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How to cite this publication

Please cite the final published version:

Steinar Birgisson, Yanbin Shen and Bo B. Iversen (2017). In operando observation of sodium ion diffusion in a layered sodium transition metal oxide cathode material, P2 Na_xCo_{0.7}Mn_{0.3}O₂. In *Chemical Communication*, 53, 1160-1163.

DOI: <http://dx.doi.org/10.1039/C6CC09415E>

Publication metadata

Title:	In operando observation of sodium ion diffusion in a layered sodium transition metal oxide cathode material, P2 Na _x Co _{0.7} Mn _{0.3} O ₂
Author(s):	Steinar Birgisson, Yanbin Shen and Bo B. Iversen
Journal:	<i>Chemical Communication</i>
DOI/Link:	http://dx.doi.org/10.1039/C6CC09415E
Document version:	Accepted manuscript (post-print)

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In operando observation of sodium ion diffusion in a layered sodium transition metal oxide cathode material, P2 $\text{Na}_x\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_2$

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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www.rsc.org/

In operando powder X-ray diffraction data reveal an unexpected structural evolution in layered P2 type $\text{Na}_x\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_2$ material during cycling. The population of single crystallographic sites sometimes increases even though sodium ions are being extracted from the structure, implying a highly cooperative diffusion mechanism. The structural evolution is shown to proceed through a series of metastable structures that cannot be predicted by thermodynamics.

Sodium-ion batteries have attracted a lot of interest due to their great potential in large scale energy storage of intermittent electricity sources such as wind and solar power. The fundamental functionality of a sodium-ion battery is determined by the properties of electrode materials. These are governed by the atomic-scale structure and they commonly determine battery properties such as energy density, rate capability and cycle life.^{1–6} Therefore, understanding the structure of the electrode material is an important step in improving battery performance. Correlating the structure directly to a specific property of a battery can be challenging using *ex situ* measurements. This is because *ex situ* measurements study the structure of the electrode material before, after, or at specific points during cycling, after the battery has been terminated and disassembled. Therefore, metastable and/or non-equilibrium conditions that might be dominant during battery operation possibly relax to a more stable condition. Understanding how the structure affects specific battery properties and observation of the structure evolution during working conditions can be obtained by *in operando* measurements, i.e. by studying the structural changes of the electrode material while the battery is being cycled.^{7–16}

Fig. 1 *In operando* PXRD during the first charge and discharge of the NCMO electrode.

Here we report an *in operando* powder X-ray diffraction (PXRD) study of a P2 type $\text{Na}_x\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_2$ (P2-NCMO) cathode material. The study covers the first charge to 4.5 V taking ~19 hours (~C/19) and the first discharge to 1.2 V taking ~8 hours (C/8), as shown in Fig. 1. Many *in operando* studies use synchrotron radiation, which means that due to time constraints the charge and discharge processes are performed at relatively high rate far from the typical working conditions of a battery. Here we use an *in operando* cell designed for conventional diffractometers,³ which due to the reflection geometry design is able to provide an excellent signal to noise ratio up to high data resolution. This allows full structure Rietveld refinements to be carried out on the individual *in operando* data sets.

The present cathode material has previously been shown to exhibit a high degree of reversibility and very good rate performance for a sodium-ion battery.¹⁷ The *in operando* PXRD probes the crystalline material in the coin cell and therefore only “observes” the electrochemical reaction of the cathode material. It is well known that the initial charge and discharge cycles of ion batteries may include additional irreversible processes on top of the primary electrochemical reaction of the electrode materials. These processes include solid electrolyte interface formation and electrolyte decomposition and can affect the measured capacity/voltage curve (CV-curve)

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Electronic Supplementary Information (ESI) available: Details about crystal structure, high potential phase formation, material synthesis, characterization, electrode preparation, *in operando* PXRD data collection and analysis. See DOI: 10.1039/x0xx00000x

by adding capacity in different voltage ranges.¹⁸ These irreversible processes are unlikely to affect the bulk structural changes in the crystalline cathode material, because they occur in the electrolyte and on the surface of the cathode. However, because of the additional reactions, the direct measurement of the capacity in different voltage ranges may not coincide perfectly with extraction/insertion of sodium ions from the crystal structure that is measured directly using *in operando* PXRD.

The P2 sodium transition metal oxide structure crystallizes in space group $P6_3/mmc$. It consists of sheets of transition metal oxide octahedrons (TMO_6) that connect by edge-sharing in two dimensions (TM-sheets). The TM-sheets stack along the crystallographic *c*-direction forming a layered structure. The sodium ions sit in two distinct prismatic sites in between the TM-sheets. One shares faces with two TMO_6 (Na_f) and one shares edges with six TMO_6 (Na_e),¹⁹ see ESI. It has been shown theoretically and experimentally that the Na_f site is thermodynamically less stable due to larger coulombic repulsion from shorter sodium to transition metal (TM) distances, ~ 2.8 Å and ~ 3.2 Å for TM to Na_f and Na_e respectively.^{20–26}

Since the first *in operando* PXRD study of the P2 type material in 2001,²⁷ many studies of P2 materials with various compositions have been reported in the literature.^{12, 15, 24, 28–39} All these studies report reversible expansion/contraction of the *c* axis and contraction/expansion of the *a/b* axis upon charge/discharge. Some studies also report reversible phase transformations at high and/or low potential. The main result in the present study is a surprising evolution of the sodium loading for each crystallographic site as determined by full structure Rietveld refinements.⁴⁰ Unusual evolution of sodium loadings for P2 type cathode materials have been reported before and shown to be rate dependent.³⁷ Here, highly non equilibrium structural evolution is shown to occur for P2-NCMO even at a relatively low current rate of $\sim C/19$.

The sodium loading of the P2-NCMO cathode material, as atomic fraction per formula unit (*x*), is presented in Fig. 2. As expected the total sodium loading decreases linearly initially due to electrons being extracted from the cathode at a constant rate. More interesting trends are revealed when the sodium loading of each crystallographic site is examined. Initially, the loading of the Na_e site decreases while the loading of the Na_f site increases. This trend continues until $x(\text{Na}_e)=0.23(2)$ and $x(\text{Na}_f)=0.33(2)$, i.e. the more unstable Na_f site is the more populated. This trend is unusual for two reasons. Firstly, extraction of sodium ions from the cathode indicates a decrease in sodium loading for both sodium sites. Different rates of extraction dependent on the relative stability of the sites can be expected but an increased loading of a more unstable site is highly unexpected.^{37, 39, 41, 42} To our knowledge this has only been shown once before, for P2 type $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ at relatively high rate of $1C$.³⁷ It has been postulated that sodium ion migration pathways in P2 sodium transition metal oxide materials is a direct pathway between adjacent prismatic sites, Na_e and Na_f .⁴³ The trend therefore indicates a highly complex cooperative mechanism for sodium

ion diffusion in the crystal structure during charging than simple extraction of the sodium ions one by one. Secondly, the sodium loading of the more unstable Na_f site eventually gets larger than for the Na_e site. Thermodynamically stable structures in this compositional range always show a higher sodium loading in the Na_e site.²⁰ This indicates non-equilibrium conditions on a structural level during charging of this material even at this low rate. Upon continued charging the sodium loadings for each of the sites evolves in an intriguing pattern of linear trends. Each linear trend is broken in a point that might coincide with the composition of a metastable structure. These metastable compositions together with their relative sodium loading of both sites are summarized in Table 1 and indicated as vertical lines in Fig. 2 and Fig. 3. Notably, only the starting material (composition 1) shows a relative sodium loading that is predicted by theoretical calculations.²⁰ This means that the whole charging process takes place under non-equilibrium conditions and thermodynamic calculations therefore cannot be used to predict what happens on a structural level during cycling of the battery. Upon discharge the same metastable compositions are observed in the reverse order except composition 2, which does not re-appear during the discharge process. Notably composition 2 appears during a two P2 phases region while charging, see below. The fact that the two phase region is not observed during discharge might explain why composition 2 is not observed upon discharge.

Fig. 2 Total *x* and values for each crystallographic site as a function of time. Filled symbols are weighted average for the two P2 phases. Also shown is the theoretically calculated *x* and cell voltage. Numbered lines (1–5) correspond to metastable compositions.

Table 1 Metastable compositions during first charging of P2-NCMO.

Point	Time [min]	Potential [V]	Na_f loading	Na_e loading	Total loading
1	0	2.4	0.22(3)	0.39(3)	0.61(4)
2	132	3.0	0.33(2)	0.23(2)	0.56(6)
3	253	3.3	0.24(3)	0.21(3)	0.45(4)
4	330	3.7	0.30(3)	0.09(3)	0.40(4)
5	572	4.1	0.10(3)	0.18(3)	0.28(4)

A potential plateau is observed between ~ 4.1 – 4.4 V ($t = 576$ – 836 min), which has been shown to be irreversible upon further cycling.¹⁷ Simultaneously, the sodium loading for both sites stagnates indicating that sodium is no longer being extracted from P2-NCMO. The stagnant sodium loading despite constant current clearly shows that the extracted/inserted sodium cannot in all cases be quantified by measured capacity. This probably also holds true for other material systems in sodium and lithium ion batteries. At the same time the unit cell parameters also stop changing. A possible explanation for these stable structural parameters is that the extraction of more sodium ions beyond this point destroys the crystalline material without changing the bulk structural parameters. However, this is not the case since the normalized scale factor obtained in the Rietveld refinements is also stable in this charging interval, see ESI. These observations suggest that something other than the crystalline P2-NCMO material is electrochemically active in the high potential window. It has been shown that the potential plateau is not due to electrolyte decomposition.¹⁷ A possible explanation for the potential plateau is that the NCMO electrode contains an amorphous part that reacts irreversibly in this potential range. Further evidence for the presence of amorphous material is shown in elemental composition data and HRTEM images in ESI.

At ~ 850 minutes the Bragg reflections from the P2-NCMO phases start to disappear and a new set of few and broad Bragg reflections appears arising from a new poorly crystalline phase termed the “Z” phase (see Fig. 1). A more detailed discussion about this phase transformation is given in ESI. Note that shortly before the appearance of the new phase, the sodium loading for the Na_e site starts to drop rapidly indicating a solid solution behaviour of the P2 phase during the phase transformation. A simultaneous solid solution and phase transformation mechanism in battery materials has been reported e.g. for LiFePO_4 .⁴⁴ Upon discharge the “Z” phase transforms completely back to the P2-NCMO phase showing that the phase transformation is fully reversible.

After ~ 1500 minutes (discharged to 1.7 V) the sodium loadings of both sodium sites have reached their original values. After that the unit cell parameters stop changing, see Fig. 3, and the sodium loading is constant within the margin of error indicating the P2-NCMO material is electrochemically inactive at lower potentials. The fact that the material restores its original structure completely upon discharge to 1.7 V indicates good reversibility and long cycling life, as has been shown before.¹⁷

Fig. 3 shows the evolution of the unit cell of the P2-NCMO cathode material during the first cycle. As shown in previous studies the a/b axes contracts while charging but the c axis expands. All unit cell parameters return to their original value upon discharge indicating a stable cycling that translates into long cycling life.¹⁷ Interestingly, two P2 phases with different c -axis values coexist in the time interval 66–242 minutes (below ~ 3.7 V). The original P2 phase transforms completely into the new phase with larger c axis as seen from the normalized scale factors obtained from Rietveld refinements, see ESI. The

longer c axis of the new P2 phase indicates that it has lower sodium loading. The P2 to P2 phase transformation has only recently been reported and its observation is only possible due to high angular and temporal resolution of the data.^{37–39} From a technical point of view it is interesting to note that it has, to our knowledge, never been reported using *in operando* PXRD data obtained on a laboratory diffractometer. During the phase transformation the c -axis of both phases changes continuously, indicating a solid solution behaviour of both phases during the phase transformation.

Fig. 3 Unit cell parameters and cell voltage as a function of time. Numbered lines (1–5) correspond to metastable compositions.

In summary, full structure Rietveld refinements of *in operando* PXRD data of P2-NCMO material have shown unexpected structural evolution upon first charge and discharge. The *in operando* data were obtained under realistic cycling conditions, and therefore give insight into how the P2 structure evolves during real battery operation. The sodium loadings of both sodium sites are shown to increase in specific intervals during first charge even though the total loading decreases. This result implies that the sodium ion diffusion during cycling is more complicated than previously thought and presumably involves cooperative mechanisms throughout the crystal structure. Highly non-equilibrium conditions are observed during first cycle, since the thermodynamically more stable site is less populated during most of the cycling. Finally, it is shown that the sodium ions do not order into thermodynamically stable structures during first cycle, even at relatively low charging rates. Instead there is evidence of an evolution between a set of metastable structures.

We gratefully acknowledge fruitful discussions with Dipankar Saha and Solveig Kjeldgaard. We also thank Espen D. Bøjesen for collecting HRTEM-EDS images. This research was supported by the Danish National Research Foundation (DNRF93).

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