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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

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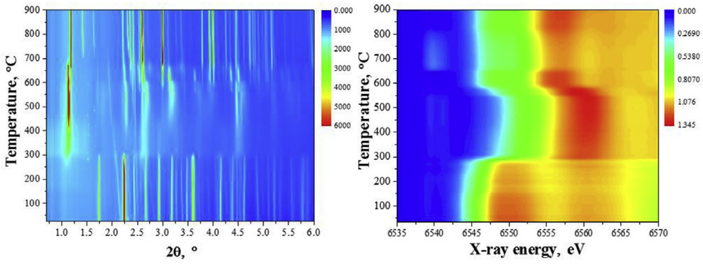
HIGHLIGHTS

- Multi intermediate phases including P3 and P′3 was observed before O′3 phase
- $NaMnO_2$ can be formed at 600 °C.
- Residue sodium carbonate doesn't have any obvious negative effect on sodium cathode.
- P2 type $Na_{2/3}MnO_2$ synthesized at 600 °C have low initial charge capacity.

GRAPHICAL ABSTRACT



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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 $Na_{2/3}MnO_2$. 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 $Na_{2/3}MnO_2$. A P2 type $Na_{2/3}MnO_2$ was synthesized at reduced temperature (600 °C). The influence of Na_2CO_3 impurity on the electrochemical performance of P2 $Na_{2/3}MnO_2$ was thoroughly investigated in our work. It was found that the content of Na_2CO_3 can be reduced by optimizing Na_2CO_3/$MnCO_3$ 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.

1. Introduction

Lithium-ion batteries have been widely used to power modern portable electronics over the past decades due to their high energy density. However, with an increasing need for large-scale energy storage system on electric vehicle and energy grid system, concern

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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 (M = 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 $[MO_2]$ 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 $Na_{2/3}MnO_2$ and P2 $Na_{2/3}MnO_2$ 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 $Na_{2/3}MnO_2$. The crystallization of P2 $Na_{2/3}MnO_2$ and P'2 $Na_{2/3}MnO_2$ 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 $Na_{2/3}MnO_2$. The results showed that O′3 type sodium manganese oxides start to form at about 600 °C. Therefore, P2 type $Na_{2/3}MnO_2$ was synthesized at reduced temperature (600 °C). The influence of Na_2CO_3 impurity on the electrochemical performance of P2 $Na_{2/3}MnO_2$ was thoroughly investigated. It was found that the content of Na_2CO_3 can be reduced by optimizing $Na_2CO_3/MnCO_3$ 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

2.1. 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).

2.2. 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 Na_2CO_3 and $MnCO_3$ 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].

2.3. 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.

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

2.4. Synthesis of P2 type $Na_{2/3}MnO_2$

$Na_{2/3}MnO_2$ was prepared by a solid-state reaction using Na_2CO_3 and $MnCO_3$ as starting materials. In a typical synthesis, Na_2CO_3 and $MnCO_3$ 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 mins to obtain a mixed powder. And the powder was then calcined at 600 °C for 10 h. To investigate the potential impact of residuals, 0.25 g of sintered powered was suspend in 10 ml deionized water for 5 mins. After the rinse, the powder was then filtered out and dried in an oven at 105 °C overnight to remove the residual water.

2.5. 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 cm^2 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 ($NaPF_6$) 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 cycler between 2.0 V and 3.8 V at different current density.

2.6. 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

3.1. In situ HEXRD

In order to understand the formation mechanism of Na_xMnO_2, *in situ* HEXRD technique was used to monitor the structure evolution during the solid-state synthesis as shown in Fig. 1a, in which red color means high intensity and blue color represents low