Synthesis and crystal structure of P-type $Na_xMn0.65Co_{0.18}Ni_{0.17}O_2$ cathode material with high capacity

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Introduction

Sodium ion batteries have attracted much attention due to the accessibility of the raw materials.

In 1980, TiS_2[1] and Na_xCoO_2[2] with layered structures were reported for use as cathode materials for sodium ion battery. Up to now, many kinds of layered materials, for example, $Na_{2/3}(Ni_{1/3}Mn_{2/3})O_2$[3], $NaFeO_2$[4], $NaMn_{1/2}Ni_{1/2}O_2$[5], $Na_{2/3}(Fe_{1/2}Mn_{1/2})O_2$[6] and so on, have been studied as the cathode materials.

Recently, we reported $Na_{0.95}Li_{0.15}(Mn_{0.55}Co_{0.1}Ni_{0.15})O_2$, prepared by by the electrochemical Li-Na ion exchange of $Li_{1.2}Mn_{0.55}Co_{0.10}Ni_{0.15}O_2$, show a high initial discharge capacity of more than 200 $mAhg^{-1}$.[7]

In this study, the $Na_xMn0.65Co_{0.18}Ni_{0.17}O_2$, prepared by solid state reaction, was found to deliver a high discharge capacity. In addition to evaluation of the electrochemical performance of the material, detailed crystal structure of as-prepared sample and structural change during charge and discharge process were also investigated.

Experimental

Sample was obtained by heating a mixture consisting of Na_2CO_3, Mn_3O_4 and $M(OH)_2$ (M = Mn, Co, Ni) in the temperature range of 600 °C and 900 °C for 10 h in air. An electrode was prepared by attaching a mixture of the active material (90 wt.%), acetylene black (5 wt.%) and polyvinylidenedifluoride (5 wt.%) to aluminum foil. The electrode was tested in a 2032-type coin cell assembled using a sodium foil anode, a separator (Celgard 2400) and electrolyte (1M $NaPF_6$ in EC/ DEC (1:1 volume ratio)). Galvanostatic charge-discharge tests were performed at 30 °C and the current density of 0.05C-rate in the potential range of 1.0–4.5 V vs. Na/Na^+. The structural change of the sample during charge and discharge process was evaluated using XRD with Mo-Kα radiation and the detailed crystal structure of the as-prepared sample was characterized by high-resolution synchrotron radiation (BL19B2, SPring8, Japan).

Results and Discussions

Figure 1 shows XRD pattern, calculated one and their difference based on the Rietveld refinements of the product synthesized at 900 °C. The crystal structure of the products was found to belong to P2-type structure. Based on the ICP analysis, the chemical formula of the sample was determined to be $Na_{0.76}Mn_{0.65}Co_{0.18}Ni_{0.17}O_2$.

Figure 2 shows the charge and discharge curves of the electrodes in the voltage range of 1.0-4.5V ($vs.Na/Na^+$) for the initial and second cycles. The second charge/ discharge capacity showed 220/218 $mAhg^{-1}$, respectively.

Figure 3 shows the changes in the lattice parameters *a* and *c* of the P2-$Na_{0.76}Mn_{0.65}Co_{0.18}Ni_{0.17}O_2$ during the initial charge and discharge process. The P2-$Na_{0.76}Mn_{0.65}Co_{0.18}Ni_{0.17}O_2$ maintained its crystal structure during charge/discharge process with 13 % *c* axis change.

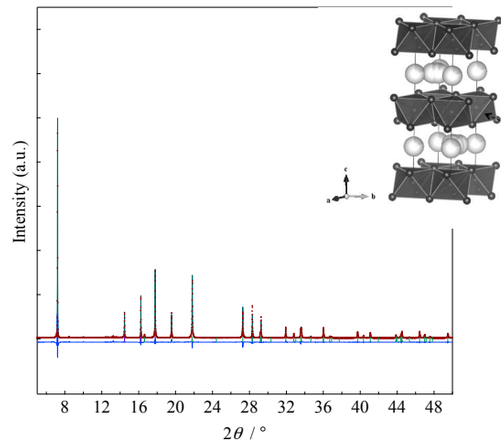

Fig.1 XRD pattern, calculated one and their difference based on the Rietveld refinements of P2-type $Na_xMn0.65Co_{0.18}Ni_{0.17}O_2$ and the structural model.

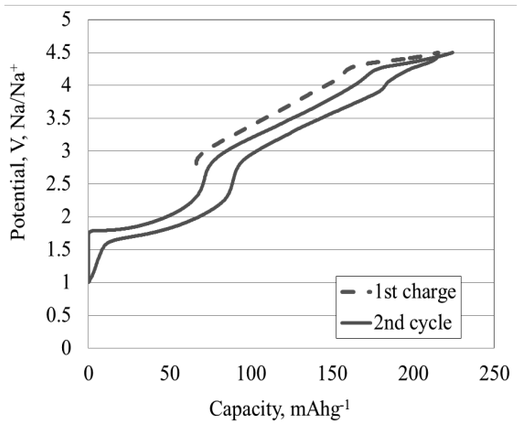

Fig.2 First and second charge / discharge curves of the.P2-type $Na_xMn0.65Co_{0.18}Ni_{0.17}O_2$.

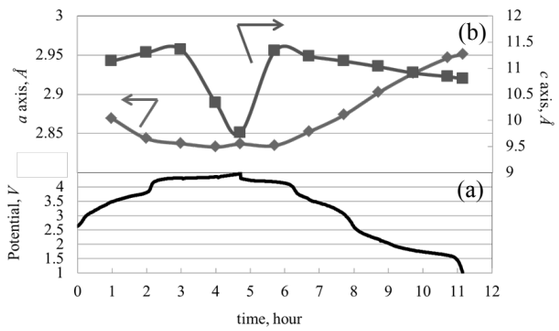

Fig.3 (a) Voltage vs. time for P2-type $Na_xMn0.65Co_{0.18}Ni_{0.17}O_2$. *in situ* X-ray cell. (b) Lattice parameters *a* and *c* vs. time corresponding to the voltage-time curve in (a). (■) *c* axis; (♦) *a* axis.

Refferences

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