Solid State Synthesis of Layered Sodium Manganese Oxide for Sodium-ion Battery by in-situ High Energy X-ray Diffraction and X-ray Absorption Near Edge Spectroscopy

Tianyuan Ma^{1, 2}, Gui-Liang Xu¹, Xiaoqiao Zeng¹, Yan Li¹, Yang Ren³, Chengjun Sun³, Steve M. Heald³, Jacob Jorne^{2, 4*}, Khalil Amine¹, and Zonghai Chen^{1*}

- 1) Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA
- 2) Materials Science Program, University of Rochester, Rochester, NY 14627, USA
- 3) X-Ray Science Division, Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA
- 4) Department of Chemical Engineering, University of Rochester, Rochester, NY 14627, USA

Corresponding author: zonghai.chen@anl.gov; Jacob.jorne@rochester.edu

Abstract

In situ high energy X-ray diffraction (HEXRD) and *in situ* X-ray absorption near edge spectroscopy (XANES) were carried out to understand the solid state synthesis of Na_xMnO_2 , with particular interest on the synthesis of P2 type $\text{Na}_{2/3}\text{MnO}_2$. It was found that there were multi intermediate phases formed before NaMnO_2 appeared at about 600 °C. And the final product after cooling process is a combination of O'3 NaMnO_2 with P2 $\text{Na}_{2/3}\text{MnO}_2$. A P2 type $\text{Na}_{2/3}\text{MnO}_2$ was synthesized at reduced temperature (600 °C). The influence of Na_2CO_3 impurity on the electrochemical performance of P2 $\text{Na}_{2/3}\text{MnO}_2$ was thoroughly investigated in our work. It was found that the content of Na_2CO_3 can be reduced by optimizing $\text{Na}_2\text{CO}_3/\text{MnCO}_3$ ratio during the solid state reaction or other post treatment such as washing with water. We expected our results could provide a good guide for future development of high performance cathode materials for sodium-ion batteries.

Keywords: *in situ* HEXRD, *in situ* XANES, solid-state synthesis, P2 type $\text{Na}_{2/3}\text{MnO}_2$, sodium ion battery, sodium deficiency

Graphical Abstract

1. Introduction

Lithium-ion batteries have been widely used to power modern portable electronics over the past decades due to its high energy density. However, with an increasing need for large-scale energy storage system on electric vehicle and energy grid system, concern about the depletion of lithium reservoir has risen [1, 2]. Recently, sodium-ion batteries (SIBs) have been considered as a possible supplemental to lithium ion batteries due to its low cost and high abundance of sodium element. Among all the cathode materials that have been studied in SIBs, layered transition metal oxides, Na_xMO_2 ($\text{M} = \text{Mn, Ni, Co}$) with their binary and ternary derivatives are of great interest due to their high specific capacities. Based on the site occupied by sodium ion, the layered transition metal oxides can be categorized into two types: P type (Prismatic site) and O type (octahedral site) [3]. Usually there will be a number after P or O, such as P2, P3 or O3, indicating the repeating unit perpendicular to $[\text{MO}_2]$ layers. P2- Na_xMO_2 with mixed transition metal [4, 5] and partial substitution of transition metal by Al, Ti, Mg, Fe [2, 6-8] tend to deliver better capacity retention because the P2 structure can be maintained for a wide range of x during charge and discharge process. Also the large interslab distance and low sodium diffusion barrier of P2 type structure is especially beneficial in terms of rate performance [9]. In order to get a better understanding of P2- Na_xMO_2 , it is important to decouple the mixing transition metals and carry out a thorough investigation on the end member of the series.

Parant et.al. have reported two polymorphs for P2- Na_xMO_2 in 1971 [10]: undistorted P2 $\text{Na}_{2/3}\text{MnO}_2$ and P2 $\text{Na}_{2/3}\text{MnO}_2$ with orthorhombic distortion. Recently, Prof. Yabuuchi and Komaba [11] have investigated how the polymorphic characteristics bring difference in electrochemical and structural properties during (de)sodiation of P2 $\text{Na}_{2/3}\text{MnO}_2$. The crystallization of P2 $\text{Na}_{2/3}\text{MnO}_2$ and P'2 $\text{Na}_{2/3}\text{MnO}_2$ is indeed highly dependent on synthesis

conditions, such as the heating process and Na/Mn ratio. Accordingly, it's highly desired to have a better understanding on the formation mechanism of Na_xMnO_2 during its solid state synthesis with the purpose of tuning its structures by controlling the synthesis condition. In this study, *in situ* high-energy X-ray diffraction (HEXRD) and *in situ* X-ray near edge spectroscopy (XANES) were utilized to explore the formation of P2 type $\text{Na}_{2/3}\text{MnO}_2$. The results showed that O3 type sodium manganese oxides start to form at above 600 °C. Therefore, P2 type $\text{Na}_{2/3}\text{MnO}_2$ was synthesized at reduced temperature (600 °C). The influence of Na_2CO_3 impurity on the electrochemical performance of P2 $\text{Na}_{2/3}\text{MnO}_2$ was thoroughly investigated. It was found that the content of Na_2CO_3 can be reduced by optimizing $\text{Na}_2\text{CO}_3/\text{MnCO}_3$ ratio during the solid state reaction or other post treatment such as washing with water. We expected our results could provide a good guide for future development of high performance cathode materials for sodium-ion batteries.

2. Experimental

***In situ* High-energy X-ray diffraction (HEXRD)**

The *in situ* HEXRD measurement was carried out at sector 11-ID-C of the Advanced Photon Source (APS) at Argonne National Laboratory while the sample was heated up to 900 °C at a heating rate of 2 °C/min. The wavelength of the X-ray beam used was 0.11165 Å. Detailed setup of the *in situ* HEXRD can be found in our previous papers [12, 13]. 2D image collected by a 2D detector was converted into 1D data for further study. Rietveld refinement of patterns was conducted using General Structure Analysis Software (GSAS).

***In situ* X-ray Absorption Near Edge Spectroscopy (XANES)**

The *in situ* XANES measurement at Mn K-edge during solid state synthesis was performed at sector 20-BM-B of APS at Argonne National Laboratory while the sample was heated up to 900 °C at a heating rate of 2 °C/min. Mixture of Na₂CO₃ and MnCO₃ were pressed into a pellet, which was then placed in the furnace for the heating treatment. A pair of Si (111) crystals was used to monochromatize the incident beam. XANES data was normalized using Athena software package [14].

Covariance analysis

The similarity between two different XRD or XANES patterns (r1 and r2) can be quantified mathematically by calculating the covariance as shown in Eq. (1) [15]. If two spectra are identical to each other, the covariance value of Eq. (1) equals to 1; if not, a number that is smaller than 1 will be given and the bigger the difference, the smaller the number is.

$$\text{CORR}(r1, r2) = \frac{\sum_i r1(i) * r2(i)}{\sqrt{\sum_i r1(i) * r1(i)} * \sqrt{\sum_i r2(i) * r2(i)}} \quad (1)$$

Synthesis of P2 type Na_{2/3}MnO₂

Na_{2/3}MnO₂ was prepared by a solid-state reaction using Na₂CO₃ and MnCO₃ as starting materials. In a typical synthesis, Na₂CO₃ and MnCO₃ with a Na to Mn atomic molar ratio of 1:1 or 0.735:1 were mixed in a high energy ball mill for 200 minutes to obtain a mixed powder. And the powder was then calcined at 600 °C for 10 hours. To investigate the potential impact of residuals, 0.25 g of sintered powder was suspended in 10 ml deionized water for 5 minutes. After the rinse, the powder was then filtered out and dried in an oven at 105 °C overnight to remove the residual water.

Electrochemical characterization

The electrodes were made by mixing 70 wt.% cathode materials, 20 wt.% C-45 carbon black and 10 wt.% polyvinylidene difluoride (PVDF) binder in N-methyl-2-pyrrolidone (NMP) and then punched into 1.5 cm² discs. Metallic Na foil was used as counter electrode and Glass Fiber was used as separator for assembling 2032 type coin cells. The electrolyte used was 1.0 M sodium hexafluorophosphate (NaPF₆) in propylene carbonate (PC) with 2 vol% fluoroethylene carbonate (FEC) as the electrolyte additive. The electrochemical tests of the cells were then characterized with MACCOR cyler between 2.0 V and 3.8 V at different current density.

Physical Characterization

Ex situ HEXRD measurement was carried out at sector 11-ID-C of the APS at Argonne National Laboratory. The wavelength of the X-ray beam used was 0.11725 Å. The morphology of the prepared samples was determined using a Hitachi S4700 scanning electron microscopy (SEM). Thermal gravimetric analysis (TGA) of samples prepared at different condition was performed with a STA 449 F3 Jupiter from room temperature to 800 °C. The heating rate was 10 °C/min and the purge was done with argon at 50 mL/min flowing rate.

3. Results and discussion

***In situ* HEXRD.** In order to understand the formation mechanism of Na_xMnO₂, *in situ* HEXRD technique was used to monitor the structure evolution during the solid-state synthesis as shown in Figure 1a, in which red color means high intensity and blue color represents low intensity. Before the *in situ* solid-state synthesis, equivalent moles (based on atomic ratio) of Na₂CO₃ and MnCO₃ were ball milled to get a well-mixed powder. According to the *in situ* HEXRD profile obtained at the beginning of the *in situ* experiment, the pellet consists of original Na₂CO₃ (PDF #

37-0451), original MnCO_3 (PDF # 44-1472) and a small amount of extra Mn_3O_4 (PDF # 24-0734), which is probably resulted from the ball milling process. From the contour plot of *in situ* HEXRD data, it can be found that the solid-state reaction mainly occurred at two different temperature ranges: 270 °C to 300 °C and 550 °C to 710 °C, which can be backed by the covariance analysis result depicted in Figure 1b. Note that a number that is smaller than 1 means difference was found between two adjacent spectra. The smaller the number, the bigger the difference is. Clearly, four obvious downward peaks can be observed at about 280 °C, 559 °C, 596 °C and 658 °C, respectively. As shown in Figure 2a, from 276 °C to 294 °C, a signature peak for a layered sodium transition metal oxide (Na_xMnO_2) with $\text{R}\bar{3}\text{m}$ structure appeared first, evidenced by its (003) peak at 1.14° . As the peak intensity of this layered material increased, a set of peaks at 1.74° , 2.23° , 2.67° , 3.19° and 3.61° corresponding to MnCO_3 disappeared while characteristic peaks for Na_2CO_3 remained visible till 720 °C with a structure change from monoclinic to hexagonal at 450 °C. At about 559 °C (Figure 2b), a peak of $\text{R}\bar{3}\text{m}$ structure, namely P3 phase Na_xMnO_2 at 1.14° shift to a lower 2θ value, indicating the formation of an unidentified phase, which is responsible for the change observed at 559 °C in covariance analysis (see Figure 1b). And then P'3 type $\text{Na}_{2/3}\text{MnO}_2$ with $\text{C}2/\text{m}$ structure was observed at about 596 °C and then disappeared at about 696 °C. This phase can be identified as P'3 type $\text{Na}_{2/3}\text{MnO}_2$, in which the prismatic site occupied by sodium ion shares face with MnO_6 octahedral on one side and edges on the other side [16]. While the unidentified phase could be a result of intergrown P'3 and P3 phase, similar to a complex structure consisting of intergrown regions of $\alpha\text{-NaMnO}_2$ and $\beta\text{-NaMnO}_2$ domains presented by Juliette et al [17]. Finally, the reaction corresponding to the last peak in covariance analysis (see Figure 1b) includes the formation of NaMnO_2 at a temperature above 600 °C and the disappearance of P'3 type $\text{Na}_{2/3}\text{MnO}_2$ at about 690 °C. The

peaks exhibited at the end of the heating (900 °C) can be ascribed to NaMnO₂ with C2/m structure and Na₃MnO₄ with P213 structure. Therefore, as shown in Figure 2b, a P3 type layered structure was formed at a relatively low temperature, i.e. 276 °C, which was then transformed into P'3 type Na_{2/3}MnO₂ with an existence of an intermediated intergrown structure of P3 and P'3 ranging from 559 °C to 596 °C. O'3 NaMnO₂ was observed from 600 °C through 900 °C, while Na₃MnO₄ start to form at about 704 °C. At 900 °C, a combination of Na₃MnO₄ and O'3 NaMnO₂ can be obtained. The evolution of sodium-contained compounds can be clearly supported by the Rietveld Refinement results shown in Figure S1.

***In situ* XANES.** In order to further understand the formation mechanism of Na_xMnO₂, *in situ* XANES was conducted to monitor changes on the chemical environment of Mn during solid-state synthesis. A pellet comprising equivalent moles of Na₂CO₃ and MnCO₃ was transformed into the *in situ* heating furnace (LINKAM Stage) before the in-situ XANES measurement started. Figure 3 shows the contour plot of the *in situ* XANES spectra and its covariance analysis. Clearly, there are also four obvious changes as shown in covariance analysis of *in situ* XANES in Figure 3b, which agreed well with *in situ* HEXRD results.

Comparison of XANES spectra at different temperature range is presented in Figure 4. The arrows indicate the increase of temperature during solid-state synthesis. At the same time, the spectra of Mn₂O₃ and MnO₂ are also plotted in Figure 4 as reference. The Mn K pre-edge can be assigned to 1s to 3d transition, which is not allowed by the electronic dipolar selection rule. There are two possible explanations for this unforbidden transition being able seen: quadrupole allowed transitions and mixing of 4p and 3d states [18, 19]. While the main edge peak can be ascribed to 1s to 4p state transition. For the spectra from 271 °C to 305 °C (See Figure 4a), there is a significant edge shift to higher energy than the Mn₂O₃ reference spectrum, suggesting that

the valence of Mn in Na_xMnO_2 with $\text{R}\bar{3}\text{m}$ formed here is far more than 3+, yet not very close to 4+ based on the distance between Na_xMnO_2 spectra (dark yellow) and MnO_2 reference spectra. As the temperature continuously increases to the point where the unidentified intermediate phase arises (see Figure 4b), the edge of the spectrum shifts to a lower energy. The average valence decrease for Mn is presumably a result of increasing x value in Na_xMnO_2 . As the Na insertion continues with temperature rising, the average valence of Mn further drops to almost 3+, presenting an edge position close to Mn_2O_3 (Figure 4c). Finally, the mean oxidative state of Mn doesn't change much as O'3 NaMnO_2 formed and P'3 type $\text{Na}_{2/3}\text{MnO}_2$ disappeared (Figure 4d), indicating that x value in this P'3 phase is very close to the actual x value in O'3 phase. Considering an x value of 0.9-1 [20] for O'3 type layered sodium cathode material, sodium ratio is fairly high in this P'3 Na_xMnO_2 .

Since our target material is P type Na_xMnO_2 , a sintering temperature at 600 °C was selected so that the content of O type structure could be minimized without compromising the crystallinity of P type cathode material based on the *in situ* HEXRD and *in situ* XANES result. Figure 5 shows the *ex situ* XRD pattern of P2 $\text{Na}_{2/3}\text{MnO}_2$ synthesized at 600 °C with a Na: Mn ratio of 1:1 presenting in the starting material. According to *in situ* HEXRD (Figure 2a), the peaks of MnCO_3 , one of the raw materials used in the solid state synthesis of P2 $\text{Na}_{2/3}\text{MnO}_2$, disappeared at about 294 °C, which coincides with its melting temperature. And when it is cooled down to room temperature from 600 °C as in our synthesis route, there are no peaks of MnCO_3 observed in the final result (Figure 5). Thus, the content of MnCO_3 in the final material should be negligible. It can be also found out from *ex situ* XRD result in Figure 5 that the as prepared sample is comprised of mainly P2 type $\text{Na}_{2/3}\text{MnO}_2$ (PDF#27-0751), a small amount of

second phase with orthorhombic structure (PDF#38-0965) and the residual Na_2CO_3 , which may have some impact on the electrochemical performance of P2 type $\text{Na}_{2/3}\text{MnO}_2$.

Electrochemical characterization. Two methods were utilized to eliminate the residual Na_2CO_3 in the final product. One way is to reduce the amount of Na_2CO_3 used during the solid-state synthesis from 43% excess to 5% excess (denoted as P2- $\text{Na}_{2/3}\text{MnO}_2$ -5%), and the other one is to rinse the final product with water (denoted as P2- $\text{Na}_{2/3}\text{MnO}_2$ -risined) [21, 22]. Figure S2 shows the SEM images of P2- $\text{Na}_{2/3}\text{MnO}_2$ prepared at different conditions. Clearly, all samples have platelet morphology with secondary particle size of 100 to 200 nm. Among the three samples, the average particle size of P2- $\text{Na}_{2/3}\text{MnO}_2$ -5% appears to slightly smaller than the other ones (Figure S2b). But the difference between P2 type $\text{Na}_{2/3}\text{MnO}_2$ (Figure S2a) and P2- $\text{Na}_{2/3}\text{MnO}_2$ -risined (Figure S2c) is small.

Figure 6 shows the electrochemical performance of P2- $\text{Na}_{2/3}\text{MnO}_2/\text{Na}$ cells; the electrolyte used in these cells was 1.0 M sodium hexafluorophosphate (NaPF_6) in propylene carbonate (PC) with 2 Vol% fluoroethylene carbonate (FEC) as the electrolyte additive. The capacity retention of these cells were measured using continuous charge/discharge cycling at a constant rate of 0.1 C (~ 0.4 mA) within the potential range between 2.0 V and 3.8 V (vs. Na^+/Na); the discharge capacity and related columbic efficiency were illustrated in Figures 6a, c and e. Figure 6a shows the discharge capacity for the cell using the P2- $\text{Na}_{2/3}\text{MnO}_2$. The initial discharge capacity of the cell was 104.8 mAh/g, and its discharge capacity was about 79.8 mAh/g after continuous charge/discharge cycling for 80 cycles (about 76% capacity retention). Considering the composition of the final active material is $\text{Na}_{2/3}\text{MnO}_2$, there might be substantial amount of residual Na_2CO_3 , one of the starting materials, remained in the final product. In order to get an idea on the effect of residual Na_2CO_3 , it would make more sense to subtract its mass when

calculating capacity. Assuming all the Mn participated in the reaction of forming $\text{Na}_{2/3}\text{MnO}_2$ and the actual ratio of Na to Mn in the material is 2/3, the capacity would be 122.7 mAh/g and 93.5 mAh/g for the 1st and 80th cycle with capacity retention of 76.2% after subtracting the mass of residual Na_2CO_3 . Compared to P2- $\text{Na}_{2/3}\text{MnO}_2$, P2- $\text{Na}_{2/3}\text{MnO}_2$ -5% exhibited 124 mAh/g initial discharge capacity with 79% capacity retention after 80 cycles. It appears that the large quantity of residual Na_2CO_3 in the electrode does not affect the electrochemical performance of active material. To further confirm this speculation, the pristine P2- $\text{Na}_{2/3}\text{MnO}_2$ material was rinsed with de-ionized water, presuming to get rid of some soluble impurities on the surface, which is confirmed by the TGA analysis later. The cycling performance of P2- $\text{Na}_{2/3}\text{MnO}_2$ -rinsed is shown in Figure 6e. It can be clearly seen that the initial discharge capacity was 120 mAh/g, very close to that of P2- $\text{Na}_{2/3}\text{MnO}_2$ -5%. More importantly, the capacity retention was improved to 89% with the rinsing process.

Figures 6b, 6d, and 6f further compare the rate capabilities of the materials prepared through different approaches. For pristine P2- $\text{Na}_{2/3}\text{MnO}_2$ material, the discharge capacity is 118 mAh/g at 0.05C and 41 mAh/g at 1C, corresponding to 138.8 mAh/g at 0.05C and 49 mAh/g at 1C after subtracting mass of residual Na_2CO_3 . Apparently the rate capability of P2- $\text{Na}_{2/3}\text{MnO}_2$ -5% has not changed much compared to P2- $\text{Na}_{2/3}\text{MnO}_2$ (Figure 6d). However, a slightly better rate capability was observed for P2- $\text{Na}_{2/3}\text{MnO}_2$ -rinsed (Figure 6f) with a 63 mAh/g capacity at 1C.

TGA analysis. TGA characterization of $\text{Na}_{2/3}\text{MnO}_2$ obtained from different approaches was also carried out to validate the role of excessive Na_2CO_3 ; the TGA results of Na_2CO_3 and $\text{Na}_{2/3}\text{MnO}_2$ samples are shown in Figure 7. Figure 7 shows that the Na_2CO_3 sample lose about 2 wt.% at a

temperature range between 100 °C and 150 °C, which was contributed from the loss of the absorbed water in Na₂CO₃. Other than the loss of absorbed water, Na₂CO₃ sample remained unchanged up to 800 °C. A multi-step weight loss was observed for all three cathode materials. Within the temperature range between 100 °C and 150 °C, all the three Na_{2/3}MnO₂ samples lose about 4 wt.% of their initial weight, mostly contributed by the absorbed water. A big discrepancy among three Na_{2/3}MnO₂ samples was observed for the reaction occurred at temperatures above 500 °C, presuming a further reaction between residual Na₂CO₃ or Na₂O with Na_{2/3}MnO₂ to form NaMnO₂ as shown in equation 2.

In the above equation, gas phase species like O₂ and CO₂ was formed; the progress of above reactions can lead to the weight loss as shown in Figure 7. Presuming the sodium cathode material obtained at 600 °C is P2-Na_{2/3}MnO₂, the sample obtained with an initial Na: Mn of 1:1 is a mixture of Na_{2/3}MnO₂ and residual Na₂CO₃ with a molar ratio of 6:1. Note that the decomposition of Na₂CO₃ is not considered here because the amount is negligible. As shown in TGA result (Figure 7), there is no obvious mass loss for Na₂CO₃ at higher temperature (especially when temperature is higher than 600 °C). Actually, as reported by Jong-wan Kim and co-workers [23], unlike Li₂CO₃, the thermal decomposition of Na₂CO₃ started from its melting point (850 °C) and continued as the temperature was increased, but at a very slow rate. Therefore, the amount of Na₂CO₃ decomposed should be negligible compared to the amount left in the P2 Na_{2/3}MnO₂ (synthesized at 600 °C). If Na_{2/3}MnO₂ further reacts with residual Na₂CO₃ at elevated temperatures, it will cause a weight loss of about 8.6 % in theory. The TGA data showed a weight loss of about 10.6 % between 500 °C and 800 °C, which is close to the theoretical number (8.6 wt.%). It can be also indicative that the actual content of sodium in the

final product is less than 2/3. In addition, the occurrence of reaction (equation 2) can result in a reduction of the valence state of manganese, agreeing well with the left shift of Mn absorption edge at a temperature above 600 °C (see Figure 3a). Therefore, the amount of weight loss in Figure 7 can be used as an indicator of the amount of residual Na-containing species that are ready to reaction of $\text{Na}_{2/3}\text{MnO}_2$. The correlation between Figure 6 and Figure 7 implies that the residual Na_2CO_3 does not have any negative impact on the electrochemical performance of the final material.

Na deficiency

The $\text{P2-Na}_{2/3}\text{MnO}_2$ cathode delivered a charge capacity of only 8.98 mAh/g during the first charge and 126.34 mAh/g during the first discharge (see Figure 8a), which is a common phenomenon in the P-type cathode materials for sodium ion battery[24]. In the following cycle, a reversible capacity of 127 mAh/g can be obtained as Na reversibly extract/insert into cathode material as shown in Figure 8b. It proves that Na content in the material is less than the nominal composition. Normally, there are two Na sites in P2 type Na_xMnO_2 , one prismatic site shares faces with MnO_6 octahedron in adjacent layers, while the other prismatic position share edges with MnO_6 octahedron in adjacent layers. Energetically, it is highly unfavorable for Na to occupy both sites simultaneously[25], leading to a less than 0.9 Na per formula[24]. In half cell, the sodium deficiency wouldn't cause any problem because it can be compensated for by metallic sodium used in anode side. However, when cathode is cycled against anode material that is lacking of excess sodium source as in full cell, reversible capacity would be defined by the amount of Na that could be de-intercalated during initial charge, which would limit practical use of this kind of cathode material. It is worth noting that x value in the intermediate phase (P'3

Na_xMnO_2) forming at 600 °C is pretty high according to XANES results as shown in Figure 4c. From practical perspective, P'3 and O type materials with higher initial Na stoichiometry are of more practical importance than P2 type $\text{Na}_{2/3}\text{MnO}_2$.

4. Conclusion

In situ high energy X-ray diffraction (HEXRD) and *in situ* X-ray absorption near edge spectroscopy (XANES) were utilized to follow the structural evolution during the solid-state synthesis of Na_xMnO_2 ; a P2 type $\text{Na}_{2/3}\text{MnO}_2$ was synthesized by sintering the material at 600 °C. Both electrochemical results and HEXRD data agree on a large amount of residual Na_2CO_3 in the material sintered at 600 °C. This implies that the low Na stoichiometry in P2 type material is not originated from the loss of Na_2CO_3 during solid-state synthesis, but from the energetic repulsion of sodium ions in adjunct prismatic sites. The electrochemical results suggest that this energy barrier can at least be partially compensated during charge/discharge to achieve a higher sodium stoichiometry. However, similar energy compensation by synthesizing the material at elevated temperatures will result in O type materials. Although the residual Na_2CO_3 shows insignificant impact on the electrochemical performance of P2 type $\text{Na}_{2/3}\text{MnO}_2$, the nature of its sodium deficiency makes it of less practical importance for sodium-ion batteries. We expected our results could provide a good guide for future development of high performance cathode materials for sodium-ion batteries.

Acknowledgement

Research was funded by U.S. Department of Energy (DOE), Vehicle Technologies Office. Support from David Howell and Tien Duong of the U.S. DOE's Office of Vehicle Technologies Program is gratefully acknowledged. Argonne National Laboratory is operated for the US Department of Energy by UChicago Argonne, LLC, under contract DE-AC02-06CH11357. Use of the Advanced Photon Source (APS) and the Center for Nanoscale Materials, including resources in the Electron Microscopy Center, was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

Figure 1. Contour plot of *in situ* HEXRD patterns collected during the solid state synthesis (a) and covariance analysis of *in situ* HEXRD profiles (b).

Figure 2. *In situ* HEXRD patterns collected (a) and phase evolution (b) during the solid state synthesis and the peak change between 1° to 1.25° from 400°C to 900°C (c)

Figure 3. Contour plot of in situ Mn K-edge XANES spectrum collected during the solid state synthesis (a) and the corresponding covariance analysis (b).

Figure 4. Normalized Mn K-edge XANES at various stages during heating: (a) from 271 to 305 °C; (b) from 542 to 554 °C ; (c) from 577 to 599 °C; (d) from 644 to 667 °C.

Figure 5. XRD pattern of P2 $\text{Na}_{2/3}\text{MnO}_2$ synthesized at 600 ° C.

Figure 6. Cycling performance at 0.1C and rate performance versus cycle number between 2.0 V and 3.8 V for $\text{Na}_{2/3}\text{MnO}_2$ synthesized with Na:Mn=1:1 (a) and (b), Na:Mn=0.735:1 (c) and (d), Na:Mn=1:1 after rinsing (e) and (f) .

Figure 7. TGA analysis of Na_{2/3}MnO₂ synthesized at different condition and Na₂CO₃ under argon atmosphere.

Figure 8. Evolution of cell voltage as a function of charge/discharge capacity in P2-Na_{2/3}MnO₂ and P2-Na_{2/3}MnO₂-rinsed during 1st cycle (a) and 2nd cycle (b) between 1.9 V and 3.8 V.

References

- [1] S.-W. Kim, D.-H. Seo, X. Ma, G. Ceder, K. Kang, *Adv. Energy Mater.* 2 (2012) 710-721.
- [2] M.D. Slater, D. Kim, E. Lee, C.S. Johnson, *Adv. Funct. Mater.* 23 (2013) 947-958.
- [3] C. Delmas, C. Fouassier, P. Hagenmuller, *Physica B & C* 99 (1980) 81-85.
- [4] D.H. Lee, J. Xu, Y.S. Meng, *Phys. Chem. Chem. Phys.* 15 (2013) 3304-3312.
- [5] D. Yuan, W. He, F. Pei, F. Wu, Y. Wu, J. Qian, Y. Cao, X. Ai, H. Yang, *J. Mater. Chem. A* 1 (2013) 3895.
- [6] D. Kim, E. Lee, M. Slater, W. Lu, S. Rood, C.S. Johnson, *Electrochem. Commun.* 18 (2012) 66-69.
- [7] J. Billaud, G. Singh, A.R. Armstrong, E. Gonzalo, V. Roddatis, M. Armand, T. Rojo, P.G. Bruce, *Energy Environ. Sci.* 7 (2014) 1387.
- [8] X. Wu, J. Guo, D. Wang, G. Zhong, M.J. McDonald, Y. Yang, *J. Power Sources* 281 (2015) 18-26.
- [9] L. Liu, X. Li, S.-H. Bo, Y. Wang, H. Chen, N. Twu, D. Wu, G. Ceder, *Adv. Energy Mater.* 5 (2015) 1500944-1500948.
- [10] J.P. Parant, R. Olazcuage, M. Devalette, C. Fouassier, E.P. Hagenmuller, 3 (1971) 1-11.
- [11] S. Kumakura, Y. Tahara, K. Kubota, K. Chihara, S. Komaba, *Angew Chem. Int. Ed.* 55 (2016) 12760-12763.
- [12] Z.H. Chen, Y. Ren, Y. Qin, H.M. Wu, S.Q. Ma, J.G. Ren, X.M. He, Y.K. Sun, K. Amine, *J. Mater. Chem.* 21 (2011) 5604-5609.
- [13] Y.C. Kan, Y. Hu, J. Croy, Y. Ren, C.J. Sun, S.M. Heald, J. Baren, I. Bloom, Z.H. Chen, *J. Power Sources* 266 (2014) 341-346.
- [14] B. Ravel, M. Newville, *J. Synchrotron Radiat.* 12 (2005) 537-541.
- [15] Y. Li, R. Xu, Y. Ren, J. Lu, H.M. Wu, L.F. Wang, D.J. Miller, Y.K. Sun, K. Amine, Z.H. Chen, *Nano Energy* 19 (2016) 522-531.
- [16] M. Yoncheva, R. Stoyanova, E. Zhecheva, E. Kuzmanova, M. Sendova-Vassileva, D. Nihtianova, D. Carlier, M. Guignard, C. Delmas, *J. Mater. Chem.* 22 (2012) 23418.
- [17] J. Billaud, R.J. Clement, A.R. Armstrong, J. Canales-Vazquez, P. Rozier, C.P. Grey, P.G. Bruce, *J. Am. Chem. Soc.* 136 (2014) 17243-17248.
- [18] S.J. Hwang, J.H. Choy, *J. Phys. Chem. B* 107 (2003) 5791-5796.
- [19] K.W. Nam, M.G. Kim, K.B. Kim, *J. Phys. Chem. C* 111 (2007) 749-758.
- [20] R.J. Clément, P.G. Bruce, C.P. Grey, *J. Electrochem. Soc.* 162 (2015) A2589-A2604.
- [21] I. Hasa, D. Buchholz, S. Passerini, J. Hassoun, *ACS Appl. Mater. Interfaces* 7 (2015) 5206-5212.
- [22] D. Buchholz, L.G. Chagas, C. Vaalma, L. Wu, S. Passerini, *J. Mater. Chem. A* 2 (2014) 13415.
- [23] J.W. Kim, H.G. Lee, *Metall. Mater. Trans. B* 32B (2001) 17-24.
- [24] R.J. Clement, P.G. Bruce, C.P. Grey, *J. Electrochem. Soc.* 162 (2015) A2589-A2604.
- [25] R. Berthelot, D. Carlier, C. Delmas, *Nat. Mater.* 10 (2011) 74-80.