**Cobalt-substituted $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$: phase evolution and a high capacity
positive electrode for sodium-ion batteries**

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Abstract

$\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ ($x=0, 0.01, 0.08, 0.11, 0.22, 0.33, 0.44$) powders are synthesized as positive electrodes for sodium-ion batteries via a thermopolymerization method. X-ray diffraction and scanning electron microscopy are used to analyze their crystal structures and particle morphologies. Galvanostatic cell cycling is used to characterize the electrochemical properties. The Co-substitution can change the structure of $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ from T-type ($x=0$) into layered P2-type ($x=0.11$) or P3-type ($x=0.44$). For the samples synthesized under our specific conditions, the particle morphology can be used as an indicator of their crystal structures: rod-like (T-type), plate-like (P2-type) and granules (P3-type). P2-type $\text{Na}_{0.44}\text{Mn}_{0.89}\text{Co}_{0.11}\text{O}_2$ allows more Na^+ intercalation into the inter-layer spacing and results in a high discharge capacity with 220 mAh g^{-1} at 12 mA g^{-1} in initial cycle, 180 mAh g^{-1} after 40 cycles in the voltage range of 2.0-4.2 V and a good rate performance

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of 104 mAh g⁻¹ at a rate of 600 mA g⁻¹ in the voltage range of 2.0-4.0 V.

Keywords: sodium ion battery; phase evolution; layered structure; sodium manganese oxide; cobalt doping.

1. Introduction

Despite of huge success of lithium-ion batteries (LIBs) in portable electronics and electric vehicles, high cost and safety concerns in some extreme environments constraint their utilization, especially for large-scale energy storage systems. Therefore, sodium ion batteries (SIBs) as alternatives to LIBs have attracted much attention owing to their abundant resources of electrode materials and significantly low cost [1-5].

Among the sodium positive electrode materials, $\text{Na}_{0.44}\text{MnO}_2$ (i.e. $\text{Na}_4\text{Mn}_9\text{O}_{18}$) with a tunnel structure is rather attractive, because the orthorhombic $\text{Na}_{0.44}\text{MnO}_2$ possesses high rate capability and good cycle stability as a positive electrode material [6-8]. It may be also applied in aqueous sodium-ion batteries [9,10]. In order to gain in-depth understanding of the structure and evolutions, and further improve its electrochemical properties, various studies have been performed in literature. For its synthesis, it has been synthesized by hydrothermal method [11], polyvinyl pyrrolidone-combustion method [12], molten-salt method [13,14] and so on. Lattice doping is also an effective way to tailor the structures and properties of electrode materials, while most doping studies on this material are focused on Ti-substituted $\text{Na}_{0.44}\text{MnO}_2$ [15, 16]. Other transition metal elements are rarely used as dopants in $\text{Na}_{0.44}\text{MnO}_2$. Herein, we report that a certain amount of Co-substitution can change the crystal structure of $\text{Na}_{0.44}\text{MnO}_2$ from tunnel-type(or T-type) into layered P2-type or P3-type, and increase substantially the electrochemical capacity of sodium storage,

where "P" refers to the Na coordination (trigonal prismatic), and "2" or "3" to the number of MO₂ slabs in the hexagonal cell [17]. More interestingly, we find the particle morphology has a clear link with the crystal structure. Furthermore, the P2-type Na_{0.44}Mn_{0.89}Co_{0.11}O₂ can deliver a rather high initial discharge capacity of 220 mAh g⁻¹ at 0.1C and retain 180 mAh g⁻¹ after 40 cycles in 2.0-4.2V.

2.Experimental

The powders with compositions Na_{0.44}Mn_{1-x}Co_xO₂ (x=0, 0.01, 0.08, 0.11, 0.22, 0.33, 0.44) were synthesized by a thermopolymerization method. 0.021 mol NaNO₃ (Sinopharm, AR), stoichiometric amounts of Co(NO₃)₃·6H₂O (Sinopharm, AR) and Mn(CH₃COO)₂·4H₂O (Sinopharm, AR) were dissolved in 90 ml deionized water to obtain aqueous solutions, into which 10 ml HNO₃ was added to avoid hydrolysis. Then 50 ml acrylic acid (Sinopharm, CR) was added into the solutions in a beaker. The solutions were heated at 180°C for 10 h in an oven to complete the thermopolymerization process, during which water was evaporated to form gels that were decomposed to produce fluffy foam-like solid products in the beaker. The products were grinded and first preheated at 500°C for 6 h to get rid of organic residues, and a subsequent heat treatment was carried out at 900°C for 10 h. All the heat treatment processes were carried out in air atmosphere. The sintered products were grinded into fine powders.

The crystalline structures of the samples were characterized by using a diffractometer (Philips X'Pert Pro Super, Cu K α radiation). The XRD patterns were

collected in a range of 2θ values from 10° to 60° at a scanning rate of $10^\circ \text{ min}^{-1}$. The Rietveld refinement was performed using the General Structure Analysis System (GSAS) program to obtain the lattice parameters and the relative contents of phases. The morphologies of the samples were studied by scanning electron microscopy (Sirion 2000, FEI) equipped with energy dispersive X-ray (EDS) microanalysis hardware.

The electrochemical properties of the $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ ($x=0, 0.01, 0.08, 0.11, 0.22, 0.33, 0.44$) powders were evaluated in 2032 type coin cells using a Na disk as the counter electrode and 1.0 M NaClO_4 in ethylene carbonate and diethyl carbonate (EC:DEC = 1:1) containing also 1.0 wt% fluoroethylene carbonate (FEC) solution as the electrolyte. The positive electrode laminates were prepared by mixing the active materials (80wt%), acetylene black (10 wt%) and PVDF (10 wt%) in N-methyl-pyrrolidinone into an electrode slurry and then casting the slurry on aluminum foil as a current collector. The cells were assembled in an argon-filled glove box with above electrode laminates as working electrodes. The separator was glass fiber (Whatman Gf/D). The cells were tested on a multi-channel battery test system (NEWARE BTS-610) with galvanostatic charge and discharge in different selected voltage ranges. Cyclic voltammetry and AC impedance spectroscopy measurements on the cells were performed with a CHI 604B electrochemical workstation.

3. Results and discussion

3.1 Crystal structures and particle morphologies of $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$

The XRD patterns of the $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ samples are shown in **Fig. 1**. Almost

all the diffraction peaks of $\text{Na}_{0.44}\text{MnO}_2$ can be indexed as an orthorhombic $\text{Na}_{0.44}\text{MnO}_2$ structure with a Pbam space group (JCPDF 27-0750). The pattern confirms the formation of well-crystallized tunnel structured $\text{Na}_{0.44}\text{MnO}_2$ (T-type), although a few extra un-identified impurity peaks appeared, which are usually observed for $\text{Na}_{0.44}\text{MnO}_2$ [13,16]. When a small amount of Co ($x=0.01$) is used to substitute Mn, an extra peak at around 16° (2θ) appears in addition to the T-type peaks. It belongs to the strongest (002) peak of a layered P-type phase. With increasing the Co content, the intensity of the P-type (002) peak becomes stronger while the peaks from the T-type structure are weakened until completely disappear at $x=0.11$. This result reveals the phase evolution process from T-type to P2-type when x changes from 0 to 0.11. The XRD pattern of $\text{Na}_{0.44}\text{Mn}_{0.89}\text{Co}_{0.11}\text{O}_2$ can be indexed into a pure P2-type $\text{Na}_{0.70}\text{MnO}_{2.05}$ phase (JCPDF27-0751) with a hexagonal $\text{P6}_3/\text{mmc}$ space group ($a = 0.29429$ nm, $c = 1.12785$ nm). It is worth noticing that a P2 phase is usually observed for sodium manganese oxide that contains relatively high sodium content, e.g. $x \geq 0.6$ [18-20]. Obviously, the Co-substitution is beneficial for the stability of layered structure, which allows the formation of a P2 phase even at a low sodium content. By further increasing x to 0.44, $\text{Na}_{0.44}\text{Mn}_{0.56}\text{Co}_{0.44}\text{O}_2$ is identified as another layered phase, i.e. P3-type structure with an $\text{R}\bar{3}\text{m}$ space group [21-23]. Thus, when $x=0.22$ and 0.33, the XRD patterns of $\text{Na}_{0.44}\text{Mn}_{0.78}\text{Co}_{0.22}\text{O}_2$ and $\text{Na}_{0.44}\text{Mn}_{0.67}\text{Co}_{0.33}\text{O}_2$ indicate a mix of P2 and P3 phases (**Fig. S1**). It can be seen clearly from **Fig. S1** that the diffraction peaks shift to higher angles with the increasing Co content, which is consistent with results of XRD Rietveld refinement. The lattice parameters and the

relative contents of P2 and P3 phases obtained from Rietveld refinement are given in **Table 1**. The lattice parameters (a, c) of $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ both for P2 and P3 phases decrease with increasing Co content. The change trend of the lattice parameters is reasonable because the ionic radius of Co^{3+} (0.063 nm) is less than that of Mn^{3+} (0.066 nm), which is also an evidence that the Co is indeed doped in the lattice.

The SEM images of the samples are presented in **Fig.2**. $\text{Na}_{0.44}\text{MnO}_2$ (**Fig.2a**) presents a typical T-type rod-like morphology with clean and smooth surface facets, suggesting that the particles are well crystallized. From $x=0$ to $x=0.11$, the particle morphology changes gradually from rods to plates. The intermediate compositions $\text{Na}_{0.44}\text{Mn}_{0.99}\text{Co}_{0.01}\text{O}_2$ (**Fig.2b**) and $\text{Na}_{0.44}\text{Mn}_{0.92}\text{Co}_{0.08}\text{O}_2$ (**Fig.2c**) are composed of both rod-like and plate-like particles. The $\text{Na}_{0.44}\text{Mn}_{0.89}\text{Co}_{0.11}\text{O}_2$ sample consists of only 2D nano-plates with a thickness of about 500 nm (**Fig.2d**), showing the typical morphology for other P2-type layered positive electrode materials, such as $\text{Na}_{0.67}\text{Mn}_{0.65}\text{Ni}_{0.2}\text{Co}_{0.15}\text{O}_2$ [24] and $\text{Na}_{2/3}\text{Mn}_y\text{Co}_{1-y}\text{O}_2$ [25]. According to above XRD analysis (**Fig.1**), the exposed parallel surfaces of these plates should be (002) planes. Furthermore, the significant difference in the particle morphology between $\text{Na}_{0.44}\text{MnO}_2$ and $\text{Na}_{0.44}\text{Mn}_{0.89}\text{Co}_{0.11}\text{O}_2$ is also a reflection of the phase evolution after the cobalt-substitution. With further increasing the doping level (Co content), the particle morphology changes from plates to small granules (**Fig.2d-2f**). It can be seen that $\text{Na}_{0.44}\text{Mn}_{0.56}\text{Co}_{0.22}\text{O}_2$ ($x=0.22$) sample consists of particles with two kinds of morphologies, i.e. mixed plates and granules, which correspond to mixed P2/P3 phases (**Fig.2e**). The $\text{Na}_{0.44}\text{Mn}_{0.56}\text{Co}_{0.44}\text{O}_2$ ($x=0.44$) sample consists of uniform

granular particles of about 100 nm in size. These morphologies evolutions are well consistent to the evolutions of crystal structures as shown by the XRD patterns (**Fig. 1**). Therefore, it is very interesting that, for $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ synthesized under our specific conditions, the particle morphology is a clear indicator of its crystal structure, i.e. rods (T-type), plates (P2-type) and granules (P3-type).

The Energy Dispersive Spectroscopy elementary mapping analysis on $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ ($x=0, 0.11, 0.44$) samples are displayed in **Fig. 3**. When $x=0$, with a selected area containing several rods (**Fig.3a**), Mn element is homogeneously distributed while Co element is not detected (**Fig.3b** and **Fig.3c**). When x increases to 0.11 (**Fig.3d**), Co element is revealed (**Fig.3f**) and becomes more obvious when $x=0.44$ (**Fig.3i**), while the Mn element is all uniformly distributed in the samples (**Fig.3e** and **Fig. 3h**). The chemical composition of the samples by the EDS analysis is shown in **Table. S1**. The results are approximately consistent with the stoichiometric ratio, and the small differences may come from the instrumental measuring errors which are within the allowable error range.

3.2 Electrochemical performance of $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$

In $\text{Na}_{0.44}\text{MnO}_2$ or $\text{Na}_4\text{Mn}_9\text{O}_{18}$ lattice, there are two types of tunnels, i.e. a large flat S-shaped tunnel containing half-filled sites for Na ions (~ 0.22) and another relatively smaller hexagonal tunnel with centrally located Na ions (~ 0.22). The crystal structure is displayed in **Fig. 4a**. The Na ions in the hexagonal sites cannot be extracted/inserted reversibly, while those in the S-shaped tunnel can be

extracted/inserted reversibly. Therefore, in the first charge step, the Na content (y) in Na_yMnO_2 can change from 0.44 to 0.22, corresponding to a specific charge capacity of 60 mAh g^{-1} , while in the subsequent cycles y changes between 0.22 and 0.66, corresponding to a specific capacity of 121 mAh g^{-1} .

The initial charge–discharge curves of $\text{Na}/\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ cells at 0.5C (60 mA g^{-1}) in the voltage range of 2.0–4.0 V are compared in **Fig. 5**. The first charge capacity of $\text{Na}_{0.44}\text{MnO}_2$ is 54 mAh g^{-1} and the subsequent reversible discharge capacity is about 111 mAh g^{-1} (**Fig. 5a**). These values are approximately consistent with above prediction. The differences are due to relatively high rate (0.5C) used. When the current is reduced to 0.1C and in 2.0–4.2 V voltage range, we can obtain the first charge capacity of 57 mAh g^{-1} and a reversible discharge capacity of 117 mAh g^{-1} (**Fig.S2a**), which are even closer to the theoretically predicted values. Also, voltage profiles with multiple plateaus are observed during the reversible Na extraction/insertion, which should be due to the multiple two-phase regions with stepwise compositions.

As discussed before, $\text{Na}_{0.44}\text{Mn}_{0.89}\text{Co}_{0.11}\text{O}_2$, as also written as $\text{Na}_4\text{Mn}_8\text{CoO}_{18}$ is a pure P2 phase with a layered structure (**Fig. 4b**). The sodium ions are sitting at layers separated by layers of MO_6 octahedrons ($\text{M}=\text{Mn}_{0.89}\text{Co}_{0.11}$ here), in principle, all of Na ions in the inter-layer spacing are accessible for electrochemical reactions. Theoretically the first charge can extract maximum 0.44 Na and reach a capacity up to 121 mAh g^{-1} if the upper cut-off voltage is sufficiently high and at a low current rate. Nevertheless, the measured first charge capacity at 0.5C is about 54 mAh g^{-1} due to

the narrow voltage window (2.0-4.0 V) (**Fig. 5d**). When the upper cut-off voltage is raised to 4.2 V, a charge capacity of 76.4 mAh g⁻¹ can be measured (**Fig. S2b**). The first charge capacity of 54 mAh g⁻¹ corresponds to the composition change from Na_{0.44}Mn_{0.89}Co_{0.11}O₂ to Na_{0.24}Mn_{0.89}Co_{0.11}O₂. Thus, in the subsequent cycles, maximum 0.76 Na per formula would be inserted/extracted, corresponding to a capacity of 209 mAh g⁻¹. At 0.5C and in the voltage range of 2.0-4.0V, we can measure a capacity of 155 mAh g⁻¹ (**Fig. 5d**). When Na_{0.44}Mn_{0.89}Co_{0.11}O₂ electrode is cycled in a wider voltage range and at a lower current rate, it can deliver a higher specific capacity. In fact, at 0.1C rate, Na_{0.44}Mn_{0.89}Co_{0.11}O₂ delivers a discharge capacity of 220 mAh g⁻¹ in 2.0-4.2 V for the first cycle (**Fig. S2b**), which is close to above predicated value 209 mAh g⁻¹. Furthermore, other than Na_{0.44}MnO₂ which gives multi-plateau voltage profiles, Na_{0.44}Mn_{0.89}Co_{0.11}O₂ delivers a more smooth charge/discharge curves. This behavior may be caused by the disordered Mn/Co arrangement, which breaks the charge ordering and/or Na⁺/vacancy ordering [16].

Na_{0.44}Mn_{0.56}Co_{0.44}O₂, as also written as Na₄Mn₅Co₄O₁₈, is identified as a pure P3 phase with a layered structure with a larger periodical length in c-direction compared to the P2 phase (**Fig. 4c**). Similar to the P2-type Na_{0.44}Mn_{0.89}Co_{0.11}O₂, it would theoretically reach a capacity of 121 mAh g⁻¹ in the first charge step. But in the limited voltage window of 2.0-4.0 V and at 0.5C, we only measure a capacity of 24 mAh g⁻¹ (**Fig. 5f**), corresponding to the composition change from Na_{0.44}Mn_{0.56}Co_{0.44}O₂ to Na_{0.35}Mn_{0.56}Co_{0.44}O₂. Thus, in the subsequent cycles we would measure a theoretical capacity of 179 mAh g⁻¹ (0.65 Na per formula). However,

due probably to the too high lower cut-off voltage at 2.0 V, we only measure a capacity of 76 mAh g⁻¹. Judging from the angle between the discharge curve and the x-axis, only a small fraction of active sodium is measured down to 2.0 V. Also, the voltage profiles are steeper than those for P2 phase. When Na_{0.44}Mn_{0.56}Co_{0.44}O₂ electrode is cycled in a wider voltage range 1.5-4.4 V at 0.1C, it can deliver a higher initial charge/discharge capacity of 44/164 mAh g⁻¹ (**Fig. S3a**). Nevertheless, because of its relatively low capacity in 2.0-4.0 V, this composition is not a focus of this paper.

When x=0.01 or Na_{0.44}Mn_{0.99}Co_{0.01}O₂, neither the charge-discharge curves nor the specific capacities have obvious change compared with those of Na_{0.44}MnO₂ (**Fig. 5b**). The voltage profiles also have the multi-plateau feature for T-type phase. It is likely that the degree of Co-substitution is too small to cause pronounced structural change, as confirmed by the XRD (**Fig. 1**) and SEM (**Fig. 2**) analyses. When the Co content (x) is increased to 0.08 or Na_{0.44}Mn_{0.92}Co_{0.08}O₂ (**Fig. 5c**), the cell displays a smooth P2-type charge/discharge curves without distinct multiple plateaus. The discharge capacity increases to 131 mAh g⁻¹.

When x=0.22, the composition becomes Na_{0.44}Mn_{0.78}Co_{0.22}O₂ or Na₄Mn₇Co₂O₁₈, while the voltage profiles combine the features of both P2 and P3 phases (**Fig. 5e**). The discharge capacity is around 97 mAh g⁻¹, which is between those of P2-type Na_{0.44}MnO₂ (155 mAh g⁻¹) and P3-type Na_{0.44}Mn_{0.56}Co_{0.44}O₂ (76 mAh g⁻¹). Also, when Na_{0.44}Mn_{0.56}Co_{0.44}O₂ electrode is cycled in a wider voltage range in 1.5-4.4 V it can deliver a higher specific capacity of 187.5 mAh g⁻¹ at 0.1C (**Fig. S3b**). In fact, there is another stoichiometric composition Na₄Mn₆Co₃O₁₈ or Na_{0.44}Mn_{0.67}Co_{0.33}O₂,

which is expected to have similar electrochemical properties of the P2 and P3 phases combination but with a capacity between 76 mAh g⁻¹ and 97 mAh g⁻¹.

The comparative cycling performances of Na_{0.44}Mn_{1-x}Co_xO₂ (x=0, 0.01, 0.08, 0.11, 0.22, 0.44) at 0.5C (60 mA g⁻¹) are shown in **Fig. 6a**. From x=0 to x=0.11, the discharge capacity of the Co-substituted samples increases with the increase of Co content. There is an extremely obvious capacity elevation in Na_{0.44}Mn_{0.89}Co_{0.11}O₂. It delivers a discharge capacity of 135.7mAh g⁻¹ after 50 cycles, that is compared to 108 mAh g⁻¹ for Na_{0.44}MnO₂. Although the cycling stability is a little poorer than the T-type Na_{0.44}MnO₂, Na_{0.44}Mn_{0.89}Co_{0.11}O₂ still exhibits a relatively stable cycle performance with a capacity retention of 87% after 50 cycles. With more Co substitutions (x=0.22, 0.44), the overall discharge capacity further decreases, but the capacity retention increases to 96% for Na_{0.44}Mn_{0.78}Co_{0.22}O₂ and 99% for Na_{0.44}Mn_{0.56}Co_{0.44}O₂ after 50 cycles. The excellent cycling stability of the latter two can be explained by the effect of Mn³⁺ replacement by Co³⁺ which alleviates the Jahn–Teller distortion and suppresses the structural stress of the materials [25].

At a low rate of 0.1C (**Fig. 6b**), Na_{0.44}Mn_{0.89}Co_{0.11}O₂ delivers a high discharge capacity of 200.5 mAh g⁻¹ for the first cycle and retains 166 mAh g⁻¹ after 40 cycles in 2.0-4.0 V. The When cycled in a wider voltage window of 2.0-4.2 V, it delivers a higher specific capacity of 220 mAh g⁻¹ for the first cycle and 180 mAh g⁻¹ after 40 cycles. On the other hand, Na_{0.44}MnO₂ delivers a quite low discharge capacity with only 117 mAh g⁻¹ at 0.1C in 2.0-4.0 V due to the limit of tunnel structure. The P2-type Na_{0.44}Mn_{0.89}Co_{0.11}O₂ reveals an overall promising electrochemical performance, and

highlighted by the high average coulombic efficiency (99.0%~100%).

The rate performances of $\text{Na}_{0.44}\text{MnO}_2$ and $\text{Na}_{0.44}\text{Mn}_{0.89}\text{Co}_{0.11}\text{O}_2$ samples in 2.0-4.0 V at various current densities are shown in **Fig. 7**. $\text{Na}_{0.44}\text{MnO}_2$ delivers a discharge capacity of 122 mAh g^{-1} at 12 mA g^{-1} and 83 mAh g^{-1} at 600 mA g^{-1} , while $\text{Na}_{0.44}\text{Mn}_{0.89}\text{Co}_{0.11}\text{O}_2$ delivers a discharge capacity of 200, 151, 138, 114 and 104 mAh g^{-1} at 12, 60, 120, 360 and 600 mA g^{-1} , respectively. The superior rate performance of $\text{Na}_{0.44}\text{MnO}_2$ can be attributed to the large diffusive tunnels of this T-type phase, which is consistent with the result of electrochemical impedance analysis (**Fig. S4**). Nevertheless, the P2-type $\text{Na}_{0.44}\text{Mn}_{0.89}\text{Co}_{0.11}\text{O}_2$ still delivers overall higher discharge capacities at all current rates. It should also be noted that such a high discharge capacity of the Co-substituted $\text{Na}_{0.44}\text{Mn}_{0.89}\text{Co}_{0.11}\text{O}_2$ is superior to most of the data of the T-type and layered positive electrode materials reported in literature (**Table. 2**). It exhibits much higher discharge capacity in a relatively narrow voltage range, suggesting a great potential application in sodium ion batteries.

Fig. S5 show the cyclic voltammograms of the initial three cycles of $\text{Na}_{0.44}\text{MnO}_2$ and $\text{Na}_{0.44}\text{Mn}_{0.89}\text{Co}_{0.11}\text{O}_2$ in 1.5-4.2 V. There are about six groups of redox peaks for the T-type $\text{Na}_{0.44}\text{MnO}_2$ (**Fig. S5a**), corresponding roughly the six voltage plateaus on its charge-discharge curves (**Fig. 5a**). For the P2-type $\text{Na}_{0.44}\text{Mn}_{0.89}\text{Co}_{0.11}\text{O}_2$, there are two groups of peaks at around 2.25 V and 3.6 V, respectively (**Fig. S5b**). They are believed to be associated with the redox reactions of $\text{Mn}^{4+}/\text{Mn}^{3+}$ and $\text{Co}^{4+}/\text{Co}^{3+}$ pairs, which are consistent to the voltage plateaus of charge-discharge curves (**Fig. 5f**).

4. Conclusions

A series of $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ ($x=0, 0.01, 0.08, 0.11, 0.22, 0.33, 0.44$) powders are synthesized by a thermopolymerization method. For the first time, we have found that the Co-substitution can gradually change the structure of $\text{Na}_{0.44}\text{MnO}_2$ from tunnel T-type ($x=0$) into layered P2-type ($x=0.11$) or P3-type ($x=0.44$). Under the specific synthesis conditions, the particle morphology of these samples can be used as an indicator of their crystal structures: rod-like (T-type), plate-like (P2) and granules (P3). T-type $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ gives charge-discharge profiles with multiple plateaus, while P2-type $\text{Na}_{0.44}\text{Mn}_{0.89}\text{Co}_{0.11}\text{O}_2$ and P3-type $\text{Na}_{0.44}\text{Mn}_{0.56}\text{Co}_{0.44}\text{O}_2$ give smooth profiles. P2-type $\text{Na}_{0.44}\text{Mn}_{0.89}\text{Co}_{0.11}\text{O}_2$ allows more Na^+ intercalation into the inter-layer spacing and results in a high discharge capacity with 220 mAh g^{-1} at a low rate in initial cycle and 180 mAh g^{-1} after 40 cycles in the voltage range of 2.0-4.2 V, and a good rate performance with 104 mAh g^{-1} at 600 mA g^{-1} in the voltage range of 2.0-4.0 V.

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Figure captions:

Fig.1 XRD patterns of Na_{0.44}Mn_{1-x}Co_xO₂ (x=0, 0.01, 0.08, 0.11, 0.22, 0.44).

Fig. 2 SEM images of Na_{0.44}Mn_{1-x}Co_xO₂, where x=0 (a),0.01 (b),0.08 (c),0.11 (d),0.22

(e), and 0.44 (f).

Fig. 3 The energy dispersive spectroscopy elementary mapping of T-type (a-c), P2-type (d-f) and P3-type (g-i) samples.

Fig. 4 Structural illustrations of T-type (a), P2-type (b) and P3-type (c).

Fig. 5 The initial two charge–discharge curves of $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$, where $x=0$ (a), 0.01 (b), 0.08 (c), 0.11 (d), 0.22 (e) and 0.44 (f).

Fig. 6 The cycling performances of $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ ($x=0, 0.01, 0.08, 0.11, 0.22, 0.44$) at 0.5C (60mA g^{-1}) (a) and $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ ($x=0, 0.11$) at 0.1C (12mA g^{-1}) (b).

Fig. 7 The rate performances of $\text{Na}_{0.44}\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ ($x=0, 0.11$)

Table 1 The lattice parameters and the relative contents of P2 and P3 phases obtained from Rietveld refinement.

Table 2 The comparison of electrochemical properties of T-type and layered positive electrode materials between this work and literature data.

Table 1

Sample	Phase	P2: Lattice parameters (Å)	P3: Lattice parameters (Å)
x=0.11	P2: 100 wt%	a=2.8740	--
	--	c=11.3196	--
x=0.22	P2: 62.95 wt%	a=2.8542	a=2.8404
	P3: 37.05 wt%	c=11.3184	c=16.9505
x=0.33	P2: 19.20 wt%	a=2.8352	a=2.8324
	P3: 80.80 wt%	c=11.3070	c=16.9424
x=0.44	P3: 100 wt%	--	a=2.8204
	--	--	c=16.9378

Table 2

Cathodes	Initial capacity(mAh g ⁻¹)	Specific capacity(mAh g ⁻¹)	Refs
T-Na _{0.44} Mn _{0.89} Ti _{0.11} O ₂	110@20mA g ⁻¹ (1.5-3.9V)	—	[16]
T-Na _{0.54} Mn _{0.50} Ti _{0.51} O ₂ @C	137.3@28mA g ⁻¹ (2.0-4.2V)	83@700mA g ⁻¹	[26]
P2-Na _x Mg _{0.11} Mn _{0.89} O ₂	174@ 12mA g ⁻¹ (1.5-4.4V)	63@610mA g ⁻¹	[27]
P2-Na _{0.67} Mn _{0.65} Ni _{0.2} Co _{0.15} O ₂	155 @12mA g ⁻¹ (1.5-4.2V)	132@120mA g ⁻¹	[24]
P2-Na _{0.6} Mn _{0.66} Ni _{0.22} Fe _{0.11} O ₂	205@15mA g ⁻¹ (1.5-4.6V)	--	[21]
O3-NaFe _x (Ni _{0.5} Mn _{0.5}) _{1-x} O ₂	133@ 12mA g ⁻¹ (2.0-4.0V)	125@120mA g ⁻¹	[28]
O3-NaLi _{0.05} (Ni _{0.25} Fe _{0.25} Mn _{0.5}) _{0.95} O ₂	180@ 17mA g ⁻¹ (1.75-4.4V)	130.9@170mA g ⁻¹	[29]
P2-Na _{0.44} Mn _{0.89} Co _{0.11} O ₂	200.5@12mA g ⁻¹ (2.0-4.0V) 220@12mA g ⁻¹ (2.0-4.2V)	138@120mA g ⁻¹ 104@600mA g ⁻¹	this work

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7