, unlike most nano-systems. The effects of the cell configuration on the rate testing are also investigated and discussed.

Materials and Methods

Synthesis of ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinels.—Ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel was prepared by a solid-state reaction from Li_2CO_3 (99.995%, Alfa Aesar), NiCO_3 (99%, Alfa Aesar), and MnO_2 (99.9%, Alfa Aesar). A stoichiometric amount of these starting materials was ballmilled for 6 h at 300 rpm with 5 mm diameter yttrium-stabilized zirconia balls. After drying, the mixture was ground and pressed into a pellet. The pellet was calcined in air at 900°C for 12 h and slowly cooled down. The product was ground and repelletized. The pellet was annealed at 700°C in air for 48 h and slowly cooled down.

XRD and SEM.—X-ray diffraction (XRD) patterns were collected using a Rigaku diffractometer equipped with $\text{Cu K}\alpha$ radiation by step scanning in the 2θ range of 10–80°. Rietveld refinement and profile matching of the powder diffraction data were performed with Fullprof using space group $P4_332$ for the ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

Scanning electron microscopy (SEM) images were collected under an accelerating voltage of 5 kV on a JEOL 6320 microscope. The powders were coated with carbon by evaporation.

Electrochemical properties.—Electrochemical cells were configured in the following way: $\text{Li}/1\text{ M LiPF}_6$ in EC:DMC = 1:1/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with carbon black (15 wt %) as conductive agent and polyethylenetetrafluoride (PTFE) (5 wt %) as binder. The electrode density is 3–4 mg/cm^2 . Two pieces of Celgard 2500, 2325, or C480 separators were used in 2016 coin cells, assembled in an argon-filled glove box, and cycled at room temperature using Maccor 4000 operating in the galvanostatic mode. To control the external pressure on the coin cell, the cell was fixed on a C-shape clamp with two stainless steel leads. The load applied on the cell could be controlled with the C-clamp and was measured by inserting a load cell (Omega Engineering Inc., LCM307-1KN) between the coin cell and the C-clamp. The relaxation of the load on the coin cell was recorded with a Keithley 2701 digital multimeter.

The capacity vs voltage was measured by potentiostatic intermittent titration (PITT) on a Solartron 1287 electrochemical interface. Steps of 10 mV were taken to fully charge and discharge the cell. The capacity was measured at each voltage step until the current was below C/100. Electric impedance spectra were collected on a Solartron 1260 impedance/gain-phase analyzer coupled to a Solartron 1287 electrochemical interface. The amplitude of the ac signal was kept at 10 mV, and the frequency ranged from 1 MHz to 10 mHz.

Computational methodology.—Energies were obtained with first principles calculations based on density functional theory (DFT). The spin-polarized generalized gradient approximation with Perdew–Wang exchange correlation, and the projector augmented-wave (PAW) method were used as implemented in Vienna ab initio simulation package (VASP).¹⁶ A plane-wave basis with a kinetic energy

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Figure 1. (Color online) XRD pattern and refinement of as-prepared ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The square root of the intensity is shown to highlight the minor peaks. The red (black) line represents the experimental (calculated) data. The residual discrepancy is shown in blue. The refinement results agree with the ordered spinel model and give $R_p = 8.76\%$, $R_{wp} = 12.8\%$, and $\chi^2 = 7.75$.

cutoff of 370 eV and a reciprocal-space k -point grid of $5 \times 5 \times 5$ were used. The $+U$ correction term in the Dudarev scheme was used with $U = 5.96$ for Ni and $U = 5.0$ for Mn.¹⁷ Structures were fully relaxed, and the nudged elastic band method was used for determining activation barriers.

Results and Discussion

Structure and morphology of the as-prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinels.—The XRD pattern of the annealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is shown in Fig. 1, with the square root of the intensity plotted to more clearly show weak peaks due to Ni/Mn ordering. Rietveld refinement gives a lattice parameter $a = 8.160$ Å, which agrees with the value reported previously for ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized in air^{8,18} but different from the value of 8.1176(2) Å reported by Pasero et al. Their sample, prepared in high oxygen pressure (120 bar),¹⁹ showed no oxygen deficiency and Ni/Mn disordering as low as 2%. As the lattice parameter increases with the presence of Mn^{3+} resulting from oxygen deficiency, it is reasonable to conclude that the ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized in air, as in this paper and in Ref. 8 and 18, has a certain amount of oxygen deficiency while retaining Ni/Mn ordering.¹⁹

The SEM of the as-prepared ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in Fig. 2 shows that the material is well crystallized with a particle size in the range of 3–5 μm.

Electrochemical tests.—**Capacity vs voltage by PITT in ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.**—Figure 3 shows capacity vs voltage measured by PITT in the as-prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The results were plotted in a manner resembling cyclic voltammograms except that the current is replaced by the capacity.²⁰ The major oxidation consists of two peaks (~ 4.73 and ~ 4.75 V), and the corresponding reduction peaks are ~ 4.71 and ~ 4.73 V. The 20 mV splitting agrees with the result obtained by Ariyoshi et al. in ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (~ 20 mV)⁸ but is much smaller than that of disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (~ 60 mV).^{9,21} The inset figure shows the additional redox couples. Below 4.7 V, there are three redox couples, $\sim 3.94/3.93$ V, $\sim 4.08/4.07$ V, and $\sim 4.40/4.33$ V, as labeled in Fig. 3. Above 4.7 V, one additional redox couple was observed at $\sim 4.90/4.88$ V. While two of these redox couples ($\sim 4.08/4.07$ V and $\sim 4.40/4.33$ V) have been reported previously in ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$,¹⁸ the other two ($\sim 3.94/3.93$ V and $\sim 4.90/4.88$ V) are found for the first time in this work. The mecha-

Figure 2. SEM of the as-prepared ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ shows an average particle size of 3–5 μm.

nisms of the additional redox couples and their possible effect on the performance of our materials are not clear at present.

Rate capability and cyclability.—The discharge rate capability is shown in Fig. 4. The C rates were calculated based on 1C = 150 mAh/g, and the charge rate was 0.5C for the high rate discharge tests and 0.2C for the 0.2C discharge. The discharge capacities are around 147, 134, and 110 mAh/g at 0.2C, 20C, and 40C, respectively. The discharge capacity at 20C decays slowly from 137 mAh/g at the 2nd cycle to 134 mAh/g at the 50th cycle (Fig. 4b), while at 40C, no obvious capacity decay was seen over 50 cycles. Coulombic efficiency was measured to be 93.1% for the first cycle upon 0.2C charge and discharge. After 50 cycles, the coulombic efficiency reaches 98.8%.

The rate capability we obtained is better than previously reported results with various synthesis methods.^{9-15,22-29} It is particularly interesting to compare with the rate capability of small particles. Shaju and Bruce synthesized ordered and disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with a particle size around 50 nm and showed high rate capability (~ 120 mAh/g at 20C and ~ 100 mAh/g at 40C for disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$; ~ 80 mAh/g at 20C and ~ 50 mAh/g at 40C for

Figure 3. (Color online) Capacity vs voltage measured upon potentiostatically charge and discharge with 10 mV steps (PITT).

Figure 4. (Color online) (a) Discharge rate performance and (b) capacity retention of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The electrode density is 3 mg/cm^2 , and the electrode contains 15 wt % carbon. Two pieces of Celgard C480 separators were used. Charge rate is 0.5C for 20C and 40C discharge and 0.2C for 0.2C discharge. Voltage window is 3–5 V.

ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.¹² The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ we synthesized shows an average particle size around 3–5 μm but better rate capability than both ordered and disordered nano- $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The fact that around 100-times larger particle shows higher rate capability strongly indicates that ion or electron transport in the particle is not the rate-limiting process at least for 40C.

The results of the rate capability in charge are shown in Fig. 5a. The discharge rate was 5C for all the cycles, and lower discharge rates did not significantly modify the subsequent charge capacity. Charge capacities for 0.2C, 1C, and 5C rates are, respectively, 149, 132, and 89 mAh/g. No significant decay was observed in 20 cycles, as shown in Fig. 5b. One major reason that the charge rate capability cannot be as high as the discharge rate capability is that the charge voltage is cut at 5 V, which is only about 0.3 V above the equilibrium voltage. Hence, polarization at a higher rate leads to a premature charge cutoff.

Effects of the cell configuration on the performance.— When testing electrode materials at a very high rate, it is important to ensure that no other components of the cell and electrode become rate-limiting. In addition, homogeneity is required in the electrode as any inhomogeneity in charging or discharging leads to higher

Figure 5. (Color online) (a) Charge rate performance and (b) capacity retention of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The electrode density is 3 mg/cm^2 , and the electrode contains 15 wt % carbon. Two pieces of Celgard 2500 separators were used. Discharge rate is 5C. Voltage window is 3–5 V.

effective rates for some fraction of the electrode and hence reduced capacities. Several aspects of the cell configuration influenced the rate performance.

The effect of the separators.— Three different separators were used for comparison. All other conditions were the same when assembling the coin cell. The rate capability and capacity retention with three different separators are compared in Fig. 6. The relevant properties of the three separators (Celgard C480, 2500, and 2325) are listed in Table I. The C480 separator gives the best performance both in rate capability and in cyclability. While C480 is the thinnest separator, the thickness difference does not seem large enough to explain the performance variation based solely on diffusion length through the separator. This is supported by the comparison of performances between Celgard 2325 and 2500, which have the same thickness but different porosities and pore sizes.

The effect of external pressure on the coin cell.— When external pressure was applied to the coin cell by squeezing the C-clamp, the load initially decayed but stabilized after some time. The relaxation is likely due to the creep of the lithium foil, separator, and binder in the positive electrode, etc.³⁰ Figure 7a shows a typical load relaxation profile when external pressure was applied. The same coin cell was pressed two times. After each pressing, the pressure during

Figure 6. (Color online) Performance comparison for three different Celgard separators. Two pieces of each type of separator were used. Charge rate is 0.5C for 20C and 40C discharge and 0.2C for 0.2C discharge. Voltage window is 3–5 V.

relaxation was recorded and the electric impedance was measured. Figure 7b shows that pressing significantly decreases the resistance that results in the semicircle in the impedance plot.

The rate capabilities under two external pressures are compared in Fig. 8. The cell, which was pressed up to about 80 psi and relaxed for 1 h, shows low rate capability (100 mAh/g at 20C and 60 mAh/g at 40C). Another cell, which was pressed up to about 240 psi and relaxed for 1 h, shows much higher rate capability (130 mAh/g at 20C and 100 mAh/g at 40C). The discharge overpotential also decreased significantly with higher pressure, which agrees with the decrease in impedance.

Gaberscek et al. pointed out that the high frequency impedance semicircle is due to the contact impedance between the current collector and the electrode.³¹ The external mechanical load improves this interface contact and improves the rate capability of the cell. Possibly, pressure on the cell also improves the Li-ion transport in electrolyte. Johns et al. showed that Li-ion transport in an electrolyte especially through the composite electrode can be rate-limiting at high rates.³² Possibly, pressure increases the penetration and wetting of the electrolyte in the composite cathode.

The effect of the carbon content in the electrode.—To investigate the effect the amount of carbon in the electrode has on the rate performance, electrodes with a 30 wt % active material, 65 wt % carbon, and a 5 wt % binder were prepared. The discharge capability of this cell, charged at 5C and discharged at various rates, is shown in Fig. 9. After 151 cycles, the discharge capacity reaches 107 mAh/g at 83C. After 202 cycles, the discharge capacity reaches 78 mAh/g at 167C. These increases in rate capability observed when diluting the active mass with more carbon are similar to what has

Figure 7. (Color online) The relaxation of external load applied on the coin cell with two sequential pressings is shown in (a). Three electric impedance spectra collected during the external load relaxation are compared in (b). Two pieces of Celgard 2325 separators were used.

been observed in LiFePO_4 ³³ and point to the electrode morphology being rate-limiting for very fast electrode materials.

First-principles calculation of lithium diffusivity in ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.—The diffusion path of Li in spinels is believed to be a three-dimensional network.^{34,35} Lithium moves from one tetrahedral site to the next by migration through a vacant octahedral site.²¹ While in a spinel such as LiMn_2O_4 , all vacant octahedral sites and the lithium migration paths are equivalent; ordering in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ creates a distinct Ni site in 4b(5/8,5/8,5/8) and a Mn site in the 12d(1/8,3/8,−1/8) position of the $P4_332$ space group.⁸ Similarly, the vacant octahedral sites are divided into 4a(1/8,1/8,1/8) and 12d(1/8,5/8,−3/8) sites. The 4a site is surrounded by three Ni and three Mn atoms, and the 12d(1/8,3/8,−1/8) site is surrounded by one Ni and five Mn atoms. Migration of lithium between tetrahedral sites occurs through intermediate vacant octahedral sites. Because

Table I. The related properties of three different Celgard separators.

Celgard separator comparison				
Type	Layers	Thickness (μm)	Porosity (%)	Pore size (μm)
C480	PP/PE/PP	21.5	50	0.038
2500	PP	25	55	0.064
2325	PP/PE/PP	25	39	0.028

Figure 8. (Color online) (a) Rate and (b) cyclability performance for different pressures loaded on the coin cell. Two pieces of 2325 separators were used. Cells were relaxed for 1 h after application of pressure.

Figure 9. (Color online) (a) Rate and (b) cyclability performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with 65 wt % carbon. Charge rate is 5C. Voltage window is 3–5 V.

each tetrahedral site is surrounded by one 4a and three 12d(1/8,3/8, -1/8) sites, two distinct lithium diffusion paths exist, as shown in Fig. 10.

The energy along both paths was calculated in supercells containing eight formula units ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a formula unit). The periodic images of the migrating lithium are approximately 8.32 Å apart. Activation barriers are determined in the dilute Li limit ($x \approx 0$) by including one Li in an otherwise delithiated cell with eight formula units and in the dilute vacancy limit ($x \approx 1$) with seven Li and one vacancy site in the cell. All lattice parameters are fixed at $x = 0$ or $x = 1$ values for the activation barrier calculations, and all internal degrees of freedom are relaxed.³⁶

Figure 11 shows the energy along the distinct migration paths in lithium-rich and vacancy-rich phases. Only the energy from the tetrahedral site to the octahedral site is plotted as the other half of the path from the octahedral site to the tetrahedral site is symmetrically equivalent. In path I, the octahedral site surrounded by three Ni and three Mn atoms is effectively the activated state with a barrier of about 416 meV in the lithium-rich phase and 536 meV in the vacancy-rich phase. In path II, the activated state is either the octahedral site (in the Li-rich phase) or the crossing through the joint oxygen triangle between the tetrahedral and octahedral sites (in the vacancy-rich phase). For this path, the activation barriers are lower

(about 351 meV in the lithium-rich phase and 305 meV in the vacancy-rich phase). The activation barrier is higher in the lithium-rich phase than in the vacancy-rich phase for path I, while the opposite is the case for path II. The electrostatic potential plays a critical role in determining the activation barrier.³⁷ In the vacancy-rich phase, less electrostatic repulsion from other Li^+ is expected to lower the barrier. Meanwhile, the change in the valence state of the nearest transition metal(s) would also influence the electrostatic repulsion.³⁸ In path II, one Ni atom changes from 2+ to 4+ upon delithiation, which would increase repulsion with the diffusing Li^+ . The results in Fig. 11b indicate that the effect of valence increase from Ni is smaller than that from Li^+ interaction, and the total barrier becomes lower upon delithiation. This is similar to what happens in Li_xFePO_4 upon delithiation³⁶ but is opposite to what happens in Li_xCoO_2 .³⁹ In path I, however, three Ni atoms change from 2+ to 4+, which increases the electrostatic repulsion more than the effect of the Li vacancies. Hence, the total barrier along this path increases upon delithiation.

The activation barriers in path II are significantly lower than those in path I both in the lithium-rich phase and the vacancy-rich phase. Because path II percolates the structure, lithium does not need to migrate through the high barrier path I. Consequently, we

Figure 10. (Color online) Schematic figure of two distinct paths for lithium migration in ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Green balls denote Li ions, and red balls denote oxygen ions. Li diffusion path I is indicated by blue arrows, and the blue ball is the 4a site in the middle of path I. Dark scarlet arrows show the Li diffusion path II with dark scarlet balls at 12d sites in the middle of path II.

Figure 11. (Color online) Calculated energy along the lithium migration paths in ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. (a) Path I defined by three Ni and three Mn around the active state; (b) path II defined by one Ni and five Mn around the active state.

use the activation energy along path II to evaluate the lithium diffusivity of this material. With a simple dilute diffusion model

$$D = a^2 \nu \exp(-E_{\text{act}}/k_B T) \quad [1]$$

where a is the lithium hopping distance, ν is the attempt frequency, and E_{act} is the activation barrier. With hopping distance $a = 3.46 \text{ \AA}$ in diffusion path II and $\nu = 10^{12} \text{ Hz}$ (typical range of phonon frequencies), the diffusivities are calculated to be $1.41 \times 10^{-9} \text{ cm}^2/\text{s}$ in the lithium-rich phase and $8.25 \times 10^{-9} \text{ cm}^2/\text{s}$ in the vacancy-rich phase.³⁶ Using the simple estimate $L^2 = Dt$ for the diffusion length, Li can migrate $\approx 3 \text{ }\mu\text{m}$ in 10 s. Our experimental results show that more than half of the theoretical capacity was obtained at a discharge rate of 167C (corresponding to 22 s) with a particle size in the range of 3–5 μm . Hence, both experiment and calculation agree and confirm the high rate capability of this material.

Our results with high loading density and 15 wt % carbon also indicate again that the intrinsic rate capability of active materials can only be measured with a highly optimized cell; as for fast materials, tested under high rates, the Li transport in the electrolyte and the composite electrode is typically rate-limiting.³² Only when the active mass is sufficiently diluted and other kinetic limitations are resolved can one observe the intrinsic rate limits of the material.

Conclusion

Ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel was prepared by a solid-state reaction. Though the particle size is several microns, this material shows high rate capability and excellent cyclability. The high rate capability observed agrees with our first-principles calculations, which show a low migration barrier for Li. Both experiment and calculation suggest that micron-sized ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ can be a high rate electrode material with an excellent density.

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