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# The novel P3-type layered $Na_{0.65}Mn_{0.75}Ni_{0.25}O_2$ oxides doped by nonmetallic elements for high performance sodium-ion batteries



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#### HIGHLIGHTS:

performance.

versible capacity.

stable P2 phase.

• A novel P3-NaMNO is synthesized via

low temperature annealing process.

• The non-metal elements doped sam-

 NaMNO-F suppresses P3-O1 phase transition and delivers a higher re-

 Boron doping can transform the NaMNO from P3 phase to a more

ples show an excellent electrochemical

#### G R A P H I C A L A B S T R A C T

 $\underbrace{ Step I \\ Sintering \\ M_{3}Ni(CO_{3})_{4}} \underbrace{ Step I \\ J.SMn_{2}O_{3}*NiO \\ } \underbrace{ Step I \\ Mixing \\ 0 \\ Sintering \\ M_{3}NiO_{3}} \underbrace{ Step II \\ Mixing \\ 0 \\ Sintering \\ M_{3}NiO_{3}} \underbrace{ Step II \\ Mixing \\ 0 \\ Sintering \\ M_{3}NiO_{3}} \underbrace{ Step II \\ M_{3}NiO_{3}} \underbrace{ Step II \\ M_{3}NiO_{3}} \underbrace{ Step II \\ M_{3}NiO_{3}} \underbrace{ M_{3}NiO_{3}} \underbrace{ M_{3}O_{3}*NiO \\ N_{3}O_{3}*NiO_{3}} \underbrace{ M_{3}O_{3}*NiO \\ N_{3}O_{3}*NiO_{3}} \underbrace{ M_{3}O_{3}*NiO_{3}} \underbrace{ M_{3}O_{3}*NiO_{3}} \underbrace{ M_{3}O_{3}*NiO_{3}} \underbrace{ M_{3}O_{3}*NiO_{3}} \underbrace{ M_{3}O_{3}*MiO_{3}} \underbrace{ M_{3}O_{3}*MiO_{3}*MiO_{3}} \underbrace{ M_{3}O_{3}*MiO_{3}} \underbrace{ M_{3}O_{3}*MiO_{3}*MiO_{3}} \underbrace{ M_{3}O_{3}*MiO_{3}} \underbrace{ M$ 

#### ABSTRACT

Due to the attractive advantage of safety and cost of sodium-ion batteries, lithium-ion batteries can be replaced by sodium-ion batteries with the ever-increasing demand of large-scale energy storage systems. However, short cycle life and poor rate performance restrict sodium-ion batteries further commercial application. Cathode materials are one of the most important components of sodium-ion batteries, which have an unparalleled effect on the electrochemical performance of sodium-ion batteries. Herein, the novel P3-Na<sub>0.65</sub>Mn<sub>0.75</sub>Ni<sub>0.25</sub>O<sub>2</sub> cathode material doped by non-metal elements is synthesized via hydrothermal method and subsequent low temperature annealing process. The as-prepared P3-Na<sub>0.65</sub>Mn<sub>0.75</sub>Ni<sub>0.25</sub>O<sub>2</sub> shows excellent electrochemical performance due to doping of non-metal elements. It can be found that fluorine doped Na<sub>0.65</sub>Mn<sub>0.75</sub>Ni<sub>0.25</sub>F<sub>0.1</sub>O<sub>1.9</sub> can distinctly suppress P3-O1 phase transition and deliver a higher reversible capacity of 163.7 mAh g<sup>-1</sup> at 0.1 C, while boron doped Na<sub>0.65</sub>Mn<sub>0.75</sub>Ni<sub>0.25</sub>B<sub>0.1</sub>O<sub>2</sub> transforms from P3 phase to a more stable P2 phase and exhibits remarkable cycle life and rate performance. Therefore, this new strategy doping by means of non-metal elements provides a significant exploration for the development of the high capacity electrode materials of sodium-ion batteries.

### ARTICLE INFO

Keywords: Sodium-ion batteries Cathode material Crystalline phase Phase transition Non-metal elements Electrochemical performance

#### 1. Introduction

The environmental pollution caused by the excessive use of traditional fossil energy has received widespread attention. Seeking green and renewable energy has been research hotspots in the field of energy storage and conversion. Lithium-ion batteries (LIBs) have already dominated the field of electric energy storage (EES) application due to the high energy density and environmental friendliness [1]. However, for the sake of safety concerns and the rapid rise in the price of lithium resources, more and more scientists are exploring the new energy storage system as an alternative to LIBs for electric energy storage [2]. Sodium-ion batteries (SIBs) are considered more promising in the large-

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scale energy storage market due to the similar electrochemical properties to LIBs, abundant resource and low cost.

Tremendous works have been made on the commercial application of SIBs. On the one hand, the electrolyte and separator with excellent electrochemical performances have been developed for SIBs. On the other hand, a number of active materials are applied to electrode materials. To date, most anode materials could exhibit more than  $200 \text{ mAh g}^{-1}$  capacity and show a stable cycle life [3]. However, the cathode materials play a vital role in the development of SIBs. Hence, how to exploit high capacity and long cycle life cathode materials are the major challenges for SIB commercialization.

Generally speaking, an excellent electrode material for LIBs/SIBs should be high discharge capacity, high initial coulombic efficiency, high rate capability, long cycle life and low cost. Up till now, a large number of significant works on cathode materials for SIBs have been reported, e.g., transition metal oxides [4], ferrocyanides [5], polyanionic compounds [6], and organic-based materials [7]. However, still many significant problems in the cathode materials, such as low specific capacity, poor cycling performance, and instability in the air, etc., need to be solved. In addition, relatively low energy density and average operating voltage all limit SIBs practical applications in the future [8]. Hence, transition metal oxides  $Na_xMO_2$  (M = Mn, Ni, Co, etc.) have received extensive attention due to the high discharge capacity, high energy density and commercial viability as cathode materials of SIBs [9].

Due to different structures,  $Na_xMO_2$  can be divided into two classes: layered structure and tunnel-structure. The tunnel-type oxides exhibit small pentagon tunnels [10], while the sodium-ions are electrochemically inactive in the small tunnels. Hosono et al. reported  $Na_{0.44}MnO_2$  only offered 140 mAh g<sup>-1</sup> when cycled in the voltage of 2.0–4.0 V [11]. In contrast, the layered oxides exhibit better electrochemical performance than tunnel oxides. According to the arrangement of the sodium layer and the transition-metal, Delmas et al. classified layered- $Na_xMO_2$  into two main groups: O3 and P2 types. The letter O refers to alkali ions occupying octahedral sites and the letter P refers to prismatic sites [7].

O3-type oxides mostly show a high reversible capacity, it is beneficial to increase the energy density of cathode materials. However, O3-type Na<sub>x</sub>MO<sub>2</sub> usually undergoes a complicated phase transition during the charge-discharge process, although the O3-type oxides exhibit stable layered structure, due to the large difference in volume among each phase, O3-type Na<sub>x</sub>MO<sub>2</sub> is demonstrated a poor cycle life. Therefore, suppressing phase transition is the most effective way to improve cycling performance of O3-type oxides at present. Yuan et al. reported that O3-Na<sub>3</sub>Ni<sub>6</sub>SbO<sub>6</sub> material shows an excellent cyclability with reversible three-phase transitions. However, a partial irreversible O3-P3-O1 phase transition is still found in O3-Na<sub>3</sub>Ni<sub>6</sub>SbO<sub>6</sub> [12]. Therefore, phase transition effect is a significant problem in O3-type Na<sub>x</sub>MO<sub>2</sub> and limits their practical applications in large-scale energy storage.

In contrast, P2-type oxides could maintain original structure during Na<sup>+</sup> insertion/extraction owing to a more open framework and direct Na-ion diffusion [13]. In addition, because P2-Na<sub>x</sub>MO<sub>2</sub> cannot react with water or carbon dioxide, P2-type oxides are normally stable in ambient atmosphere. However, limited sodium storage content cannot provide sufficient sodium-ion during charge-discharge process, thus most P2-type oxides can only deliver a low reversible capacity. For example, the P2-Na<sub>2/3</sub>[Ni<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> only displays 86 mAh g<sup>-1</sup> during the first discharge process in the voltage window of 2.0–4.0 V [14]. Therefore, P2-type Na<sub>x</sub>MO<sub>2</sub> is likely to be less competitive commercially.

During the long period of academic research on layered oxides, it has been found that the crystalline phase largely influences the electrochemical performance of layered oxides. Hence, developing a new crystalline phase will become an effective strategy for improving the electrochemical performance of layered oxides. The P3 and P2 phases have the same sodium accommodation as the prismatic sites and the O3 phase always transforms to the P3 phase during charge and discharge process [13]. Thus, P3 phase is a special crystalline phase which is related to both P2 and O3 phases. The local environment of the Na ions at prismatic sites, along with the particular diffusion pathway determines the unique electrochemical kinetics of P3 phase. In addition, P3 phase layered oxides have nearly the same excellent structural stability as P2 phase, thus, P3 phase layered oxides show a better cycle life and rate performance than O3 phase. Moreover, P3 phase layered oxides provide a higher sodium content than P2 phase and show a higher discharge capacity. However P3 phase shows also a higher sodium diffusion barrier than P2 phase [13]. The large radius of Na ions could destroy the structure of P3-type layered oxides during Na<sup>+</sup> intercalation/deintercalation. Fortunately, recent works have shown that the reasons for structural degradation and the low initial coulomb efficiency can be attributed to the redox activities on oxygen anions [15-18], because the lattice oxygen is irreversibly converted into oxygen, most layered oxides do not exhibit a satisfactory cycle life. Thus, optimizing Na-ions migration paths and electrochemical properties of P3-type oxides to meet the requirements of SIBs practical applications in energy storage become the current development trend.

Up to now, substantial improvements have been made in the electrochemical properties of layered-NaxMO2, such as element-doping, nanostructure design or carbon-coating [19-22], especially elementsubstitution has received extensive attention due to effective improvements in electrochemical performance. For example, NaNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/</sub> <sub>3</sub>O<sub>2</sub> shows a capacity retention of 100% after 50 cycles [23]. In contrast,  $Na[Ni_{0.5}Mn_{0.5}]O_2$  exhibits a bad cycling behavior with 85% capacity retention after 50 cycles [24]. At the same time, non-metallic element doping has also been used to improve the electrochemical properties of electrode materials [25]. Moreover, non-metallic element doping could suppress the redox activities on oxygen anions, which has attracted extensive attention. Particularly, non-metallic element doping has been widely studied in the lithium-rich layered oxides [26,27], Li et al. proposed that the reversibility of the oxygen redox in Li<sub>2</sub>RuO<sub>3</sub> can be suppressed via incorporating boron atoms. B<sub>0.15</sub>-Li<sub>2</sub>RuO<sub>3</sub> shows a remarkable cycling behavior with 90% capacity retention after 100 cycles [28]. Lee et al. reported the partial substitution of fluorine for oxygen in the interstitial sites of layered oxides could reduce the oxygen redox activity, thereby stabilizing the structure of the materials [29].

In this work, based on the high abundance and low cost of the manganese and the inherent stability of the Mn<sup>4+</sup> oxidation state, and the high specific capacity of Na<sub>x</sub>NiO<sub>2</sub>, firstly, the nickel-substituted manganese-based P3-type layered oxide by a low temperature annealing process was prepared. Because of the synergetic function of various metal ions when introducing Ni<sup>2+</sup> into transition metal layer, the spherical  $Na_{0.65}Mn_{0.75}Ni_{0.25}O_2$  (denoted hereafter NaMNO) with special crystalline phase could deliver 160 mAh g<sup>-1</sup> reversible capacity and show a more stable cycle life than the most layered oxides cathode materials of SIBs. Secondly, in order to further improve the electrochemical properties of the cathode material, we introduced non-metallic element like fluorine and boron respectively into sample to suppress the redox activities on oxygen anions and stabilize the lavered structure. It has been found that the sample Na<sub>0.65</sub>Mn<sub>0.75</sub>Ni<sub>0.25</sub>F<sub>0.1</sub>O<sub>1.9</sub> (denoted hereafter NaMNO-F), which doped with fluorine, shows a higher reversible capacity and better cycle life; while the boron doping sample  $Na_{0.65}Mn_{0.75}Ni_{0.25}B_{0.1}O_2$  (denoted hereafter NaMNO-B) shows superior cycle performance and rate performance.

#### 2. Experiment section

# 2.1. Preparation of nickel-substituted manganese-based P3-type layered oxides

Layered oxides NaMNO, NaMNO-F, NaMNO-B were synthesized by a solid-state reaction method using manganese-nickel oxide precursor,



Fig. 1. Illustration for the designed route to synthesize NaMNO-F/B.

Table 1The results of ICP-OES and IC.

Material samples	Element content (%)						
	Na	Mn	Ni	F	В		
NaMNO	14.53	40.12	14.17				
NaMNO-F	14.37	40.04	14.06	0.0186			
NaMNO-B	14.55	40.01	14.33		0.0108		

sodium carbonate, sodium fluoride and Boric acid. The precursor is obtained by hydrothermal and sintering, the manganese chloride and nickel chloride in the molar ratio of 3:1 were dissolved into ethylene glycol and stirred for 2h, then adding an excess of ammonium bicarbonate under stirring for 30 min, the mixture was transferred to the hydrothermal reactor and reacted at 180 °C for 18 h in a high temperature oven. Filtering the obtained decomposition solution and washing with deionized water and ethanol. The obtained powder was transferred to an oven and dried at 60 °C for 12 h. The dried material was calcined at 550 °C for 6 h in an open-air muffle furnace with 2 °C/ min to synthetic precursor: 1.5Mn<sub>2</sub>O<sub>3</sub>·NiO. Sodium fluoride as a source of fluorine and boric acid as a source of boron were grinded respectively with precursor and sodium carbonate (transition-metal: sodium = 1:1.05), then the mixtures was dried at 40 °C and calcined at 700 °C for 10 h in a muffle furnace with 4 °C/min, Rapidly cooled (5 °C/ min) to room temperature. The products finally stored under inert atmosphere (see Fig. 1.).

#### 2.2. Characterization

In order to obtain the accurate composition of each chemical composition of the products, chemical analysis of the synthesized materials was performed with an inductively coupled plasma optical emission spectrometer (ICP-OES, DIONEX-ICS-1100, America). Furthermore, determination of fluoride ion content of sample material by ion chromatography (IC, DIONEX-ICS-5000, America). The crystalline structure was characterized by X-ray diffraction (XRD, Model D8-Advance, Germany) using the Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) at 40 mA and 40 kV over the 2 $\theta$  range from 10° to 90°. The particle morphology and particle size distribution studies were carried out with field emission scanning electron microscope (FESEM, Hitachi S-4800). The microstructure and element distribution of particle was observed by high resolution transmission electron microscopy and the EDX mapping (JEM-2100F microscope operating at 200 kV). The element valence was determined by X-ray photoelectron spectroscopy (XPS, Thermo-250XI, CN).

#### 2.3. Electrochemical measurement

Positive electrodes were prepared by mixing 10 wt% of Super P (SP), 80 wt% of active material and 10 wt% of PVDF in N-methyl-2pyrrolidone (NMP) and coating the slurry on Al foil. The active material mass loading in the electrodes was about  $2 \text{ mg cm}^{-2}$ . The button cells were assembled in an argon filled glovebox. Sodium metal was used as counter and reference electrodes, and the metal sodium was cut from sodium chunks (99.8%, Aladdin) and then made into sodium tablets. The positive electrodes separated from the negative electrode 3 sheets of glass fiber disks. which are soaked with a  $1 \mod L^{-1}$  solution of NaClO<sub>4</sub> in an ethylene carbonate (EC)/propylene carbonate (PC) mixture (1/1 v/v). Cells were cycled galvanostatically at different constant current rates between 2.0 and 3.75 V in Neware battery tester (BTS-XWJ-6.44S-00052 Neware, Shenzhen, China). Cyclic voltammetry (CV) tests were performed at a scan rate of  $0.1 \text{ mV s}^{-1}$  between 2.0 and 3.75 V (vs Na<sup>+</sup>/Na). CV measurements were conducted using an electrochemical workstation (CHI660e Chenhua, China). The EIS was also recorded using the same instrument over the frequency range from 100 kHz to 10 mHz, while the disturbance amplitude was 5 mV. All the electrochemical measurements were carried out at 25 °C.

#### 3. Results and discussion

The elemental compositions of the as-prepared materials are examined from the ICP-OES and tabulated in Table1. It can be seen from Table 1 that the content of each element is consistent with the initial design.

The morphologies of the as-prepared precursor, NaMNO, NaMNO-F and NaMNO-B are shown in Fig. 2. The precursor material shows a uniform spherical morphology in Fig. 2(a), moreover, higher magnification SEM images suggest that each sphere is made up of primary nanoparticles. As shown in Fig. 2(b)–(d), three product samples all show the micron-sized spherical morphology, and the size of spherical particles are about  $1 \mu m$ . Usually, the appropriate size of particle is



Fig. 2. (a) SEM images of precursor: 1.5Mn<sub>2</sub>O<sub>3</sub>·NiO, (b) NaMNO, (c) NaMNO-F, (d) NaMNO-B.



Fig. 3. The XRD patterns and Rietveld plots of (a) NaMNO, (b) NaMNO-F, (c) NaMNO-B, (d) observation of the P3-type crystal structure along the b axis, (e) observation of the P3-type crystal structure along the c axis, (f) observation of the P2-type crystal structure along the b axis, (g) observation of the P2-type crystal structure along the c axis.

more beneficial to increase the tap density of the electrode material [30]. In contrast with NaMNO, after sintering with sodium carbonate, the spherical particles are made up of nano-sized sheet-like primary particles. It will be more beneficial to enhance electrolyte infiltration and improve coulombic efficiency.

In order to further analyze the crystal structure of the as-prepared materials, the XRD patterns and Rietveld refinement of NaMNO, NaMNO-F, NaMNO-B samples are shown in Fig. 3. Fig. 3(a) and 3(b) shows the XRD patterns and Rietveld plots of NaMNO and NaMNO-F, and all the observed patterns are indexed to a rhombohedral lattice with space group R3m. Obviously, the diffraction peak positions of NaMNO-F are in good agreement with NaMNO, which indicates that the fluorine-doped does not change the crystal structure of the original material. The Rietveld refinement are calculated on the basis of the P3- $Na_{0.62}Ti_{0.37}Cr_{0.63}O_2$  model structure [13] and the refinement results are R<sub>wp</sub> of 8.63% and 9.15%, respectively. Fig. 3(c) shows the XRD patterns and Rietveld plots of NaMNO-B, all of the diffraction lines could be indexed to the P2-type structure with space group P63/mmc. By utilizing the P2-Na\_{0.67}Mn\_{2/3}Ni\_{1/3}O\_2 model [31], the refinement result is R<sub>wp</sub> of 8.72%. In Fig. 3(a)–(c), the observed patterns are in accordance with the calculated pattern, and no impurity peaks are observed in all XRD patterns. Detailed crystallographic data on refined NaMNO, NaMNO-F and NaMNO-B are compared in Table 2.

Fig. 3(d) and (f) demonstrate the crystal structure of P3-NaMNO and P3-NaMNO-F and the oxygen stacking order is ABBCCA, one MeO<sub>6</sub> octahedron and three edges, three MeO<sub>2</sub> sheets per unit cell (Fig. 3d) have prisms sharing one face with MeO<sub>6</sub> octahedra of the next layer, and only one sodium site (Fig. 3e). The crystal structures of P2-type NaMNO-B are shown in Fig. 3(f) and (g), characterized by ABBA oxygen stacking including two MeO<sub>6</sub> octahedra per unit cell (Fig. 3b), sharing edges with six MeO<sub>6</sub> octahedra or either sharing faces with two MeO<sub>6</sub> octahedra of adjacent slabs, and offer two different sites for Na-ions. The results of Fig. 3(a) and (b) prove that the fluorine-doped does not change crystalline structure of the material. In contrast, the crystalline structure has changed dramatically after the introduction of boron atoms and the phase transition of P3-P2 is observed, which has never been reported in the same literatures. Because of the radius of  $B^{3+}$  ions is only 0.27 Å, thus, interstitial-site doping is possible and the M-O bonds are lengthened due to the strong B-O bonds, inducing the local prism geometrical distortion [27]. Furthermore, the P3 and P2 phases have the same sodium accommodation as prismatic sites. Hence, it is possible that the boron-doped material undergoes a P3-P2 phase

Tal	ble	2

Lattice 1	parameters	of P2	and P3	bhase	samples	after	Rietveld	refinement

Sample	NaMNO		NaMNO-F		NaMNO-B	
Phase	P3		P3		P2	
Space Group	R3m		R3m		P63/mmc	
Cell parameters	a (Å)	2.86133	a (Å)	2.86455	a (Å)	2.88325
-	b (Å)	2.86133	b (Å)	2.86455	b (Å)	2.88325
	c (Å)	16.65310	c (Å)	16.65038	c (Å)	11.14412
	α (°)	90	α (°)	90	α (°)	90
	β (°)	90	β (°)	90	β (°)	90
	γ (°)	120	γC	120	γ (°)	120
	Volume (Å <sup>3</sup> )	118.076 (15)	Volume (Å <sup>3</sup> )	118.865 (10)	Volume (Å <sup>3</sup> )	80.231 (8)
R-factors	R <sub>wp</sub> (%)	8.63	R <sub>wp</sub> (%)	9.15	R <sub>wp</sub> (%)	8.72
	R <sub>p</sub> (%)	6.84	R <sub>p</sub> (%)	6.42	R <sub>p</sub> (%)	7.45
	$\chi^2$	1.36	$\chi^2$	1.42	$\chi^2$	1.27



Fig. 4. (a) TEM image of NaMNO, (b) HRTEM image of NaMNO and (c) the fast Fourier transform pattern, (d-g) distribution of elements in the NaMNO, (h) TEM image of NaMNO-F, (i) HRTEM image of NaMNO-F and (j) the fast Fourier transform pattern, (k) the characteristic EDX spectrum of NaMNO-F (l-p) distribution of elements in the NaMNO-F, (q) TEM image of NaMNO-B, (r) HRTEM image of NaMNO-B and (s) the fast Fourier transform pattern, (t) the characteristic EDX spectrum of NaMNO-B, (u-y) distribution of elements in the NaMNO-B.

transition.

The structure of samples is further characterized by transmission electron microscope (TEM). Fig. 4(a), (h) and (q) are corresponded to the TEM images of NaMNO, NaMNO-F and NaMNO-B, respectively. TEM images further confirm the sphere structure of three product samples. The fast Fourier transform (FFT) patterns and representative high-resolution TEM results of three sample materials are shown Fig. 4(b–c), (i–j) and (r–s), respectively. As in Fig. 4(c), the crystal lattice fringe spacing is 2.37 Å, it corresponds to the (0 1 2) lattice plane of NaMNO. As shown in Fig. 4(i) and (j), the (0 1 2) lattice plane also is observed in NaMNO-F with crystal lattice fringe spacing is 2.37 Å. The (0 1 2), (0 0 6) and (1 0 4) lattice plane are belong to P3-type structure with R $\bar{3}m$  space group which has been reported in the literature [13,32]. As a contrast, the (0 1 2), (0 0 4) and (1 0 1) lattice plane in Fig. 4(i) are belong to P2-type structure with P63/mmc space group. The (1 0 1) lattice fringe spacing is 2.43 Å. Hence, the TEM images are consistent with the XRD refinement results. The characteristic EDX spectrum of NaMNO-F is shown in Fig. 4(k), the result proves the existence of fluorine in the sample material. And similarly, the characteristic EDX spectrum which is shown Fig. 4(t) proves the boron existence in NaMNO-B. The elements distribution in the samples was characterized by EDX-mapping. Fig. 4(d–g), (l–P) and (u–y) are corresponded to EDX-mapping results of NaMNO, NaMNO-F and NaMNO-B, respectively. All elements demonstrate a similar homogeneous distribution in the all measured area according to EDX-mapping results.

XPS measurements show the more information about the oxidation state of transition-metal ions in the NaMNO, NaMNO-F and NaMNO-B. The spectra are shown in Fig. 5. Through referencing the C 1s line to 284.85 eV to correct the binding energies for specimen charging. As shown in Fig. 5(a), the absence of other impurity and the presence of



Fig. 5. XPS spectra of (a) survey spectrum, (b) Na 1s, (c) F 1s, (d) B 1s, (e) Mn 2p, (f) Ni 2p, (g) O 1s for sample materials.

Na, Mn, Ni and O as well as C from the reference are proved by the NaMNO survey spectra. In addition, the presence of F and B are proved in the respective spectra of two sample materials. The dominant peaks at which binding energies of 643.8 and 855.7 eV are assigned to  $Mn^{4+}$  and Ni<sup>2+</sup> [33]. Fig. 5(b) shows the fitting and deconvolution of Na (1s) spectrum and the binding energy (BE) of 1071 eV which is good consistent with the values reported the similar cathode materials [34]. As shown in Fig. 5(c) and (d), the characteristic peaks in which binding energies of 685.7 and 192 eV are attributed to F<sup>-</sup> and B<sup>3+</sup>. Because the F 1s binding energy value obtained from NaF is about 683.5 eV [35], F-

ions can be confirmed to be derived from M-F and there is no NaF in the NaMNO-F after annealing. Similarly, no other peaks were observed in survey spectra of NaMNO-B, it proves that B<sup>0</sup> is not existent in NaMNO-B. Accordingly, this indirectly proves that boron element has incorporated into the material structure.

The Mn 2p XPS spectra of three sample materials are shown in Fig. 5(e), the Mn 2p spectrum has two main characteristic peaks of  $2p_{1/2}$  at 654.4 eV and  $2p_{3/2}$  at 642.8 eV, indicating the dominant Mn(IV) cation in three sample materials. The less obvious peaks at 653.3 and 641.8 eV, which are attributed to Mn(III) cation can be also observed. However, the ratio of Mn(III) and Mn(IV) in the three sample materials is different. As shown in Fig. 5(e), the ratio of Mn(III) and Mn(IV) is the largest in NaMNO-F and the smallest in NaMNO-B since fluorine doping can effectively reduce the average valence of Mn [29]. Thus, NaMNO-F shows the highest capacity during the first charge process.

Fig. 5(f) shows the Ni 2p XPS spectra, the peak located at about 854.3 eV is assigned to Ni  $2p_{3/2}$  and a small peak at about 862.0 eV is corresponded to Ni(II) cation. The existence of Ni<sup>3+</sup> is proved by the less prominent peak at 855 eV. As shown in Fig. 5(e) and (f), no obvious peak displacement occurred after fluorine or boron doping, it shows that the oxidation state species of the transition metal ions is not changed after the doping of non-metal ions. Moreover, Ni<sup>3+</sup> and Mn<sup>3+</sup> ions in the lattice may be caused by valence degradation [36]. The two oxygen contributions are shown in the high resolutions spectrum for the O 1s region (Fig. 5g). Usually, the peak at 529.6 eV is typical of metal oxygen bonds (lattice oxygen) and the peak at 531.2 eV is usually associated with surface species including chemisorbed oxygen, hydroxyls or under coordinated lattice oxygen [37,38]. The surface oxygen is reduced after doping F because F-ions are electronegative and it repels the adsorption of electronegative surface oxygen. More lattice oxygen exposure is beneficial to improve the electrochemical activity of NaMNO-F. In contrast, the B-ions with multiple positive charges could attract electronegative surface oxygen, thus, surface oxygen increased after doping B in NaMNO-B. A large amount of surface oxygen accumulation on the material surface will inhibit the transformation of lattice oxygen to surface oxygen. Therefore, boron doping suppresses the oxidation reduction of oxygen anions and stabilizes the structure of the material.

The electrochemical performance of NaNMO, NaMNO-F and NaMNO-B are evaluated by assembling sodium half cells. The electrochemical properties of three samples as the cathode materials are first investigated by CV curves. Fig. 6(a-c) exhibit the CV curves of the NaMNO, NaMNO-F and NaMNO-B electrodes between 1.5 and 4.0 V versus Na<sup>+</sup>/Na at a scan rate of  $0.1 \text{ mV s}^{-1}$ . From CV curves of NaMNO, it can be found that there are four pair of obvious oxidation/ reduction peaks. The reduction/oxidation peaks at 1.8/2.1 V correspond to the redox couples of  $Mn^{3+}/Mn^{4+}$ . And the peaks at 3.1/3.2 V and 3.2/3.3 V are assigned to the redox couples of Ni<sup>3+</sup>/Ni<sup>4+</sup> and Ni<sup>2+</sup>/Ni<sup>3+</sup>. It's worth noting that the NaMNO shows a pair of strong reduction/oxidation peaks (3.58/3.70 V vs Na<sup>+</sup>/Na), which correspond to the P3-O1 phase transition [12]. It is known that the phase transition is apparently not beneficial to maintain the material structure stability during Na<sup>+</sup> intercalation/deintercalation. And CV curves of NaMNO-F does not exhibit reduction/oxidation peaks corresponding to the P3-O1 phase transition, it demonstrates the suppression of the phase transition after F doping. It's probably because the stronger M-F bonds can maintain the stability of the material, and thus the structural variation is difficult to occur. Furthermore, CV curves of NaMNO-F shows greater graphic area than which of NaMNO, thus, NaMNO-F could exhibit a higher capacity. As shown in Fig. 6(c), the reduction/oxidation peaks of  $Mn^{3+}/Mn^{4+}$  are 1.8/2.0 V. The potential difference is 0.2 V, which is less than 0.3 V of NaMNO and NaMNO-F. Therefore, NaMNO-B has a smaller electrode polarization and will exhibit a better rate performance and kinetics characteristic. In addition, the closer overlapping of the CV curves of NaMNO-F and NaMNO-B confirm a higher reversibility of Na<sup>+</sup> sodiation/de-sodiation than NaMNO. However, the peak



Fig. 6. The first three consecutive cyclic voltammograms of (a) NaMNO, (b) NaMNO-F, (c) NaMnO-B, (d) the first charge and discharge profiles of samples, (e) the sencond charge and discharge profiles of samples, cycling performance of samples at (f) 0.2 C, (g) 0.5 C, (h) 1 C, (i) rate performance of samples, (j) Nyquist plots of samples recorded at open circuit voltage.

intensity of the reduction/oxidation peaks decreases, which are at 3.1/3.2 V and 3.2/3.3 V, hence the corresponding charge and discharge platforms are no longer obvious for NaMNO-F and NaMNO-B samples.

Fig. 6(d) shows the charge and discharge performance of NaMNO, NaMNO-F and NaMNO-B as cathode materials. When cycled at 0.1 C, the NaMNO. NaMNO-F and NaMNO-B samples exhibit the initial discharge capacities of 156.3, 163.7 and  $150 \text{ mAh g}^{-1}$  in the voltage window of 1.5-3.75 V, respectively, which are close to the theoretical capacity  $(170 \text{ mAh g}^{-1})$ . Among three samples, the NaMNO-F shows the highest discharge capacity, based on XPS analysis this may be more electrochemically active Mn<sup>3+</sup> participating in redox reactions. In contrast, because the introduction of boron inhibits the redox of oxygen, the NaMNO-B exhibits a lower discharge capacity. In order to obtain the complete charge and discharge platforms for three samples, the charge and discharge curve of the second cycle for each sample is shown in Fig. 6(e), three samples exhibit charge capacities of 181, 180 and  $175 \text{ mAh g}^{-1}$ , respectively, corresponding to the coulombic efficiency of 85.5%, 86.1% and 85.7%. The extra charge capacity might be assigned to the oxidative decomposition of sodium propyl carbonate generated the formation of a solid electrolyte interphase or involving oxygen redox couples [39,40]. As shown in Fig. 6(e), the charge and discharge platforms of samples perfectly correspond to the results of CV.

The cycling performances of NaMNO, NaMNO-F and NaMnO-B at 0.2 C, 0.5 C and 1 C are shown in Fig. 6(f-h). When the three samples cycle at 0.2 C, the initial reversible capacities are 133.3, 136.9, and 123.7 mAh g<sup>-1</sup>, respectively. After 100 cycles, the capacities retentions are 75.1%, 83.1% and 86.2%, respectively. All the samples show good cycle stability. Although NaMNO demonstrates maximum capacity fading, NaMNO shows a much-improved cycle performance compared with the same type of materials in the literature [31]. In addition, NaMNO-F and NaMNO-B show a higher initial coulombic efficiency, demonstrating that NaMNO-F and NaMNO-B have fewer side reactions during charge and discharge. The reversible capacities are 122.4, 128.0, and 115.7 mAh  $g^{-1}$  at the current densities of 0.5 C, after 200 cycles, the capacity fades are 0.225%, 0.13% and 0.085% per cycle, respectively. Similarly, when the samples cycled at 1 C, NaMNO-F and NaMNO-B also show a better cycle performance than NaMNO, while NaMNO-B exhibits the best cycle life among three samples.

Fig. 6(i) illustrates a C-rate test, the current densities from 0.1 C to 1 C within 1.5–3.75 V. As shown in Fig. 6(i), NaMNO shows unsatisfactory rate performance. When the current rate comes back to 0.1 C again, the discharge capacities could be almost recovered to the initial values except NaMNO. Moreover, NaMNO-B shows a capacity rising slightly since the material fully activated in the previous cycle.

In addition, the electrochemical impedance spectroscopy (EIS) measurements are fitted using the equivalent circuit given in Fig. 6(j). EIS measurements are carried out after 3 cycles at 0.1 C. The EIS plots are consisted of a slope line at low frequency and a semicircle at high frequency. In general, the slop line at low frequency range is the Warburg impedance (Zw), which is concerned with Na<sup>+</sup> diffusion in the particles of the electrode material. The semicircle at the higher frequency range reflects the charge transfer resistance (R<sub>ct</sub>), R<sub>ct</sub> is associated with the electrochemical kinetics of material. The intercept of the semicircle with the Z' real axis is related to uncompensated ohmic resistance (R<sub>s</sub>). It corresponds to the resistance between the electrolyte and cathode interface. After fitting, R<sub>s</sub> values of NaMNO, NaMNO-F and NaMNO-B are 5.71, 4.55 and 4.21  $\Omega$ , respectively. However, NaMNO shows maximum R<sub>ct</sub> value of about 384.3  $\Omega$ , NaMNO-F and NaMNO-B show a lower R<sub>ct</sub> values of 159 and 74.7  $\Omega$ .

#### 4. Conclusion

A kind of novel P3-Na<sub>0.65</sub>Mn<sub>0.75</sub>Ni<sub>0.25</sub>O<sub>2</sub> cathode materials for the application of SIBs is successfully synthesized via hydrothermal method and low temperature annealing process. The Na<sub>0.65</sub>Mn<sub>0.75</sub>Ni<sub>0.25</sub>O<sub>2</sub> cells

show an initial specific discharge capacity of 156.3 mAh  $g^{-1}$  at 0.1 C. In order to further improve the electrochemical performance of NaMNO, doping non-metallic elements (F and B) into this kind of P3 materials shows distinct significance. Especially, fluorine doping can effectively reduce the average valence of Mn, hence, more electrochemically active Mn<sup>3+</sup> is involved in the charge and discharge process, thus, NaMnO-F shows a higher reversible capacity. Furthermore, fluorine doping can successfully suppress P3-O1 phase transition and the stronger M-F bonds can be maintained in the cyclic process, thus, NaMnO-F exhibits a better cycle performance. Besides, boron doping can suppress the oxidation reduction of oxygen anions and stabilize the structure of the material, moreover, boron doping can transform the material from P3 phase to a more stable P2 phase, thus NaMNO-B demonstrates an excellent rate performance and cycle life. Apparently, non-metallic element doping is an effective strategy to improve the electrochemical performance of the cathode material, and NaMNO with fluorine or boron doping can clearly enhance discharge capacity, rate capability and cyclic stability.

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