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Rate Dependent Performance Related to Crystal Structure Evolution of $Na_{0.67}Mn_{0.8}Mg_{0.2}O_2$ in a Sodium-Ion Battery

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S *Supporting Information*

ABSTRACT: Sodium-ion batteries are considered as a favorable alternative to the widely used lithium-ion batteries for applications such as grid-scale energy storage. However, to meet the energy density and reliability that is necessary, electrodes that are structurally stable and well characterized during electrochemical cycling need to be developed. Here, we report on how the applied discharge current rate influences the structural evolution of $Na_{0.67}Mn_{0.8}Mg_{0.2}O_2$ electrode materials. A combination of *ex situ* and *in situ* X-ray diffraction (XRD) data were used to probe the structural transitions at the discharged state and during charge/discharge. *Ex situ* data shows a two-phase electrode at the discharged state comprised of phases that adopt *Cmcm* and *P6₃/mmc* symmetries at the 100 mA/g rate but a predominantly *P6₃/mmc* electrode at 200 and 400 mA/g rates. *In situ* synchrotron XRD data at 100 mA/g shows a solely *P6₃/mmc* electrode when 12 mA/g charge and 100 mA/g discharge is used even though *ex situ* XRD data shows the presence of both *Cmcm* and *P6₃/mmc* phases. The *in situ* data allows the Na site occupancy evolution to be determined as well as the rate of lattice expansion and contraction. Electrochemically, lower applied discharge currents, e.g., 100 mA/g, produce better capacity than higher applied currents, e.g., 400 mA/g, and this is related in part to the quantity of the *Cmcm* phase that is formed near the discharged state during a two-phase reaction (*via ex situ* measurements), with lower rates producing more of this *Cmcm* phase. Thus, producing more *Cmcm* phase allows access to higher capacities while higher rates show a lower utilization of the cathode during discharge as less (if any) *Cmcm* phase is formed. Therefore, this work shows how structural transitions can depend on the electrochemically applied current which has significant ramifications on how sodium-ion batteries, and batteries in general, are analyzed for performance during operation.
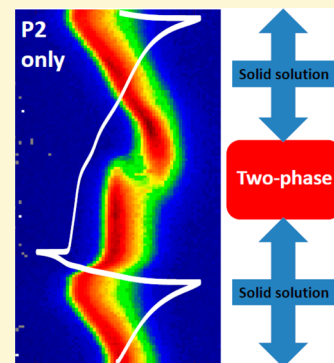
■ INTRODUCTION

Sodium-ion batteries (NIBs) are currently being reinvestigated following their inception in 1980s[1] due to the increasing energy demand and the requirement to find alternatives to Li-ion storage. This requirement is further motivated by the elevated price of Li as well as the relatively limited and politically controlled character of Li-sources.[2,3] Sodium-ion batteries have the potential to be perfect candidates for the next generation of batteries due to their high abundance (6th most abundant element in Earth) and wide distribution, giving them excellent economic viability. Notably, Na-ion batteries may find important use in large-scale grid systems (where energy density is a less prominent factor) which store energy from renewable and intermittent sources such as solar and wind.

Currently, cathode materials for NIBs are the most actively researched. Structures that form layered oxides, of the type Na_yMO_2 (where M is a first-row transition metal or a combination of transition metals), are shown to be promising cathode materials for Na-ion batteries due to their high reversible capacity, and for M = Fe and Mn, cost and safety.[2−4] These materials share many common features with their Li-counterparts despite the larger size of Na. Sodium layered oxides are typically identified using Delmas' notation[5] P2, P3, O3, etc., where P and O indicate the Na sites (P = trigonal prismatic and O = octahedral) and the number relates to the transition metal layers within the unit cell. From this classification, numerous studies have been reported for P2-type Na_yMO_2 materials demonstrating their higher capacities, diffusion rate, and better cyclability than that of the O3 structure.[6]

In 1999, Paulsen and Dahn reported an exhaustive study on P2-sodium manganese oxide compounds[7] after reports from

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Parant et al., two decades prior, first showed evidence of this phase while elucidating the phase diagram of Na_xMnO_2.[8] Even then, these authors anticipated that Li and transition metal doping in P2-$Na_yMn_xM_zO_2$ reduces the Mn^{3+} Jahn−Teller distortion which in turn, increases its temperature stability range. Billaud et al. more recently reported the P2-type $Na_{0.67}Mn_{1−x}Mg_xO_2$ material, where $0 \leq x \leq 0.2$, exhibits a capacity of 175 mA h/g with excellent capacity retention. They attributed the high cycle efficiency to the Mg dopant, albeit with the trade-off of less capacity (150 mA h/g for $Na_{0.67}Mn_{0.8}Mg_{0.2}O_2$).[9] Furthermore, Mg prevented Mn^{3+}/Mn^{4+} ordering within the structure during charge/discharge which was reflected in a reduction of the sharp drops of voltage in the electrochemical curves. Shortly after, Yabuuchi et al. reported on the performance of P2-type $Na_{2/3}Mg_{0.28}Mn_{0.72}O_2$, showing capacities (>200 mA h/g)[10] higher than those expected for the Mn^{3+}/Mn^{4+} redox couple. A possible explanation given for these results was a reversible oxygen redox reaction, analogous to O3-type lithium-excess manganese oxides.[11] This material, however, showed poor cyclability with a drop in capacity to 150 mA h/g after just 30 cycles.

To our knowledge, there are few reports in the literature showing enhanced fast-rate performance in sodium layered cathode materials. Kim et al. reported superior rate capability for $Na_{0.85}Li_{0.17}Ni_{0.21}Mn_{0.64}O_2$ (a capacity of 65 mA h g^{-1} at a rate of 25 C).[12] More recently, Komaba and co-workers reported a large reversible capacity (>100 mA h/g) for $NaFe_{1/2}Co_{1/2}O_2$ after 50 cycles for a 30 C rate (7.23 A/g) in the voltage range, 2.5−4 V.[13]

Here, we report variable-rate discharge cycling studies on P2-$Na_{0.67}Mn_{0.8}Mg_{0.2}O_2$ electrodes. Galvanostatic measurements coupled with *in situ* and *ex situ* X-ray diffraction (XRD) data have been used to demonstrate the effects of the current in the electrochemical performance of this material which, in turn, is intrinsically related to the structural phases observed during cycling.

■ EXPERIMENTAL SECTION

Electrochemical performance of $Na_{0.67}Mn_{0.8}Mg_{0.2}O_2$ has been evaluated using CR2032 coin cells. Electrode active materials were mixed with carbon black as conductive agent and polyvinylidene fluoride (PVDF) as binder in a 80:10:10 ratio. The slurry of the composite was made by using *N*-methylpyrrolidone (NMP), and then, the mixture was coated on aluminum foil which acts as current collector. Coated aluminum foils were dried at 120 °C for 2 h in a vacuum oven. Electrodes of 12 mm diameter were punched out of the coated foil and pressed under a load of 4 tons. After pressing the electrodes, these were again dried in a vacuum oven at 120 °C for 2 h. 1 M $NaPF_6$ in ethylene carbonate and propyl carbonate (EC/PC, 1:1 vol %) was used as electrolyte, and sodium metal was used as reference electrode. Galvanostatic cycling was performed in the voltage region of 1.5−4 V on a Maccor battery tester. Charging of all samples was performed at 12 mA/g, and discharging was performed at different rates, viz., 100, 200, and 400 mA/g. Initially, variable electrode loading was used (e.g., 1.1, 3.2, and 1.1 mg for 100, 200, and 400 mA/g discharge rates, respectively; see Figures S1 and S2); however, for better comparison between applied current rates, electrode loadings were kept consistent at 4.3 ± 0.5 mg. Extended galvanostatic cycling for 100 charge/discharge cycles was undertaken with the above discharge rates, and cells were opened in the discharged state (i.e., ∼1.5 V) at the end of 100 cycles. Electrode loadings for these cells at the 100 and 400 mA/g discharge rate were 1.1 and 3.2 mg for the 200 mA/g discharge rate. Coated Al foils were washed with electrolyte solvent and dried inside the glovebox. Al foils with electrode were mounted on the sample holder and covered with the Kapton foil

before collecting XRD data. XRD data were collected using Cu Kα radiation on a Bruker D8 Advance X-ray diffractometer equipped with a LYNXEYE detector. The discharged state of electrodes extracted from *in situ* cells (see below) at the charge rate of 12 mA/g and discharge rates of 100 and 200 mA/g were collected using a PANalytical Empyrean diffractometer with Cu Kα radiation. Electrodes were mounted in an airtight dome sample holder inside the glovebox and transferred to the instrument. Two $x \geq 0.5$ (vertical) and $4 x \leq 0.5$ (vertical) mm incoming X-ray slits were used for this experiment, and further details are presented in the Discussion section of this work.

An alternative method to prepare samples for *ex situ* diffraction measurements on the first charge/discharge was used to increase the quantity of the active material in the X-ray beam and thus improve XRD signal. Pellets of active material, super S carbon, and Kynar Flex 2801 (a copolymer based on PVDF) binder in a mass ratio of 75:18:7 were used, and after cycling, the electrodes were washed and dried in a similar manner to the coated electrodes. The extracted powders were then transferred to 0.5 mm glass capillaries. *Ex situ* powder XRD measurements for the first cycle were performed on a Stoe STADI/P diffractometer operating in capillary mode, with FeKα_1 radiation (λ = 1.936 Å), and data were collected overnight. Rietveld refinements of the structural models and XRD data were carried out using the program Topas Academic.[14]

The positive electrodes for *in situ* measurements were manufactured by mixing 80% wt. $Na_{0.67}Mn_{0.8}Mg_{0.2}O_2$ active material, 10% wt. conductive carbon (Super C65), and 10% wt. PVDF. A few mL of NMP were added, and the resulting slurry was stirred for 1 h. This slurry was then coated on an aluminum foil using similar techniques to that described above. Coin cells with 3 mm diameter holes in the casing and 5 mm diameter holes in the stainless spacer were used for the construction of the coin cells for the *in situ* measurements. The coin cells contained Na metal (∼1 mm thickness), glass fiber separator with 1 M $NaClO_4$ in EC/PC (1:1 wt %) electrolyte solution. *In situ* synchrotron X-ray diffraction experiments were performed within 1−2 days after cell construction. Further details regarding coin cell construction and beamline setup can be found in refs 15−20.

For the electrochemical tests in coin cells, the electrode loadings were kept consistent at 4.3 ± 0.5 mg for the discharging rates of 100, 200, and 400 mAh/g. It is worthwhile to note that $NaClO_4$ electrolyte can be dangerous as it is sensitive to shocks, and for the development of commercial batteries, an alternative electrolyte is preferable. Note that following the drying step under vacuum, the samples were minimally exposed to air (<1 min) if at all. If transportation of samples or electrodes was required, they were transported in inert conditions and further dried under vacuum prior to cell construction. This was to avoid CO_2 and moisture uptake into these samples as recently evidenced.[21]

In situ synchrotron XRD data were collected on the Powder Diffraction beamline[22] at the Australian Synchrotron with a λ of 0.68954(2) Å, determined using the NIST 660b LaB_6 standard reference material. Data were collected continuously in 4.4 min acquisitions on the coin cell in transmission geometry throughout the charge/discharge cycles. The coin cells were first charged to 4 V at 12 mA/g, then discharged to 1.5 V at 100 mA/g, and charged again to 4 V at 12 mA/g. This corresponds to 0.1−0.2 C on charge and ∼1 C on discharge, and the electrode loading was 3 mg. Rietveld refinements were carried out using the GSAS[23] software suite with the EXPGUI[24] software interface.

■ RESULTS AND DISCUSSION

Electrochemical Performance of $Na_{0.67}Mg_{0.2}Mn_{0.8}O_2$ at Different Rates of Discharge. Galvanostatic charge/discharge curves of the samples at various discharge rates are shown in Figure 1. During the first charge, which corresponds to the extraction of sodium from $Na_{0.67}Mg_{0.2}Mn_{0.8}O_2$, the Mn^{3+}/Mn^{4+} oxidation process leads to a charging capacity of ∼35 mAh/g. During the first discharge, which corresponds to sodium insertion into $Na_xMg_{0.2}Mn_{0.8}O_2$, due to the presence of
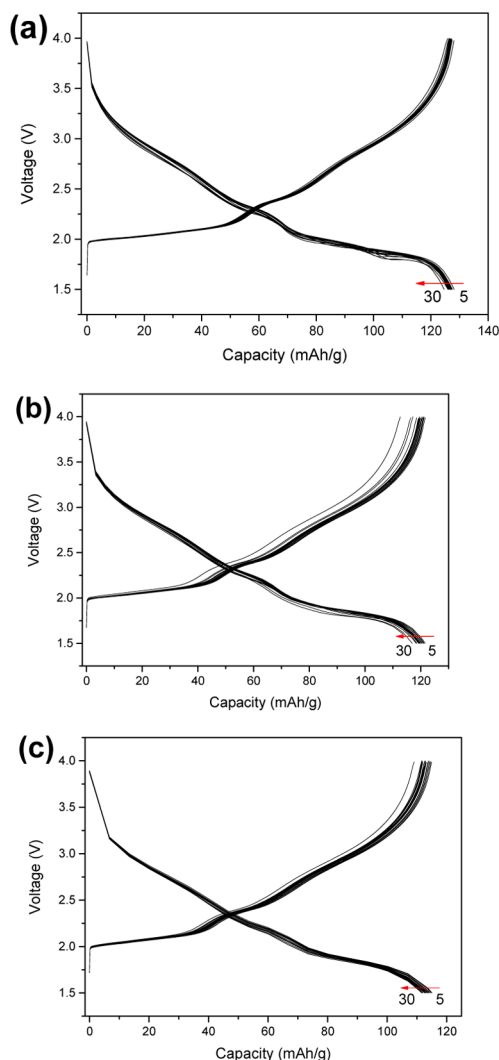
Figure 1. Potential profiles of the $Na_{0.67}Mn_{0.8}Mg_{0.2}O_2$ electrode charged at 12 mA/g and discharged at (a) 100, (b) 200, and (c) 400 mA/g. Profiles from the 5th to 30th cycles are shown.
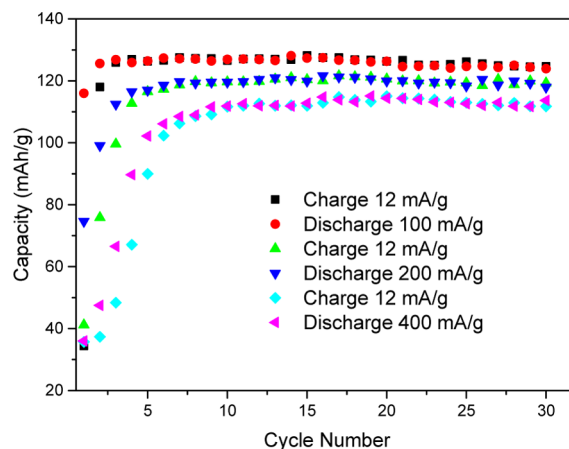

Figure 2. Capacity retention at 12 mA/g charge and 100, 200, and 400 mA/g discharge rates for electrode loading of 4.3 ± 0.5 mg.

the sodium metal as the source of the sodium ions, a greater amount of sodium ions is inserted into the structure compared to the amount extracted during first charge. This leads to high discharge/charge capacities on the second cycle and subsequent cycling. Interestingly, independent of the discharge rate, a large voltage plateau was observed below 2.0 V that contributes significantly to the total capacity.

Cycling performance of the material at different rates of discharge is shown in Figure 2 with two different electrode loadings. Samples were discharged at 100 (low), 200 (moderate), and 400 mA/g (high) rates. Comparing the rates of discharge, the measured capacity from the highest to lowest follows 100 mA/g > 200 mA/g > 400 mA/g using both electrode loads. After 30 cycles at the 4.3 ± 0.5 mg electrode loading, the capacity using discharge rates of 100, 200, and 400 mA/g was 125, 120, and 114 mAh/g, respectively. The observed capacities at these discharge rates are similar which sugges changes when increasing applied discharge rate.

The data presented here are from reproducible cells with very similar electrode loading. We note, however, that there is variation during cell construction (e.g., calandering of the foils and loading density) which does impact electrochemical
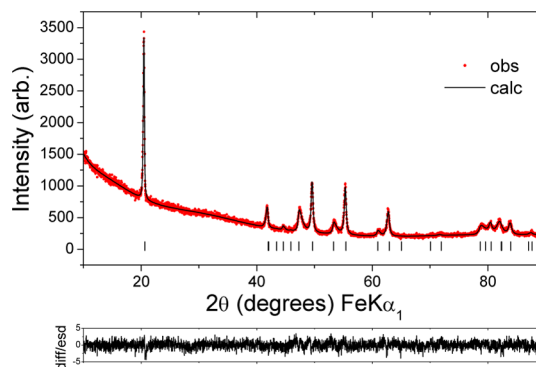
performance and cannot be completely neglected. It is interesting to note that one series of cells appeared to show optimal performance at the 200 mA/g discharge rate; however, on further analysis, this appeared to be a result of the electrode loading (see Figures S1 and S2). In any case, in order to understand the mechanisms responsible for the current-rate dependent behavior, we have analyzed the samples by *ex situ* X-ray diffraction (XRD) after 1 and 100 cycles in the fully discharged state at different rates and *in situ* XRD with 12 mA/g charge and 100 mA/g discharge. The *ex situ* data essentially represent extracted data after charge/discharge cycling while the *in situ* data represent the optimal conditions found from the electrochemical results, Figures 1 and 2.

***Ex Situ* Structural Analysis.** XRD data were obtained from samples extracted at various points on the first charge–discharge cycle at a rate of 10 mA/g. Rietveld refinement of structural models with the data from all points on the first charge revealed that the hexagonal P2 structure (space group $P6_3/mmc$) was maintained to full charge, with no formation of the OP4 phase which is observed for lower Mg contents.[9] A smooth contraction in Mn(Mg)–O bond lengths was observed on sodium extraction accompanying a contraction in *a* and expansion in *c* lattice parameters. The plateau around 2 V on discharge is associated with a transition to an orthorhombic phase (space group *Cmcm*). A profile fit is shown in Figure 3, and refined parameters are given in Table 1. It should be noted

Figure 3. Fitted powder XRD pattern for $Na_{0.92(1)}Mn_{0.8}Mg_{0.2}O_2$ at the end of discharge. Dots represent the observed data, and the solid line is the calculated pattern. The lower line is the difference/esd. Tick marks indicate the allowed reflections.

Table 1. Refined Crystallographic Parameters for Na$_{0.92}$Mn$_{0.8}$Mg$_{0.2}$O$_2$^{a}

atom	Wyckoff symbol	x/a	y/b	z/c	SOF	B$_{iso}$
Na1	4c	0	0.310(2)	0.25	0.86(1)	1.2(−)
Na2	4c	0	0	0.25	0.055(8)	1.2(−)
Mn1/Mg1	4a	0	0	0	0.8/0.2	0.5(−)
O1	8f	0	0.655(2)	0.0907(10)	1	0.6(−)

^{a}space group *Cmcm*. a = 2.8944(6) Å, b = 5.3928(10) Å, c = 10.801(3) Å, R$_{wp}$ = 4.80%, R$_e$ = 4.54%, R$_p$ = 3.69%.

that the magnitude of the orthorhombic distortion at the end of discharge is significantly smaller than that observed for lower Mg contents.[9] In addition, the Mn(Mg)−O bond lengths show a smaller Jahn−Teller distortion with apical bond lengths of 2.102(11) Å and in-plane distances of 1.938(8) Å, compared to 2.345(3) and 1.936(2) Å for 5% Mg.

The key aspect the first cycle illustrated was the formation of the orthorhombic *Cmcm* phase at 2 V (Table 1 and Figure 3). To observe the discharged products in more detail, cells were cycled 100 times and extracted at the end of discharge. Initial comparison of the 002 type reflections as a function of discharge rate shows obvious split reflections in the case of the sample discharged at 100 mA/g while higher rates of discharge, 200 and 400 mA/g, do not show obvious splitting (Figure 4a). Rietveld analysis was used to model the phases, and the fit to the data obtained from the sample discharged at 100 mA/g is shown in Figure 4b with further structural details presented in Table 2. The amount of the *Cmcm* phase that forms at the end of discharge decreases as the current rate is increased, with the cell discharged at 400 mA/g showing a wholly *P6$_3$/mmc* electrode. Therefore, there appears to be a current-dependent formation of the *Cmcm* phase at the end of discharge with slower current rates favoring the formation of this phase, while higher current rates show a predominant *P6$_3$/mmc* phase.

In addition to the phase fractions and lattice parameters presented in Table 2, refinements were performed to approximate the sodium content in the respective phases. Na content was found to increase from 0.68 to 0.75 in the *P6$_3$/mmc* phase obtained after discharging at 400 mA/g to discharging at 200 mA/g. This corresponds to the greater capacity observed during cycling for discharge at 200 mA/g compared to 400 mA/g.

Correlating the current-dependent formation of the *Cmcm* phase (Figure 4) to the observed current-dependent electrochemical behavior (Figure 1), it appears that the formation of a significant amount of the *Cmcm* phase at the end of discharge at 100 mA/g is desirable for the performance of these electrodes. Electrochemically, there is insufficient charge transfer at the 200 and 400 mA/g rates to capture or extract the entire charge/discharge capacity of the battery. At the discharge rates of 100 and 200 mA/g, there exists a mix of *Cmcm* and *P6$_3$/mmc* phases, but the electrode would have sufficient time to relax or phase separate during extraction and subsequent XRD data analysis; therefore, *in situ* XRD was used to study the real-time behavior of the electrode to determine the precise structural evolution of the electrode at the 100 mA/g discharge rate.

In Situ Synchrotron XRD Structural Analysis at 100 mA/g Discharge. *Initial Structural Characterization.* The cathode in the coin cell adopts a layered structure in the hexagonal space group *P6$_3$/mmc* symmetry; a P2-type structure[25] and the reported structural model[8,10] were used as a starting point for analysis. No evidence of CO$_2$ or water uptake[21] was found with the collected data. Other models, e.g., O3, were trialed but the P2-type structure gave the best fit.
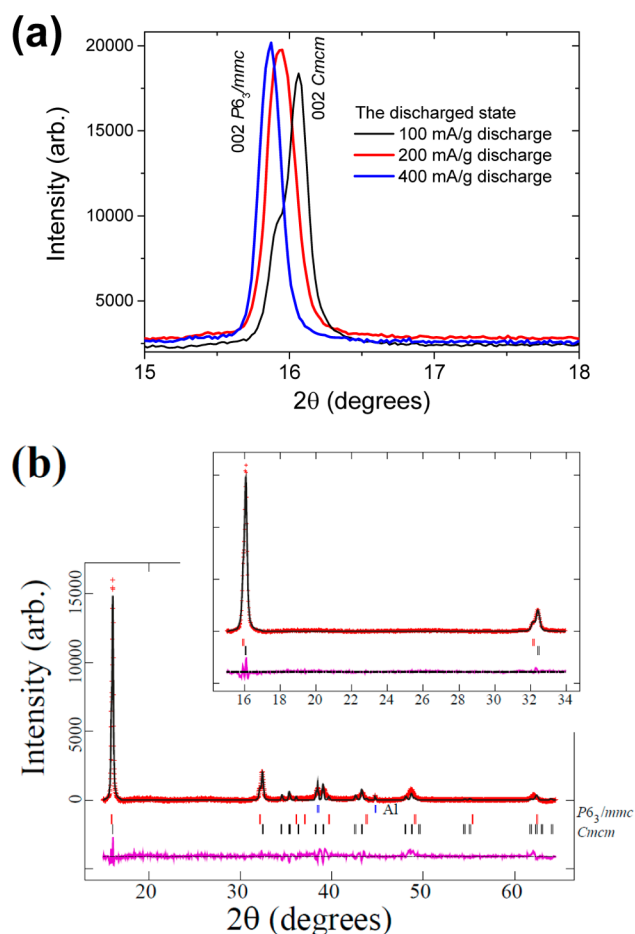

(a)

(b)

Figure 4. (a) The evolution of the 002 type reflection of extracted electrodes at different discharge rates after 100 cycles of charge/discharge. The two phase behavior is clearly evident during the 100 mA/g discharge while it is predominantly single phase for higher discharging rates. (b) Rietveld refined fit of the *P6$_3$/mmc* and *Cmcm* models and Al to the *ex situ* XRD data set of the 100 mA/g discharged sample. Data are shown as crosses, the calculated Rietveld model as a line through the data, and the difference between the data and the model as the line below the data. The vertical reflection markers are for the phases labeled. The inset in (b) shows the fit to the two structural models.

Reflections arising from the aluminum current collector and sodium anode were excluded as their positions did not overlap with many cathode reflections. The background, scale, and lattice parameters were refined initially, and the Mg/Mn site was modeled with 0.2/0.8 occupation. Two Na sites were present Na(1) with x = y = 0 and z = 1/4 and Na(2) with x = 1/3, y = 2/3, and z = 3/4, and Na(1) shows lower occupancy than the Na(2) site. Atomic parameters were refined, starting with independently refined atomic displacement parameters (ADPs), oxygen z positional parameter, and sodium site occupancy factors (SOFs). Note, sodium ADPs and SOFs were

Table 2. Comparative Parameters from the Structural Analysis of Extracted Electrodes from the Discharged State Using Different Current Rates

		lattice parameters *Cmcm*			lattice parameters *P6₃/mmc*	
extracted from	phase fraction *Cmcm*: *P6₃/mmc*	a	b	C	a	c
12/100 mA/g	3.7(3):1	2.9081(4)	5.1848(9)	11.0354(7)	2.8726(9)	11.135(2)
12/200 mA/g	0.34(2):1	2.9080(5)	5.2336(7)	11.078(1)	2.9136(5)	11.1370(8)
12/400 mA/g	0.002(2):1 all *P6₃/mmc*				2.9177(3)	11.1690(4)

not simultaneously refined; SOFs were refined and fixed, and then, the ADPs refined and fixed and so on. In conjunction, profile terms were refined. The structural model fitted well with the data but showed a large mismatch in the 100, 110, and 103 reflections. Fourier maps were used to illustrate what could cause these mismatches. The difference Fourier map (observed − calculated) is shown in Figure 5a,b; in this case, the Na sites
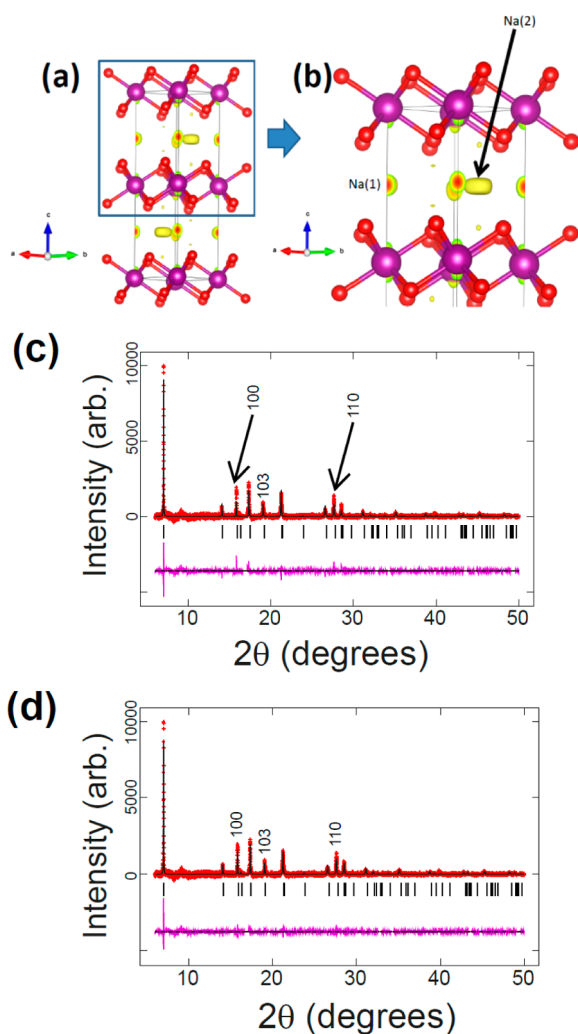
were set to 0, and the positive Fourier density is shown. There appears to be Fourier density around the Mn/Mg site and at the Na(1) and Na(2) sites, further confirming the P2 structure. Interestingly, the Fourier density on the Na(2) site has a distinct nonspherical shape suggesting that this site should be modeled using anisotropic ADPs or reflecting the disordered nature of this site.[26] The inclusion of a preferred orientation term along the 100 axis (0.719(4)) improves the fit (see Figure 5c,d), lowers the Na content on both sites to unrealistic values (Na(1) = 0.162(5) and Na(2) = 0.216(8)), and pushes the oxygen positional parameter to a very low value of z = 0.0704(5) but has little influence on the other parameters. The final refined lattice and atomic parameters based on the fits without the preferred orientation term (Figure 5c) are shown in Table 3.

Table 3. Refined Crystallographic Parameters for Na₀.₆₄₍₁₎Mn₀.₈Mg₀.₂O₂

atom	Wyckoff	x	y	Z	SOF	isotropic ADP (×100)/Å²
Na(1)	2	0	0	0.25	0.240(6)	1.08[a]
Na(2)	2	1/3	2/3	0.75	0.40(1)	6.00[a,b]
Mn(1)	2	0	0	0	0.8	0.34[a,c]
Mg(1)	2	0	0	0	0.2	0.34[a,c]
O(1)	4	1/3	2/3	0.0803(5)	1	1.40[a]

[a]Refined alternatively to SOFs and refined and fixed. [b]Can be modeled anisotropically as 2.01, 1.00, 0.0, 2.01, 0.0, 13.9. [c]Constrained to be equal. Space group = *P6₃/mmc*, in Figure 5c, without preferred orientation 34 refinement parameters, χ^2 = 1.63, R_p = 2.57%, wRp = 3.78%, a = 2.8717(1), c = 11.1811(2) Å.

Phase Evolution. The phase evolution during charge/discharge/charge is predominantly solid solution with a small two-phase region or plateau (orange shading) as shown in Figure 6 for the 002 and 110 reflections. On visual inspection, the electrode does not phase separate (e.g., both *P6₃/mmc* and *Cmcm* orthorhombic phases existing or transforming between each other) on discharge. During the solid solution regions, the changes in the 2θ-value of the 002 reflection are opposite to changes in 110 reflection; e.g., as the 002 2θ-value increases, the 110 2θ-value decreases. This suggests an anisotropic evolution of the lattice parameters within this Na composition.

It is interesting to note that the Mg/Mn ordering observed by Yabuuchi et al.[10] is observed in these data by the 1/3,1/3,0 reflection. This ordering is persistent throughout the charge/discharge cycles (Figure 6c) suggesting that the Mg/Mn ordering does not change during cycling. Additionally, this ordering is observed in the first and second phase (discussed below). Note this reflection sits directly above the amorphous feature due to carbon black and PVDF in the electrode mix which reduces its signal-to-noise ratio.

Taking a closer look at the two-phase region, using stacked plots (Figure 7), the relative similarity of the two-phases
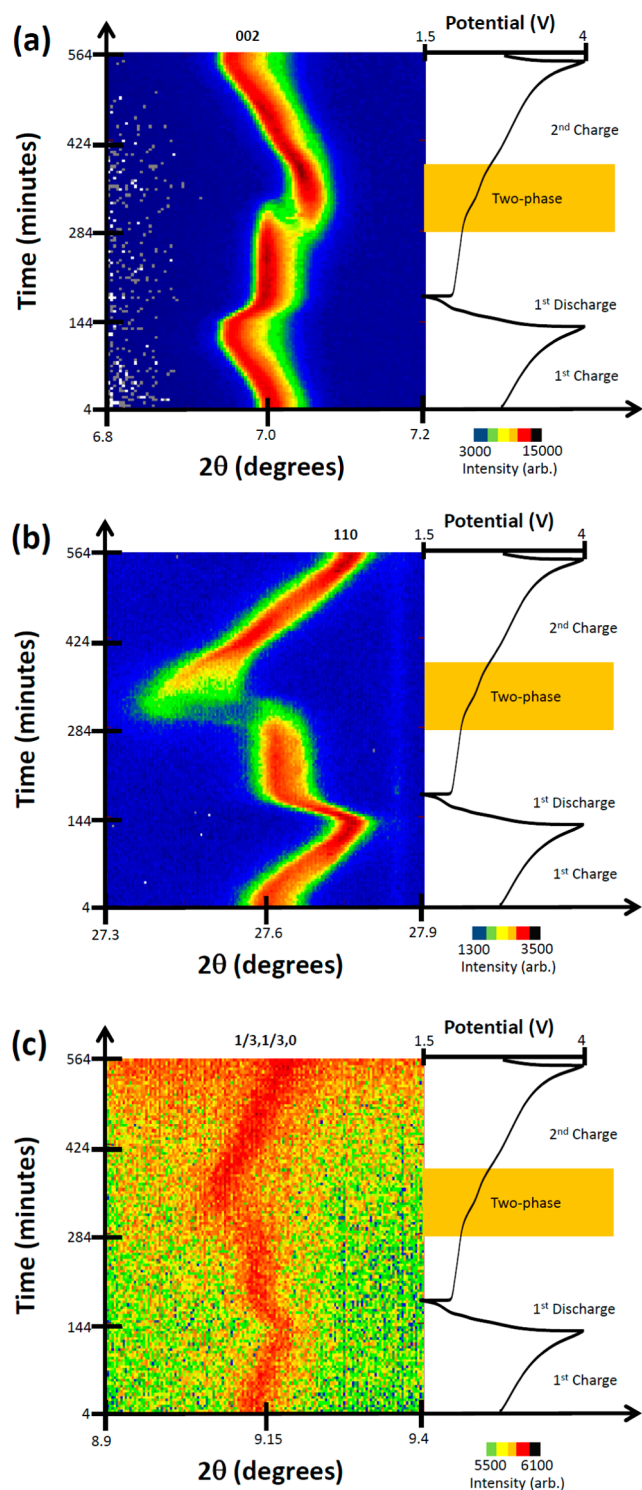
Figure 5. (a, b) The crystal structure of the cathode at OCP with Fourier intensity illustrated when the Na occupancy is set to zero. Mn/Mg is purple, oxygen is red, Fourier intensity is yellow, and the sites are labeled. Rietveld refined fit of the structural model to the initial *in situ* synchrotron XRD data set (c) without and (d) with a preferred orientation term. Data are shown as crosses, the calculated Rietveld model as a line through the data, and the difference between the data and the model as the line below the data. The vertical reflection markers are for P2-Na₀.₆₇Mn₀.₈Mg₀.₂O₂ and the arrows indicate in (c) the 100 and 110 reflections.

Figure 6. Selected 2θ regions of *in situ* synchrotron XRD data highlighting the evolution of the (a) 002, (b) 110, and (c) 1/3,1/3,0 (Mn/Mg ordering[10]) reflections by a color scale and the potential profile (right). The orange shaded box highlights the two-phase region showing the disappearance and appearance of reflections.
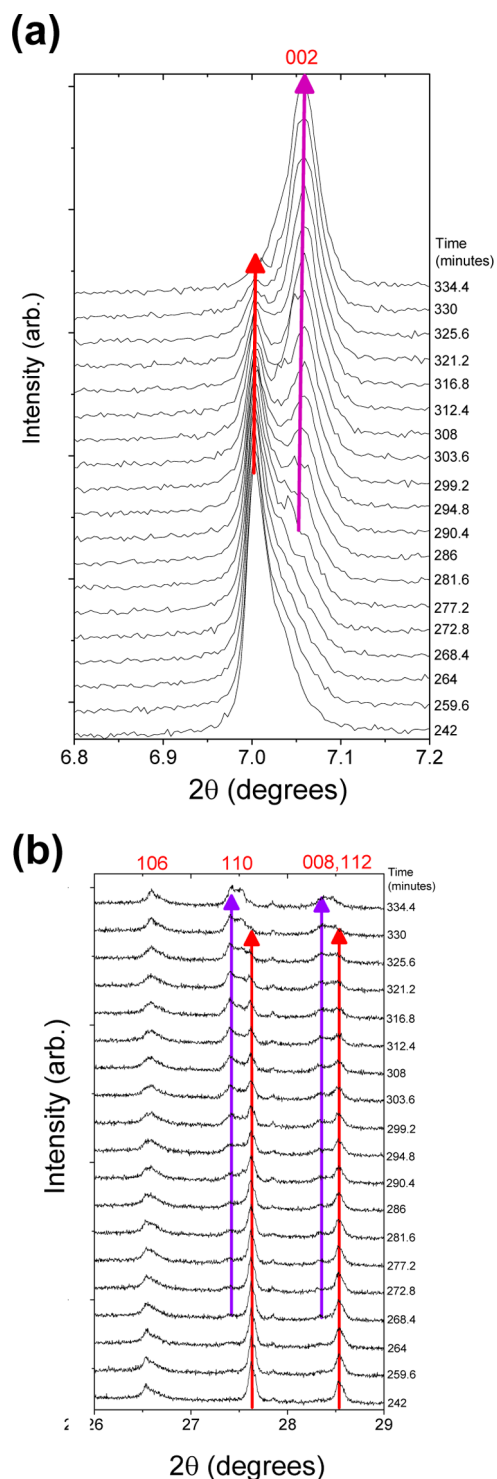

Figure 7. Snapshots via a stacked plot of the *in situ* data of the (a) 002 and (b) 106, 110, and 008, 112 reflections with time shown on the right-hand side of each graph. The red arrows indicate the disappearance of reflections from initial phase (phase 1), and the purple reflections are the new reflections which show subtle changes in the 2θ-value during the same region.

becomes more apparent. The two-phases adopt the same symmetry and feature only subtle differences in the atomic parameters, predominantly sodium content similar to findings for $LiCoO_2$[27,28] and $Na_{3-y}V_2O_2(PO_4)_2F$[18,19] where two-phase regions are characterized by Na/Li-rich and Na/Li-poor phases. Note the first phase disappears with minimal change in 2θ-value

(or lattice parameters; see red arrow in Figure 7) while the second phase appears and shows a small change in 2θ-value (see purple arrow in Figure 7) during the two-phase region. The change in 2θ-value is minute but suggests a simultaneous presence of multiple phase transitions, two-phase and solid
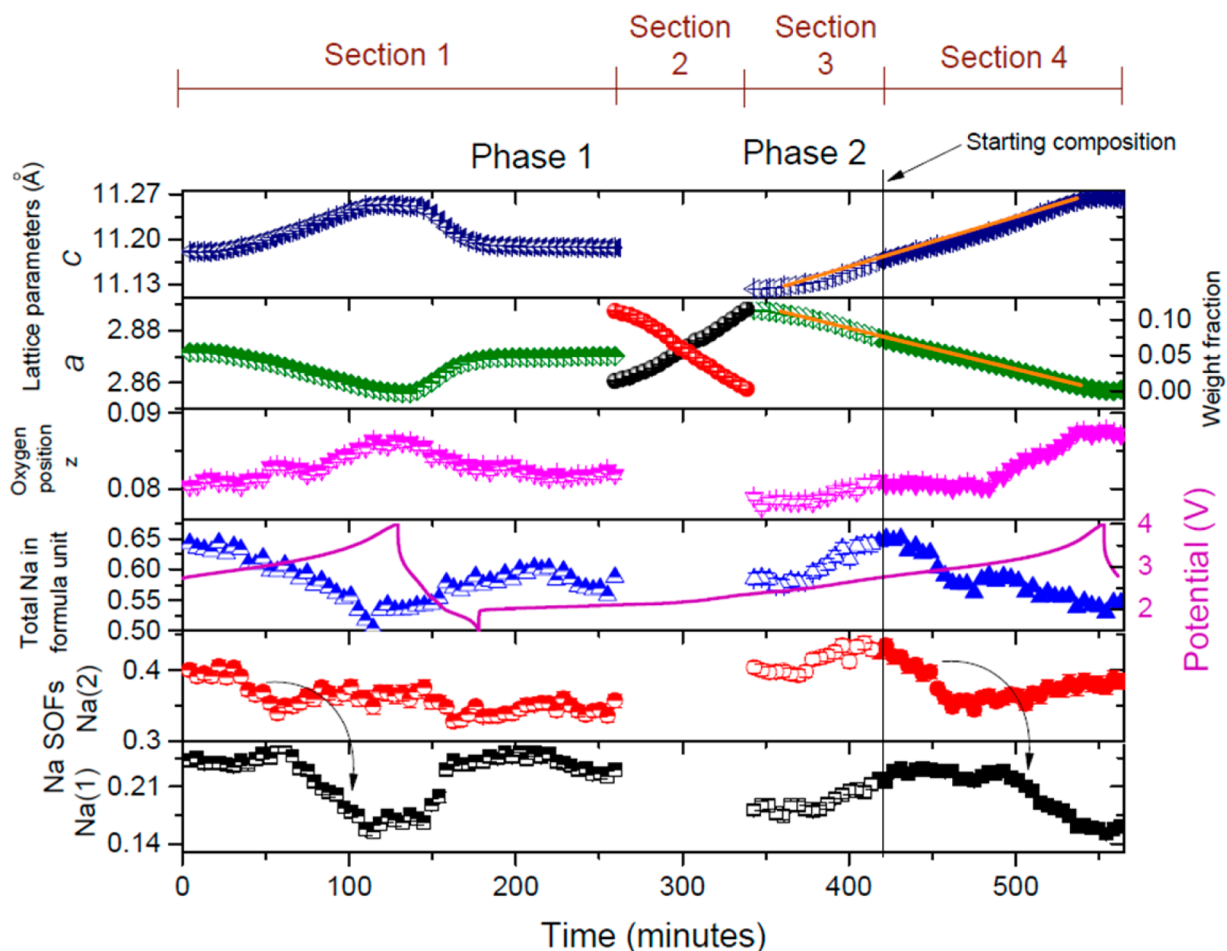
Figure 8. Evolution of the lattice parameters a and c in olive diamonds and blue triangles, respectively; the phase fractions of the initial or 1st phase and the 2nd phase in red and black balls, respectively; the oxygen positional parameters in magenta triangles; the total sodium content in the formula unit in blue triangles; the Na SOFs of the Na(1) and Na(2) sites in black squares and red circles, respectively; the potential profile in purple. Half-filled symbols represent section 1 which encompasses the charge from OCP, discharge, and initial 2nd charge process. The two phase region shown by only the black and red balls are considered as section 2. The section following the two-phase section is section 3 where the 2nd phase evolves in a rather anomalous fashion with respect to the sodium parameters, and this section features open symbols. The final section, section 4, features filled symbols and begins from the composition and voltage that is equivalent to the OCP composition and voltage, as indicated by the straight line.

solution, similar to that observed recently by *in situ* neutron powder diffraction experiments with LiFePO$_4$ cathodes.[29] Note the simultaneous phase transition region is very small in this cathode.

Detailed Structural Evolution during Battery Function. For the sequential refinements, 4 sections were defined. The first section until the two-phase reaction begins (half-filled symbols in Figure 8) corresponds to charge, discharge, and part of the subsequent charge; the second section is the two-phase region (spheres in Figure 8); the third section leads up to the original Na$_{0.67}$Mn$_{0.8}$Mg$_{0.2}$O$_2$ composition on the second charge (open symbols in Figure 8); the last section is the reminder of charge (closed symbols in Figure 8).

During first charge, a contracts while c expands until near charged state where both a and c begin to stabilize around $a = 2.8563(1)$ and $c = 11.2528(3)$ Å. During the fast discharge, a expands while c contracts and then stabilizes with $a \sim 2.87$ and $c \sim 11.18$ Å and minimal change is observed during the initial stages of second charge. This leads to the two-phase region (discussed below). At the end of the two-phase region, a and c are at their highest and lowest values, respectively, higher and lower than the original cathode and after discharging. Here, a is

2.8879(1) and c is 11.1233(2) Å and the potential is 2.36 V. From this point on, a contracts while c expands during the reminder of charge. Notably, the contraction of a appears to be slightly more linear than the expansion of c as highlighted by the straight lines in Figure 8. This may be intricately tied to the evolution of the sodium atomic parameters. The original composition of the cathode returns close to the open circuit potential (OCP) at 2.72 V (compared below). Interestingly, the charged cathode on the second charge resembles the charged electrode on the first charge remarkably well suggesting robust and repeatable structural transitions during these processes.

On charge, the Na content drops from 0.64(1) at OCP to 0.50(1) near the first charged state, corresponding to a change in Na content of the order of ~0.15. The electrochemically derived capacity for charge was 30 mAh g^{-1} which corresponds to a slightly lower change in Na content of ~0.14 Na. However, taking into account surface reactions and noting that the refinement was a constrained refinement, the values give a good indication of the evolution. Interestingly, the first 60 min of charge at 12 mA/g from OCP results in most of the sodium extraction occurring from the Na(2) site, which is then "transferred" to the Na(1) site for the reminder of charge as

indicated by the arrow in Figure 8. On the fast discharge, the sodium insertion occurs solely on the Na(1) site and the Na(2) occupancy remains the same. This suggests that sodium extraction occurs first from the Na(2) followed by the Na(1) site, while insertion occurs first to the Na(1) site. This shows that the Na(1) site has Na extracted from and inserted into near the charged state. However, sodium does not reinsert or transfer to the Na(2) site on charge. Even on subsequent charge, the Na(2) site remains fairly constant. Thus, Na(1) appears to carry the charge in this region (near first charged state, discharge, initial second charge). The inability to extract more sodium from the Na(2) site during the initial part of the second charge may be the reason that the two-phase region is observed. The two-phase region acts to redistribute Na between the two crystallographic sites. This is evidenced after the two-phase region, where the Na occupancy is larger on the Na(2) site and smaller on the Na(1) compared to the beginning of the two-phase region. It appears that there is a need for Na redistribution that instigates the two-phase region.

In the two-phase region (section 2), the first phase and a second phase with slightly different lattice parameters and sodium content are active. The a and c lattice parameters and volume are 2.8879(1) and 11.1233(1) Å and 80.343(3) Å^3, respectively, at the end of the two-phase region (2nd phase), and at the beginning, they are 2.8702(1) and 11.1869(2) Å and 79.814(3) Å^3 (1st phase). Thus, the a lattice parameter expands, while c shrinks and the overall volume increases. The second phase appears to be an expanded version of the initial first phase. Table 4 shows the major differences between the phases.

Table 4. Refined Crystallographic Parameters for $Na_{0.582(11)}Mn_{0.8}Mg_{0.2}O_2$ before the Onset of the Two-Phase Region and $Na_{0.578(11)}Mn_{0.8}Mg_{0.2}O_2$ (Bold) After the Two-Phase Region

atom	Wyckoff	x	y	z	SOF	isotropic ADP ($\times 100$)/Å^2
Na(1)	2	0	0	0.25	0.228(7)	1.08[a]
					0.179(6)	**0.53[a]**
Na(2)	2	1/3	2/3	0.75	0.354(9)	6.00[a,b]
					0.399(9)	**6.99[a,b]**
Mn(1)	2	0	0	0	0.8	0.34[a,c]
						0.13[a,c]
Mg(1)	2	0	0	0	0.2	0.34[a,c]
						0.13[a,c]
O(1)	4	1/3	2/3	0.0816(5)	1	1.40[a]
				0.0786(5)		**1.36[a]**

[a]Refined alternatively to SOFs and refined and fixed. [b]Can be modeled anisotropically. [c]Constrained to be equal. Prior to two-phase region 34 refinement parameters, $\chi^2 = 1.65$, $R_p = 2.59\%$, wRp = 3.83%, $a = 2.8702(1)$, $c = 11.1869(2)$ Å. After the two-phase region 34 refinement parameters, $\chi^2 = 1.44$, $R_p = 2.43\%$, wRp = 3.34%, $a = 2.8880(1)$, $c = 11.1234(2)$ Å.

The one factor that appears at odds with the charge/discharge profile is the third section which is shown by the open symbols in Figure 8, following the two-phase region. Here, the sodium content on both sites and overall increases, and this occurs during charge where sodium extraction should be occurring. The speculative explanation for this behavior can be that the presence of surface Na layers (following the two-phase region) allow for sodium extraction giving rise to the change in potential and charge process, while a small proportion of the surface Na equilibrates and locates onto the sites within the structure, increasing the bulk Na content. The c lattice parameter appears to be slightly nonlinear in this region which may provide further insight for future work. Further work is required to rationalize the behavior in this region of the charge process. In any case, following the $Na_{0.67}Mn_{0.8}Mg_{0.2}O_2$ composition on the second charge (section 4), the behavior observed from OCP to the first charge (section 1) is essentially reproduced.

Comparing the initial phase in the coin cell at the open circuit potential (OCP) at 2.72 V and the structure in the subsequent charge at 2.72 V, there are minimal differences in the structure. Table 5 shows the atomic parameters for the structure at 2.72 V. The differences are minute: a OCP is 2.8717(1) compared to 2.8771(1) Å at the next 2.72 V on charge; c OCP is 11.1812(2) compared to 11.1672(2) Å; volume OCP is 79.854(3) compared to 80.055(3) Å^3. The similarities in the structure show its ability to reversibly insert/extract Na, with only a small expansion of a contraction of c noted at the same states of charge.

■ DISCUSSION

Overall, the structural transitions are reversible, and at the 12 mA/g charge and 100 mA/g discharge, there are single and two phase reactions occurring but the P2-type structure is preserved. At this rate, there is no evidence of the Cmcm phase on discharge via these in situ measurements. From the ex situ measurements, it was concluded that the lack of the Cmcm phase and preservation of the P2 structure leads to lower capacities of the $Na_{2/3}Mn_{0.8}Mg_{0.2}O_2$ cathode at 12/200 and 12/400 mA/g compared to 12/100 mA/g rates. However, the lack of the Cmcm phase during in situ experiments suggests a minute quantity may form under continuous operation at 12/100 mA/g.

A concern with the coin cell used in this work, containing circular Kapton-tape covered holes to allow X-ray transmission, as compared to cells with Be windows or the AMPIX cell,[30] is the potential for a "lag effect" of the electrochemical reaction in the region of the hole. In other words, the XRD pattern is taken of a region that may be behind the true electrochemistry of the cell. In order to test this, in situ cells with the $Na_{0.67}Mn_{0.8}Mg_{0.2}O_2$ electrode were tested offline under two conditions at the 200 mA/g discharge rate. The first cell was discharged to 1.5 V and allowed to rest before another discharge to 1.5 V was applied, and this process was repeated 5 times. The second cell was just discharged to 1.5 V. Both cells were immediately extracted (~15 min, via a quick transfer to the glovebox). XRD data were collected using two slits that control the dimension of the incoming X-ray beam on the sample. The first data set was collected with an incoming slit of $2\ x \leq 0.5$ (vertical) mm dimension which was centered on the central part of the electrode and the second data set with a slit of $4\ x \leq 0.5$ (vertical) mm. The patterns clearly show the presence of a two phase electrode (see Figure S3). For the 100 mA/g discharge rate electrode using this slit configuration, a similar two-phase electrode is observed but with a slightly different phase composition (see Figure S4). The two phase electrode at the 100 and 200 mA/g discharge rate in combination with the in situ synchrotron XRD data at the 100 mA/g discharge rate suggest that the process of electrode extraction allows the electrode to relax to a state that is not t[...] kinetic state but rather closer to the thermodynamically sta[...]

Table 5. Refined Crystallographic Parameters for $Na_{0.64(1)}Mn_{0.8}Mg_{0.2}O_2$ at 2.72 V on Second Charge

atom	Wyckoff	X	y	z	SOF	isotropic ADP ($\times 100$)/Å^2
Na(1)	2	0	0	0.25	0.218(6)	0.53[a]
Na(2)	2	1/3	2/3	0.75	0.421(10)	6.99[a,b]
Mn(1)	2	0	0	0	0.8	0.13[a,c]
Mg(1)	2	0	0	0	0.2	0.13[a,c]
O(1)	4	1/3	2/3	0.0808(5)	1	1.36[a]

[a]Refined alternatively to SOFs and refined and fixed. [b]Can be modeled anisotropically. [c]Constrained to be equal. Space group = $P6_3/mmc$, 34 refinement parameters, $\chi^2 = 1.69$, $R_p = 2.57\%$, wRp = 3.90%, $a = 2.8771(1)$, $c = 11.1672(2)$ Å.

state with two-phases present. Only slight variations in peak intensity are found between the 2 and 4 mm slits indicating that the regions with the Kapton window does not "lag" significantly behind the majority of the electrode as expected for these materials. In addition, there are significant differences in phase composition (see Figures S3 and S4) between the electrodes that are straightly discharged at 100 and 200 mA/g and sequentially discharge rest-discharged, further illustrating the role electrode relaxation has on the processes under investigation. It is important to note that *in situ* (*operando*) processes can detail kinetic information, while extracting electrodes for *ex situ* studies can result in the convolution of the actual electrode state and any relaxation mechanisms that occur.[31]

At 12 mA/g discharge, the material delivers around 150 mAh/g[9] and the *Cmcm* phase is formed at the discharged state. As the discharge current rate is increased, there is an observed capacity loss, as there is less capacity that is extracted from the electrode; thus, less of the *Cmcm* phase is formed at the discharged state. In other words, more of the *Cmcm* phase is formed at the 12 mA/g than the 100 mA/g discharge rate. The loss of capacity is a commonly seen occurrence as current rate is increased.[32] Coupling this behavior with the *in situ* XRD data, which shows that the *Cmcm* phase is not formed at the 100 mA/g discharge rate under continuous operation in contrast to *Cmcm* formation in *ex situ* studies, suggests reaction kinetics plays a critical role.

The question of kinetics near the discharged state remains a complex problem. The rate limiting process and the process that limits capacity can be the nucleation and growth of the *Cmcm* or P2 phase in all the particles (one particle can be P2 while another in *Cmcm*) or within particles (e.g., core/shell of P2 and *Cmcm* phases);[33−35] related to the diffusion of sodium in the P2 and *Cmcm* phases; lattice avoidance of the two phase mechanism;[29,30] electronic/ionic conductivity of the electrode particle surface and bulk; or combinations of these processes to name a few options. Further work is required to rationalize such intricacies.

If one considers the percentage of the *Cmcm* phase formed for the 100, 200, and 400 mA/g discharge, there is a distinct reduction in quantity from ~78 and 25 to less than 0.2%, respectively (see Table 2 for ratios), *via ex situ* data after 100 cycles. Factoring in the *in situ* data collected at a discharge rate of 100 mA/g with no evidence of the *Cmcm* phase, the most likely cause of the formation of the *Cmcm* phase at 100 and 200 mA/g is electrode relaxation and extraction. On the basis of this information and the recorded capacity at 400 mA/g, it is reasonable to suggest that the electrode does not reach the state of charge required where the *Cmcm* phase can form, and thus, any electrode relaxation will result in the P2 phase being maintained at 400 mA/g.

Sodium extraction (and insertion) often results in phase transitions, some dramatic and some minimal, during battery charge (or discharge) in this family of layered compounds.[13,17,36] Typically, as the current rate is increased, the amount of sodium extracted (or inserted) decreases which corresponds to a lower measured energy density or capacity. During the charge process in $Na_{0.67}Mn_{0.8}Mg_{0.2}O_2$, there is a phase transition between two P2-type or hexagonal $P6_3/mmc$ phases and this results in minimal structural change. In contrast, the hexagonal $P6_3/mmc$ to orthorhombic *Cmcm* phase transition near the discharged state appears to be one of the most significant factors that influence capacity and the largest structural change exhibited by this electrode. These phases are often referred to as P2 and P'2, respectively, and are also observed in other P2-type electrodes.[13,36] The details of the hexagonal $P6_3/mmc$ to orthorhombic *Cmcm* transition are elegantly detailed in ref 36 which shows that with increasing Jahn−Teller active Mn^{3+} a cooperative distortion occurs that promotes this phase transition. Similar to the work on the $Na_xFe_{0.5}Mn_{0.5}O_2$, there appears to be a two-phase mixture at the end of discharge *via ex situ* measurements,[36] but our *in situ* and *ex situ* findings suggest that this is a rate dependent reaction which does not occur at higher applied discharge rates.

■ CONCLUSIONS

The discharge current rate can influence the electrochemical performance of electrodes, and there is a structural reason attributable to this in the case of $Na_{0.67}Mn_{0.8}Mg_{0.2}O_2$ electrodes. The transition of the $P6_3/mmc$ to the *Cmcm* phase at the discharged state is in part responsible for the marginally superior electrochemical performance with a discharge rate of 100 mA/g compared to the discharge rates of 200 and 400 mA/g. Although in an *ex situ* experiment, the *Cmcm* phase is clearly present at the discharged state with a 100 mA/g discharge rate; under real cell conditions (e.g., nonequilibrium), the *Cmcm* phase is not formed at the discharged state. The *Cmcm* phase does begin to form if the electrode is extracted from the cell, suggesting that the 100 mA/g discharge rate inhibits the formation of the *Cmcm* phase under continuous cycling conditions. From a chemical point-of-view, the nucleation and growth of the *Cmcm* phase and subsequent removal enhances the capacity of the electrochemical process, e.g., allowing sodium to be inserted into the *Cmcm* phase and thus increasing capacity. At higher discharge rates of 400 mA/g, there is insufficient utilization of the electrode which can lead to lower capacities compared to the 100 and 200 mA/g discharge rate. Therefore, the two-phase phase electrode or moving toward a two-phase electrode at the discharged state appears to be a prerequisite for better cycling performance. The current-rate dependent performance is intricately linked to the structure of electrodes and characterizing this link will allow researchers and industry to maximize the performance of

electrode materials. A synergy is required between the electronic controls of current rate during operation and the expected structural-electrochemical performance parameters.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b02142.

> Galvanostatic cycling, capacity versus cycle number of electrodes with different loadings, and *ex situ* XRD analysis of electrodes extracted from coin cells with holes covered by Kapton tape (PDF)

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Notes

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