Preparation of Y-Doped La$_2$Ti$_2$O$_7$ Flexible Self-Supporting Films and Their Application in High-Performance Flexible All-Solid-State Supercapacitor Devices

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ABSTRACT: Flexible all-solid-state supercapacitors have drawn more attention owing to the rapid growth of wearable electronic equipments. Herein, we have succeeded in synthesizing a series of Y-doped lanthanum titanate flexible self-supporting films (LSF-$x$, 0.1 $\leq$ $x$ $\leq$ 0.5) and investigating the change of microstructures, morphological characteristics, and lattice structures of these films affected by different Y-doping contents. To further determine the optimum Y-doping content, we have explored the electrochemical properties of working electrodes prepared by LSF-$x$ (0.1 $\leq$ $x$ $\leq$ 0.5) samples as the main active material. As the LSF-0.2 electrode has the best areal capacitance of 1.3 F·cm$^{-2}$ at 2 mA·cm$^{-2}$, we use the LSF-0.2 electrodes and PVA$-$Na$_2$SO$_4$ gel to fabricate a flexible all-solid-state supercapacitor device. This device has a high areal capacitance of 255.9 mF·cm$^{-2}$ at a current density of 2 mA·cm$^{-2}$ with a high cell voltage of 2.1 V, while the corresponding energy density is 156.8 $\mu$Wh·cm$^{-2}$ with a power density of 2.1 mW·cm$^{-2}$. Moreover, it also shows a long cycling life and outstanding flexibility. Therefore, the LSF-0.2 sample can be used as an excellent energy-storage material for a wearable electronic device.

1. INTRODUCTION

Over the last few decades, as the smart bracelet, foldable mobile phone, flexible electronic display, and other wearable electronic equipment have been broadly applied in all areas of our daily lives, the development of flexible electronic device has drawn much attention of scientific and technological researchers. To meet the growing demand of lightweight design, portability, and low manufacturing cost for flexible electronic equipment, high-performance flexible power sources have become one of the research focuses. Among them, the flexible supercapacitors have been considered as the appropriate device because of their higher power density and longer cycling performance than those of lithium-ion batteries. Although the flexible supercapacitors exhibit superior advantages such as small size, high flexibility, and lightweight, these devices still have some challenges like low energy density and unsatisfactory reliability. According to the equation $E = 1/2CV^2$, the energy density can be improved by enlarging the capacitance and operating voltage of the supercapacitor. Hence, we are able to synthesize a flexible supercapacitor electrode material with ultrahigh energy-storage ability to enhance the capacitance and potential windows first, and then we can improve the security of the device through fabricating the all-solid-state supercapacitor.

To satisfy the needs of an all-solid-state supercapacitor, the development of novel flexible electrode materials for them has become the current intense pursuit. In recent years, it has been reported that some electrode materials such as carbon materials, transition-metal oxides (TMO)/compound oxides, and electrically conductive polymers have been widely used for flexible all-solid-state supercapacitors. In particular, compared with carbon and electrically conductive polymers materials, TMO/compound oxides have attracted tremendous interests owing to their higher capacitance, better energy density, and environmental friendliness. Although a wide
variety of TMO/compound oxides have been applied broadly for all-solid-state supercapacitors, these composite flexible electrodes often limit the utilization of the active electrode materials, for example, Wang et al. have prepared a typical flexible all-solid-state supercapacitor (FSC) based on mesoporous Bi$_2$MoO$_6$ quasi-nanospheres (MBIN) on an activated carbon cloth (ACC) hybrid electrode for improving the energy-storage density and cyclic stability, and the MBIN/ACC flexible electrodes displays an ultrahigh mass capacitance.21 Lei’s research group has reported the successful growth of α-Fe$_2$O$_3$ nanosheets on the CS electrode position followed by low-temperature thermal annealing, and α-Fe$_2$O$_3$ on CS displays high specificity that is 1.7-times higher than that of the CS substrate;20 Li et al. have synthesized NiCo$_2$O$_4$/C core–shell nanoneedles grown on a Ni foam by a simple route and applied in supercapacitors, and the electrode exhibits excellent rate capability and remarkable cycling stability;21 Haiqun Chen’s research group has prepared a composite consisting of Mn$_{0.1}$Ni$_{0.9}$MoO$_4$ mesoporous nanorods and reduced graphene oxide (Mn$_{0.1}$Ni$_{0.9}$MoO$_4$/rGO), which is assembled into a symmetrical all-solid-state device as electrode material, with alkaline poly(vinyl alcohol) as a solid-state electrolyte.22 These research studies show that because of the rigid nature of oxides, the TMO/compound oxides that can simultaneously reduce the obtainable energy and power density have to be decorated on conductive soft carriers for the application in flexible supercapacitors.23 As a result, synthesizing a new self-supporting oxide film with excellent flexibility, large capacity, and outstanding energy density would be an effective solution to meet the demands of the development of flexible all-solid-state supercapacitors.

In the past decades, various kinds of oxides have been widely used for the supercapacitors as active electrode materials.24–28 Among them, the pyrochlore compounds show a variety of interesting physical and chemical properties such as high electrical conductivity, good elemental flexibility, and oxygen-vacancy structure.29–31 Because the previous study indicates that oxygen vacancies have been regarded as the charge-storage sites of compound oxides, A$_2$B$_2$O$_7$-type lanthanum titanate (LTO) can be used as outstanding electrochemical energy-storage material.32 To apply LTO as the main active material to flexible all-solid-state supercapacitors, we can prepare a flexible self-supporting film of LTO, which can also significantly increase the electrochemistry performance and the mechanical property of the flexible device. Moreover, according to the mechanism of oxygen intercalation, the number of oxygen vacancies of LTO can be obviously improved by doping a tertiary component into A or B site of LTO.34,35 As the increase of oxygen vacancies may enhance the capacitance of LTO, we can modify the energy-storage ability of LTO flexible self-supporting films by doping the transition-metal element Y.36–38 In addition, the electrospinning combined with the low-temperature sintering technology is practiced to synthesize these Y-modified self-supporting materials.

In this research, we report the synthesis of a series of Y-doped LTO flexible self-supporting films with rich-oxygen-vacancy structure by a sol–gel-assisted electrospinning method followed with low-temperature calcination. The La$_x$Y$_{1-x}$Ti$_2$O$_7$ flexible self-supporting films (when $x = 0.1, 0.3, 0.4, 0.5$) were denoted as LSF-0.1, LSF-0.2, LSF-0.3, LSF-0.4, and LSF-0.5, respectively. Besides, the change of the microstructure, morphological characteristics, element composition, and electrochemical property of LSF-$x$ influenced by Y doping was further explored using XRD, SEM, TEM, BET, XPS, and an electrochemical workstation. Because the LSF-0.2 sample showed the highest areal capacitance (1307 mF·cm$^{-2}$ at 2 mA·cm$^{-2}$) compared with the others, we fabricated a symmetrical LSF-0.2//LSF-0.2 flexible all-solid-state supercapacitor device using a soft-matter substrate and an LSF-0.2 flexible self-supporting film. In addition, this device exhibited high areal capacitance (255.9 mF·cm$^{-2}$ at 2 mA·cm$^{-2}$), large energy density (156.8 μWh·cm$^{-2}$ at 2.1 mW·cm$^{-2}$), long cycling stability, and excellent flexibility.

2. EXPERIMENTAL SECTION

2.1. Preparation of the Precursor Films. In this study, we prepared the precursor solution using poly(vinylpyrrolidone) (PVP, $M_w = 1\, 300\, 000$), La(NO$_3$)$_3$·6H$_2$O (≥99.0%), titanium tetraisopropanolate (TTIP), and Y(NO$_3$)$_3$ (≥99.5%), and all of these materials were purchased from Aladdin, China. First, La(NO$_3$)$_3$·6H$_2$O (≥99.0%), Y(NO$_3$)$_3$, and TTIP were weighed based on the molar ratio of 2:1:x=2−x, respectively, and these drugs were dissolved into a mixture of absolute ethanol, deionized water, and acetic acid (weight ratio, 5:4:1) in a weight ratio of 1:1. We marked this mixture solution as solution A. In addition, we dissolved 15 wt % PVP in a mix solution of deionized water and absolute ethanol in a weight ratio of 1:1, and stirred for 4 h to form a homogeneous solution at room temperature. This mix solution was marked as solution B. To form the precursor solution for electrospinning, we added the solution A into solution B (weight ratio of 1:2) and continuously stirred for about 2 h until clear. After that, as shown in Figure 1, we applied this precursor solution to prepare the precursor films by the electrospinning method. All of the processing parameters of the electrospinning process were determined as follows: the flow rate was 0.3 mL·h$^{-1}$, the positive potential was 15 kV (HD90, high voltage power supply, China), and the distance between the needle tip and the collector was 15 cm.

Figure 1. Schematic illustration of the fabrication processes of LSF-$x$ precursors using the electrospinning method.
carefully studied the change of morphologies and the structure of LSF-x (0.1 ≤ x ≤ 0.5) films with different proportions of Y doping using transmission electron microscopy (TEM, FEI Tecnai G20), scanning electron microscopy (SEM, Cam Scan2600 FE), X-ray photoelectron spectroscopy (XPS, PHI-5000 Versaprobe), and the powder X-ray diffraction (XRD, Rigaku-D/max, Cu Kα), respectively.

2.3. Electrochemical Measurements. The working electrodes were prepared by attaching a series of LSF-x (0.1 ≤ x ≤ 0.5) films on the carbon fabric. Poly(vinylidene fluoride) (PVDF), which was dissolved in n-methyl pyrrolidone (NMP) at 5 wt %, served as a binder for electrodes in this process. In addition, we studied the electrochemical measurements of these electrodes using a CHI760E (Shanghai Chenhua, China) workstation with a three-electrode system in a 1 M Na2SO4 electrolyte solution. In this test system, the platinum wire was the counter electrode and the saturated calomel electrode (SCE) was the reference electrode. Moreover, the flexible all-solid-state supercapacitor device was assembled by two symmetrical electrodes. Then, the PVA–Na2SO4 gel was used as a solid electrolyte in this device, and the weight ratio between PVA and Na2SO4 was 5:7. The flexible all-solid-state supercapacitor device was tested by a two-electrode system.

We calculated the areal capacitance \( C \), F·cm\(^{-2}\) of the working electrode using the following equation based on the GCD curves

\[
C = \frac{1}{t} \int I_0 dt \left/ (a \Delta V) \right.
\]

In this equation, \( I_0 \) is the impressed current, \( a \) (cm\(^2\)) is the area of all working electrodes, \( dt \) is the cycle time, and \( \Delta V \) is the voltage range of each scan.

The energy density \( E \) and power density \( P \) of the device can be calculated using the following two equations

\[
E = \frac{1}{2} CV^2
\]

\[
P = \frac{3600 \times E}{t}
\]

As mentioned above, \( C \) is the areal specific capacitance of the device (F·cm\(^{-2}\)), \( V \) is the voltage (V), and \( t \) is the discharge time (s).

3. RESULTS AND DISCUSSION

3.1. Investigation of the Effect of Y Doping. To further confirm the best content of Y in LSF-x (0.1 ≤ x ≤ 0.5), we have thoroughly investigated the effects of Y doping with different proportions on the microstructure, morphological characteristics, and element composition of these LSF-x samples. In this study, these tests have been carried out using XRD, SEM, TEM, and XPS, and the results are shown as follows.

3.1.1. Crystal Structure. The crystal structures of LSF-x (0.1 ≤ x ≤ 0.5) samples with different contents of Y element are characterized by X-ray diffraction (XRD) patterns in a 2θ range between 15 and 90°, as illustrated in Figure 2a. From these patterns, we can observe four clearly main characteristic peaks of LSF-0.1, LSF-0.2, and LNF-0.3 samples, which correspond to the orientations of (−210), (400), (−212), and (410) planes, respectively. These peaks are in agreement with the standard card (JCPDS No. 28-0517) of a pyrochlore-type structure \( \text{La}_2\text{Ti}_2\text{O}_7 \) with a cubic lattice system. Besides, this image also shows that intensity of these characteristic peaks is decreased with the increase of Y doping. When \( x = 0.4 \), although these characteristic peaks still remain, their intensities become weaker and the boundary between them is not clear. While the content of \( x \) is increased to 0.5, the LSF-0.5 presents no clear characteristic peaks, which can be explained by the changes from a crystalline to amorphous structure of the sample. These results indicate that the crystallinity of the LSF-x (0.1 ≤ x ≤ 0.5) samples is inversely proportional to the Y-doping proportion, and the trend of crystallization reduces with the increasing Y-doping content until the formation of an amorphous structure. The great changes of the crystal system and the lattice distortion in this doping progress can be attributed to the Jahn–Teller effect. In general, the cationic radius between A sites and B sites in LTO becomes mismatched when Y replaces Ti at B sites, and this mismatch may cause the dramatic distortion in the crystal structure. What is more, excess of Y doping may change crystallization conditions of pyrochlore-type \( \text{La}_2\text{Y}_x\text{Ti}_{2-x}\text{O}_7 \) compounds and influence the precipitation of the main crystal phase. Due to the positive relationship of the number of oxygen vacancies with the crystallinity, the low crystallization degree of the \( \text{La}_2\text{Y}_x\text{Ti}_{2-x}\text{O}_7 \) sample may reduce its energy-storage ability. Hence, we cannot dope too much Y element into \( \text{A}_2\text{B}_2\text{O}_7 \)-type lanthanum titanate (LTO).
Moreover, we calculate the grain sizes of LSF-\(x\) (0.1 \(\leq x \leq 0.5\)) samples by Scherrer’s formula to explore the connection between grain growth and the Y-doping ratio. As shown in Figure 2b, the grain size is proportional to the content of the Y element when 0.1 \(\leq x \leq 0.4\). Due to the even distribution of Y element in the precursor in the form of ions, the crystal lattice may grow with increasing Y doping, which can lead to the increase of grain size. However, the smaller grain size of the LSF-0.5 sample than the others suggests that nanofibers just begin to form crystal nuclei. This result agrees with the previous analysis.

3.1.2. Surface Morphology. The morphologies of the LSF-\(x\) (0.1 \(\leq x \leq 0.5\)) samples are further investigated by SEM measurement and are exhibited in Figure 3a–e. These images show that the surfaces of LSF-0.3 and LSF-0.4 samples tend to be smooth and consist of well-developed grains, while the surfaces of LSF-0.1 and LSF-0.2 samples are according to their degree of crystallinity. Owing to the lattice distortion, the amorphous structure grows in quantity with the increase of Y doping until the LSF-x sample is unable to form a complete pyrochlore structure.

To further investigate the LSF-\(x\) (0.1 \(\leq x \leq 0.5\)) samples, we have characterized their nanostructure and crystalline characteristics using HRTEM, and these results are exhibited in Figure 4. The graphs in Figure 4a–e correspond to the TEM photos of LSF-0.1, LSF-0.2, LSF-0.3, LSF-0.4, and LSF-0.5, respectively. These images show that all samples are made of particles or crystallites with a close connection, and their sizes are influenced by the variation of Y proportion. As 0.1 \(\leq x \leq 0.4\), the grain sizes of LSF-x samples increase with the growth of Y content, and their homogeneous particles also change to inhomogeneous. For the LSF-0.5 sample, the particle sizes sharply decline, owing to the formation of the amorphous structure in excessive levels of Y doping. Besides, Figure 4f–j exhibits the lattice fringes of LSF-\(x\) (0.1 \(\leq x \leq 0.5\)) samples. As shown in Figure 4f,g, the LSF-0.1 and LSF-0.2 samples both display clear lattice fringes, and their interplanar spacing is 0.172 and 0.196 nm, respectively. However, excessive Y doping can damage the lattice structure of LSF-x. The little change of LSF-0.3 sample lattice can be proved by the minor bending of its lattice fringes in Figure 4h, and its interplanar spacing grows up to 0.216 nm at the same time. Moreover, an interplanar spacing of the LSF-0.4 sample observed from Figure 4i is 0.241 nm, while the bend, crack, and malposition of its lattice fringes can well determine the occurrence of lattice distortion. In addition, no complete lattice fringe shown in Figure 4j indicates that the LSF-0.5 sample has an amorphous structure, which is in good agreement with the above-mentioned results. In conclusion, although Y doping can improve the number of oxygen vacancies, we should maintain the Y content at an appropriate level.

3.1.3. XPS Analyses. To determine the change regularity of the composition and the valence state of LSF-x (0.1 \(\leq x \leq 0.5\)) samples with different Y-doping proportions, we investigate these samples by performing the XPS analyses. As shown in Figure 5a, these XPS spectra of LSF-x (0.1 \(\leq x \leq 0.5\)) samples prove the presence of La, Ti, and Y elements. From Figure 5b, we can observe two spin–orbit characteristic peaks of all LSF-x (0.1 \(\leq x \leq 0.5\)) samples, which can be divided into Y \(3d_{3/2}\) and Y \(3d_{5/2}\) peak area, the change of the peak intensity suggests that the LSF-0.5 sample has an amorphous structure, which is in good agreement with the above-mentioned results. In conclusion, although Y doping can improve the number of oxygen vacancies, we should maintain the Y content at an appropriate level.

![Figure 3. SEM images of (a) LSF-0.1, (b) LSF-0.2, (c) LSF-0.3, (d) LSF-0.4, and (e) LSF-0.5.](image-url)
chemisorbed oxygen species (hydroxyl groups, $O^-$) consist of La–OH, Y–OH, and Ti–OH peaks. Generally, because the hydroxyl groups adsorbed by LSF-$x$ ($0.1 \leq x \leq 0.5$) samples can be regarded as evidence of the existence of oxygen vacancies, the increase of the $O^-$ peak area can further prove the growth of oxygen vacancies after doping. These results are well accorded with a previous study.

3.2. Electrochemical Properties. 3.2.1. Effects of $Y$ Content. In this study, we have prepared the LSF-$x$ ($0.1 \leq x \leq 0.5$) electrodes as working electrodes using the corresponding LSF-$x$ ($0.1 \leq x \leq 0.5$) samples. To investigate the effects of Y-doping proportion on the electrochemical performance of LSF-$x$ ($0.1 \leq x \leq 0.5$) samples, the electrochemical workstation has been used to explore the electrochemical behavior of working electrodes by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) measurements, and the AC impedance method.
The CV curves of LSF-x (0.1 \leq x \leq 0.5) electrodes measured in a 1 M Na2SO4 aqueous solution at a scan rate of 50 mV s^{-1} with a three-electrode system are manifested in Figure 6a. Because the larger CV curve integral area represents the higher specific capacitance, the LSF-0.2 electrode may possess the best electrochemical property compared with the other LSF-x (0.1 \leq x \leq 0.5) electrodes. Moreover, Figure S1 exhibits the CV curves of all LSF-x (0.1 \leq x \leq 0.5) electrodes tested in a 1 M Na2SO4 aqueous solution at various scan rates ranging from 5 to 100 mV s^{-1}. Generally, these curves all display a deformed rectangle shape with a pair of remarkable redox peaks, and the potential range is -0.85 to 1.25 V versus the reference electrode (vs SCE). Based on the oxygen intercalation mechanism, these peaks can correspond to the conversion of Ti^{3+}/Ti^{4+}. The reversible redox reaction can be described as following

\[ \text{Ti}^{3+} + \text{H}_2\text{O} \xrightarrow{\text{charge\ discharge}} \text{Ti(OH)}^{3+} + \text{H}^+ + e^- \]  

(4)

For definitely stating this energy-storage mechanism, the schematic diagrams of oxygen intercalation of LSF-x (0.1 \leq x \leq 0.5) samples are shown in Figure S2. According to this image, it can be observed that oxygen ions at the surface can be absorbed and migrated to oxygen vacancies in the bulk structure through the lattice. Although the reversible redox reactions of Ti^{3+}/Ti^{4+} occurred in the lattice, the composition of main elements and crystal lattice still remains the same in this process. Hence, these oxygen vacancies in LSF-x (0.1 \leq x \leq 0.5) samples are considered as the main charge-storage sites for the pseudocapacitive process, and the redox reaction can be known as a topotactic reaction. As the previous analyses indicate that the amount of oxygen vacancies in LSF-x (0.1 \leq x \leq 0.5) samples is multiplied along with the increase of Y doping; the Y doping can improve the electrochemical performance of samples. However, a large proportion of Y doping can cause the lattice distortion of LSF-x (0.1 \leq x \leq 0.5) samples. As a result, to obtain the best energy-storage property, consideration must be given to both the degree of crystallinity and the number of oxygen vacancies.

Figure 6b shows the GCD curves of all LSF-x (0.1 \leq x \leq 0.5) samples tested at a current density of 2 mA cm^{-2} with the potential window of -0.85 to 1.25 V (vs SCE) in a 1 M Na2SO4 aqueous solution. Due to the reversible redox process of pseudocapacitance, all of the curves do not have a mirror symmetry, which is in good agreement with the CV consequences. Since the energy-storage performance of all LSF-x (0.1 \leq x \leq 0.5) electrodes can be estimated by comparing the relevant discharging time, the LSF-0.2 electrode with the longest discharge time in these GCD curves suggests the best. Furthermore, the GCD curves of LSF-0.1, LSF-0.2, LSF-0.3, LSF-0.4, and LSF-0.5 electrodes have been measured at various current densities to further investigate their electrochemical behaviors (Figure S3a–e). These GCD curves of the same sample display an approximate shape under different current densities, showing that all electrodes can have the good electrochemical ability at a high power density.
determine the above results, we have calculated the corresponding areal capacitance of LNF-\(x\) electrodes by these GCD curves of all of the LSF-\(x\) (0.1 \(\leq x \leq 0.5\)) electrodes at different current densities, ranging from 2 to 25 mA cm\(^{-2}\) according to eq 1, and these results are exhibited in Figure 6c. In this image, the LSF-0.2 electrode shows the best capacitance with the highest value of 1307 mF cm\(^{-2}\) (324 F g\(^{-1}\)), and this result can further confirm this oxygen intercalation mechanism.

To further explore the electrochemical properties of LSF-\(x\) (0.1 \(\leq x \leq 0.5\)) electrodes affected by the change of the \(Y\) content, the frequency response of electrodes has been studied by carrying out the electrochemical impedance spectroscopy technique (EIS) test at open-circuit potential. As shown in Figure 6d, the Nyquist plots of all LSF-\(x\) (0.1 \(\leq x \leq 0.5\)) electrodes are both consisted of two regions. In the high-frequency range, there are five Warburg semicircles with different radii, while the five corresponding straight lines with a slope of 60° are exhibited in the low-frequency range. For the purpose of analyzing the properties of energy storage and dissipation, we have fitted the equivalent circuit according to the EIS data using the Z-View computer software. The equivalent circuit is presented in the inset of Figure 6d, and the values of solution resistance (\(R_s\)), double-layer capacitance between the solution and the electrode (\(C_{dl}\)), charge-transfer resistance between the solution and the electrode (\(R_{ct}\)), pseudocapacitance of the electrode (\(C_p\)), and Warburg impedance (\(W_r\)) are calculated and listed in Table S1. From this table, we can observe that \(R_s\) values of various electrodes are close, about 4.2 \(\Omega\). Besides, since the low \(R_{ct}\) value suggests the fast charge and discharge rates, these data can also be applied to judge the oxygen intercalation capability. In conclusion, these results obtained from the table are in very good agreement with the changing trend of electrochemical properties of LSF-\(x\) (0.1 \(\leq x \leq 0.5\)) electrodes influenced by \(Y\) doping.

3.2.2. Electrochemical Performance of the All-Solid-State Device. As the LSF-0.2 electrode shows better areal capacitance values than other working electrodes, the symmetric flexible all-solid-state supercapacitor devices are prepared by two LSF-0.2 electrodes with the PVA–Na\(_2\)SO\(_4\) gel as the solid electrolyte. As exhibited in Figure S4, the thickness of the LSF-0.2 sample used in this device is around 23.7 \(\mu\)m, while the mass density of the film is 3.2 mg cm\(^{-2}\).

To further investigate the electrochemical performance of this all-solid-state device, the CV curves of the device are measured by cyclic voltammetry at various scan rates and are shown in Figure 7a. These CV curves obtained at different scan rates both have nearly rectangular shapes and maintain almost the same shape under different integral areas. This result indicates that the all-solid-state device has a safe, stable, and fast charge–discharge performance. Furthermore, this LSF-0.2//LSF-0.2 flexible all-solid-state supercapacitor device shows a high stable voltage window of 2.1 V, which is much higher than the previous studies as follows: 1.8 V for NiFe\(_2\)O\(_4\)@rGO//NiFe\(_2\)O\(_4\)@rGO (PVA–KNO\(_3\) gel),\(^{38}\) 1.0 V for rGO/CNT-c//rGO/CNT-c (PVA–H\(_2\)SO\(_4\) gel),\(^{39}\) 2.0 V for MnO\(_2\)/CNTs/cellulose//MnO\(_2\)/CNTs/cellulose (PVA–H\(_2\)SO\(_4\) gel),\(^{40}\) 1.8 V for MnSe@CT//MnSe@CT (PVA/LiCl hydrogel),\(^{41}\) 1.8 V for Ni–Co//CP//AC (PBI–KOH gel),\(^{42}\) and 1.2 V for AC//AC (PGPPE).\(^{43}\)

To study the energy-storage ability of the LSF-0.2//LSF-0.2 flexible all-solid-state device, we need to calculate the areal specific capacitances through eq 1. Consequently, we have...
tested the LSF-0.2//LSF-0.2 flexible all-solid-state device by the galvanostatic charge–discharge method at different current densities and the GCD curves are exhibited in Figure 7b. These GCD curves measured at different current densities ranging from 2 to 25 mA cm\(^{-2}\) show similar shapes, indicating a high Coulombic efficiency of the all-solid-state device. Then, the specific capacity of the device referred by mass is shown in Figure S5. Moreover, Figure 7c shows the corresponding volumetric power densities \((P_{v})\) and mass-power densities \((P_{m})\) when the corresponding volumetric power densities \((P_{v})\) and mass-power densities \((P_{m})\) are 66.1 Wh cm\(^{-3}\) and 49 Wh kg\(^{-1}\), respectively. Moreover, corresponding to previous data, the maximum volumetric energy densities \((E_{v})\) and mass-energy densities \((E_{m})\) are 0.89 W cm\(^{-3}\) and 656.3 W kg\(^{-1}\), respectively. In addition, to compare the devices studied before, we give the examples as follows: WMCNTs-WO\(_{3}\)-GO//WMCNTs-WO\(_{3}\)-GO (27.7 Wh kg\(^{-1}\) at 250 µW cm\(^{-2}\)),\(^{35}\) Cu(OH)\(_{2}\)/CPCC//AC/CC (49 µWh cm\(^{-2}\) at 0.6 mW cm\(^{-2}\)),\(^{46}\) FPCSLP\(_{54}\)//FPCSLP\(_{44}\) (72.5 µWh cm\(^{-2}\) at 250 µW cm\(^{-2}\) at 250 µW cm\(^{-2}\)),\(^{47}\) Cu/Carbon-NF//Cu/Carbon-NF (41 µWh cm\(^{-2}\) at 280 µW cm\(^{-2}\)),\(^{48}\) and s-MnO\(_{2}\)/MoS\(_{2}\)//s-MnO\(_{2}\)/MoS\(_{2}\) (38 µWh cm\(^{-2}\) at 500 µW cm\(^{-2}\)).\(^{49}\) Besides, the energy-storage performance of the state-of-the-art supercapacitors, which are calculated based on the mass, are listed as follows: 80MnFe\(_{2}\)O\(_{4}\)-20rGO//80MnFe\(_{2}\)O\(_{4}\)-20rGO (27.7 Wh kg\(^{-1}\) at 250 µW cm\(^{-2}\)),\(^{30}\) Mn\(_{3}\)O\(_{4}\)/rGO//AC (36.76 Wh kg\(^{-1}\) at 500 W kg\(^{-1}\)),\(^{24}\) NiCo\(_{2}\)S\(_{4}\)//rME/PPY//Fe\(_{2}\)O\(_{3}\)//ME/PPY (20.1 Wh kg\(^{-1}\) at 159.4 W kg\(^{-1}\)).\(^{52}\) MS-CMTBs//MS-
and presented in Figure 8c. It can be noticed that the values of the device corresponding to each bending angles are calculated after bending, the areal capacitances of may decrease a lot. To further con with the increase of the bending angle. While this bent device charge

\[
C_F = \frac{Q}{N_{QrGO/CF}} = 50.7 \text{ Wh kg}^{-1}\
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Table S1: the values of the equivalent circuit fitted for EIS spectra of LSF-x electrodes; Figure S1: the cyclic voltammograms (CVs) of (a) LSF-0.1, (b) LSF-0.2, (c) LSF-0.3, (d) LSF-0.4, and (e) LSF-0.5 electrodes at various sweep rates of 5–100 mVs⁻¹; Figure S2: the mechanism of oxygen intercalation into LSF-x; Figure S3: the galvanostatic charge–discharge (GCD) curves of (a) LSF-0.1, (b) LSF-0.2, (c) LSF-0.3, (d) LSF-0.4, and (e) LSF-0.5 electrodes at different current densities of 2–25 mA cm⁻²; Figure S4: the cross-sectional SEM images of (a) LSF-0.2 and (b) piece of the LSF-0.2 flexible thin film; Figure S5: the specific capacity of the LSF-0.2//LSF-0.2 device referred by mass; Figure S6: the galvanostatic charge–discharge (GCD) curves of the LSF-0.2//LSF-0.2 device at the 1th, 1000th, and 10 000th cycles; and Figure S7: the power density of energy density of the LSF-0.2//LSF-0.2 device in a Ragone plot.

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4. CONCLUSIONS

In summary, the LaₓY₂₋ₓTi₃₋ₓO₇ flexible self-supporting films (0.1 ≤ x ≤ 0.5) have been successfully synthesized by electrosprinning combined with the low-temperature sintering technology in this research. To investigate the variety of crystal structures of LSF-x influenced by different proportions of Y doping, we have applied the XRD, SEM, TEM, and XPS measurement on these samples. These results suggest that the oxygen-vacancy numbers increase with the growth of Y-doping content, we have explored the electrochemical properties of working electrodes prepared by LSF-x (0.1 ≤ x ≤ 0.5) samples. As the LSF-0.2 electrode shows a higher areal capacitance of 1.3 F cm⁻² in a 1 M Na₂SO₄ electrolyte than the other electrodes, x = 0.2 can be considered as the best doping ratio. As a result, we have fabricated the symmetric flexible all-solid-state supercapacitor device using two LSF-0.2 electrodes as working electrodes and PVA–Na₂SO₄ gel as the solid electrolyte, and this device has a high areal capacitance of 255.9 mF cm⁻² at a current density of 2 mA cm⁻². Moreover, the maximum value of the energy density of this device is 156.8 μWh cm⁻² with a low corresponding power density of 2.1 mW cm⁻². In addition, this all-solid-state device also shows a long cycle life and outstanding flexibility, which can be conducive to extend the application range of the device. Thus, we have prepared a new energy-storage material with excellent flexibility for a wearable energy-storage device in this study.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03402.

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Notes

The authors declare no competing financial interest.

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