Graphical Abstract

**Lithium-substituted sodium layered transition metal oxide
fibers as cathodes for sodium-ion batteries**

Abstract

Na layered transition metal oxide fibers with/without partial Li substitution were prepared by the combination of a novel centrifugal spinning method and thermal treatment. Compared to the Li-free fibers, the Li-substituted Na layered transition metal oxide fiber cathodes exhibit higher capacities, better cycling stability and enhanced rate capability. Among the studied Li-substituted Na layered transition metal oxide fibers, $\text{Na}_{0.8}\text{Li}_{0.4}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ demonstrates the best overall electrochemical performance. The highest capacity of 138 mAh g^{-1} is achieved at 15 mA g^{-1} . As the current density increased to 75 and 300 mA g^{-1} , $\text{Na}_{0.8}\text{Li}_{0.4}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ fibers still deliver high capacities of 113 and 94 mAh g^{-1} , respectively. This specific fiber composition also yields stable cycling performance and superior rate performance at various current densities between 15 to 600 mA g^{-1} . The results suggest that partial Li substitution is an effective method to stabilize the structure of the Na layered transition metal oxide cathodes and hence enhance the electrochemical performance. It is also demonstrated that centrifugal spinning can be an attractive technology for mass production of micro-sized, fibrous electrodes.

Keywords: Sodium-ion battery, cathode, centrifugal spinning, sodium layered transition metal oxide, lithium substitution

1. Introduction

Currently, lithium-ion batteries (LIBs) are considered as one of the most widespread energy storage devices due to their desirable features including high energy density, high operating potential, long cycle life, low self-discharge, and wide temperature window. LIBs have been extensively used as the power source for portable electronics, hybrid electric vehicles, and plug-in hybrid electric vehicles (PHEVs).^{1,2} However, the reducing size of Li reserves, rising cost for Li supplies and arguably geographical limitation of Li resources together hinder the vast adoption of LIBs.³⁻⁵ Consequently, the identification of alternative energy storage systems is presently required as a valid step leading to the development of economically sustainable rechargeable batteries. Among various potential candidates, sodium-ion batteries (SIBs) appear to be a feasible alternative to LIBs due to the substantially lower cost and higher abundance of Na, which ranks the 6th most abundant element in the Earth crust. Na's similar chemistry to Li and its advantageous cost-effectiveness make SIBs a promising energy storage device of choice for large-scale, grid storage applications.⁵

Recently, many types of materials have been investigated as potential cathodes for SIBs, including transition metal fluorides (NaMF_3 , $\text{M} = \text{Fe, Mn, Ni, Ti, Co, V}$)^{6,7}, phosphate (NaFePO_4)^{8,9}, fluorophosphates (NaVPO_4F , $\text{Na}_2\text{FePO}_4\text{F}$)^{10,11}, and NASICON-type compounds ($\text{Na}_3\text{V}_2(\text{PO}_4)_3$)^{12,13}. In addition to the above-mentioned materials, Na layered transition metal oxides have become a group of attractive cathode candidate for SIBs mainly because Na (1.06 Å) has a larger ionic radius than Li (0.76 Å) and the octahedral or prismatic coordination in this group of materials is generally

preferable for Na.^{14,15} Na layered transition metal oxides can be categorized in two major groups: O3 and P2 type, in which Na ions are accommodated respectively at octahedral and prismatic sites, respectively.^{14,16,17} O3 type Na layered transition metal oxides, including NaCrO_2 ¹⁸, NaVO_2 ¹⁹, $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ²⁰, $\text{NaTi}_{0.5}\text{Ni}_{0.5}\text{O}_2$ ²¹, and $\text{NaNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ²², are all electrochemically active, but exhibit reversible capacities lower than 125 mAh g^{-1} . Generally, the P2-type Na layered transition layered transition metal oxides appear to achieve higher capacities as cathodes in SIBs than their O3-type rivals.^{14,17,23–29} Notably, Yabuuchi synthesized P2-type $\text{Na}_{2/3}\text{Fe}_{1/2}\text{Mn}_{1/2}\text{O}_2$ and achieved a reversible capacity of 190 mAh g^{-1} at 12 mA g^{-1} in a voltage range between 1.5 and 4.2 V.¹⁷ More recently, Hasa and co-worker prepared P2-type $\text{Na}_{0.5}\text{Ni}_{0.23}\text{Fe}_{0.13}\text{Mn}_{0.63}\text{O}_2$ and this cathode shows an initial discharge capacity of up to 200 mAh g^{-1} at 15 mA g^{-1} and over 150 mAh g^{-1} at 100 mA g^{-1} in a voltage window of 1.5–4.6 V.¹⁴

Li-rich, Mn-excess material $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ can deliver a high reversible capacity of over 250 mAh g^{-1} when used as a LIB cathode, which is about 68% of its theoretical capacity and is higher than the capacities of many other cathode materials.³⁰ As the SIB counterpart of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$, $\text{Na}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ also has the potential to deliver large capacity, but has not yet been reported in the literature. Therefore, we prepared this new cathode material that shares similar chemistry with $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ and investigated its electrochemical performance. The theoretical capacity of $\text{Na}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ is approximately 307 mAh g^{-1} if Na is fully extracted from the material. Notably, the P2-type Na layered transition metal

oxides are generally characterized by high capacity with limited cyclability, while the O3-type electrodes exhibit lower capacity but deliver better cycle life. Hence, it becomes critically important to develop Na layered transition metal oxides that can simultaneously have high reversible capacity and extended cycle life. In both P2 and O3-type cathodes, partial substitution of transition metals with Li in the transition metal layer was reported as an effective approach to improve their structural stability and therefore greatly enhance the electrochemical performance such as cycling stability and rate capability.^{31–37} Herein, we prepared Li-substituted Na layered transition metal oxide fibers by a novel centrifugal spinning technology combined with thermal treatment in air. A series of Li-substituted Na layered transition metal oxide fibers, with various Na and Li contents were synthesized by changing the stoichiometric ratios between Na and Li salts in the precursor solutions. The resultant Li-substituted Na layered transition metal oxide fibers were found to exhibit the P2-layered structure. These Li-substituted Na layered transition metal oxide fibers demonstrated significantly improved electrochemical performance, as compared with the pristine cathode material without partial Li substitution ($\text{Na}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$). Among the studied Li-substituted Na layered transition metal oxide fibers, $\text{Na}_{0.8}\text{Li}_{0.4}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ exhibited the most superior electrochemical performance. This cathode showed the highest reversible discharge capacity of 138 mAh g⁻¹ at a current density of 15 mA g⁻¹. At higher current densities of 75 and 300 mA g⁻¹, this cathode retained high capacities of 113 and 94 mAh g⁻¹, respectively. Stable cycling performance was achieved for the cathode after repeating charging and discharging for

50 cycles at 15 mA g⁻¹, 100 cycles at 75 mA g⁻¹ and 200 cycles at 300 mA g⁻¹. In a relatively stressful current range from 15 to 600 mA g⁻¹, the cathode also exhibited good rate capabilities. These results demonstrate that partial Li substitution is an effective method to stabilize the material structure and improve the electrochemical performance of Na layered transitional metal oxide cathodes and Li-substituted Na layered transition metal oxide fibers fabricated via centrifugal spinning can be used as a promising cathode material candidate in SIBs.

2. Materials and Methods

2.1 Material preparation

Sodium nitrate (NaNO₃, 99.0%), lithium nitrate (LiNO₃, 99.99%), nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O), manganese(II) nitrate tetrahydrate (Mn(NO₃)₂·4H₂O), cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O) N, N-dimethylformide (DMF), 1-methyl-2-pyrrolidinone (NMP) were purchased from Sigma-Aldrich Chemical Company (USA). Polyacrylonitrile (PAN, 150,000 g mol⁻¹), BTY175 battery conductive additive, and polyvinylidene fluoride (Solef 5130) were purchased from Pfaltz & Bauer Inc., Blue Nano Inc., and Solvay, respectively. All chemicals were used as received.

To prepare the precursor fibers, PAN powder was firstly dissolved into DMF solvent with a weight percentage of 12 wt. %. After the PAN/DMF solution was stirred

for over 24 hours, sodium, nickel, manganese and cobalt nitrates were mixed into the solutions stoichiometrically and stirred for another 24 hours to obtain homogeneous precursor solutions. Four precursor solutions were made, in which the molar ratio between Na and Li were 1.2:0, 1.0:0.2, 0.8:0.4 and 0.6:0.6, while the ratio of Ni, Mn and Co in the precursor solutions was kept constant at 0.15:0.55:0.1. In the precursor solutions, the total weight percentage of the metal nitrates with respect to PAN was 40 wt. %. The precursor fibers were then prepared by a novel centrifugal spinning approach. During centrifugal spinning, the precursor solutions were firstly loaded into the spinneret. The spinneret has 3 cm diameter and multiple 0.4 cm-diameter nozzles. After the solutions were injected into the spinneret, a rotational speed of 4,000 rpm was applied to produce precursor fibers. The fibers were deposited on aluminum collectors which are located radially to the spinneret with a 10 cm distance.

Li-substituted Na layered transition metal oxide fibers were prepared by calcinating the precursor fibers in a two-step method. Firstly, the precursor fibers were treated in air at 500 °C for 5 hours with 2 °C min⁻¹ heating rate to decompose the nitrates. Then, the intermediate precursor fibers were further heated to 900 °C with 2 °C min⁻¹ heating rate and held for 10 hours to form the Li-substituted Na layered transition metal oxide fibers, while in the meanwhile, the PAN component was completely decomposed.

The molar ratio between Ni, Mn, Co and O was kept constant in all four calcinated samples (0.15:0.55:0.1:2), while the molar ratio between Na and Li varied. For simplicity, we denoted $\text{Na}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$, $\text{Na}_{1.0}\text{Li}_{0.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$, $\text{Na}_{0.8}\text{Li}_{0.4}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$, and $\text{Na}_{0.6}\text{Li}_{0.6}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ as $\text{Na}_{1.2}\text{-NMCO}$, $\text{Li}_{0.2}\text{-}$

$\text{Na}_{1.0}\text{-NMCO}$, $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$, and $\text{Li}_{0.6}\text{-Na}_{0.6}\text{-NMCO}$, respectively. Similarly, the reference sample $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ was denoted as $\text{Li}_{1.2}\text{-NMCO}$.

2.2 Structural analysis

The morphology of Li-substituted Na layered transition metal oxide fibers were investigated using field emission scanning electron microscope (FESEM-JEOL 6400F SEM at 5 kV). X-ray diffraction (XRD, Rigaku Smartlab, $\text{Cu K}\alpha$, $\lambda = 1.544 \text{ \AA}$) was conducted to characterize the crystal structures of Li-substituted Na layered transition metal oxide fibers. The XRD patterns were obtained within a 2θ range of $5\text{-}90^\circ$ and a step size of 0.02° .

2.3 Electrochemical evaluation

The electrochemical behavior of Li-substituted Na layered transition metal oxide fibers was evaluated using coin cells (CR2032-type). The working electrodes were synthesized by mixing Li-substituted Na layered transition metal oxide fibers (70 wt. %) with conductive additive (BTY 175, 20 wt. %) and polyvinylidene fluoride (PVDF, Solef 5130, 10 wt. %) in N-methyl-2-pyrrolidone (NMP) solvent. Then, the prepared slurries were casted onto carbon-coated aluminum foil (the current collector) and vacuum-dried overnight. The dried electrodes were cut from the carbon-coated foil using a puncher with a diameter of $1/2''$. Na foil was cut directly from pure Na dry stick

for use as the counter electrode. The working electrodes and Na counter electrode were partitioned by glass fiber separator (Whatman GF/D glass microfiber filters) impregnated with electrolyte consisting of 1 M NaClO₄ in solvent composing of ethylene carbonate (EC) and dimethyl carbonate (DMC) by a volume ratio of 1:1. Prior to the electrochemical tests, the cells were kept rested over 24 hours.

Galvanostatic charge/discharge performance were investigated by Arbin BT2000 battery tester in a voltage range of 4.2-1.5 V vs Na⁺/Na at current densities of 15, 75 and 300 mA g⁻¹. The rate capabilities of Li-substituted Na layered transition metal oxide fibers were investigated at various current densities from 15 to 600 mA g⁻¹.

3. Results and discussion

PAN/nitrate precursor fibers were prepared via a novel centrifugal spinning technology that enables rapid fiber production. Figure 1a sketches the lab-scale centrifugal spinning instrument used in the present study. The centrifugal spinning instrument mainly includes a Teflon spinneret with multiple fine nozzles, high speed motor equipped with DC motor controller, and aluminum collectors. To prepare the precursor fibers, the precursor solutions containing PAN and different amounts of Na, Li, Ni, Mn, and Co nitrates were fed into the spinneret through the top opening, and then high-speed rotation was applied. When the rotational speed accelerated to a value at which the centrifugal force can overcome the surface tension of the precursor

solutions, liquid jets were initiated from the nozzles on the spinneret. During the movement in a circular trajectory course, the liquid jets were stretched and the solvent (DMF) gradually evaporated. Finally, dried precursor fibers deposited onto the rod-shaped collectors. Two leather pieces can be found in Figure 1a, and they were installed to generate lifting air so that the fibers were collected on the upper area of the spinning platform, forming freestanding nonwoven mats that were easy to remove. Figure 1b illustrates the precursor fibers prepared via centrifugal spinning. The precursor fibers contain PAN as the polymer carrier, and homogeneously distributed metal salts within the fibers. The precursor fibers were thermally treated in air in a two-step treatment: the first step at 500 °C facilitated the decomposition of the metal nitrates, while the second step at 900 °C allowed the formation of Li-free or Li-substituted Na layered transition metal oxide fibers. The schematic illustration of the as-synthesized Na or Li-substituted Na layered transition metal oxide fibers is shown in Figure 1c. The centrifugal spinning route used in the present study is novel and promising in the preparation of fibrous Na layered transition metal oxide electrode materials, mainly because this spinning technology uses well-mixed precursor solutions that accommodates uniform metal ion distribution in the final product. So far, most reported fibrous electrode materials were prepared by electrospinning, which is slow, unsafe, and high cost.³⁸ To the best of our knowledge, centrifugal spinning has not been used in sodium-ion battery electrode preparation. Compared with electrospinning, centrifugal spinning can generate fine fibers from more concentrated polymer solutions so that less solvent is needed. This method also avoids the use of high voltage, which is a safety concern in electrospinning.

More importantly, centrifugal spinning can produce tens of grams of fine fibers per nozzle per hour, and such high production rate is at least two orders of magnitude higher than that of electrospinning.^{38–40} Overall, the above-mentioned advantages make centrifugal spinning an attractive approach for both academia and industry due to its large production rate, high safety, and low cost. Therefore, we used this rapid and scalable method for preparing fibrous electrode materials, and the results obtained in this study can potentially provide a solution to industrial, mass production of fibrous electrodes.

The morphologies of as-spun PAN/nitrate precursor fibers and the resultant Li-substituted Na layered transition metal oxide fibers with various Na and Li contents were examined by SEM. The SEM images of representative Li-substituted Na layered transition metal oxide fibers with a specific composition of $\text{Li}_{0.4}\text{Na}_{0.8}\text{-NMCO}$ and the corresponding precursor fibers are shown in Figure 2. It is seen from Figures 2a and b that the typical precursor fibers show smooth surface without bead formation. The precursor fibers are continuous and overlay with each other to form a 3D network structure with interconnected pores between the fibers. The average diameter of the precursor fibers is about $3\mu\text{m}$. The as-spun precursor fibers were thermally treated in air with a two-step treatment at $500\text{ }^{\circ}\text{C}$ and $900\text{ }^{\circ}\text{C}$, respectively, to form Li-substituted Na layered transition metal oxide fibers. Figures 2c and d demonstrate the morphology of the as-prepared $\text{Li}_{0.4}\text{Na}_{0.8}\text{-NMCO}$ fibers. It is seen that after the two-step thermal treatment, the obtained $\text{Li}_{0.4}\text{Na}_{0.8}\text{-NMCO}$ fibers lose the smooth surface structure and are no longer continuous. The average fiber diameter shrinks from $3\mu\text{m}$ to $1\mu\text{m}$ due to

the removal of the polymer component and the decomposition of the nitrates. The resultant fibers still maintain a short fibrous structure and 1D architecture. In recent LIB and SIB material studies, employing 1D nano-/micro-structure becomes an attractive method to improve the electrochemical performance of electrode materials. In bulk electrode materials, active particles tend to aggregate due to their high surface energy, resulting in the formation of large secondary particles. The inner part of the aggregated particles is difficult to be utilized and barely contributes to the electrode capacity because of the insufficient electrode-electrolyte contact. In contrast, the 1D structured electrode materials show unique fibrous architecture and interconnecting nature, and can hinder the self-aggregation of active particles. Compared to traditional electrode materials, the 1D structure electrode materials possess large effective electrode-electrolyte contact area and better electrolyte wettability during cycling, which contribute to enhanced electrochemical performance. Moreover, the unique 1D structure provides well-guided and shortened transport pathways for both ions and electrons, facilitating rapid and efficient ionic/electronic transport and resulting in improved electrochemical performance.⁴¹⁻⁴⁴ In the present study, $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$ fibers can potentially facilitate sufficient electrode-electrolyte contact and rapid ionic/electronic transportation throughout the material, which in turn lead to reduced electrochemical impedance and enhance electrochemical performance.

The crystal structures of Li-free and Li-substituted Na layered transition metal oxide fibers were investigated using XRD and results are given in Figure 3. For comparison, the XRD pattern of Na-free $\text{Li}_{1.2}\text{-NMCO}$ particles is also provided. In the

XRD pattern of $\text{Na}_{1.2}\text{-NMCO}$ fibers (curve 3a), major peaks are identified at 2-theta angles of 16.0° , 32.3° , 36.3° , 39.9° , 44.0° , 49.3° , 62.3° , 65.1° and 67.5° and these peaks are characteristic peaks for typical P2-type Na layered transition metal oxides.^{14,24,25} For the XRD pattern of the reference sample ($\text{Li}_{1.2}\text{-NMCO}$ particles, curve 3e), strong diffraction peaks are observed at 2-theta angles of 18.8° , 37.1° , 44.9° , 49.0° , 59.0° , 64.7° , 65.5° , and 68.8° . These diffraction peaks are typical for Li-rich Mn-based oxide cathodes in Li-ion batteries and can be attributed to the $\alpha\text{-NaFeO}_2$ structure.^{45,46} It is seen from curves 3b, c and d that as the relative content ratio of Na/Li decreases from 1.0/0.2, 0.8/0.4 to 0.6/0.6, the diffraction peaks representing Na-free $\text{Li}_{1.2}\text{-NMCO}$ increases, indicating that these Li-substituted Na layered transition metal oxide fibers are solid solutions of $\text{Li}_{1.2}\text{-NMCO}$ in $\text{Na}_{1.2}\text{-NMCO}$ with various stoichiometric ratios.

The electrochemical performance of both Li-free and Li-substituted Na layered transition metal oxide fibers is evaluated using galvanostatic charge-discharge tests within a voltage range of 4.2-1.5 V at a current density of 15 mA g^{-1} and the results are demonstrated in Figure 4. It is seen that the initial charging of all four cathode materials proceeds predominantly in two stages. In the first stage, the voltage increases to above 2 V rapidly, and then shows a potential plateau between 2 and 3.8 V. When the electrode is further charged from 3.8 to 4.2 V, a second voltage plateau appear from 4 to 4.2 V, however, this charge plateau becomes less apparent in the following charge curves. For Na-free Li-rich, Mn-excess oxide cathodes such as $\text{Li}_{1.2}\text{-NMCO}$, the initial charge curve generally displays a charge plateau at 4.4 to 4.6 V, which is attributed to the irreversible extraction of Li from Li_2MnO_3 of the solid solution cathode materials.⁴⁵ This charge

plateau is usually absent from the second charge curve and the irreversible reaction results in the irreversible capacity loss of the first cycle. Similarly, the charge plateau at 4 to 4.2 V in the Li-substituted Na layered transition metal oxide fibers can be ascribed to possible Na/Li extraction from the as-prepared solid solution cathodes. The initial charge capacities of $\text{Na}_{1.2}\text{-NMCO}$, $\text{Li}_{0.2}\text{-Na}_{1.0}\text{-NMCO}$, $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$, and $\text{Li}_{0.6}\text{-Na}_{0.6}\text{-NMCO}$ fibers are 144, 204, 280 and 237 mAh g^{-1} , respectively, while the corresponding initial discharge capacities are 94, 135, 124 and 125 mAh g^{-1} , respectively. All the Li-substituted Na layered transition metal oxide fibers exhibit higher initial discharge capacities than that of the pristine $\text{Na}_{1.2}\text{-NMCO}$ fibers. The electrochemical performance of $\text{Na}_{1.2}\text{-NMCO}$, $\text{Li}_{0.2}\text{-Na}_{1.0}\text{-NMCO}$, $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$, and $\text{Li}_{0.6}\text{-Na}_{0.6}\text{-NMCO}$ fibers was further investigated at a medium current density of 75 mA g^{-1} and a high current density of 300 mA g^{-1} in a potential window of 4.2 to 1.5 V. The charge-discharge curves obtained at 75 and 300 mA g^{-1} can be seen in Figures S1 and S2, respectively. Comparing Figures S1 and S2 with Figure 4, it is seen that the charge-discharge curves at the medium and high current densities show similar charge/discharge plateaus to those found in the low current density tests, suggesting the good rate capability of these cathode materials.

Figure 5 compares the cycling performance of Li-free and Li-substituted Na layered transition metal oxide fibers at current densities of 15, 75 and 300 mA g^{-1} within a potential window of 4.2 to 1.5 V. It is seen from Figure 5a that at a current density of 15 mA g^{-1} , reversible capacities of 94, 135, 124 and 125 mAh g^{-1} are delivered in the first cycle for $\text{Na}_{1.2}\text{-NMCO}$, $\text{Li}_{0.2}\text{-Na}_{1.0}\text{-NMCO}$, $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$, and $\text{Li}_{0.6}\text{-Na}_{0.6}\text{-NMCO}$.

NMCO fibers, respectively. After repeatedly charge and discharge for fifty cycles, specific capacities of 71, 93, 79 and 86 mAh g⁻¹ are sustained for Na_{1.2}-NMCO, Li_{0.2}-Na_{1.0}-NMCO, Li_{0.4}-Na_{0.8}-NMCO, and Li_{0.6}-Na_{0.6}-NMCO fibers, respectively. All the Li-substituted Na layered transition metal oxide fibers show higher specific discharge capacities in all 50 cycles. Although the Li_{0.2}-Na_{1.0}-NMCO fibers maintain the highest discharge capacity of 93 mAh g⁻¹ after fifty cycles, the highest specific capacity of 138 mAh g⁻¹ is achieved at the third cycle of Li_{0.4}-Na_{0.8}-NMCO fibers. The Li-substituted Na layered transition metal oxides exhibit a slightly increasing trend in the discharge capacities for the first several cycles, indicating this type of cathode materials might need a long activation process before the highest utilization is reached. The cycling performance of Na_{1.2}-NMCO, Li_{0.2}-Na_{1.0}-NMCO, Li_{0.4}-Na_{0.8}-NMCO, and Li_{0.6}-Na_{0.6}-NMCO fibers at 75 mA g⁻¹ is compared in Figure 5b. After a hundred charge-discharge cycles, the specific discharge capacities of Na_{1.2}-NMCO, Li_{0.2}-Na_{1.0}-NMCO, Li_{0.4}-Na_{0.8}-NMCO, and Li_{0.6}-Na_{0.6}-NMCO fibers are 69, 96, 91 and 93 mAh g⁻¹, respectively, corresponding to capacity retentions of 80%, 83%, 81% and 89%. Figure 5c displays the cycling performance of the cathode materials at 300 mA g⁻¹ for two hundred cycles. All cathode materials show insignificant capacity loss during the prolonged cycling tests: after two hundred cycles, the specific capacities retained for Na_{1.2}-NMCO, Li_{0.2}-Na_{1.0}-NMCO, Li_{0.4}-Na_{0.8}-NMCO, and Li_{0.6}-Na_{0.6}-NMCO fibers are 53, 70, 75 and 63 mAh g⁻¹, corresponding to capacity retentions of 79%, 82%, 81% and 82%, respectively. These results show that Li-substituted Na layered transition metal oxide fibers yield higher discharge capacities and better cycling stability, indicating that the partial Li

substitution is an effective approach to sustain the structural stability of the Na layered transition metal oxide cathodes and therefore leads to enhanced electrochemical performance.

The rate performance of Li-free and Li-substituted $\text{Na}_{1.2}\text{-NMCO}$ fibers was examined in a voltage window of 4.2 to 1.5 V with various current densities of 15, 30, 75, 150, 300 and 600 mA g^{-1} and the results are shown in Figure 6a. Figures 6b, c, d and e provide the corresponding voltage profiles at each current density. It is seen that when the current density increases, lower capacities are obtained for all four cathode materials, however, the charge-discharge curves maintain the same trend. For $\text{Na}_{1.2}\text{-NMCO}$ fibers, specific discharge capacities of 100, 76, 65, 58, 50 and 42 mAh g^{-1} , respectively, are obtained at current densities of 15, 30, 75, 150, 300 and 600 mA g^{-1} . At the highest current density of 600 mA g^{-1} , $\text{Na}_{1.2}\text{-NMCO}$ fibers retain 42% of the original capacity at 15 mA g^{-1} . As the current density returns to 15 mA g^{-1} , the discharge capacity goes back to 85 mAh g^{-1} , corresponding to 85% of the initial discharge capacity. On the contrary, the three Li-substituted Na layered transition metal oxide fibers demonstrate higher discharge capacities at all current densities, compared to $\text{Na}_{1.2}\text{-NMCO}$ fibers. Among all the studied cathode materials, $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$ fibers exhibit the best rate performance and deliver reversible capacities of 140, 119, 105, 94, 82 and 68 mAh g^{-1} , respectively, at 15, 30, 75, 150, 300 and 600 mA g^{-1} . At 600 mA g^{-1} , $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$ fibers maintain 49% of the original capacity at 15 mA g^{-1} . As the current density retrieves at 15 mA g^{-1} , $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$ fibers show a discharge capacity of 127 mAh g^{-1} , corresponding to 91% of the initial capacity value.

The significantly enhanced electrochemical performance of the Li-substituted Na layered transition metal oxide fibers is largely contributed by the Li stabilizing effect in the transition metal layers of the materials. Several studies reported partially substitution of Na with Li and the results suggest that such method is effective in improving the electrochemical performance for SIB cathode materials.^{31–37} Li substitution strategy has been applied in both P2 and O3 type materials. It is commonly believed that the substituted Li ions share the adjacent transition metal sites with Mn and Ni ions, which results in minimal anti site disorder. In this way, the added Li in the cathode materials is expected to stabilize the transition metal layer and counter the movement of Ni into the Na layer during repeated Na intercalation and deintercalation.^{31,34,37} Therefore, the substituted Li in the structure can help prevent phase transformation and mitigate structural degradation during cycling, resulting in improved electrochemical performance. In the present study, various stoichiometric proportions between Li and Na were investigated to determine the optimum composition. The electrochemical performance of Na_{1.2}-NMCO, Li_{0.2}-Na_{1.0}-NMCO and Li_{0.4}-Na_{0.8}-NMCO gradually improves due to the effect of partial Li substitution. However, for Li_{0.6}-Na_{0.6}-NMCO, the Li concentration is too high and the excess Li leads to the formation of more Li₂MnO₃ impurities, which in turn reduces the electrode capacity.³⁵ Therefore, it is determined that the composition Li_{0.4}-Na_{0.8}-NMCO has the optimum stoichiometric proportion among all the Li-substituted Na layered transition metal oxide fiber cathodes studied in this work.

So far, most Na layered transition metal oxide cathodes for SIBs were prepared in the form of small particles and their specific capacities ranged from 100 to 200 mAh g⁻¹ at low current densities.¹⁴⁻²⁹ The highest specific capacity achieved for the fibrous cathodes prepared in the present study is 140 mAh g⁻¹, which is medium among the reported capacity values. However, in most reported studies, the cycling performance of the cathode materials was evaluated at low to medium current densities (<100 mA g⁻¹) with limited cycling numbers (<50 cycles).¹⁴⁻²⁹ Since long-term cyclability and rate capability are important for the practical application of SIBs, the cycling performance of Na_{1.2}-NMCO, Li_{0.2}-Na_{1.0}-NMCO, Li_{0.4}-Na_{0.8}-NMCO and Li_{0.6}-Na_{0.6}-NMCO fibrous cathodes was evaluated at medium (75 mA g⁻¹) and high (300 mA g⁻¹) current densities for 100 and 200 cycles, respectively, in the present study. The obtained capacity retentions range from 80% to 90%, which is satisfactory for SIB cathodes. Moreover, comparing the capacity retention values of the fibrous cathodes in this study with other Na layered transition metal oxide cathodes for the same cycle number (*i.e.*, 50 cycles), the achieved capacity retentions fall in the range between 90% to 96%, which is higher than most reported results, giving the condition that the current densities used in this study are higher than those used in literature.¹⁴⁻²⁹ Therefore, the fibrous structure employed in this study is effective in improving the electrochemical performance of Na layered transition metal oxide cathodes.

4. Conclusions

Na layered transition metal oxide fibers with/without partial Li substitutions were synthesized via centrifugal spinning with subsequent heat treatment. Various fibrous cathodes with different Na/Li stoichiometric ratios were obtained by changing the contents of Na and Li salts in the precursor solutions. Compared to the $\text{Na}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ fibers, the Li-substituted Na layered transition metal oxide fibers show higher capacities, better cycling stabilities and improved rate performance. Among the studied cathode materials, $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$ fibers exhibits the most superior electrochemical performance: they deliver the highest capacities of 138 mAh g^{-1} at 15 mA g^{-1} , 113 mAh g^{-1} 75 mA g^{-1} , and 94 mAh g^{-1} at 300 mA g^{-1} , respectively. In a stressful current range between 15 to 600 mA g^{-1} , $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$ fibers maintain 49% of the original capacity at the highest current density of 600 mA g^{-1} , and retrieves 91% of its initial capacity as the current density returns to 15 mA g^{-1} . It is therefore demonstrated that partial Li substitution in the Na layered transition metal oxide fibers can be considered as an effective route to improve the structural stability and enhance the electrochemical performance of the Na layered transition metal oxides. Moreover, centrifugal spinning can be a promising approach in the fabrication of micro-sized fibrous electrode materials due to its high cost effectiveness and scale-up capability.

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Captions of figures

Figure 1. Schematic illustration of (a) centrifugal spinning instrument, (b) a centrifugally-spun PAN/nitrate precursor fiber, and (c) a Li-substituted Na layered transition metal oxide fiber.

Figure 2. SEM images of PAN/nitrate precursor fibers for $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$ (a, b), and corresponding $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$ fibers (c, d).

Figure 1. XRD patterns of $\text{Na}_{1.2}\text{-NMCO}$ fibers (a), $\text{Li}_{0.2}\text{-Na}_{1.0}\text{-NMCO}$ fibers (b), $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$ fibers (c), $\text{Li}_{0.6}\text{-Na}_{0.6}\text{-NMCO}$ fibers (d), and $\text{Li}_{1.2}\text{-NMCO}$ particles (e).

Figure 4. Charge-discharge curves of $\text{Na}_{1.2}\text{-NMCO}$ fibers (a), $\text{Li}_{0.2}\text{-Na}_{1.0}\text{-NMCO}$ fibers (b), $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$ fibers (c), and $\text{Li}_{0.6}\text{-Na}_{0.6}\text{-NMCO}$ fibers (d). The current density was 15 mA g^{-1} .

Figure 5. Cycling performance of $\text{Na}_{1.2}\text{-NMCO}$, $\text{Li}_{0.2}\text{-Na}_{1.0}\text{-NMCO}$, $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$, and $\text{Li}_{0.6}\text{-Na}_{0.6}\text{-NMCO}$ fibers at current densities of 15 (a), 75 (b) and 300 (c) mA g^{-1} .

Figure 6. Rate capabilities of $\text{Na}_{1.2}\text{-NMCO}$, $\text{Li}_{0.2}\text{-Na}_{1.0}\text{-NMCO}$, $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$, and $\text{Li}_{0.6}\text{-Na}_{0.6}\text{-NMCO}$ fibers in a current range of 15 to 600 mA g^{-1} (a); corresponding voltage profiles of $\text{Na}_{1.2}\text{-NMCO}$ fibers (b), $\text{Li}_{0.2}\text{-Na}_{1.0}\text{-NMCO}$ fibers (c), $\text{Li}_{0.4}\text{-Na}_{0.8}\text{-NMCO}$ fibers (d), and $\text{Li}_{0.6}\text{-Na}_{0.6}\text{-NMCO}$ fibers (e).

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