Triclinic $Na_{3.12}Co_{2.44}(P_2O_7)_2$ as a High Redox Potential Cathode Material for Na-Ion Batteries

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ABSTRACT

Two types of sodium cobalt pyrophosphates, triclinic $Na_{3.12}Co_{2.44}(P_2O_7)_2$ and orthorhombic $Na_2CoP_2O_7$, are compared as high-voltage cathode materials for Na-ion batteries. $Na_2CoP_2O_7$ shows no electrochemical activity, delivering negligible capacity. In contrast, $Na_{3.12}Co_{2.44}(P_2O_7)_2$ exhibits good electrochemical performance, such as high redox potential at *ca.* 4.3 V (vs. Na/Na^+) and stable capacity retention over 50 cycles, although $Na_{3.12}Co_{2.44}(P_2O_7)_2$ delivered approximately 40 mA h g^{-1}. This is attributed to the fact that $Na_2CoP_2O_7$ (~3.1 Å) has smaller diffusion channel size than $Na_{3.12}Co_{2.44}(P_2O_7)_2$ (~4.2 Å). Moreover, the electrochemical performance of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ is examined using Na cells and Li cells. The overpotential of Na cells is smaller than that of Li cells. This is due to the fact that $Na_{3.12}Co_{2.44}(P_2O_7)_2$ has a smaller charge transfer resistance and higher diffusivity for Na^+ ions than Li^+ ions. This implies that the large channel size of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ is more appropriate for Na^+ ions than Li^+ ions. Therefore, $Na_{3.12}Co_{2.44}(P_2O_7)_2$ is considered a promising high-voltage cathode material for Na-ion batteries, if new electrolytes, which are stable above 4.5 V vs. Na/Na^+, are introduced.

Keywords : Na-ion batteries, Cathode, Off-stoichiometry, Pyrophosphate

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1. Introduction

Recently, Na-ion batteries have been considered as a promising alternative to Li-ion batteries because abundance in sodium precursors can lead to a cost reduction [1-4]. In addition, the existence of a database of electrode materials for Li-ion batteries can promote the development of electrode materials for Na-ion batteries, since the chemistry of Na-ion batteries is similar to that of Li-ion batteries. Drawing inspiration from previously reported cathode materials for Li-ion batteries, many research groups have reported various cathode materials for Na-ion batteries. These include Na_xCoO_2 [5,6], Na_xCrO_2 and Na_xNiO_2 [7], α-$NaFeO_2$ [8], Na_xVO_2 [9, 10], $Na_{0.44}MnO_2$ [11], $Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$ [12], $Na_{1-x}Ni_{0.5}Mn_{0.5}O_2$ [13], $NaCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ [14], $NaMPO_4$ (M=Fe, Mn) [15], A_2MPO_4F (A = Na, Li, M = Fe, Mn, Co, Ni) [16], $NaVPO_4F$ [17], $Na_{1.5}VOPO_4F_{0.5}$ [18], $Na_3V_2(PO_4)_2F_3$ [19,20], $Na_3Fe_3(PO_4)_4$ [21], $Na_2FeP_2O_7$ [22], *t*-$Na_2(VO)P_2O_7$ [23], and $Na_2MnP_2O_7$ [24,25]. Our group also reported a new pyrophosphate cathode material (triclinic $Na_{4-α}M_{2+α/2}(P_2O_7)_2$ where $2/3 \leq α \leq 7/8$ and M = Fe, $Fe_{0.5}Mn_{0.5}$, or Mn) and showed promising electrochemical performance including negligible capacity fading over 60 cycles and good rate performance [26]. Then, Niu *et al.* and Chen *et al.* optimized the electrochemical performance of $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ [27,28]. However, its specific energy (3.0 V × *ca.* 85 mA h g^{-1}) is still smaller than that of $LiFePO_4$ (3.4 V × *ca.* 160 mA h g^{-1}), which is used in Li-ion batteries. Not only $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ but the majority of cathode materials for Na-ion batteries display lower energy densities when compared to those used in Li-ion batteries; thus, an improvement in energy density is vital for commercialization of Na-ion batteries. This can be achieved by either increasing the reversible capacity or the redox potential. It is well known that the redox potential of Co^{2+}/Co^{3+} in phosphate-based

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materials for Li-ion batteries is higher than those of Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} [29]. Therefore, in this report, we introduce the Co analogue ($Na_{3.12}Co_{2.44}(P_2O_7)_2$) of triclinic $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ as a high-voltage cathode material for the improvement in energy density. Moreover, triclinic $Na_{3.12}Co_{2.44}(P_2O_7)_2$ was also compared with orthorhombic $Na_2CoP_2O_7$ to investigate the effect of crystal structure on electrochemical performance. It was known that three crystal structures of sodium cobalt pyrophosphates ($Na_2CoP_2O_7$) exist: orthorhombic ($Pna2_1$), tetragonal ($P4_2/mmm$), and triclinic (P-1) structures [30-32]. Whereas the electrochemical performance of nanosized orthorhombic $Na_2CoP_2O_7$ has been reported [33], the synthesis and electrochemical performance of triclinic $Na_{3.12}Co_{2.44}(P_2O_7)_2$ have not yet been studied to the best of our knowledge. Furthermore, we demonstrate that $Na_{3.12}Co_{2.44}(P_2O_7)_2$ has an appropriate channel size for Na^+ ions through comparison of the electrochemical behaviors of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ in Na-ion and Li-ion cells.

2. Experimental

2.1 Synthesis

Triclinic $Na_{3.12}Co_{2.44}(P_2O_7)_2$ and orthorhombic $Na_2CoP_2O_7$ were synthesized through a conventional solid-state method. Stoichiometric amounts of sodium carbonate (Na_2CO_3, Sigma-Aldrich, ≥ 99.5%), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich, 98+%), and ammonium phosphate dibasic (($NH_4)_2HPO_4$, Sigma-Aldrich, 98+%) were mixed, and then heated at 300°C for 6 hours and 600°C for 12 hours in Ar atmosphere.

2.2. Chemical de/sodiation processes

Chemical oxidations of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ (as well as the electrochemical charging processes) to $Na_{3.12-x}Co_{2.44}(P_2O_7)_2$ (x = ~1) and $Na_{3.12-y}Co_{2.44}(P_2O_7)_2$ (y = ~2) is performed using nitronium tetrafluoroborate (NO_2BF_4, 95+%, Sigma-Aldrich) with equimolar amounts, stirred with acetonitrile (AN) solvent for 3 hours, then filtered and washed with ethanol. In the same way, sodium iodide (NaI, ≥ 99.5%, Sigma-Aldrich) is added for chemical reduction (electrochemical discharging processes) with AN, stirred for 5 hours. Changes in atomic composition of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ were estimated using an inductively coupled plasma-mass spectrometer (ICP-MS, Perkin-Elmer NexION 350D).

2.3 Materials characterization

Powder X-Ray diffraction (XRD) data were collected on a Bruker D2 Phaser diffractometer using Cu-Kα radiation (λ=1.5418 Å) operated from 2θ = 10 - 80°. Rietveld refinements were performed using powder XRD patterns with the TOPAS program. The morphologies of powders were examined using the Hitachi S-4800 Field Emission Scanning Electron Microscopy (FE-SEM).

2.4 Electrochemical characterization

Each active material (70 wt.%) was mixed with carbon black (Super-P, 15 wt.%) and polyvinylidene fluoride (PVdF, 15 wt.%) in 1-methyl-2-pyrrolidinone solvents (NMP, Sigma-Aldrich, anhydrous, 99%). The slurries were coated on Al foil as a current collector. Electrochemical performances of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ and $Na_2CoP_2O_7$ were examined using coin cells (CR2032 type). Na and Li metals were used as counter electrodes for Na-ion and Li-ion half-cells, respectively. A 0.8 *M* solution of sodium hexafluorophosphate ($NaPF_6$) dissolved in a mixture (1:1, v/v) of ethylene carbonate (EC) and propylene carbonate (PC), with 5 wt.% of fluoroethylene carbonate (FEC) and 1 wt.% of tris(trimethylsilyl)phosphite (TMSP) additives, and 1.3 *M* of lithium hexafluorophosphate ($LiPF_6$) dissolved in a mixture (3:2:5, v/v/v) of ethylene carbonate, ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) were used as electrolytes for Na-ion and Li-ion half-cells, respectively. Galvanostatic experiments were performed at the current density of 4.75 mA g^{-1} (*ca.* 0.05 C-rate) in the voltage ranges from 2.4 to 4.5 V vs. Na/Na^+ and from 2.7 to 4.8 V vs. Li/Li^+. Furthermore, the potentiostatic intermittent titration technique (PITT) was performed to estimate diffusion coefficients. The potential step of 10 mV was applied at various depth of discharge states. Each potential step was applied until the current density was less than 0.75 mA g^{-1}. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 300 kHz to 1 mHz with voltage amplitude of 5 mV using the BioLogic SP-150.

3. Results and Discussion

Two types of sodium cobalt pyrophosphates, triclinic $Na_{3.12}Co_{2.44}(P_2O_7)_2$ and orthorhombic $Na_2CoP_2O_7$, were synthesized through a conventional

(a)

(b)
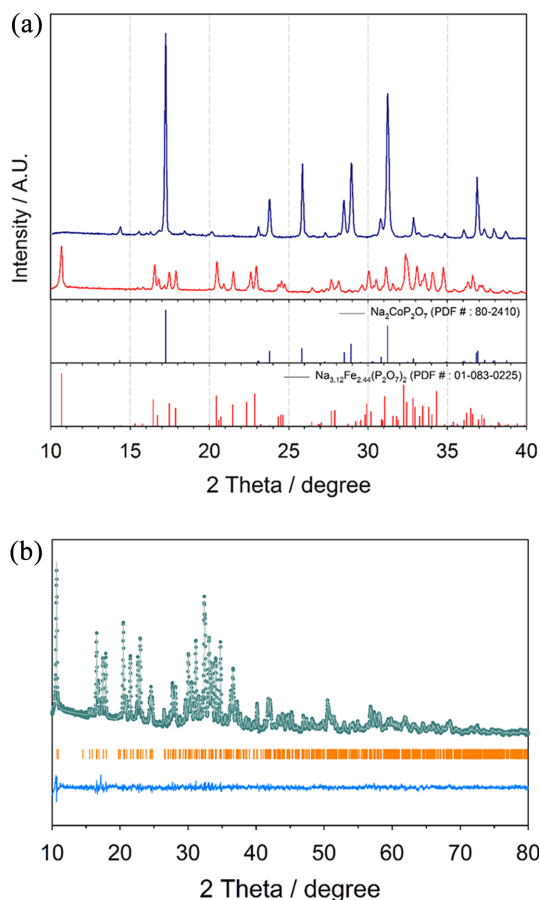
Fig. 1. XRD patterns of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ and $Na_2CoP_2O_7$ powders, and (b) Rietveld refinement of $Na_{3.12}Co_{2.44}(P_2O_7)_2$.

Table 1. Lattice parameters of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ obtained by Rietveld refinement with agreement factors.

| Parameters	$Na_{3.12}Co_{2.44}(P_2O_7)_2$
a / Å	6.37314(11)
b / Å	9.96077(16)
c / Å	10.96801(20)
α / °	64.4518(13)
β / °	85.9552(16)
γ / °	73.5350(15)
Volume / Å^3	565.126(19)
R_p / %	1.04
R_{wp} / %	1.38
χ^2	1.47

solid-state method via heating at 600°C under Ar. Fig. 1(a) shows the X-ray diffraction (XRD) patterns of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ and $Na_2CoP_2O_7$, indicating that they contained no impurities. We performed the Rietveld refinement to determine the lattice parameters of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ (Fig. 1(b) and Table 1). This revealed that $Na_{3.12}Co_{2.44}(P_2O_7)_2$ has a crystal structure similar to triclinic $Na_{3.12}Fe_{2.44}(P_2O_7)_2$. However, a slight distortion was observed due to the different ionic size between Co and Fe. As shown in the crystal structure images (Fig. 2(a), (b), and (c)), $Na_{3.12}Co_{2.44}(P_2O_7)_2$ is composed of two centrosymmetrical crowns of $Co_2P_4O_{20}$ and $Co_2P_4O_{22}$, and has three dimensional diffusion channels along the [100], [010], and [101] directions. On the other hand, ort-

horhombic $Na_2CoP_2O_7$ has a layered crystal structure having a two-dimensional diffusion path perpendicular to the [010] direction (Fig. 2(d)).
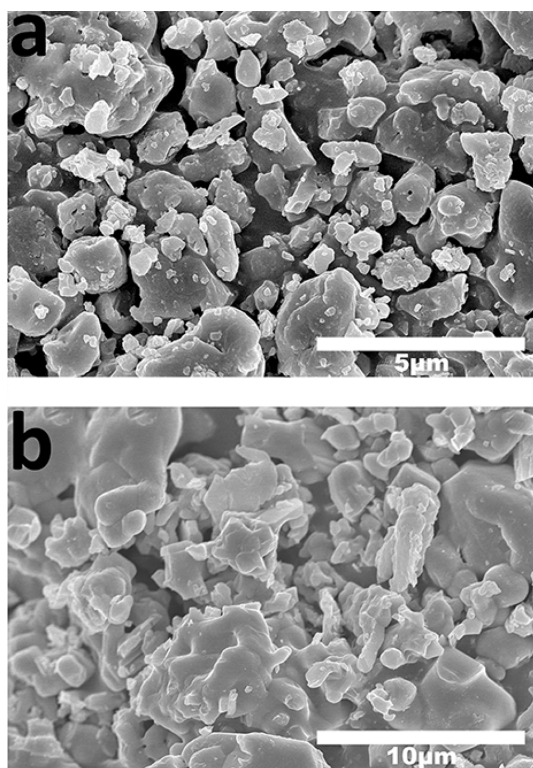
We compared the electrochemical performances of triclinic $Na_{3.12}Co_{2.44}(P_2O_7)_2$ and orthorhombic $Na_2CoP_2O_7$, as shown in Fig. 3. Na metal and a 0.8 *M* solution of $NaPF_6$ dissolved in a mixture solvent of EC and PC 1:1 (v/v) were used as a counter electrode and electrolyte, respectively. FEC and TMSP were added as electrolyte additives to improve the electrochemical stability of electrolytes at high voltages [34]. As shown in the voltage profiles and dQ/dV plots of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ (Fig. 3(a) and (b)), two plateaus were observed at very high redox potentials of ~3.9 and 4.3 V vs. Na/Na$^+$. This implies that $Na_{3.12}Co_{2.44}(P_2O_7)_2$ exhibited a higher redox potential than $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ (~3.0V vs. Na/Na$^+$). Although $Na_{3.12}Co_{2.44}(P_2O_7)_2$ delivered a smaller reversible capacity (approximately 40 mA h g^{-1}) than $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ (~ 85 mA h g^{-1}), this is attributed to the upper limit of the charging voltage (4.5 V vs. Na/Na$^+$) due to the severe electrolyte decomposition above 4.5 V. $Na_{3.12}Co_{2.44}(P_2O_7)_2$ also showed excellent reversibility with negligible capacity fading over 50 cycles, although the coulombic efficiency was not sufficiently high because of electrolyte decomposition (Fig. 3(d)). In contrast to triclinic $Na_{3.12}Co_{2.44}(P_2O_7)_2$, layered $Na_2CoP_2O_7$ did not deliver any observable reversible capacity in the voltage range between 2.4 and 4.5 V vs. Na/Na$^+$ (Fig. 3(c)). The poor electrochemical activity of $Na_2CoP_2O_7$ is attributed to very slow kinetics result-
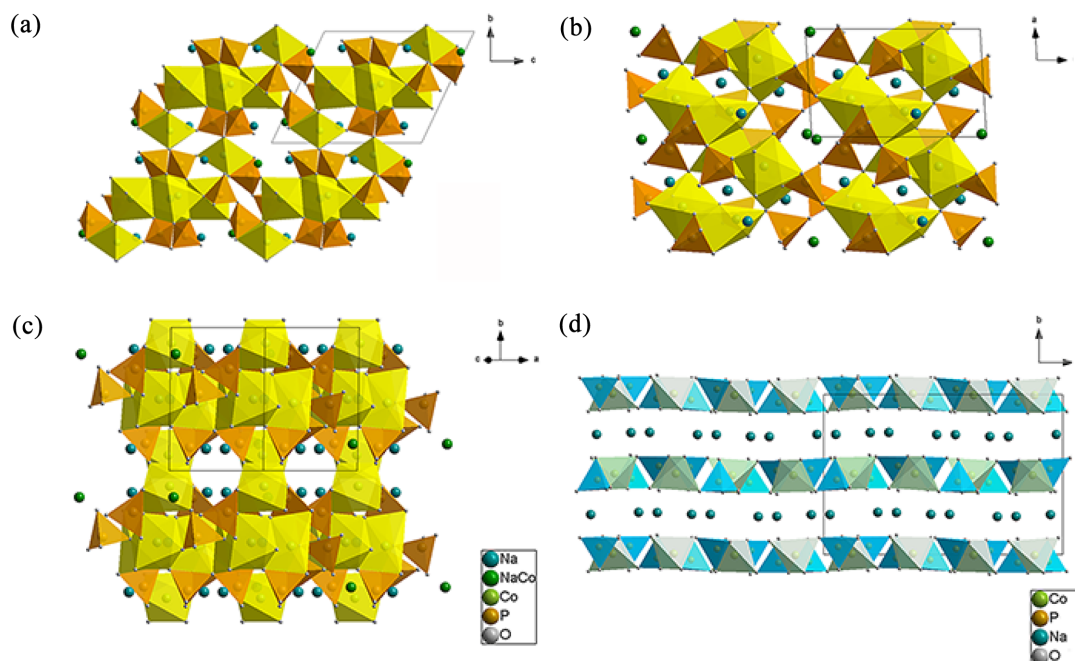
Fig. 2. Crystal structures of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ along the (a) [100], (b) [010], and (c) [101] directions and crystal structure of (d) $Na_2CoP_2O_7$ along the [100] direction.
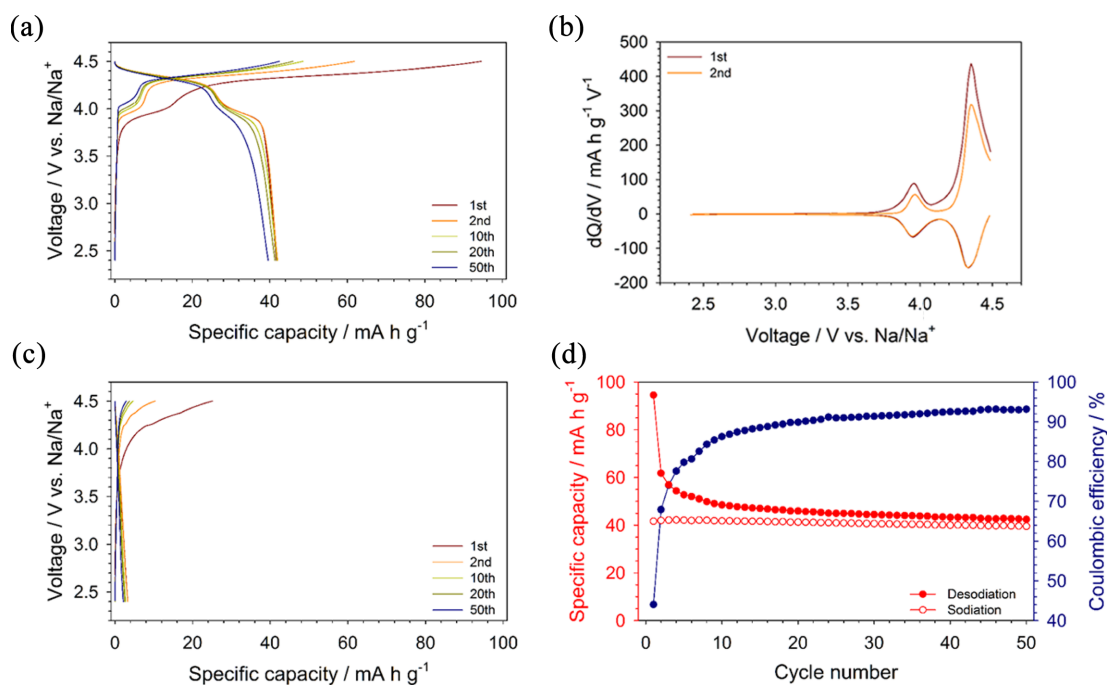
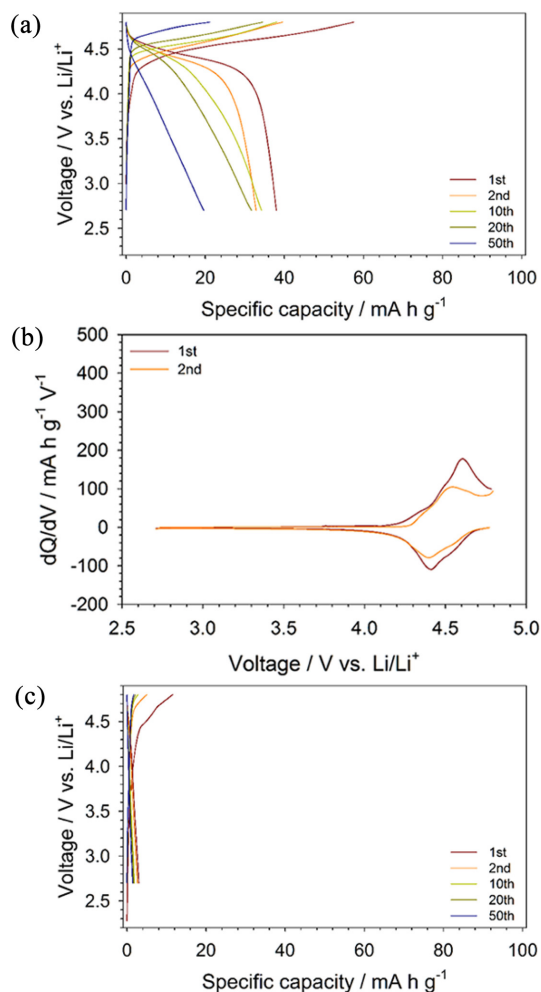**Fig. 3.** (a) Voltage profiles and (b) dQ/dV plots of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ for Na-ion cells, (c) voltage profiles of $Na_2CoP_2O_7$ for Na-ion cells, and (d) cycle performance and coulombic efficiency of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ for Na-ion cells.

Fig. 4. SEM images of (a) $Na_{3.12}Co_{2.44}(P_2O_7)_2$ and (b) $Na_2CoP_2O_7$ powders.

Fig. 5. (a) Voltage profiles and (b) dQ/dV plots of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ for Li-ion cells, and (c) voltage profiles of $Na_2CoP_2O_7$ for Li-ion cells.

ing from the high activation energy for the diffusion of Na^+ ions due to the small channel size (~3.1 Å); note that the channel size of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ is ~4.2 Å. Since $Na_{3.12}Co_{2.44}(P_2O_7)_2$ and $Na_2CoP_2O_7$ have similar particle sizes that ranges from hundreds of nanometers to a few micrometers, as shown in the SEM images (Fig. 4), the different electrochemical activities of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ and $Na_2CoP_2O_7$ were not due to the difference in the particle sizes.

Moreover, $Na_{3.12}Co_{2.44}(P_2O_7)_2$ and $Na_2CoP_2O_7$ were examined as cathode materials for Li-ion batteries (Fig. 5). Li metal and a 1.3 *M* solution of $LiPF_6$ dissolved in a mixture solution of EC: EMC: DEC (3:2:5, v/v/v) were used as a counter electrode and electrolyte, respectively. Li-ion cells of $Na_2CoP_2O_7$ still exhibited no electrochemical activity in the voltage range between 2.7 and 4.8 V vs. Li/Li^+ (Fig. 5(c)), which is consistent with the result of Na-ion cells. Li-ion cells of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ delivered a reversible capacity of approximately 40 mA h g^{-1}

(Fig. 5(a)), which is similar to its Na-ion cells. However, when compared to the performance for Na-ion cells, $Na_{3.12}Co_{2.44}(P_2O_7)_2$ exhibited a larger polarization and poorer capacity retention for Li-ion cells, as shown in the dQ/dV plots (Fig. 3(b) and 5(b)). It is notable that the overpotential of Na-ion cells was smaller than that of Li-ion cells, despite the fact that Na^+ ions are larger than Li^+ ions. To understand this behavior, diffusion coefficients and charge transfer resistances were investigated using PITT and EIS, respectively (Fig. 6). The diffusion coefficients (*D*) were calculated using the equation below with the

(a)

(b)
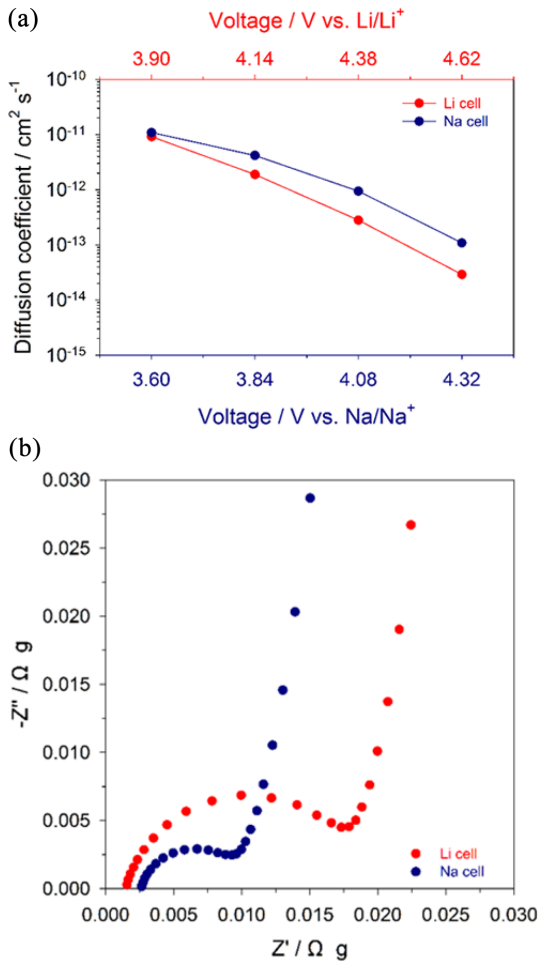
Fig. 6. (a) Diffusion coefficients of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ for each cells. (b) Nyquist plots of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ using symmetric cells for Na-ion and Li-ion cells.

assumption of the finite diffusion to exclude the effect of surface roughness of particles:

$$i = \frac{2nFAD\Delta C}{a}exp\left[\left(-\frac{\pi^2 D}{a^2}\right)t\right]$$

where n is an equivalent amount of electrons, F is Faraday constant, A is the surface area of particles, ΔC is the concentration gradient, and a is a particle radius. The diffusion coefficients of Li^+ and Na^+ ions in $Na_{3.12}Co_{2.44}(P_2O_7)_2$ were measured using current transients obtained from the PITT (Fig. 6(a)) [35-37]. Diffusion coefficients were calculated from the slopes ($-\pi^2 D/a^2$) of ln(imp) vs. t. Interestingly, the

diffusion coefficients of Na^+ ions were higher than those of Li^+ ions in $Na_{3.12}Co_{2.44}(P_2O_7)_2$. This suggests that the large channel size of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ is more suitable for larger Na^+ ions than Li^+ ions. This behavior is consistent with Na^+-conducting β-alumina [38-40]; the activation energy of Na^+ ions for ionic diffusion in β-alumina is lower than that of Li^+ ions. This is attributed to the fact that the smaller Li^+ is less stable in large sites with a high coordination number, resulting in stronger binding with oxygen than that in the case of Na^+. In addition, to compare the charge transfer resistances of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ between Na cells and Li cells, we performed the EIS analysis using symmetric cells comprising two identical fully charged electrodes. This revealed that Na-ion cells have a smaller charge transfer resistance than Li-ion cells (Fig. 6(b)). For these reasons, $Na_{3.12}Co_{2.44}(P_2O_7)_2$ showed better electrochemical performance for Na-ion batteries, indicating that the structure of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ is more suitable for Na-ion batteries.

Since the high charging voltage inevitably leads to the oxidative decomposition of the electrolyte, the electrochemical reaction mechanism of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ was investigated through chemical sodiation and desodiation. The redox potentials of oxidizing and reducing agents must be above and below a redox potential of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ (*ca.* 3.9 and 4.3 V vs. Na/Na^+), respectively. For this reation, NO_2BF_4 (V (NO_2^+/NO_2) = ca. 4.8 V vs. Na/Na^+) and NaI (V (I_2/I^-) = ca. 3.1 V vs. Na/Na^+) were used for chemical desodiation and sodiation, respectively [41]. The sequential formation of $Na_{3.12}Co_{2.44}(P_2O_7)_2 \rightarrow Na_{2.5}Co_{2.44}(P_2O_7)_2 \rightarrow Na_{2.0}Co_{2.44}(P_2O_7)_2 \rightarrow Na_{2.65}Co_{2.44}(P_2O_7)_2 \rightarrow Na_{2.75}Co_{2.44}(P_2O_7)_2$ was obtained via repetitive desodiation and sodiation using equimolar NO_2BF_4 and NaI, respectively. The amount of Na and Co in $Na_{3.12-x}Co_{2.44}(P_2O_7)_2$ was measured by ICP analysis (Fig. 7(a)). Then, we obtained the XRD patterns of those compositions, as shown in Fig. 7(b). The XRD peaks gradually and reversibly shift as x in $Na_{3.12-x}Co_{2.44}(P_2O_7)_2$ increased and decreased, and we also observed no evidence for a two-phase mixture of the end member phases. This implies that the $Na_{3.12}Co_{2.44}(P_2O_7)_2$ electrode proceeds in a one-phase reaction. This solid solution behavior of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ was also confirmed by the appearance of sloping voltage profiles (Fig. 3(a)).
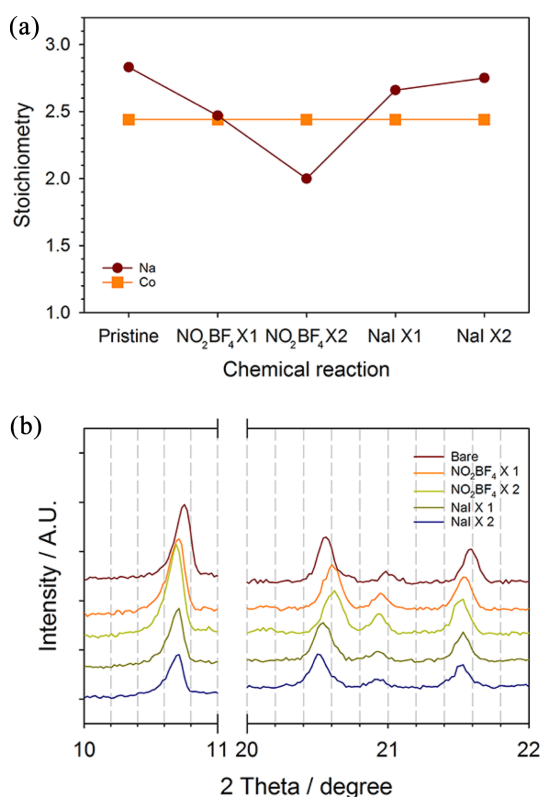
Fig. 7. (a) Atomic composition (ICP-MS) of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ during repetitive chemical desodation with NO_2BF_4 and sodiation with NaI, and (b) the corresponding XRD patterns of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ during chemical desodation and sodiation. Numbers in legends indicate the number of repeating times for chemical desodation and sodiation, respectively.

4. Conclusions

We synthesized two types of sodium cobalt pyrophosphates, triclinic $Na_{3.12}Co_{2.44}(P_2O_7)_2$ and orthorhombic $Na_2CoP_2O_7$, through a conventional solid-state method via heating at 600°C under Ar. $Na_{3.12}Co_{2.44}(P_2O_7)_2$ and $Na_2CoP_2O_7$ were examined as high-voltage cathode materials for Na-ion batteries. Whereas $Na_2CoP_2O_7$ showed no electrochemical activity, $Na_{3.12}Co_{2.44}(P_2O_7)_2$ exhibited good electrochemical performance, such as high redox potential at *ca.* 4.3 V (vs. Na/Na$^+$) and stable capacity retention over 50 cycles, although $Na_{3.12}Co_{2.44}(P_2O_7)_2$ delivered approximately 40 mA h g^{-1}. This is attributed to the fact that $Na_2CoP_2O_7$ (~3.1 Å) has smaller diffusion channel size than $Na_{3.12}Co_{2.44}(P_2O_7)_2$ (~4.2

Å). Moreover, we compared the electrochemical performances of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ between Na cells and Li cells. Na cells showed smaller overpotential than Li cells. This is due to the fact that $Na_{3.12}Co_{2.44}(P_2O_7)_2$ displayed a smaller charge transfer resistance and higher diffusivity for Na$^+$ ions when compared to Li$^+$ ions. This implies that the large channel size of $Na_{3.12}Co_{2.44}(P_2O_7)_2$ were more appropriate for Na$^+$ ions than Li$^+$ ions. Therefore, $Na_{3.12}Co_{2.44}(P_2O_7)_2$ is considered a promising candidate for a high-voltage cathode material. We believe that the high energy density of Na-ion batteries can be achieved with $Na_{3.12}Co_{2.44}(P_2O_7)_2$ if stable electrolytes above 4.5 V vs. Na/Na$^+$ are developed.

Acknowledgment

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