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

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

<table>
<thead>
<tr>
<th>Citation</th>
<th>Ma, Xiaohua, Byoungwoo Kang, and Gerbrand Ceder. &quot;High Rate Micron-Sized Ordered LiNi$<em>{0.5}$Mn$</em>{1.5}$O$_4$.&quot; Journal of The Electrochemical Society 157, no. 8 (2010): A925. © 2010 ECS - The Electrochemical Society.</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Published</td>
<td><a href="http://dx.doi.org/10.1149/1.3439678">http://dx.doi.org/10.1149/1.3439678</a></td>
</tr>
<tr>
<td>Publisher</td>
<td>Electrochemical Society</td>
</tr>
<tr>
<td>Version</td>
<td>Final published version</td>
</tr>
<tr>
<td>Accessed</td>
<td>Thu Jan 03 03:47:17 EST 2019</td>
</tr>
<tr>
<td>Citable Link</td>
<td><a href="http://hdl.handle.net/1721.1/82611">http://hdl.handle.net/1721.1/82611</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>Article is made available in accordance with the publisher's policy and may be subject to US copyright law. Please refer to the publisher's site for terms of use.</td>
</tr>
<tr>
<td>Detailed Terms</td>
<td></td>
</tr>
</tbody>
</table>
High Rate Micron-Sized Ordered LiNi$_{0.5}$Mn$_{1.5}$O$_4$

Xiaohua Ma, Byoungwoo Kang, and Gerbrand Ceder

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

Ordered LiNi$_{0.5}$Mn$_{1.5}$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 $\sim$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 $10^{-8}$–$10^{-9}$ 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.

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 LiNi$_{0.5}$Mn$_{1.5}$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$_2$ ($\sim$620 Wh/kg) and LiFePO$_4$ ($\sim$591 Wh/kg), LiNi$_{0.5}$Mn$_{1.5}$O$_4$ ($\sim$658 Wh/kg) gives a higher specific energy than many commercialized compounds.

Previous work in the literature has distinguished between two types of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ depending on the ordering of Ni/Mn in the octahedral sites.8 Most investigators have shown disordered LiNi$_{0.5}$Mn$_{1.5}$O$_4$ to have better rate capability and cyclability than ordered LiNi$_{0.5}$Mn$_{1.5}$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 LiNi$_{0.5}$Mn$_{1.5}$O$_4$. While Shaju and Bruce showed high rate capability and cyclability with 50 nm LiNi$_{0.5}$Mn$_{1.5}$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 LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with high rate capability (about 80 mAh/g at 30C) and good cyclability.15 In their composition, however, 20% of the Ni$^{2+}$/Ni$^{4+}$ redox couple at 4.7 V is replaced by the Mn$^{3+}$/Mn$^{4+}$ redox couple at 4.1 V, which reduces the total energy density.

In this paper, we showed results on micron-sized ordered LiNi$_{0.5}$Mn$_{1.5}$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 LiNi$_{0.5}$Mn$_{1.5}$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 LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinels.— Ordered LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel was prepared by a solid-state reaction from Li$_2$CO$_3$ (99.95%, 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 Cu Kα radiation by step scanning in the 20 range of 10–80°. Rietveld refinement and profile matching of the powder diffraction data were performed with Fullprof using space group P4$_3$32 for the ordered LiNi$_{0.5}$Mn$_{1.5}$O$_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: Li/1 M LiPF$_6$ in EC/DMC = 1:1/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with carbon black (15 wt %) as conductive agent and polyethylene tetrafluoride (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
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. 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 LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinels.—The XRD pattern of the annealed LiNi$_{0.5}$Mn$_{1.5}$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 LiNi$_{0.5}$Mn$_{1.5}$O$_4$ synthesized in air, as in this paper and in Ref. 8,18 but different from the value of 8.1176 Å reported by Pasera 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 LiNi$_{0.5}$Mn$_{1.5}$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.10

The SEM of the as-prepared ordered LiNi$_{0.5}$Mn$_{1.5}$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 LiNi$_{0.5}$Mn$_{1.5}$O$_4$.—Figure 3 shows capacity vs voltage measured by PITT in the as-prepared LiNi$_{0.5}$Mn$_{1.5}$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 ($\approx -4.73$ and $\approx -4.75$ V), and the corresponding reduction peaks are $\approx -4.71$ and $\approx -4.73$ V. The 20 mV splitting agrees with the result obtained by Ariyoshi et al. in ordered LiNi$_{0.5}$Mn$_{1.5}$O$_4$ ($\approx -20$ mV).5 but is much smaller than that of disordered LiNi$_{0.5}$Mn$_{1.5}$O$_4$ ($\approx -60$ mV).9,21 The inset figure shows the additional redox couples. Below 4.7 V, there are three redox couples, $\approx -3.94/3.93$ V, $\approx -4.08/4.07$ V, and $\approx -4.40/4.33$ V, as labeled in Fig. 3. Above 4.7 V, one additional redox couple was observed at $\approx -4.90/4.88$ V. While two of these redox couples ($\approx -4.08/4.07$ V and $\approx -4.40/4.33$ V) have been reported previously in ordered LiNi$_{0.5}$Mn$_{1.5}$O$_4$,18 the other two ($\approx -3.94/3.93$ V and $\approx -4.90/4.88$ V) are found for the first time in this work. The mechanisms 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 mA/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 mA/h/g at 0.2C, 20C, and 40C, respectively. The discharge capacity at 20C decays slowly from 137 mA/h/g at the 2nd cycle to 134 mA/h/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.9,12,22-29 It is particularly interesting to compare with the rate capability of small particles. Shaju and Bruce synthesized ordered and disordered LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with a particle size around 50 nm and showed high rate capability ($\approx 120$ mA/h/g at 20C and $\approx 100$ mA/h/g at 40C) for disordered LiNi$_{0.5}$Mn$_{1.5}$O$_4$; $\approx 80$ mA/h/g at 20C and $\approx 50$ mA/h/g at 40C for
ordered LiNi$_{0.5}$Mn$_{1.5}$O$_4$. The LiNi$_{0.5}$Mn$_{1.5}$O$_4$ we synthesized shows an average particle size around 3–5 μm but better rate capability than both ordered and disordered nano-LiNi$_{0.5}$Mn$_{1.5}$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 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. 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
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. 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. 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 been observed in LiFePO4 and point to the electrode morphology being rate-limiting for very fast electrode materials.

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

<table>
<thead>
<tr>
<th>Celgard separator comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>C480</td>
</tr>
<tr>
<td>2500</td>
</tr>
<tr>
<td>2325</td>
</tr>
</tbody>
</table>

**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.

**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.
each tetrahedral site is surrounded by one 4a and three 12d/H2O849
sites, two distinct lithium diffusion paths exist, as shown in
Fig. 10. The energy along both paths was calculated in supercells con-
taining eight formula units/LiNi0.5Mn1.5O4 as a formula unit/H2O849
LiNi0.5Mn1.5O4. The periodic images of the migrating lithium are approximately 8.32 Å
apart. Activation barriers are determined in the dilute Li limit
x
0
by including one Li in an otherwise delithiated cell with eight
formula units and in the dilute vacancy limit
x
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 tet-
rahedral 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 octa-
hedral 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 op-
posite 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 bar-
rier becomes lower upon delithiation. This is similar to what hap-
gets in LiFePO4 upon delithiation 36 but is opposite to what hap-
ens in Li2CoO2. 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

---

(a) 

(b) 

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

(a) 

(b) 

Figure 9. (Color online) (a) Rate and (b) cyclability performance of
LiNi0.5Mn1.5O4 with 65 wt % carbon. Charge rate is 5C. Voltage window is
3–5 V.
use the activation energy along path II to evaluate the lithium diffusivity of this material. With a simple dilute diffusion model

$$D = \alpha^2 \nu \exp(-E_{\text{act}} / k_B T)$$

where \(\alpha\) is the lithium hopping distance, \(\nu\) is the attempt frequency, and \(E_{\text{act}}\) is the activation barrier. With hopping distance \(a = 3.46\) Å in diffusion path II and \(\nu = 10^{12}\) Hz (typical range of phonon frequencies), the diffusivities are calculated to be \(1.41 \times 10^{-6}\) cm²/s in the vacancy-rich phase and \(8.25 \times 10^{-7}\) cm²/s in the vacancy-rich phase.\(^{96}\) Using the simple estimate \(L^2 = D t\) for the diffusion length, Li can migrate \(\approx 3 \mu m\) in 1 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 \(\mu m\). 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 LiNi_{0.5}Mn_{1.5}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 LiNi_{0.5}Mn_{1.5}O_{4} can be a high rate electrode material with an excellent density.

Acknowledgment

This work was supported by the MRSEC program of the National Science Foundation under grant no. DMR-0819762 and by the Batteries for Advanced Transportation Technology (BATT) program under contract no. 6806960.

Massachusetts Institute of Technology assisted in meeting the publication costs of this article.

References