NaMn$_{2-x}$Ni$_x$O$_4$ Derived from Mesoporous LiMn$_{2-x}$Ni$_x$O$_4$: High-Voltage Spinel Cathode Materials for Na-Ion Batteries

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Sodium ion batteries are a topic of emerging interest, as the low cost and high natural abundance of sodium precursors provide a specific advantage over commercial lithium ion batteries. Comparatively, sodium-ion batteries suffer from lower operating voltages, making the development of suitable high voltage positive electrodes key to enabling sodium chemistry capable of direct replacement for modern lithium ion storage devices. Herein, we investigate disordered nickel doped manganese spinels (Na$_{1-x}$Mn$_{2}$Ni$_x$O$_4$) as a positive electrode for sodium ion battery applications. Due to the kinetic limitations of the sodium deinsertion reaction into Na$_{1-x}$Mn$_{2}$Ni$_x$O$_4$ the effect of both temperature and the electrochemical cycling window are studied revealing a unique reaction pathway and potential optimization routes for further study.

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Increasing interest in large-scale electrochemical energy storage for grid applications has prompted the investigation of battery chemistries that are more cost-effective as compared to commercial Li-ion technology. Due to the large abundance and associated low costs of sodium precursors, sodium-ion batteries have been widely investigated over recent years. Investigations into positive electrodes for sodium ion batteries (SIBs) have produced a number of different electrode chemistries capable of reversible Na$^+$ deinsertion. In particular, the manganese oxides have demonstrated a number of possible host structures suitable for reversible cycling of Na$^+$, with the majority of attention being generally confined to layered compounds consisting of transition metal doped P2, P3, and O3 type structures. However, there still remain certain drawbacks in utilizing such SIBs for commercial applications, as reversible Na$^+$ deinsertion requires large open structures due to the physically larger ionic radii of Na$^+$ (~1.0 Å) relative to that of Li$^+$ (0.59 Å). Of particular concern is the lower voltage of SIBs using traditional chemistries imparted by the Na/Na$^+$ redox, which is approximately 0.33 V higher than that of Li/Li$^+$. Table I considers a competitive analysis of various cathode chemistries of potential interest for SIBs, and although suffering from a reduction in gravimetric and volumetric capacity when comparing against LIBs, movement from lithium to sodium chemistries offers considerable advantages in terms of cost and raw material abundance making them far more practical for electrical grid applications.

Due to the large foundation of research on lithium-ion cathode materials, it is desirable to potentially utilize such promising structures for analogous cathodes in SIBs. The spinel structure has been widely studied, and offers facile Li$^+$ deinsertion by nature of the 3D interdiffusional pathways. However, the large ionic size differences between Li$^+$ and Na$^+$ have demonstrated considerable difficulty in the implementation of sodium analogues to existing Li-based compositions; yet the spinel structure has proven to successfully accommodate Na$^+$ following initial delithiation onto the vacant tetrahedral sites, further expanding the scope of feasible host structures for SIBs.

Earlier investigations into the delithiated spinel (λ-MnO$_2$) structure have demonstrated limited utility in a sodium ion cell due structural destabilization with extended cycling beyond the first few cycles, consistent with results obtained from first principle studies. Additional work on λ-MnO$_2$ in aqueous sodium cells has shown that for large format devices show further cost advantages over conventional energy storage solutions; however, they are ultimately restricted by the limited electrochemical stability window of the aqueous electrolyte. Nevertheless, the spinel structure offers a very stable and robust framework uniquely capable of accommodating Na$^+$ onto the vacant tetrahedral sites. Our recent work into the investigation of Na$^+$ insertion into the high voltage spinel λ-Mn$_{1.4}$Ni$_0.6$O$_2$ (λ-MNO) has exhibited full theoretical capacity and retention of the spinel structure during the first discharge reaction, and has identified nickel-doped manganese spinels as a potential cathode material for SIBs. The Na$^+$ insertion into λ-MNO has shown that the initial Na$^+$ insertion reaction takes place by a combined two-phase/single-phase reaction as characterized by operando XRD. Utilization of the nickel-doped λ-MNO in this case has both increased the operating voltage and improved the structural stability over the pure manganese spinel. The question then becomes whether or not reversible Na$^+$ deinsertion is possible within the spinel framework, and if appreciable capacity can be maintained over a substantial lifetime.

λ-MNO may prove to be advantageous over conventional layered compounds, as the MnO$_6$ octahedral network form a robust octahedral network capable of alkali ion insertion with minimal phase transformations. However, both the structural stability and cycle efficiencies are of key importance in order to realize the full potential of λ-MNO as a sodium positive electrode. Herein, the λ-MNO structure is further evaluated as a potential positive electrode for SIBs; while the initial insertion mechanism is understood, the governing principle(s) behind reversible Na$^+$ deinsertion are investigated by structural and electrochemical techniques.

Experimental

Pure lithium spinel powders were prepared with compositions of LiMn$_{1.56}$Ni$_{0.44}$O$_4$ and LiMn$_{1.5}$Ni$_{0.5}$O$_4$ for the disordered and ordered spinels (Fd-3m and P4,32, respectively), FTIR analysis and X-ray diffraction (XRD) analysis were utilized to verify the characteristic vibrational modes, phase purity and lattice parameter of the lithium spinel samples. With respect to XRD, lattice parameters were calculated utilizing an internal silicon reference using a Bruker D8 Advance diffractometer (Cu Kα, λ = 1.5406 Å). FTIR analysis was performed using a ThermoScientific Nicolet 6700 spectrometer, and multipoint Brunauer-Emmett-Teller (BET) measurements were made using N$_2$ adsorption in a micrometrics ASAP 2020 system.

Free standing positive electrodes were made by a plastic electrode casting technique with 69.8% active material, 3.8% conductive carbon (SP, MMM) and 6% poly(vinylidene fluoride-co-hexafluoropropylene) (Kynar 2801, Elf Atochem) binder along with 20% propylene carbonate (PC) plasticizer under dry atmosphere. Positive electrodes were punched into disks, extracted (by treatment with diethyl ether) and dried under vacuum at 120 °C before being.
Results

Disordered (Fd-3m) and ordered (P4$_3$32) lithium spinel electrodes were characterized both electrochemically and by powder X-ray diffraction (XRD). Respective lattice parameters of 8.166 Å and 8.160 Å for the disordered and ordered spinels were obtained using an internal silicon standard, and are in good agreement with those previously reported. BET surface areas of the disordered and ordered spinels were 5.7 m$^2$/g and 4.6 m$^2$/g respectively. Within the following sections λ-MNO derived from disordered (Fd-3m) and ordered (P4$_3$32) lithium spinels and their corresponding sodiated analogues (Na$_x$-MNO) are abbreviated as F$_x$-MNO, P$_x$-MNO, FNa$_x$-MNO and PNa$_x$-MNO respectively.

In order to assist the reader through the progression of this work, Figure 1 is provided, broadly summarizing the mechanistic pathways for the ordered (P4$_3$32) and disordered (Fd-3m) spinels as a result of the physical and electrochemical characterization techniques mentioned throughout this manuscript. Within Figure 1, segments marked by bold arrows indicate a two-phase reaction (between two (F/P)Na$_x$-MNO spinel compositions) and those shown as thin arrows mark a Na$^+$ deinsertion by a solid-solution mechanism. Dashed segments correlate to data collected following an extended open circuit period at full discharge for (F/P)Na$_x$-MNO.

The initial Na$^+$ insertion of FNa$_{0.88}$MNO takes place by a two-phase reaction (F$_3$-MNO $\rightarrow$ FNa$_{0.88}$MNO) followed by Na$^+$ insertion by a single-phase reaction (0.88 < x < 1.0) in FNa$_x$-MNO) saturating the remaining 8a tetrahedral sites as discussed in a previous work. Recovery of the original F$_x$-MNO structure is only realized when activating a kinetically sluggish two-phase reaction that occurs beyond 4.25 V, after which, the following discharge then proceeds in the same manner as the original Na$^+$ insertion. These kinetic limitations prevent complete desodiation of the FNa$_x$-MNO structure, thereby largely limiting discharge capacities of successive cycles to a narrow Na$^+$ deinsertion range of ca. 0.55 < x < 1.0. When incomplete desodiation has taken place, an alternative pathway is identified during the following sodiation. This alternative reaction pathway (downward arrow from 4.25 V in Figure 1) is purely single-phase in nature, as inserted Na$^+$ act to prop open the spinel structure, facilitating a relatively fast solid-solution type behavior.

The ordered PNa$_x$-MNO spinel follows a similar trend in which the final reformation of the P$_x$-MNO structure is dependent on an additional two-phase reaction occurring beyond 4.25 V. Additional two-phase reactions are also observed below 4.25 V indicating a difference in the reaction pathway between ordered and disordered spinels during Na$^+$ deinsertion.

As will be discussed, FNa$_x$-MNO begins to

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Table I. Competitive analysis of select cathode compositions.

| Cathode Material | Ah/kg | Wh/kg | Ah/L | Wh/L |
|------------------|-------|-------|------|------|
| LiMn$_{0.56}$Ni$_{0.44}$O$_4$ | 146.8 | 690.3 (4.7 V) | 667.5 | 3137.2 (4.7 V) |
| NaMn$_{0.56}$Ni$_{0.44}$O$_4$ | 135.0 | 486.0 (3.6 V) | 600.5 | 2161.8 (3.6 V) |
| NaFe$_3$ | 197.3 | 493.2 (2.5 V) | 745.3 | 1863.3 (2.5 V) |
| O3-NaCoO$_2$ (Δx = 1.0) | 295.0 | 678.6 (2.3 V) | 748.5 | 1721.5 (2.3 V) |
| O3-NaV$_2$O$_4$ (Δx = 0.5) | 147.5 | 339.3 (2.3 V) | 374.2 | 860.7 (2.3 V) |
| O3-NaCoO$_2$ (Δx = 1.0) | 235.2 | 646.8 (2.75 V) | 1175.5 | 3232.7 (2.75 V) |
| O3-NaCo$_{0.5}$V$_{0.5}$O$_2$ | 116.7 | 323.4 (2.75 V) | 587.7 | 1616.3 (2.75 V) |
| P2-Na$_{0.66}$MnO$_2$ | 140.0 | 480.0 (3.0 V) | 433.6 | 1300.8 (3.0 V) |
| P2-Na$_{0.66}$Mn$_{0.5}$Fe$_{0.5}$O$_2$ | 190.0 | 522.5 (2.75 V) | 515.6 | 1418.0 (2.75 V) |

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Figure 1. Schematic reaction pathway of dis/ordered sodium spinel cathodes constructed from a compilation of ex-situ/operando X-ray diffraction, and potentiostatic intermittent titration technique (PITT) data. Bold segments indicate two-phase regions, and thin arrows indicate single-phase deinsertion mechanisms. Dashed arrows imply an additional 10 hour open circuit voltage (OCV) period imparted at the end of the first discharge. Schematic not drawn to scale.
follow a very similar trend when relaxing at open circuit in the fully discharged state, suggesting additional kinetic considerations.

Here, it is convenient to expand on the electrochemical differences between the lithium and sodium spinels; in particular, the observed reaction voltages that will be discussed in the following sections, and validation of the site occupancy for Li/Na. Regarding the latter, validation of the Na⁺ occupancy on the 8a tetrahedral sites may be validated by XRD analysis, in which the increased intensity of the (220) spinel reflection gives a definitive picture as to the tetrahedral site idated by XRD analysis, in which the increased intensity of the (220) spinel reflection gives a definitive picture as to the tetrahedral site

occupancy relative to both the vacant λ-phase, and lithium spinel(s). Such analysis is provided in an earlier work, which when combined with the observed charge/discharge capacities, becomes clear that migration of either Mn/Ni onto the 8a sites is not feasible. Of particular interest is the significant difference in redox voltage observed for the Na⁺ de/insertion reaction, which deviates from the expected 0.3 V difference in standard redox potentials between Li/Li⁺ and Na/Na⁺. It is evident that added energetic penalties/barriers exist when incorporating Na into the 8a sites, as the specific lattice site energies and steric considerations are considerably different between Li⁺ and Na⁺, contributing to a significant deviation in voltage. The following sections hereby consider the specific challenges that arise when extracting Na⁺ from the 8a tetrahedral sites, and the various reaction mechanism(s) at play.

**Reaction mechanisms of FNaₓ-MNO by high-resolution electrochemistry.** Potentiostatic intermittent titration technique (PITT) was utilized as a low rate, near equilibrium electrochemical technique to identify the Na⁺ de/insertion reaction mechanisms. Figure 2 shows the PITT data of Fₓ-MNO during the first two discharge/charge (2.0–4.25 V) cycles (Figure 2a and Figure 2b respectively) and a following high-voltage (4.5–2.0 V) charge/discharge cycle (Figure 2c).

During the first discharge, a non-Cottrellian current response is observed across a range of 10 mV steps (3.65–3.60 V) indicating a multi-phasic reaction taking place during the initial Na⁺ insertion reaction (Fₓ-MNO → FNa₀.₈₇MNO) followed by Na⁺ insertion via a solid-solution mechanism to a final composition FNa₁.₀MNO; consistent with our previous work. The following deinsertion reaction to 4.25 V is characteristically single-phase, as seen by the current response. Although the rate of the PITT protocol is extremely low, the deinsertion reaction reaches an upper charge limit, reaching only 82% charge capacity with the remaining 18% of tetrahedral sites occupied by Na⁺ (Na₀.₁₈MNO). The limited extent of the charge reaction provides a direct explanation for the large drop in observed discharge capacities beyond the initial discharge, and due to the extremely slow-rate afforded by the PITT protocol, it is likely that additional energetic barriers are preventing the complete desodiation reaction.

During the second cycle (Figure 2b) a small multi-phasic reaction is initially observed during discharge, otherwise proceeding by a sluggish single-phase insertion mechanism. Across the 3 PITT cycles, discharge capacities show gradual degradation, presumably due to the concerns with electrolyte stability and the prolonged exposure at high voltage during PITT cycling. Similar to the first cycle, the extent of desodiation for Figure 2b reaches the same upper limit as in the previous cycle, providing confidence that additional energy barrier(s) is/are preventing further desodiation. The following discharge taking place between Figure 2b and Figure 2c (not shown) no longer demonstrates any multiphasic characteristics, showing a purely single-phase insertion mechanism occurring throughout the entire potential range. It is therefore assumed that Na⁺ de/insertion within FNaₓ-MNO occurs primarily by a single-phase reaction mechanism within 2.0–4.25 V under the quasi equilibrium conditions imparted by the PITT protocol.

Figure 2c considers the effects of increasing the potential cutoff to 4.5 V during the PITT protocol. Charging to 4.5 V induces additional two-phase reactions that can be observed both during charge and discharge. The reformed two-phase reaction during discharge is remarkably similar to the two-phase reaction seen during the initial sodiation of the Fₓ-MNO; indicating that the previous charge was successful in extracting a significant amount of the entrapped Na⁺. Two non-Cottrellian regions are seen in Figure 2c: (1) during charge at 4.37 V and (2) during the subsequent discharge at 3.65 V. It should
be noted that due to the extent of desodiation, which extends to negative “Nax” values, there is also a significant amount of electrolyte decomposition that is evident. While the observed reaction at high-voltage may be due to reaction(s) occurring within the electrolyte, the re-established non-Cottrellian region at 3.6 V during the subsequent discharge is a good indication that the observed reaction at 4.37 V during desodiation is related to reformation of the original P-T-MNO structure. In other words, the high-voltage charge was successful in extracting the majority of the 18% of entrapped Na+, and the two-phase reaction seen at 3.65 V describes a similar reaction as seen during the first cycle.

In addition to the high-voltage PITT data shown in Figure 2c, cells subjected to the same PITT protocol using additional electrolytes demonstrated similar characteristics. This was performed to see if any improvements in the anodic electrolyte decomposition component of the high voltage reaction could be enabled. While the alternative electrolytes demonstrated significant electrolyte decomposition, cells exhibited a single large two-phase re-sodiation region following the 4.5 V charge segment. This finding gives further confidence that the high-voltage non-Cottrellian current response observed in Figure 2c is not simply a side reaction associated with the composition of the electrolyte. This conclusion will be further supported by XRD results presented later in this manuscript.

Of the electrolyte compositions investigated, none afforded an appreciable improvement in the anodic oxidation of the electrolytes over the 1 M NaClO4-PC:FEC (2 vol %) composition used herein. In summary, the PITT results indicate that full desodiation of the spinel structure is limited by the need to initiate an additional two-phase reaction to yield the P-T-MNO phase. Initiation of the two-phase desodiation reaction is only apparent above 4.3 V under near equilibrium PITT conditions, motivating elevated temperature/voltage-cutoff studies throughout the following sections.

Reaction mechanisms of PNa x-MNO by high-resolution electrochemistry.—P-T-MNO was cycled under similar PITT conditions in order to probe the reaction mechanism(s) under quasi-equilibrium conditions. Figure 3 provides the first two PITT discharge/charge cycles of P-T-MNO vs. Na/Na+ at 24°C between 2.5–4.45 V. P-T-MNO progresses initially by a two-phase Na+ insertion reaction onto the 8a tetrahedral sites across a voltage range of 3.69–3.62 V, similar to the disordered spinel discussed above. Despite the slower rate afforded by the PITT conditions, initial discharge capacity only realizes ca. 81% theoretical capacity (123.6 mAh/g), implying that a considerable amount of residual P-T-MNO remains in the following cycle. As will be discussed, residual P-T-MNO plays a significant role during initial cycling, and introduces significant differences in rate capability between the two spinels.

Following the first discharge (Figure 3a), the voltage profile during the charge reaction closely resembles that of a two-phase reaction, with a very flat profile and prolonged duration at individual 10mV steps. However, only a single non-Cottrellian region is observed at 3.86 V, indicating a minor multi-phasic reaction. This reaction proceeds to completion relatively quickly, (compared to the initial discharge reaction) and the remaining voltage steps reveal relatively slow solid-solution deinsertion behavior. A distinct voltage plateau can be seen at 4.44 V during charge (2) of Figure 3a), which also displays a non-Cottrellian current response. Additional operando data (provided in later sections) further supports the formation of a two-phase reaction within this 0.1 > Nax > 0.05 compositional range during desodiation, implying an additional phase transformation taking place at high-voltage.

The second discharge (Figure 3b) demonstrates a large single non-Cottrellian response at 3.75 V, and although occurring at a higher voltage than the initial discharge reaction, it is attributed to the reformation of the initial discharge reaction (P-T-MNO → PNa0.95MNO) (as shown later by operando XRD) as additional PITT cycling of P-T-MNO within 2.0–4.25 V does not demonstrate the same two-phase behavior beyond the initial discharge. The reformation of a non-Cottrellian response following the high-voltage cutoff is believed to imply that a significant amount of Na+ has been removed from the spinel structure, enabling the second cycle to follow a similar reaction pathway as the initial discharge, with additional support provided in the later sections. The continued presence of a non-Cottrellian

Figure 3. Potentiostatic intermittent titration technique of P4332 Nax-MNO vs. Na cell during the first (a) and second (b) cycles. Cell was cycled at 24°C with 10 mV potential steps and a 0.25 mA/g current cutoff between 2.0–4.25 V and 2.0–4.5 V respectively.
Figure 4. Scaled intensity plot (a) and corresponding voltage profile (c) of in-operando XRD FNa\textsubscript{x}-MNO within the first two cycles. Add voltage range. Scaled intensity plot (b) and voltage profile (d) of high voltage charge/discharge cycle following relaxation at full discharge. Add voltage range Bragg peaks are labeled at the top of (a-b) with asterisks marking aluminum and beryllium diffraction peaks from the in-situ cell. Dashed lines are added to regions pertaining to a single-phase reaction, and solid lines are oriented toward the product of the two-phase reaction. Lines M1 through M5 serve as guidelines with respect to the voltage profile. M3 and M5 indicate the onset of a two-phase reaction.

response throughout the second charge (3.87 and 3.88 V) is in agreement with observations made during the first cycle, likely indicating a ‘small’, yet reversible, two-phase reaction interrupting an overall single-phase deinsertion mechanism.

Na\textsuperscript{+} deinsertion mechanisms of FNa\textsubscript{x}-MNO by operando X-ray diffraction.—To further validate the reactions seen in the previous PITT results, operando XRD was utilized during galvanostatic cycling (3mA/g). Similar studies on P\textsubscript{x}-MNO/PNa\textsubscript{x}-MNO were also conducted, and are summarized in the following sections. XRD measurements were taken on a continuous basis such that the change in composition (Na\textsubscript{x}) throughout each scan was less than 3%, presumably introducing negligible effects on the diffraction spectra.

Figures 4a, 4b consider only the 311, 222, and 400 spinel reflections as they offer the greatest signal-to-background ratio. Within Figure 4a, (hkl) reflections denote the FNa-MNO phase. Within Figure 4a, markers and arrows are used to indicate the reaction progression, with solid and dashed arrows representing two-phase and single-phase reaction mechanisms respectively. Here, and in similarly constructed scaled intensity figures, diffraction peaks are visualized from a top-down view (best read left-to-right, bottom-to-top), observing peak position as a function of both time and cell voltage.

During the first two cycles (shown in Figures 4a, 4c) the FNa-MNO phase is consumed by a two-phase reaction, further succeeded by a Na\textsuperscript{+} insertion reaction via solid-solution within the sodiated FNa-MNO spinel during the first discharge. The following desodiation, and second cycle all together, follow a strictly single-phase Na\textsuperscript{+} deinsertion mechanism as can be seen by the systematically shifting nature of the Bragg peaks. Operando measurements are in good agreement with the first two-cycles seen within the PITT data mentioned earlier, consistently describing a similar reaction mechanism progression, and building further confidence in the proposed reaction pathway.

After three cycles, the in-situ cell was restarted using a 4.5 V potential cutoff after relaxing at full discharge for several hours. Figure 4b examines the structural evolution within FNa\textsubscript{x}-MNO during the 4.5–2.0 V charge/discharge cycle. The charge reaction proceeds initially via a single-phase deinsertion mechanism, followed by a minor two-phase reaction (Marker M3) at ca. 4.0 V. In fact, this is only realized when considering the enlarged peak breadths of the 311, 222, and 400 peaks, and is assumed that such broadening in the XRD spectra is a result of convoluted peaks; best describing a two-phase reaction between two spinels of similar composition due to the consistent broadening across all measured Bragg reflections. Following the short two-phase reaction, the reaction mechanism continues along a single-phase pathway. Note that, as opposed to the PITT results and previous operando XRD data during the first two cycles, providing ample time in a fully discharged state, introduces minor two-phase reactions similar to those seen for PNa-MNO.

The two-phase reaction seen during discharge follows a similar reaction pathway (single-phase/two-phase(minor)/single-phase progression). However, the two-phase reaction formed during discharge is notably more evident, as there is a sizable difference in 2\textdegree{} positions of the spinel reflections, indicating a considerably larger difference in lattice parameter between the two spinel phases. The emergence of this 4.0 V two-phase reaction is only apparent for FNa\textsubscript{x}-MNO cathodes which are cycled after extended periods at open circuit in the discharged state, and shows remarkable similarities with the reaction pathway and specific voltages seen for the ordered spinel, potentially indication similar processes taking place.

Elevated temperature was used to further enhance reaction kinetics during operando XRD measurements, enabling the high-voltage two-phase reaction described earlier by PITT. Here, operando XRD measurements were not utilized under PITT conditions as the evolution of current in PITT is unpredictable and can lead to considerable spread in the Na content during the course of a single scan. Figure 5 provides a scaled intensity plot of the 311, 222, and 400 Bragg reflections with the corresponding voltage profile at 50 °C. The FNa\textsubscript{1.0}MNO cathode was fully discharged in a coin cell at 3mA/g to 2.0 V at 50 °C prior to being assembled in the in-situ cell. During the subsequent charge in the in-situ cell, Na\textsuperscript{+} deinsertion takes place within a single-phase seen by the constantly shifting Bragg peaks. At 4.0 V, (shown by marker M1) a two-phase reaction is initiated,
generating a second spinel phase with an approximate lattice parameter of 8.04 Å. Elevated temperature provides considerably better Na⁺ diffusion kinetics, as the two-phase reaction forms a heavily depleted sodium spinel (≤5% Na occupancy), and it is expected that complete recovery of the F₃-MNO is feasible by these means. However, within Figure 5, the in-situ cell was forcibly switched to discharge prior to reaching a 4.5 V cutoff in order to preserve the electrolyte from further oxidation. It is of interest that the two-phase reaction at 50 °C occurs at voltages significantly lower than those needed under near equilibrium PITT conditions (24 °C), indicating a large temperature dependence.

As the discharge reaction is initiated, an immediate decrease in X-ray intensity of Bragg reflections is observed (Figure 5a) combined with a large nucleation overpotential (Figure 5b); supportive of a two-phase reaction. Due to sensitivity limitations of the XRD setup, the secondary spinel phase is not measurable by XRD until some time afterwards (Marker M3). This resulting two-phase reaction occurs at ca. 3.3 V, and despite occurring at a lower voltage compared to the initial Na⁺ insertion reaction, is presumed to be equivalent to that seen for the initial sodiation reaction. Further considerations are covered in the Discussion section of this paper.

In summary, the collection of ambient and elevated temperature operando studies support the development of a two-phase discharge reaction upon sufficient desodiation of the FNaₓ-MNO spinel. The high-voltage two-phase reaction presents itself as the rate-limiting step, accounting for the major reduction in cell capacity beyond the first discharge.

Operando XRD comparisons.—Operando XRD was used to systematically measure structural changes within the dis/ordered spinel cathodes. A comparative summary of operando XRD measurements across (F/P)Naₓ-MNO cells is provided in Figure 6. Relative changes in lattice parameters are calculated with respect to the initial (F/P)λ-MNO and fully sodiated (F/P)Naₓ-MNO spinels for Figures 6a, 6b, 6d, 6f respectively. Operando cells were cycled at a current rate of 3mA/g at 20 °C between 2.0–4.25 V (Figures 6a, 6d), 20 °C with a 10 hour open circuit period following the initial discharge between 2.0–4.25 V (Figures 6b, 6e), and 50 °C between 2.0–4.45 V (Figures 6c, 6f) respectively. Inserted sodium (Naₓ) values are based off of relative lattice parameters assuming a linear relationship as described by Vegard’s law due to competing electrolyte degradation that renders electrochemically derived Naₓ values to be considerably unreliable, especially at high-voltage/high temperature.

Figures 6a, 6d consider the change in relative lattice parameter for the dis/ordered spinels, respectively, throughout the first two cycles within 2.0–4.25 V at 20 °C. During the initial discharge, a two-phase reaction is observed between the disordered and ordered spinels, producing sodiated spinels 0.44 Å and 0.43 Å larger than the (F/P)λ-MNO phases respectively. Contrasting behaviors between the disordered and ordered spinels can be readily observed, as sodiation within the P₃-MNO phase proceeds only to ca. PNa₀.93MNO as opposed to the F₃-MNO leaves appreciable amounts of P₃-MNO behind, providing incremental capacity throughout the following cycles as shown later on. The remaining P₃-MNO phase provides a physical account for the reduced discharge capacity of P₃-MNO, only providing incremental capacity to subsequent cycles as demonstrated in the following section.

Following charge/discharge cycles further emphasize the difference in reaction pathway between (F/P)Naₓ-MNO and PNaₓ-MNO as evidenced by the gradual and abrupt shifts in lattice parameter of Figure 6d. The Na⁺ de/insertion behavior of PNaₓ-MNO draws a sharp contrast against the purely single-phase nature of FNaₓ-MNO under 24°C galvanostatic conditions. However, much like PNaₓ-MNO, additional minor two-phase reactions can be observed in FNaₓ-MNO when relaxing at open circuit in the fully discharged state as seen in Figure 6b. While FNaₓ-MNO consistently demonstrates this hysteric dependence on relaxation time, PNaₓ-MNO retains the same reaction pathway independent of relaxation time (Figure 6e). This behavior may be related to possible migration of Na⁺ onto adjacent 16c sites and is the subject of future investigations. It should be noted that the
lower voltage cutoff is sufficient for such 16c migrations to occur, as a lower voltage reaction is clearly apparent in Figure 2 at approximately 2 V.

Overall, all cells (dis/ordered) cycled at ambient temperatures consistently observe desodiation limitations, as lattice parameters are consistently ca. 0.20–0.25 Å larger than their respective (F/P)-MNO spinels at the end of charge, indicating residual Na⁺ occupancy; consistent with PITT results. The remaining Na⁺ in the (F/P)Na₂-MNO structure demonstrate an additional energetic barrier preventing complete desodiation, which is not realized until activating an additional two-phase reaction as seen by operando XRD (Figure 5a) and PITT (Figure 2c and Figure 3b). (F/P)Na₂-MNO cathodes demonstrate an abrupt change in lattice parameter during discharge (at 50 °C) as kinetic barriers surrounding the desodiation reaction are largely mitigated (Figures 6c, 6f). The two-phase reaction seen on discharge produces a sodiated spinel phase of approximate composition Na₀.₈₈MNO and Na₀.₉₃MNO for the disordered and ordered spinels respectively. The abrupt change in lattice parameter during discharge (at 50 °C) is consistent with PITT results. The remaining Na⁺ spinels at the end of charge, indicating residual Na⁺ occupancy; consistent with PITT results. The remaining Na⁺ in the (F/P)Na₂-MNO structure demonstrate an additional energetic barrier preventing complete desodiation, which is not realized until activating an additional two-phase reaction as seen by operando XRD (Figure 5a) and PITT (Figure 2c and Figure 3b). (F/P)Na₂-MNO cathodes demonstrate an abrupt change in lattice parameter during discharge (at 50 °C) as kinetic barriers surrounding the desodiation reaction are largely mitigated (Figures 6c, 6f). The two-phase reaction seen on discharge produces a sodiated spinel phase of approximate composition Na₀.₈₈MNO and Na₀.₉₃MNO for the disordered and ordered spinels respectively. The sodiated spinels formed during the two-phase reaction are equivalent to those observed during the initial discharge reaction for (F/P)-MNO, and provides further support that full theoretical capacity can be maintained beyond the first discharge. These findings suggest that the observed two-phase reactions during the initial sodiation are primarily a result of the large difference in lattice parameter between the vacant and sodiated spinel structures, potentially indicating that rate capabilities can be further optimized by enlarging the (F/P)-MNO unit cell such that the slow two-phase reactions are suppressed in favor of single-phase insertion mechanisms.

It is apparent that the two-phase reactions may impart considerable kinetic barriers to practical performance. In order to quantify the extent of these contributions, diffusion coefficients were calculated from the obtained PITT data and shown in Table II. While calculations are based on ‘traditional’ coulometric titration considerations, their results offer a relative benchmark between the ordered and disordered spinels. Na⁺ mobility exhibits a consistent difference of ca. 3 orders of magnitude when relating the diffusion coefficients between the two-phase and single-phase regions described herein, prompting a desire to push Na⁺ de-insertion mechanisms toward a purely single-phase behavior throughout the entire 0 < Na⁺ < 1 compositional range. Further considerations are provided in the Discussion section.

Constant current + constant voltage cycling.—Cycling studies of (F/P)-MNO cathodes at 3mA/g rate (24 °C) with constant voltage segments imparted at the end of charge using a 1.0 and 2.0 mA/g current cutoff were implemented in order to assess the overall reversibility of the Na⁺ de-insertion reaction. Results are shown in Figure 7. All cells show a marked reduction in specific capacity after the first discharge cycle. This is directly related to the aforementioned difficulty in extracting Na⁺ from the dis/ordered spinels, generally requiring activation of a high-voltage two-phase reaction discussed earlier. Both 2.0 and 2.5 V lower potential cutoffs were utilized to examine any contribution the Mn⁴⁺/Mn³⁺ redox reaction (induced by the designed stoichiometry of the initial LMNO spinel) may have on the overall cyclability. Representative voltage profiles are provided for the first three cycles of the disordered and ordered spinels (Figures 7b, 7d respectively) demonstrating the periodic increase in upper voltage cutoff (4.25, 4.35, 4.45 V). After the third cycle, cells were constantly cycled utilizing a 4.45 V upper potential cutoff. For F₃-MNO samples (Figure 7a), cells discharged to 2.0 V had an initial discharge capacity between

![Graphs showing cycling performance](image)

Table II. Calculated diffusion coefficients of potentiostatic intermittent titration technique data during the initial Na⁺ insertion reaction into disordered and ordered (F/P)-MNO cathodes.

| Cycle Type                  | F₃-MNO | P₃-MNO |
|-----------------------------|--------|--------|
| 1st cycle, two-phase sodiation | 1.61 E-16 | 4.67 E-16 |
| 1st cycle, single-phase sodiation | 5.05 E-13 | 8.26 E-13 |
| 2nd cycle, two-phase desodiation | 6.32 E-17 | 1.96 E-16 |
| 2nd cycle, two-phase sodiation | 1.84 E-16 | 6.93 E-17 |

aReported diffusion coefficients during the initial discharge are averaged across the multiple 10mV steps where a two-phase behavior was observed.
132–141 mAh/g (Na$_{a_0} = 0.867–0.928$ respectively), and 124–129 mAh/g (Na$_{a_0} = 0.813–0.849$ respectively) when discharged to 2.5 V.

For P$_{F_0}$-MNO cells (Figure 7c), initial discharge capacities are notably low at 112 mAh/g and 97 mAh/g for both the 2.0 and 2.5 V potential cutoffs respectively. This relatively low initial capacity suggests a finite amount of unreacted P$_{F_0}$-MNO phase remaining at the end of the initial discharge, consistent with previous operando XRD data discussed above. While the P$_{F_0}$-MNO cells demonstrated relatively poor cycling characteristics when compared against P$_{P_0}$-MNO, P$_{F_0}$-MNO cells discharged to 2.0 V exhibit a comparatively high discharge capacity throughout the first ca. 10 cycles of operation than those (P$_{F_0}$-MNO) discharged to 2.5 V. This suggests that the residual P$_{F_0}$-MNO is contributing to minor additions in discharge capacity beyond the first cycle, also seen by changes in relative intensities throughout operando studies.

Differences in cycling performance across the various constant voltage current cutoffs may also suggest contrasting failure mechanisms between the disordered and ordered spinels, potentially related to slightly higher surface area and Mn$^{3+}$ content of the disordered spinel. An extensive analysis on specific failure mechanisms is beyond the scope of this work, and left for future study.

Overall, cells maintain appreciable cycle efficiency of ca. 90–95%, with a gradual reduction in performance. Most of this reduction in performance is likely associated to the degradation of the NaClO$_4$-PC:FEC electrolyte as evidenced by the discoloration of electrolyte upon cell disassembly. Additional ex-situ XRD analysis on cells cycled beyond 50 cycles indicate that the spinel structure is maintained without evidence of structural decomposition or formation of additional phases, clearly demonstrating that the Na$^+$ insertion reaction into the (F/P)Na$_{a_0}$-MNO structure is highly reversible.

**Discussion**

The combined utilization of electrochemical and structural characterization give a definitive progression of the varying reaction mechanisms observed for the (F/P)Na$_{a_0}$-MNO spinels. It is important to note that approximate compositions (Na$_{a_0}$) of sodium spinels within this section are based primarily on XRD data, and as such, are provided as an approximate value due to limited sensitivity and resolution as compared to electrochemical data. Considering P$_{F_0}$-MNO, the initial Na$^+$ insertion reaction occurs by a two-phase reaction, producing a sodiated spinel of nominal composition Na$_{0.88}$Mn$_{1.56}$Ni$_{0.44}$O$_4$, which is in close agreement with our previous report.

The sodiated spinel thereby continues via a solid-solution insertion process, saturating all available 8a sites of the spinel structure. While full theoretical capacity can be achieved in the disordered spinel, galvanostatic and PITP cycling exhibit a dramatic ‘loss’ in capacity beyond the first discharge cycle due to incomplete depopulation of the 8a sites, effectively narrowing the reversible Na$^+$ de/insertion compositional range. This is seen throughout Figures 6a, 6d as final lattice parameters do not reach their initial (F/P)Na$_{a_0}$-MNO values, indicating significant Na$^+$ occupancy within (F/P)Na$_{a_0}$-MNO.

P$_{P_0}$-MNO proceeds in a very similar manner, demonstrating a two-phase sodiation reaction (P$_{P_0}$-MNO → Na$_{0.88}$Mn$_{1.56}$Ni$_{0.44}$O$_4$) followed by a minor single-phase reaction of remaining tetrahedral sites. However, due to considerable differences in the rate capability between (F/P)Na$_{a_0}$-MNO, the initial two-phase reaction only reaches full capacity when considerable thermal energy (50°C) is provided, otherwise leaving behind a finite amount of the P$_{P_0}$-MNO phase. As noted by Figure 7b, the residual P$_{P_0}$-MNO phase is presumably consumed throughout the subsequent cycles, accounting for incremental capacity during the first ca. 10 cycles. Here it is important to note that although the calculated diffusion coefficients would suggest similar, if not better Na$^+$ mobility in the ordered spinel, the opposite is frequently observed. One should not consider the latter comment conclusive, as the diffusion coefficient results are modeled for Na$^+$ diffusion within a single-phase and is not a sufficient treatment for multiphase reactions, as additional interpretation of the phase boundary mobility is necessary. Small changes in the non-intrinsic, process dependent, physical structure of the crystallites may influence boundary mobility, and a more detailed treatment is left for future works.

Following the initial discharge, additional two-phase reactions are observed both during charge and discharge (Na$_{0.61}$-MNO ↔ Na$_{0.86}$-MNO; Na$_{0.63}$-MNO → Na$_{0.86}$-MNO). In fact, similar two-phase reactions are also observed in FNa$_{a_0}$-MNO (FNa$_{0.66}$-MNO → FNa$_{0.86}$-MNO; FNa$_{0.63}$-MNO → FNa$_{0.86}$-MNO) for the charge and discharge reactions.

**Figure 7.** Constant current with constant voltage discharge capacities and profiles of disordered (a + b) and ordered (c + d) sodium spinel. Cells were cycled at 24°C with a 2.0 V and 2.5 V lower potential cutoff (red and black respectively) and with 1.0 and 2.0 mA/g constant voltage current cutoffs. Cells were cycled with increasing potential cutoffs during charge (4.25, 4.35, 4.45 V) during the first three cycles, and maintained a 4.45 V charge cutoff throughout the lifetime of the cell.
that the following discharge cycle(s) are able to utilize all available metal ion optimization clear: It is desirable to (1) achieve full extraction of Na$^+$
place via a single-phase reaction, making the pathway toward optimization

demonstrates considerable kinetic advantages when de/insertion takes
charging to high (>4.25 V) voltages. Following complete desodiation, the
original discharge reactions ($F\lambda\text{-MNO} \rightarrow \text{FNa}_{0.93}\text{-MNO} \& P\lambda\text{-MNO} 
\rightarrow \text{PNa}_{0.93}\text{-MNO}$) are observed, enabling full theoretical discharge
capacity beyond the first cycle.

Figure 8 considers a detailed reaction pathway for the ($F/P$)$\text{Na}_{x}$
MNO considering specific phase compositions between single/two-
phase reactions described herein. Notations and schemes are consis-
tent with those mentioned for Figure 1. Pathways (a) through (c) describe
the specific structural evolution when relaxing for several hours at full discharge, operating on a continual basis at 24°C, and at 50°C respectively.

In summary, the sodiation of high voltage ($\text{Mn}_2\text{xNi}_1\text{O}_4$) spinel has proven to be reversible and presents itself as a viable host material for high power sodium-based chemistries. We identify that despite the facile nature throughout the majority of the de/sodiation reaction, there are considerable energetic barriers preventing complete desodiation of the spinel structure. Extensive XRD and PITT study reveal that the root of this limitation is manifested in a two-phase reaction apparent in both the disordered and ordered spinels yielding the vacant ($F/P$)$\text{Na}_{x}\lambda\text{-MNO}$ structures respectively. Upon sufficient Na$^+$
extraction, a two-phase sodiation reaction is once again established; producing ($F/P$)$\text{Na}_{x}\lambda\text{-MNO}$ phases equivalent to those seen during the initial discharge reaction, and indicating a high degree of reversibility & robustness of the spinel structure. Comparatively, Na$^+$
mobility demonstrates considerable kinetic advantages when de/insertion takes
place via a single-phase reaction, making the pathway toward opti-
mization clear: It is desirable to (1) achieve full extraction of Na$^+$, such that the following discharge cycle(s) are able to utilize all available 8a sites. (2) Modify the spinel structure such that Na$^+$
de/insertion takes place solely by a single-phase insertion reaction, circumvent-
ing the slow, rate-limited two-phase reaction(s) described earlier. And
(3) identify an electrolyte composition that is stable throughout the working potential range.

Conclusions

Delithiated ordered ($P4_3_2_1$) and disordered ($Fd-3m$) $\lambda$-
$\text{Mn}_2\text{xNi}_1\text{O}_4$ spinels were investigated as a potential positive electrode material for sodium-ion batteries. A combination of electrochemical and structural data enabled an account of the reaction progression regarding the specific Na$^+$ de/insertion reactions taking place within the vacant ($F/P$)$\lambda\text{-MNO}$ structure. Due to considerable differences in rate capability, Na$_{x}\text{Mn}_{2.16}\text{Ni}_{1.84}\text{O}_4$ (FNa-MNO) spinel is identified as a suitable positive electrode for Na-ion batteries, as both an appreciable discharge capacity can be maintained, and the spinel framework has proven capable of accommodating the large strains associated with reversible Na$^+$ cycling. Here, observed differences in ‘rate capability’ are believed to be linked to any one (or more) of the following factors: (1) The active surface area of ($F/P$)$\lambda\text{-MNO}$, (2) the differences in lattice parameter between the $F\lambda\text{-MNO}$ and $P\lambda\text{-MNO}$ spinels, and (3) differences in the $Mn^{3+}$/oxygen stoichiometry between the initial disordered and ordered lithium spinels.

Preliminary data comparing the disordered and ordered sodium spinels demonstrate the superior performance of the disordered (Fd-3m) structure. However, additional attention should be drawn to the poor kinetics of the Na$^+$ de/insertion reaction and the high potentials/temperatures used to regenerate the vacant ($F/P$)$\lambda\text{-MNO}$ spinel structure. As complete desodiation is only possible by maintaining quasi-equilibrium conditions (PITT), or by elevated temperature studies (50°C) it is desirable to further modify the spinel electrode or crystal structure in order to facilitate complete reversible Na$^+$
de/insertion onto the (F/P)$\lambda\text{-MNO}$ host structure(s).

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