Sodium insertion cathode material $\text{Na}_{0.67}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ with excellent
electrochemical properties

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Abstract

Layered-structured ternary oxide $\text{Na}_{0.67}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ is synthesized as cathode material for sodium-ion batteries. Using a liquid nitrogen quenching process during the synthesis procedure, a $\text{Na}_{0.67}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ powder with a mixed P2-O3 structure is obtained, and then characterized. The $\text{Na}/\text{Na}_{0.67}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ cell delivers a reversible capacity of 167 mA h g^{-1} and exhibits excellent cycling and rate performances without abnormal initial coulombic efficiency.

Keywords: sodium-ion battery; P2 phase; cathode; mixed structure; coulombic efficiency

1. Introduction

In recent years, sodium ion batteries (NIBs) are targeting large-scale energy storage owing to their abundant resources of electrode materials and significantly low cost [1-5]. Transition metal oxides with layered structures such as Na_xMO_2 ($\text{M} = \text{Co}, \text{Ni}, \text{Mn}, \text{Cr}, \text{Fe}, \text{V}$) are of great interest as cathode materials for rechargeable sodium ion batteries, because the layered structures allow the reversible insertion and extraction of sodium ions. Different from layer-structured cathodes LiMO_2 , in which the lithium ions occupy an octahedral site between the $[\text{MO}_2]$ layers, the sodium ions in Na_xMO_2 tend to occupy an octahedral site (O) or a prismatic site (P) between the $[\text{MO}_2]$ layers, since the radius of sodium ions is larger than that of lithium ions. As a result, Na_xMO_2 possesses several layered polymorphs in which oxide-ion layers stack in different manners as ABCABC (O3), ABBA (P2), ABBCCA (P3), and so on. The determinant of the structure is the proportion of sodium ion in initial composition [6].

Among various layered polymorphs of Na_xMO_2 , P2- Na_xMO_2 is the most widely studied one, in which the sodium ions occupy a prismatic site. The P2-type Na_xMO_2 examples are $\text{Na}_{0.67}[\text{Mn}_{0.65}\text{Ni}_{0.15}\text{Co}_{0.2}]\text{O}_2$ [7], $\text{Na}_{0.67}[\text{Mn}_{0.65}\text{Fe}_{0.2}]\text{O}_2$ [8], $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ [9], $\text{Na}_{2/3}\text{Co}_{2/3}\text{Mn}_{1/3}\text{O}_2$ [10], $\text{Na}_{2/3}\text{Co}_{1-y}\text{Mn}_y\text{O}_2$ [11], and $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ [12], and they show good electrochemical properties. However, their high capacity can only be reached in the second cycle of a half-cell $\text{Na}_x\text{MO}_2/\text{Na}$ because of the initial Na-deficient compositions. Such an abnormality in the initial coulombic efficiency (over 100%) is not desirable for a cathode material in a practical full cell. Here, a liquid nitrogen quenching process is introduced into the synthesis

procedure to obtain a $\text{Na}_{0.67}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ powder composed of mainly P2 phase and slightly O3 phase. Compared to a pure P2-phase sample with same composition, different quenching processes result in different structures. This P2-O3 ternary cathode material shows higher capacity, more excellent cycling and rate performances without the abnormality of initial coulombic efficiency.

2. Experimental

P2- $\text{Na}_{0.67}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ powders were synthesized by a one-step solid-state reaction method. 3.551 g Na_2CO_3 (2% excess, purity:99.5%) and 9.124 g coprecipitated precursor $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_x$ (Elementec Ltd in Suzhou) were mixed in ethanol by roller ball milling with 70 g zirconia balls (5mm in diameter) for 20 h and dried at 120°C in an electric oven. The mixture was calcined at 900°C for 10 h in air in an electric furnace, then immediately diverted into the liquid nitrogen to obtain sample A. For comparison, the same powder was cooled naturally in the furnace to obtain sample B. Sample C was synthesized by the same process as sample B, but with a different composition $\text{Na}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$. All samples were stored in argon atmosphere.

The crystalline structures of the samples were characterized using a diffractometer (Philips X'Pert Pro Super, Cu $K\alpha$ radiation). The XRD spectra were collected in a range of 2θ values from 10° to 70° at a scanning rate of 10° min⁻¹. The morphologies and Energy Dispersive Spectroscopy (EDS) of the samples were studied by scanning electron microscopy (SEM, JSM-6390 LA, JEOL). The

compositions of sample A and sample B were also analyzed by Inductive Coupling Plasma (ICP, Optima 7300 DV).

The electrochemical properties of the layered cathode materials were evaluated in 2032 type coin cells using a Na disk as the counter electrode and 1.0 M NaClO₄ in PC solution as the electrolyte. The cathode laminates were prepared by mixing the active materials (84 wt%), acetylene black (8 wt%) and PVDF (8 wt%) in N-methyl-pyrrolidinone into electrode slurries and then casting the slurries on aluminium foil collector. The typical mass loading of the active material within the laminate is 2 mg cm⁻². The cells (CR2032 size) were assembled in an argon-filled glove box (MBRAUN LAB Master 130) with above electrode laminates as working electrodes and a glass fiber (whatman Gf/D) as the separator. The cells were tested on a multi-channel battery test system (NEWARE BTS-610) with galvanostatic charge and discharge in different selected voltage ranges.

The cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS) measurements of the cells were measured on a CHI 660D electrochemical workstation. The CV tests were performed with fresh half-cells in the voltage range of 1.5-4.4 V vs. Na/Na⁺ for three times at a scan rate of 0.1 mV s⁻¹. The EIS tests were performed with a 5 mV AC signal in the frequency range of 0.01-10000 Hz. To measure the total impedance of the cells, a galvanostatically cycling (voltage range 1.5-4.4V) was carried for three times and then discharge to 3.5 V.

3. Results and discussion

The X-ray diffraction (XRD) analysis (**Fig. 1a**) indicates that sample B obtained with natural cooling shows a pure P2 crystal structure with a space group P63/mmc (JCPDS No. 54-0894) where the sodium ions occupy two distinct prismatic sites in $\text{Na}_{0.67}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ (**Fig. 1b**). The sample C with the composition $\text{Na}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ shows the pattern of a pure O3 phase that can be indexed to R-3m space group with the $\alpha\text{-NaFeO}_2$ structure (JCPDS No. 54-0887), in which the sodium ions occupy octahedral sites. Interestingly, the pattern of sample A is composed of the diffraction peaks mainly from P2 but also slightly from O3. It has been found that different cooling processes can influence the presence of manganese vacancies, which leads to different crystallography [13, 14]. Inductively Coupled Plasma (ICP) analysis indicates that the real compositions of sample B is $\text{Na}_{0.625}[\text{Ni}_{0.416}\text{Co}_{0.203}\text{Mn}_{0.381}]\text{O}_2$, while sample A is $\text{Na}_{0.641}[\text{Ni}_{0.410}\text{Co}_{0.205}\text{Mn}_{0.385}]\text{O}_2$. Thus, with different cooling procedures, the compositions of sample A and sample B are similar but their structures are different. A similar P2-O3 composite $\text{Na}_{0.66}\text{Li}_{0.18}\text{Mn}_{0.71}\text{Ni}_{0.21}\text{Co}_{0.08}\text{O}_{2+\delta}$ was also synthesized using different precursors by Zhou et al [15], indicating that the P2-O3 composite has better electrochemical properties.

All samples consist of particles of about 1~2 μm with irregular shapes (**Fig. 2**). Those two samples for the SEM analysis were prepared by dispersing the powders onto conductive tapes (**Fig. 2a** and **2b**). As shown in **Fig. 2c** and **Fig. 2d**, if the SEM samples are prepared by first dispersing the powders in ethanol and then releasing a few drops of the dispersed solution onto conductive tapes supported on an aluminum foil, the surfaces of the particles look different compared to those of dry powders (**Fig.**

2a and **2b**). It suggests that those samples can react with ethanol so that the sodium can be dissolved to a large extent. The ratios of the metal ions of those two samples are $\text{Na}_{0.074}\text{Ni}_{0.416}\text{Co}_{0.193}\text{Mn}_{0.391}$ and $\text{Na}_{0.068}\text{Ni}_{0.385}\text{Co}_{0.193}\text{Mn}_{0.422}$, respectively, which are confirmed by our EDS analysis. In fact, it has been reported that $\text{Na}[\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}]\text{O}_2$ can react with moisture and carbon dioxide in the air [16]. Hence, it is necessary for those samples to be cooled in liquid nitrogen during the preparation and stored in argon atmosphere.

Different from normal cathode materials, the P2-type cathodes such as sample B here show different charge-discharge curves for the first and subsequent cycles because of its lack of sodium (**Fig. 3a** and **3b**). It leads to an apparently abnormal coulombic efficiency of over 100%, which is impossible in a practical full cell [17]. Sample B shows a reversible capacity of 123 and 143 mAh g^{-1} in a voltage range of 1.5-4.2 V and 1.5-4.4 V, respectively. It should be noted that these capacities cannot be achieved in a full cell. However, sample A with the mixed P2-O3 phases shows different cycling behaviors in the first and second charge-discharge curves with a coulombic efficiency of less than 100% (**Fig. 3c** and **3d**). It delivers a reversible capacity of 138 and 164 mAh g^{-1} in a voltage range of 1.5-4.2 V and 1.5-4.4 V, respectively.

Looking into the detailed sodium insertion and extraction steps, both samples have five redox couples between 1.5 V and 4.0 V (**Fig. 4a** and **4b**), which is similar to those of O3-type $\text{Na}[\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}]\text{O}_2$ [16], corresponding to the redox reactions from Ni^{2+} and Ni^{3+} in the Na-rich discharged states to Ni^{4+} in the Na-depleted charged

states. The redox couples over 4.0 V correspond to $\text{Co}^{3+} \rightleftharpoons \text{Co}^{4+}$, which are accompanied by a phase transition from P2 to OP4 with poor reversibility for both samples [12]. The most significant difference between A and B is their charge-discharge behaviors in the low potential range, in which a plateau at around 2.4 V is detected for sample A. This plateau is observed in O3-type materials such as NaNiO_2 [18], $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [19], and $\text{Na}[\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}]\text{O}_2$ [16], indicating that a small quantity of O3 phase in sample A plays an important role. A sloping curve is measured near 2.0 V for sample B, which is observed in other P2-type materials. When charged to 4.0 V, a capacity of 114 mAh g^{-1} is measured (**Fig. 3c**), corresponding to 0.44 mole Na^+ per mole of sample A. This matches exactly to the 4.0 V-charged state $\text{Na}_{0.205}[\text{Ni}_{0.410}\text{Co}_{0.205}\text{Mn}_{0.385}]\text{O}_2$ in which all the Ni ions are present in Ni^{4+} while Co ions still in Co^{3+} . Thus, the capacity above 4.0 V must correspond to the redox couple of $\text{Co}^{3+}/\text{Co}^{4+}$.

Table 1 lists the electrochemical data of the first cycle of the half-cells Na/A, Na/B and Na/C in different voltage ranges. Generally, sample B has a coulombic efficiency of exceeding 100%, which is not achievable in a full cell. For sample A, such an abnormal efficiency (121%) is measured in a narrow voltage range (1.5-4.0 V). It becomes “normal” when the voltage range is enlarged to 1.5-4.2 V (82%) or 1.5-4.4 V (85%). The coulombic efficiency is “normal” for sample C but with rather low efficiency (78%, 63% and 46%), meaning very poor cycling performances.

The cycling behavior of the P2-O3 sample A also shows much better stability than the P2-phase sample B (**Fig. 5a** and **5b**). In the voltage range of 1.5-4.2 V, the

capacity of sample B decreases gradually from 123 mAh g⁻¹ initially to 75 mAh g⁻¹ after 55 cycles (a retention of 61%). If the upper cut-off voltage is 4.4 V, its capacity fades more rapidly from 143 mAh g⁻¹ initially to about 28 mAh g⁻¹ after 70 cycles. For sample A, its capacity changes from 138 mAh g⁻¹ initially to 122 mAh g⁻¹ after 100 cycles (1.5-4.2 V) and 164 mAh g⁻¹ initially to 116 mAh g⁻¹ after 100 cycles (1.5-4.4 V). Such an electrochemical performance is better than other P2-type materials with high capacity, such as Na_{0.67}[Mn_{0.65}Ni_{0.15}Fe_{0.2}]O₂ (204 mAh g⁻¹, 80% retention after 30 cycles) [8], Na_x[Fe_{1/2}Mn_{1/2}]O₂ (190 mAh g⁻¹, 80% retention after 30 cycles) [12]. To our knowledge, the cycling performance of sample A in the voltage range of 1.5-4.2 V is the best in literature for a cathode material of sodium-ion batteries.

Although the two samples (A and B) have the same composition Na_{0.67}[Ni_{0.4}Co_{0.2}Mn_{0.4}]O₂, their high-rate performances are entirely different (**Fig. 6a** and **6b**). In the voltage range of 1.5 to 4.2 V, sample B delivers the discharge capacities of 124, 110, 87, 64, 35 and 20 mAh g⁻¹ at 0.1, 0.2, 0.5, 2 and 5 C, respectively, whereas sample A delivers the discharge capacities of 140, 139, 134, 129, 121 and 91 mAh g⁻¹ at 0.1, 0.2, 0.5, 1, 2 and 5 C, respectively. Obviously, sample A is much better than sample B in terms of rate performance. Also, in the voltage range of 1.5 to 4.4 V, the rate performances of both samples become slightly worse. Nevertheless, sample A still retains 125 mAh g⁻¹ at 2 C, corresponding to 76% of its capacity at 0.1 C.

The comparative measurements of the electrochemical impedance spectra of the

half-cells Na/A and Na/B (**Fig. 7**) can explain their difference in the rate performance. The intercept at the Z' axis in the high frequency refers to R_s , which includes electrolyte solution resistance and electric contact resistance. The semicircle in the high and middle frequency ranges is due to the charge transfer resistance (R_{ct}) and its corresponding constant-phase-angle element (Q_{ct}) at the interfaces of the electrolyte and the electrodes. The sloping line in the lower frequency represents sodium-ion diffusion resistance in electrode bulk, namely the Warburg impedance (W)[20]. Clearly, the R_{ct} of sample B is about 10 times larger than that of sample A, which is consistent with the rate performance results (**Fig. 6a** and **6b**). The impedance spectrum of sample A can be fit to two semicircles, corresponding to the charge-transfer processes, i.e. R_{ct} and Q_{ct} , which can be further fit to two semicircles with R_{ct1} , Q_{ct1} , R_{ct2} and Q_{ct2} as shown in **Fig. 7a**. It can indirectly suggest this sample is a mix of two phases. This is likely caused by the different Ni^{4+} contents in sample A and sample B. The segmental phase of sample A is O3 phase which contains less amount of Ni^{4+} than P2 phase. More Ni^{4+} ions in P2 phase (sample B) may oxidize the electrolyte to a larger extent and thus form a thicker surface layer on the electrode. The thicker surface layer suppresses the charge transfer process and the R_{ct} increases largely as measured here. Therefore, this P2-O3 composite can stabilize the surface of the active material.

4. Conclusions

In summary, a layer-structured ternary cathode material

$\text{Na}_{0.67}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ with P2-O3 mixed phases is fabricated by a simple solid-state reaction process with a quenching procedure. It exhibits a considerably high reversible capacity of 164 mAh g^{-1} with an average voltage of 3.1 V versus sodium metal, meaning that the energy density is estimated to be 510 Wh kg^{-1} , which is comparable to that of LiFePO_4 (about 530 Wh kg^{-1} versus Li) [21]. It also shows excellent cycling stability and rate performance in the voltage range of 1.5 to 4.2 V. We believe that the results shown here prove that this material can be used in sodium-ion batteries for large-scale applications with a comparable electrochemical performance to the present large-scale lithium-ion batteries.

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Figure captions:

Fig. 1 a) XRD patterns of sample A (blue), sample B (red) and sample C (black). b) Schematic crystal structure of P2 phase.

Fig. 2 SEM images of sample A (a, c) and sample B (b, d). For SEM analysis, the powders were either dispersed directly on conductive tapes (a, b) or dispersed first in ethanol (c, d).

Fig. 3 The first and the second charge-discharge curves at 0.1 C rate of sample B (a, b) and sample A (c, d) in the voltage ranges of 1.5-4.2 V (a, c) and 1.5-4.4 V (b, d).

Fig. 4 CV curves of sample A (a) and sample B (b) in the voltage ranges of 1.5-4.4 V and at a scan rate of 0.1 mV s⁻¹.

Fig. 5 The cycling performances of sample A and sample B in the voltage ranges of 1.5-4.2 V (a) and 1.5-4.4 V (b). The coulombic efficiency data for sample A are also given in (a) and (b).

Fig. 6 The rate performances of sample A and sample B in the voltage ranges of 1.5-4.2 V (a) and 1.5-4.4 V (b).

Fig. 7 Nyquist plots of half-cells Na/A (a) and Na/B (b) which are discharged to 3.5 V at 4th cycle. The black scattered points are original data, the red lines are fitting curve. Insets are the equivalent circuits and fitting results.

Table 1 Electrochemical data of the first cycle of half-cells Na/A , Na/B and Na/C in different voltage ranges

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table 1

Electrochemical property		1.5-4 V	1.5-4.2 V	1.5-4.4 V
Sample A	Charge capacity / mAh g ⁻¹	108	168	196
	Discharge capacity / mAh g ⁻¹	131	138	164
	Coulombic efficiency	121%	82%	84%
Sample B	Charge capacity / mAh g ⁻¹	70	84	134
	Discharge capacity / mAh g ⁻¹	110	123	143
	Coulombic efficiency	157%	146%	107%
Sample C	Charge capacity / mAh g ⁻¹	120	179	205
	Discharge capacity / mAh g ⁻¹	93	112	94
	Coulombic efficiency	78%	63%	46%