Facile Fabrication Hierarchical Pore Structure $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13-x}\text{Sr}_x\text{O}_2$
Nanofiber for High-Performance Cathode Materials in Li-ion Battery

Yu Zhang, Xingyu Li, Tianjiao Zhu, Shulan Ma, Huifeng Li and Genban Sun

The long-cycle life cathode material plays a key role in terms of energy and power density for lithium-ion battery. In this work, a series of Sr-doped hierarchical porous nanofiber structure $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13-x}\text{Sr}_x\text{O}_2$ are synthesized via electrospinning combined with high temperature solid phase technology. As a result, Sr-doping can enhance the cyclic performance, suppress the voltage decay and stabilize the structure. With the incorporation of Sr, not only the crystal structure and morphology of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13-x}\text{Sr}_x\text{O}_2$ are slightly changed, but also both the specific capacity and discharge voltage of the Li rich cathode are stabilized upon cycling. When $x = 0.03$, $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13-x}\text{Sr}_x\text{O}_2$ delivers an initial discharge capacity of 213 mAh g$^{-1}$ and a capacity retention of 94.16 % at the 100th cycle. The influence of the percentage of doped Sr on the performance of the battery is analyzed. Rational Sr doping technology is an effective way to improve the electrochemical performance of Li rich manganese based material.

Introduction

Because of the energy shortage and the emergence of portable electronic equipment and electric vehicles, rechargeable lithium-ion batteries (LIBs) have attracted wide attention and played a leading role in energy storage. Compared to other energy storage devices, lithium-ion batteries possess numerous advantages, such as high energy density, long cycle life and environmental benignity. Cathode material plays a key role in terms of energy and power density for a LIBs. Lithium-rich manganese-based layered oxide, usually denoted as $x\text{Li}_2\text{MnO}_3\cdot(1-x)\text{LiMO}_2$ ($M = \text{Mn, Co, Ni, etc}$), is considered to be the most promising cathode material because it can deliver a discharge capacity up to 250 mAh g$^{-1}$, which is significantly greater than the current commercialized cathode materials. According to reports, these materials integrate two different local structures into a solid solution, one with a rhombohedral LiMO$_2$ (space group R-3m) and the other with a monoclinic Li$_2$MnO$_3$ (space group C2/m). When charged to potentials higher than 4.5 V, these materials are able to achieve their high specific capacity, which is associated with the irreversible activation of Li$_2$MnO$_3$. However, these Li-rich cathodes have fatal drawbacks, such as large irreversible capacity loss at the initial cycle, voltage decays and layered-to-spinel phase transformation during cycling, which directly impede the commercialization of Li-rich cathodes in high-energy-density lithium-ion batteries.

To improve the electrochemical properties of these Li-rich cathode materials, considerable endeavors have been devoted. One possible strategy is surface modification. For instance, coating the lithiated metal fluoride or oxide with nano-sized is a versatile method, it can avoid direct contact between active materials and electrolyte, and effectively inhibit interfacial side reactions. Zhao et al. synthesized the LiF/Fe, nanoparticles coated Li-rich Li$_2$[Li$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$]O$_2$ cathode via a facile aqueous solution process, and this novel composite cathode showed high electrochemical performance. Kobayashi et al. reported that the discharge capacity can achieve higher than 310 mAh g$^{-1}$ through surface modification of Li$_2$[Li$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$]O$_2$ with Al$_2$O$_3$. Besides, decorating the surface of Li-rich cathode materials with spinel membrane is another tactic to improve battery performance. Wu et al. reported an ultrathin spinel membrane-encapsulated layered lithium-rich cathode, where the voltage decay and thermal instability were found to be alleviated. However, the surface modification cannot obstruct the voltage degradation upon cycling led by the layered-to-spinel phase transformation.

There are indications that doping or substituting additional ions such as Al$^{3+}$, Mg$^{2+}$, K$^{+}$, Mo$^{6+}$, Y$^{3+}$ and La$^{3+}$ into lithium-rich Mn-based materials could availably stabilize the host structure. Nayak et al. substituted Mn in Li cathode materials Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ by Al and reported that Al substitution has a bulk stabilizing effect on the layered LiMO$_2$ phase. Yu et al. synthesized La-doped lithium-rich layered oxide materials Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ (x = 0.01, 0.02, 0.03). This material exhibits 93.2 % capacity retention after 100 cycles at 1 C. Moreover, La doping can stabilize the layered framework upon long term cycling and suppress voltage fading. Sun et al. reported a Y-doped layered cathode material Li$_{1.2}$Ni$_{0.54}$Mn$_{0.13}$Y$_{0.03}$O$_2$ with better electrochemical performance. Y-doping not only decreases electrochemical polarization and charge-transfer resistance, but also enhances the ability of Li$^{+}$ diffusion.

Strontium (Sr) has been used as substitution element in many cathode materials, such as LiCoO$_2$, LiNi$_x$Co$_y$O$_2$ and LiMnO$_2$, for Sr$^{2+}$ possess large radius and keep inactive during the electrochemical
process. To the best of our knowledge, Li-rich materials are composed by LiMnO component and LiNi1/3Co1/3Mn2/3O4 component and the ternary component plays an important role in the electrochemical process. Thus, Sr substitution for partial redox active Co in the LiNi1/3Co1/3Mn2/3O4 component of Li-rich material may reduce the initial discharge capacity, but it expands and stabilizes the pathway for intercalation and deintercalation of Li+ which can enhance the rate capacity and suppress the voltage and capacity fading during cycling.

In this work, a series of the Li-rich Sr-doped nanofiber structure Li1-xMn0.54Ni0.13Co0.13Srx0.03O2 were synthesized via electrospinning combined with high temperature solid phase reaction technology. The effects of Sr substitution for partial Co on the structure, morphology, electrochemical properties and electron conductivity of the Li1-xMn0.54Ni0.13Co0.13O2 are systematically studied.

Experimental

Sample synthesis
The Sr-doped layered Li1-xMn0.54Ni0.13Co0.13Srx0.03O2 (x=0, 0.01, 0.03, 0.05) nanofibers cathode materials were synthesized by the combination of electrospinning and a subsequent heat treatment. The 1.6 g of Polyacrylonitrile (PAN) was dissolved in 15 ml of N,N-dimethylformamide (DMF) solution with stirring for 12 h to obtain a homogeneous solution, here marked as solution A. The designated compositions with stoichiometric amount of LiCH4COO·2H2O, Ni(CH3COO)·4H2O, Co(CH3COO)·4H2O, Mn(CH3COO)·4H2O and Sr(CH3COO)·4H2O were dissolved in 10 ml of DMF solution with stirring for 12 h, here marked as solution B. Then, solution A and solution B were mixed together with continuous stirring for 12 h at ambient temperature until a homogeneous electrospinning solution was obtained. Next, the mixed solution was subjected to electrospinning with a flow rate of 5 ml·h⁻¹ and a distance of 15 cm between the tip and collector. Under a voltage of 13 kV, a white as-spun nanofibers film was collected on an aluminum foil. Finally, to obtain crystallized cathode materials with nanofibers, the white as-spun nanofibers film were initially stabilized at 280 °C for 4 h and then calcined at 800 °C for 12 h in air with a heating rate of 2 °C·min⁻¹.

Structural characterization
The crystal phase of the materials was characterized by Powder X-ray diffraction (XRD, Shimadzu XRD-7000, Cu Kα radiation, Japan) with a scan rate of 5 Min⁻¹ from 10 to 80 (2θ). The morphology and further structural characteristics of these cathode materials were observed by field emission scanning electron microscope (FESEM, Hitachi SU8010, Japan) and high-resolution transmission electron microscope (HRTEM, JEM-2010, JEOL, Japan). Raman spectroscopic studies of materials were carried out using a microscopic confocal Raman spectrometer (LabRAMArinis, Horiba Jobin Yvon) equipped with a 532 nm He-Ne laser, and the scanning range was from 200 to 1000 cm⁻¹. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, America) was performed to determine the surface chemical states of the samples. Inductively coupled plasma-atomic emission spectrum (ICP-AES, Jarrel-ASH, ICP-9000) was employed to analyze the chemical compositions of as-prepared samples.

Electrochemical characterization
The electrochemical properties of Li1-xMn0.54Ni0.13Co0.13Srx0.03O2 (x=0, 0.01, 0.03, 0.05) were examined by using coin-type cells CR-2032. The electrodes were prepared by mixing the active materials (80 wt%), conductive acetylene black (10 wt%) and polyvinylidene fluoride (PVDF) (10 wt%) in N-methyl-2-pyrrolidone and stirred for 1 h to obtain slurry. The slurry was evenly coated on aluminum foil and dried at 110 °C for 12 h in vacuum oven. The cells were assembled in an Ar-filled glovebox (M.Braun, Labstar, Germany) with lithium foil as the counter electrode, Celgard 2400 as the separator, and the 1 M LiPF6 in ethyl carbonate (EC) and diethyl carbonate (DEC) (volume ratio is 1:1) as the electrolyte. Galvanostatic charge-discharge tests were implemented at room temperature on the Neware (China) battery test system in the voltage range from 2.0 V to 4.8 V vs Li+/Li (1 C = 280 mA g⁻¹).

Results and discussion

Materials composition and structure
The atomic compositions of as-obtained material are confirmed by inductive coupled plasma (ICP) technique, and the elemental analysis results are tabulated in Table 1. According to the results, the composition of the as-synthesized materials are found to be very close to the targeted compositions. Especially, the concentration of Sr in each sample is agreement with the nominal stoichiometry and the Co content decreases with the increase of Sr, as expected.

Fig. 1a demonstrates the X-ray diffraction (XRD) patterns of the obtained Li1-xMn0.54Ni0.13Co0.13Srx0.03O2 (x = 0, 0.01, 0.03, 0.05) powders. The diffraction peaks of all samples, except 2θ=20~25°, can be indexed as the hexagonal α-NaFeO2 layered structure with an R-3m space group.24,36 These weak diffraction peaks at 2θ=20~25° are considered to be related to the super lattice cation ordering of LiMnO2 in the transition metal layers, confirm the existence of LiMnO2.47 There is a slight peak shift but no noticeable impurity phase in the XRD patterns, which reveals the Sr doping is valid but it does not change the crystal structure significantly. Meanwhile, two pairs of the (006)/(012) peaks and the (108)/(110) peaks are well split, suggests the formation of a well-ordered layered structure for all samples with Sr-doping.27

The Raman spectra of pristine (Li1-xMn0.54Ni0.13Co0.13O2) and the modified (Li1-xMn0.54Ni0.13Co0.13Sr0.03O2) samples are shown in Fig. 1b. Both

Table 1 The theoretical and experimental results of Li: Mn: Ni: Co: Sr molar ratios of the electrode materials according to ICP analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical molar ratios of Li: Mn: Ni: Co: Sr</th>
<th>Experimental molar ratios of Li: Mn: Ni: Co: Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li1.2Mn0.54Ni0.13Co0.13O2</td>
<td>1.2:0.54:0.13:0.13:0.02</td>
<td>1.190:0.552:0.129:0.134:0.04</td>
</tr>
<tr>
<td>Li1.2Mn0.54Ni0.13Co0.12Sr0.03O2</td>
<td>1.2:0.54:0.13:0.12:0.01</td>
<td>1.196:0.591:0.129:0.125:0.011</td>
</tr>
<tr>
<td>Li1.2Mn0.54Ni0.13Co0.10Sr0.05O2</td>
<td>1.2:0.54:0.13:0.10:0.03</td>
<td>1.200:0.589:0.130:0.095:0.033</td>
</tr>
<tr>
<td>Li1.2Mn0.54Ni0.13Co0.08Sr0.05O2</td>
<td>1.2:0.54:0.13:0.08:0.05</td>
<td>1.216:0.586:0.129:0.083:0.050</td>
</tr>
</tbody>
</table>
samples present three characteristic Raman bands of Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_{2}$ at around 429, 484, and 598 cm$^{-1}$ in the range of 100-1000 cm$^{-1}$. The weak Raman band which appears at 429 cm$^{-1}$ is ascribed to the vibration of monoclinic LiMnO$_2$ phase. The other two Raman bands at around 484 cm$^{-1}$ and 598 cm$^{-1}$ are assigned to the $E_g$ and $A_g$ vibration mode of Raman-active LiMnO$_2$ phase, respectively. Obviously, in the Raman spectra of un-doped (Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_{2}$) and Sr-doping (Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$Sr$_{0.03}$O$_{2}$) sample, the position and intensity of the three bands are barely the same, which indicates that the Sr-doping does not change the structure of the Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$Sr$_{0.03}$O$_{2}$ sample significantly again.

Microscopic morphology

The morphology of pristine and Sr-doped (Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$Sr$_{0.03}$O$_{2}$) samples is investigated by scanning electron microscopy (SEM). Fig. 2(a) shows the SEM image of the precursor nanofibers of Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_{2}$. Fig. 2(b), 2(c), and 2(d) are SEM images of Sr-doped samples with x=0.01, x=0.03, and x=0.05, respectively. The SEM images indicate that the Sr-doping results in a slight change in the morphology of the nanofibers.
(x=0, 0.01, 0.03, 0.05) samples were characterized by scanning electron microscopy (SEM). As being seen from Fig. 2, four different types of cathode materials with complex one dimension (1D) nanofiber structures have been successfully prepared by electrospinning technology. The inset of Fig. 2a displays the as-spun precursor nanofiber with a smooth surface and continuous uniform features with an average diameter of around 800 nm. After calcination at 800 centigrade degree, the diameter of 1D nanofiber structures decreases to around 700 nm and a large amount of pores are generated, which might be caused by the decomposition of metal precursor and removal of polymer components. With the incorporation of Sr ion, the morphology of materials is not distinctly changed and the nanofiber structure remains well. However, it is worth pointing out that the diameter of nanofiber materials with different Sr concentration exhibit slight difference, which is mainly due to the secondary particle average size increasing slightly with the increases of Sr component.

Fig. 3 The image of Li$_{1-x}$Mn$_{0.8}$Ni$_{0.2}$Co$_{0.8}$Sr$_{x}$O$_{2}$ (a) TEM, (b) HRTEM. (c-g) EDS elemental mapping with respect to Mn, Co, Ni, Sr, receptivity. (h) Fast Fourier transform patterns of the selected area in image (b).

The detailed crystal structure and elements distribution in Sr-doped samples were further investigated by high-resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS) elemental mapping. Fig. 3a shows the TEM images of a randomly selected Li$_{1-x}$Mn$_{0.8}$Ni$_{0.2}$Co$_{0.8}$Sr$_{x}$O$_{2}$ particle, which is nanofiber morphology composed of primary particles. According to the elemental mapping displayed in Fig. 3c-f, different elements in Li$_{1-x}$Mn$_{0.8}$Ni$_{0.2}$Co$_{0.8}$Sr$_{x}$O$_{2}$ sample with respect to Mn, Co, Ni and Sr are uniformly distributed throughout the nanofibers, and Fig. 4 also exhibits the SEM image and the corresponding EDS elemental mapping for the un-doped sample. The elemental mapping further demonstrates that the Sr element successfully entered into the bulk of the material. From the HRTEM image in Fig. 3b, the lattice fringes of (111), (131) and (020) corresponding to the monoclinic structure. Fig. 3h is the Fast Fourier transform (FFT) pattern taken from Fig. 3b. The FFT image is geometricaly equivalent to a diffraction pattern and the appeared
Fig. 4 The SEM image and the corresponding EDS elemental mapping of Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$.

Fig. 5 XPS spectra of (a) Mn 2p, (c) Ni 2p and (e) Co 2p for sample Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$. XPS spectra of (b) Mn 2p, (d) Ni 2p and (f) Co 2p and Sr 3d for sample Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$Sr$_{0.03}$O$_2$. 
reflections can be indexed to the monoclinic structure (C2/m) of Li$_3$MnO$_2$.

**XPS analysis**

The oxidation states of the transition metals (Mn, Ni, Co and Sr) in the $x=0$ and $x=0.03$ samples were examined by X-ray photoelectron spectroscopy (XPS). The corresponding spectra of Mn 2p, Co 2p, Ni 2p and Sr 3d are presented in Fig. 5. As shown in Fig. 5(a-f), the peak positions of Mn 2p$_{3/2}$, Ni 2p$_{3/2}$ and Co 2p$_{3/2}$ for two samples are very close to the data reported in references, indicating the presence of Mn$^{2+}$, Ni$^{3+}$ and Co$^{4+}$ in two samples. The notable difference can be seen from the inset in Fig. 5(f) that in the binding energy region from 125 to 140 eV, sample Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.10}$Sr$_{0.03}$O$_2$ exhibits one strong peaks at about 134.5 eV, which could be well assigned to Sr 3d. It is well demonstrated that the Sr element is present in sample Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.10}$Sr$_{0.03}$O$_2$ in the form of Sr$^{2+}$.

**Electrochemical performance**

The electrochemical performance of these cathode materials were investigated by assemble cells and the galvanostatic charge-discharge cycling was conducted at 28 mA g$^{-1}$ in the voltage range of 2.0-4.8 V. Fig. 6(a-d) display the selected charge-discharge voltage profiles from the 1$^\text{st}$ to 100$^\text{th}$ cycles for sample Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.10}$Sr$_{0.03}$O$_2$ with doping ratio $x = 0, 0.01, 0.03, 0.05$, respectively. Clearly, during the first charging processes of these cathode materials, all profiles display a gradual increase in the voltage before 4.5 V along with a plateau at about 4.5 V. The smooth voltage ramp before 4.5 V could be correspond to the process of Ni$^{2+}$ and Co$^{3+}$ being oxidized to Ni$^{4+}$ and Co$^{4+}$, and Li$^+$ being extracted from LiMO$_2$ component. Their high capacity was explained as being due to cumulative cationic ($M^{n+} \leftrightarrow M^{(n+1)+}$) and anionic
(2O^2- \rightarrow (O^2_2)^{-}) reversible redox processes.\(^3\) Tarascon and coworkers have suggested that oxidation of oxygen generally results in the pairing of O ions, resulting in an effective 2O^2-/O^{-} redox couple, which is stabilized against evolution as oxygen gas in the presence of 4d and 5d TMs due to the increased TM–O hybridization and improved band alignment over 3d TMs.\(^3\) William E. Gent et al. proposed that the properties arise from a strong coupling between anion redox and cation migration, which show that partially reversible transition metal migration decreases the potential of the bulk oxygen redox couple by > 1 V, leading to a reordering in the anionic and cationic redox potentials during cycling.\(^7\)

Moreover, the first charging specific capacity of all the electrodes were found to be higher than 330 mAh g\(^{-1}\), except for the Li\(_{1-x}\)Mn\(_{0.5+x}\)Ni\(_{0.5-x}\)Co\(_{0.5}\)Sr\(_{x}\)O\(_{2}\) electrodes. These results indicate that appropriate amount of Sr doping does not influence the charging specific capacity and the initial activation process of the monoclinic LiMnO\(_2\) phase in the first cycle. However, the first discharge specific capacities are found to be about 266, 231, 213 and 195 mAh g\(^{-1}\), and the corresponding coulombic efficiencies are 80.6 %, 70 %, 62.6 % and 69.6 % for Li\(_{1-x}\)Mn\(_{0.5+x}\)Ni\(_{0.5-x}\)Co\(_{0.5}\)Sr\(_{x}\)O\(_{2}\), Li\(_{1-x}\)Mn\(_{0.5+x}\)Ni\(_{0.5-x}\)Co\(_{0.5}\)Sr\(_{x}\)O\(_{2}\), Li\(_{1-x}\)Mn\(_{0.5+x}\)Ni\(_{0.5-x}\)Co\(_{0.5}\)Sr\(_{x}\)O\(_{2}\), and Li\(_{1-x}\)Mn\(_{0.5+x}\)Ni\(_{0.5-x}\)Co\(_{0.5}\)Sr\(_{x}\)O\(_{2}\) electrodes, respectively. The relatively low initial coulombic efficiency for the Sr doped cathode materials is ascribed to that the discharge capacity decreases with an increase in the Sr amount in these Li-rich cathodes whereas the charging capacity only slightly changes. According to previous studies, the decrease in the discharge capacity is possible related to that the substitution of a certain percentage of Co by Sr, which reduces the amount of Co redox species in the active mass.\(^36\) As can be seen from the comparison of the selected voltage curves of all electrodes, the discharge specific capacity of the sample is becomes more and more concentrated as the amount of the Sr increases, indicating that the effect of Sr doping on stabilization materials is valid.

Fig. 6e presents the cycle performance of all electrodes at 28 mA g\(^{-1}\) rates in the potential range 2.0–4.8 V. As can be seen from Fig. 6e, the un-doped materials delivered an initial discharge capacity of 266 mAh g\(^{-1}\) and decreased to 174 mAh g\(^{-1}\) after 100 cycles, which gives the capacity retention is 64.5 %. On the contrast, the Sr-doped electrodes (Li\(_{1-x}\)Mn\(_{0.5+x}\)Ni\(_{0.5-x}\)Co\(_{0.5}\)Sr\(_{x}\)O\(_{2}\), x=0.01, 0.03, 0.05) exhibit better cycling performance, and their capacity retention at the end of 100 cycles are 80.53 %, 94.16 % and 96.8 %, respectively. One attributes the voltage fade to the change of transition metal redox activities upon extended electrochemical cycling, and the other considers that structural re-arrangement leads to the significant drop of the discharge voltage.\(^7\)

Anionic redox also leads to capacity loss and structural degradation, as well as voltage hysteresis, which shows the importance of controlling anionic redox reactions.\(^37\) In order to investigate the effect of Sr doping on voltage decay, Fig. 6f compares the discharge meddle voltage profiles of four electrodes. It can be seen that the undoped electrode exhibits a rapid voltage degradation with the discharge meddle voltage decreasing from 3.46 V (1st cycle) to 2.73 V (100th cycle, ΔE=0.73 V) after 100 cycles at 28 mA g\(^{-1}\). For Li\(_{1-x}\)Mn\(_{0.5+x}\)Ni\(_{0.5-x}\)Co\(_{0.5}\)Sr\(_{x}\)O\(_{2}\), (x=0.01, 0.03, 0.05) electrodes, the discharge meddle voltage change upon cycling are 0.52 V, 0.39 V and 0.31 V, respectively. With the increase of the Sr doping ratio, the voltage change gradually decreases. Hence, the discharge voltage decay is effectively suppressed by Sr doping.

The first CV profiles of Li\(_{1-x}\)Mn\(_{0.5+x}\)Ni\(_{0.5-x}\)Co\(_{0.5}\)Sr\(_{x}\)O\(_{2}\), x=0, 0.01, 0.03, 0.05) are tested in the voltage range of 2.0–4.8 V vs. Li+/Li at a sweeping rate of 0.1 mV/s. as shown in Fig. 7a. As can be seen from Fig. 7a, during the charge of the first cycle, there are two oxidation peaks at around 4.0 and 4.6 V. The 4.0 V peak is corresponds to the oxidation of Ni\(^2+\) to Ni\(^3+\) and Co\(^2+\) to Co\(^3+\), which due to the extraction of Li\(^+\) from LiMO\(_2\). While the second sharp peak around 4.6 V originates from irreversible electrochemical activation of LiMnO\(_2\) component. During the following discharge process, the reduction peaks around 4.25 and 3.7 V correspond to the reduction of Ni\(^3+\) and Co\(^3+\), respectively. Besides, we can be observe that all samples display a pair of reversible redox peaks at 3.25 V, in consistent with the oxidation and reduction reaction of Mn\(^2+\)/Mn\(^4+\). Fig. 7b shows the impedance spectra of Li\(_{1-x}\)Mn\(_{0.5+x}\)Ni\(_{0.5-x}\)Co\(_{0.5}\)Sr\(_{x}\)O\(_{2}\) (x=0, 0.01, 0.03, 0.05) before cycle at open circuit potential. The inset in Fig. 7b exhibits the corresponding equivalent circuit model for fitting, where Rs, Rct, CPE, and Zsw represent the resistance of electrolyte, the charge transfers resistance, the double layer capacitance, and the Warburg resistance, respectively. The Rct value of Li\(_{1-x}\)Mn\(_{0.5+x}\)Ni\(_{0.5-x}\)Co\(_{0.5}\)Sr\(_{x}\)O\(_{2}\) (x=0, 0.01, 0.03, 0.05) are 132.66 Ω, 116.88 Ω, 113.04 Ω, 112.43 Ω respectively, indicating that Sr-doping improves the conductivity of the sample.

To further reveal the electrochemical reactions that occurred during the cathode charging and discharging processes, the cyclic voltammetry were shown in Fig. 8a. It can be seen that the two anodic peaks at 3.27 V, 3.69 V and 4.32 V, 4.72 V, respectively, during the 1st and 2nd cycle, are assigned to the oxidation of Mn\(^2+\) to Mn\(^4+\) and Ni\(^2+\) to Ni\(^4+\), respectively. In addition, the cathodic peaks at 3.25 V, 3.67 V, 4.25 V and 4.67 V, respectively, are attributed to the reduction of Mn\(^4+\) to Mn\(^2+\) and Ni\(^4+\) to Ni\(^2+\). The area enclosed by the anodic and cathodic peak for Mn\(^4+\)/Mn\(^2+\) and Ni\(^4+\)/Ni\(^2+\) reactions decreased in magnitude upon cycling, which show that the partial re-oxidation of Li\(^+\) from LiMO\(_2\).

Fig. 7 (a) CV profiles of the first cycles of Li\(_{1-x}\)Mn\(_{0.5+x}\)Ni\(_{0.5-x}\)Co\(_{0.5}\)Sr\(_{x}\)O\(_{2}\), (x=0, 0.01, 0.03, 0.05). (b) EIS spectra of Li\(_{1-x}\)Mn\(_{0.5+x}\)Ni\(_{0.5-x}\)Co\(_{0.5}\)Sr\(_{x}\)O\(_{2}\), (x=0, 0.01, 0.03, 0.05).
cycling, the differential capacity vs. voltage (dQ/dV) plots related to the 2nd and 50th cycles of all the electrodes are calculated from the numerical data observed in discharge profiles, as illustrated in Fig. 8. It is notable that the dQ/dV peaks corresponding to discharge profiles exhibit a distinct change upon the addition of Sr. There are three electrochemical processes centered at ~4.5 V, ~3.7 V and lower than 3.5 V. Among them, the most dominant cathodic peaks appearing between 2.5 V and 3.2 V belong to the Mn⁴⁺/Mn³⁺ redox activity, which are related to the layered-to-spinel phase transformation and deterioration of the generated spinel-like phase. Therefore, comparing the cathodic peak potentials between the 2nd and 50th cycles is very necessary. As can be seen from Fig. 8, for un-doped electrodes, the cathodic peaks of Mn⁴⁺/Mn³⁺ around 3.3 V transfer to a much lower voltage below 3.0 V after 50 cycles, which indicates the presence of spinel phase in the host structure. However, for the Li₃Mn₉Sr₄Ni₀₀₀Co₀₀₀O₂₀₀₀₀ electrolyte, the decrease of cathodic peak potential after 50 cycles is 0.21 V, which is much lower than those for the un-doped or slightly doped electrodes. These findings show that incorporation of suitable amount of Sr not only improves the capacity retention but also stabilizes the discharge voltage upon cycling.

Conclusions

To summarize, a facile way of synthesizing Sr doping hierarchical porous nanofiber structure lithium-rich material Li₃Mn₉Sr₄Ni₀₀₀Co₀₀₀O₂₀₀₀₀ was proposed. The Sr can be induced into Co site via electrospinning combined with high temperature solid phase technology. The Sr substitution for Co can enhance the cyclic performance, suppress the voltage decay and stabilize the structure. It is worth noting that the Li₃Mn₉Sr₄Ni₀₀₀Co₀₀₀O₂₀₀₀₀ material displays an initial discharge capacity of 213 mAh g⁻¹ and the capacity retention is up to 94.16% after 100 cycles. Moreover, with the increase of Sr doping ratio, the voltage change after 100th cycle gradually decreases (ΔE=0.73 V for un-doped material and ΔE=0.31 V for Li₃Mn₉Sr₄Ni₀₀₀Co₀₀₀O₂₀₀₀₀). Thus, the structural stability of the material is effectively improved and the voltage decay is mitigated. Therefore, based on this work, these Sr-doping lithium-rich nanofibers with hierarchical pore structure materials will provide an effective and promising strategy for the synthesis of high energy density cathode materials for lithium ion batteries.

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Compliance with ethical standards

Conflict of interest: The authors declare no conflict of interest.

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