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Enhancement in the Electrochemical Performance of Strontium (Sr)-Doped LaMnO$_3$ as Supercapacitor Materials

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Abstract: In this study, Strontium (Sr)-doped perovskite lanthanum manganite (La$_{1-x}$Sr$_x$MnO$_3$) nanoparticles were prepared by the sol–gel method and used as electrode materials of supercapacitors. Microstructures, morphologies, and electrochemical properties of the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), a transmission electron microscope (TEM), Brunauer–Emmett–Teller (BET) surface area measurements, cyclic voltammetry (CV), and galvanostatic charge/discharge (GCD) cycling. Investigations demonstrated that the La$_{0.85}$Sr$_{0.15}$MnO$_3$ nanoparticles had a maximum specific capacitance of 185.5 F/g at a current density of 0.5 A/g and a low charge transfer resistance (0.38 Ω) in 3 M KOH aqueous electrolyte solutions. La$_{0.85}$Sr$_{0.15}$MnO$_3$ electrode yields the highest capacitance behavior because of the larger specific surface area, lower charge transfer resistance, and higher concentration of oxygen vacancy. This result demonstrates that Sr doping significantly improved the electrochemical properties of the LaMnO$_3$ system. The anion-intercalation mechanism was examined by a charge–discharge process. This provides a promising electrode material for supercapacitors.

Keywords: sol–gel method; LaMnO$_3$; electrode materials; electrochemical properties

1. Introduction

Due to the escalating global energy crisis and environmental pollution, the development of innovative and high-efficiency energy storage technologies has drawn substantial interest. To this end, electrochemical energy storage systems, such as lithium batteries and supercapacitors, offer enormous opportunities for lowering the use of fossil fuels and pollution [1–3] because of their quick discharging and charging times, significant power density, and extended cycle life. Specifically, supercapacitors have been identified as the best energy storage technology method, attracting substantial interest. However, compared to batteries, the practical applications of supercapacitors are limited because of their lower energy density. Therefore, considerable effort has been made toward the design of electrode materials for high-energy-density supercapacitors to address this limitation [4–6].

On the other hand, studies have shown that supercapacitor electrode materials considerably influence their electrochemical performance, prompting the extensive exploration of carbon compounds, conductive polymers, and metal oxides which have been extensively explored as electrochemical devices [7,8]. Among these compounds, metal oxides have attracted great interest because of their high energy concentration and more consistent electrochemical characteristics [9]. Metal oxides such as Ru$_2$O$_5$, MnO$_2$, NiCo$_2$O$_4$, Co$_3$O$_4$, V$_2$O$_5$, and Fe$_3$O$_4$ have also been considered as important primary materials because of their tunable surface morphology, different flexible oxidation states, and high structural stability [10–16]. Perovskite materials have become an important component in solid oxide fuel cells as well due to their excellent electrical and ionic properties [17]. Due to these materials having many oxygen vacancies that allow charge storage, their electronic and
ionic conductivity satisfy the requirements of supercapacitors; thus, perovskite materials are even more preferable as supercapacitor electrode materials.

In a previous study, Mefford et al. [18] reported the anion insertion technique for LaMnO$_3$ perovskite as a supercapacitor electrode material for the first time. Based on their findings, researchers have been drawn to lanthanide-based perovskite materials due to their excellent thermal stability, simple manufacturing, oxygen preservation, low price, and high electrical conductivity [19–21]. The oxygen vacancies in perovskite are considered as charge storage sites for pseudocapacitance [20]. Therefore, the energy densities of perovskite supercapacitors could be maximized by increasing the oxygen vacancies. The oxygen-vacancy concentration in perovskite oxides can be tailored by partial substitution on A-site and/or B-site, resulting in effective control over the crystal structure, electrical conductivity, and electrochemical performance [22–26]. Doping is an effective way to alter the oxygen vacancies in a LaMnO$_3$ matrix [22–25,27]. For instance, Ma et al. [24] showed that the specific capacitance of the La$_{0.85}$Sr$_{0.15}$MnO$_3$ electrode (129.0 mF/cm$^2$) was greater than that of LaMnO$_3$ (32.6 mF/cm$^2$). Then, Alexander et al. [28] used a low-valence A-site doping concept to synthesize La$_{1-x}$Sr$_x$MnO$_3$–δ perovskite materials with high charge storage, which proved that La$_{0.2}$Sr$_{0.8}$MnO$_{2.7}$ had the highest specific capacitance. Lu et al. [29] reported the results of a preliminary study of the pseudocapacitance features of strontium-doped lanthanum manganite. They reported no capacitance degradation after 1000 cycles and a specific capacitance of 56 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$. The above-mentioned results show that Strontium (Sr) doping varied when LaMnO$_3$ had maximum specific capacitance. Therefore, exploring the impact of Sr doping on the electrochemical performance of LaMnO$_3$ perovskite materials is interesting and necessary.

Due to the sol–gel method with the advantages of rapid preparation of nanomaterials, it was easy to evenly and quantitatively incorporate some trace elements. To this end, the sol–gel method was used to create several La$_{1-x}$Sr$_x$MnO$_3$ (x = 0, 0.05, 0.1, 0.15, and 0.2) formulations, after which the impact of the properties and structural morphology of La$_{1-x}$Sr$_x$MnO$_3$ (x = 0, 0.05, 0.1, 0.15, and 0.2) on its electrochemical performance was determined. Investigations revealed that 185.5 F/g was the highest specific capacitance of the investigated La$_{0.85}$Sr$_{0.15}$MnO$_3$ nanoparticles.

2. Experimental Section
2.1. Material Preparation

The specific experimental procedure for synthesizing the La$_{1-x}$Sr$_x$MnO$_3$ (x = 0.0, 0.05, 0.1, 0.15, and 0.2) samples using the sol–gel method is as follows: Firstly, the mass of the citric acid monohydrate (≥99.5%) is 0.4224 g, and the mass of La(NO$_3$)$_3$·6H$_2$O (≥99.9%), MnCl$_2$·4H$_2$O (≥99%), and Sr(NO$_3$)$_2$ (≥99.5%) according to stoichiometric ratios of La$_{1-x}$Sr$_x$MnO$_3$ were simultaneously solubilized in 30 mL of deionized water in turn and stirred for 24 h to obtain a clear solution. Next, the transparent solution was then dehydrated in an oven at 80°C for 72 h. Finally, the obtained solid powders were thoroughly ground, moved to a tube furnace, calcined in air at a heating rate of 5°C/min from room temperature to 700°C, and then held at 700°C for 2 h to yield La$_{1-x}$Sr$_x$MnO$_3$ (x = 0.0, 0.05, 0.1, 0.15, and 0.2).

2.2. Characterization

The thermal decomposition temperature of the samples was determined by employing a thermogravimetry analysis (Diamond TG/DTA, Perkin Elmer S. A., Waltham, MA, USA). First, with continuous ventilation, a part of every item weighing 4–6 mg was treated at 800°C and a scan temperature of 15°C min$^{-1}$, and then, the stages of generated nanoparticles were assessed through X-ray powder diffraction (D8 Advance, Bruker, Karlsruhe, Germany) with a checking width of 20°–60° and a reading speed of 6°/min. Subsequently, microstructures of materials were studied utilizing a field-emission scanning electron microscopy (FE-SEM, Merlin Compact, Carl Zeiss, Oberkochen, Germany) and a transmission electron microscope (TEM, 2100F, JEOL, Shoshima City, Japan). The Brunauer–Emmett–Teller (BET)
surface area and pore size distribution were measured using a N$_2$ adsorption–desorption physisorption analyzer (ASAP 2020, Micromeritics, Norcross, Ga, USA). The compositions’ items, as well as molecular valency of the specimens, were evaluated through X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific K-Alpha, Waltham, MA, USA). XPS with an Al K alpha X-ray source was used to examine the valence distributions of the samples.

2.3. Electrochemical Measurements

The active material (80 wt.%), acetylene black (10 wt%), and polyvinylidene fluoride (PVDF, 10 wt.%) were blended in N-methylpyrrolidone (NMP) for 24 h. The mass of the active materials used is 100 mg, and the volume of NMP is about 0.5 mL. A 1 mg active material was pasted onto carbon paper (1 cm × 1 cm) current collector and baked in a vacuum stove at 80 °C for 24 h to produce electrodes that need evaluation. Afterward, a three-electrode system with a Hg/HgO reference electrode, comprising a 3 M KOH mixture as the electrolyte, was utilized to investigate the electrochemical behavior of electrodes, followed by recordings of the electrochemical impedance spectra (EIS), cyclic voltammetric (CV) curves, and constant current charge–discharge (GCD) curves of the manufactured electrodes from an analyzer (CHI660E). The specific capacity of an electrode was calculated from the GCD curves using Equation (1):

$$C_s = \frac{I\Delta t}{m\Delta V}$$  \hspace{1cm} (1)

where $C_s$ is the specific capacitance (F g$^{-1}$), $I$ is the specific current (A), $\Delta t$ is the time for discharge (s), $m$ is the mass of the active material (g), and $\Delta V$ is the potential range (V).

3. Results and Discussion

3.1. Microstructure and Morphology

While this study assessed the thermal decomposition temperature of La$_{1-x}$Sr$_x$MnO$_3$ precursors ($x = 0.0, 0.05, 0.1, 0.15, and 0.2$) using thermogravimetric assessment, that of the LaMnO$_3$ precursors were examined at an environment temperature of 50–800 °C with the temperature being increased at 15 °C/min. Figure 1a demonstrates the TG curve of the LaMnO$_3$ precursor. Investigations revealed a 15 wt.% drop in the weight of the LaMnO$_3$ precursors at 250 °C, mostly attributable to the evaporation of the natural solvents, gas, and humidity from the surface. At 380 °C, however, the precursor’s weight reduced rapidly due to the breakdown of the citric acid monohydrate, La(NO$_3$)$_3$·6H$_2$O, MnCl$_2$·4H$_2$O, and Sr(NO$_3$)$_2$; then, at temperatures of more than 650 °C, the weight of the precursor remained unchanged. These findings indicate that thermal decomposition temperatures should exceed 650 °C. Therefore, a calcination temperature of 650 °C was adopted for the La$_{1-x}$Sr$_x$MnO$_3$ precursors. However, XRD studies indicated that LaMnO$_3$ was not synthesized, causing the calcination temperature to be raised to 700 °C, with subsequent XRD patterns proving that LaMnO$_3$ had been produced. In this investigation, La$_{1-x}$Sr$_x$MnO$_3$ precursors were thus synthesized at a calcination temperature of 700 °C.

On the other hand, Figure 1b illustrates the XRD system of La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0, 0.05, 0.1, 0.15, and 0.2$) samples held at 700°C for 2 h. In contrast to the standard card (PDF 50–0297), all peaks at 23.0°, 32.6°, 40.1°, 46.7°, 52.7°, and 58.2°, which belonged to the (110), (200), (220), (130), and (024) crystal planes, respectively, appeared to correlate with those of LaMnO$_3$; no additional peaks were visible. This finding suggests that samples of La$_{1-x}$Sr$_x$MnO$_3$ were achieved at the specified calcination temperature. Investigations also revealed that the (200) deviation peaks of La$_{1-x}$Sr$_x$MnO$_3$ examples moved to the left as the Sr doping concentration increased. In addition, per the Bragg formula, 2d sinθ = nλ (where d is the crystal plane area, θ is the angle of incidence, λ is the wavelength, and n is the count of reflection levels), the lattice constant of La$_{1-x}$Sr$_x$MnO$_3$ samples was also raised with increasing Sr doping because the ionic radius of Sr (1.18 Å) was greater than that of La (1.06 Å) [24].
In contrast, the morphologies of La$_{1-x}$Sr$_x$MnO$_3$ (x = 0.0, 0.05, 0.1, 0.15, and 0.2) specimens are illustrated in Figure 2a–e. The graphs demonstrate that the La$_{1-x}$Sr$_x$MnO$_3$ samples had a homogeneous particle distribution and tiny grain size; the grain sizes of the La$_{1-x}$Sr$_x$MnO$_3$ nanoparticles reduced as Sr doping increased because the lattice flaws in the La$_{1-x}$Sr$_x$MnO$_3$ nanoparticles rose as Sr doping increased, negatively affecting grain expansion and lowering grain size [30]. Subsequently, TEM was used to assess the effect of Sr doping on the La$_{1-x}$Sr$_x$MnO$_3$ nanoparticle’s structure by characterizing the morphology of LaMnO$_3$ and La$_{0.85}$Sr$_{0.15}$MnO$_3$ samples. The results are shown in Figure 2f–i. Figure 2f,h shows that LaMnO$_3$ and La$_{0.85}$Sr$_{0.15}$MnO$_3$ samples comprised fine nanoparticle stacks with small grain sizes and uniform distribution; the grain size of the La$_{0.85}$Sr$_{0.15}$MnO$_3$ sample (~25 nm) was considerably smaller than that of the LaMnO$_3$ sample (~50 nm). Furthermore, the electron diffraction patterns of both the LaMnO$_3$ [Figure 2g] and La$_{0.85}$Sr$_{0.15}$MnO$_3$ [Figure 2i] samples showed concentric ring patterns, indicating the polycrystalline nature of the LaMnO$_3$ and La$_{0.85}$Sr$_{0.15}$MnO$_3$ samples. Then, the XRD data proposed that each ring can be assigned to various planes, as seen in the relevant images.

![Graph](image1.png)

**Figure 1.** (a) TG curve of the LaMnO$_3$ precursor and (b) XRD pattern of La$_{1-x}$Sr$_x$MnO$_3$ (x = 0.0, 0.05, 0.1, 0.15, and 0.2).

![Images](image2.png)

**Figure 2.** SEM images of (a) LaMnO$_3$, (b) La$_{0.95}$Sr$_{0.05}$MnO$_3$, (c) La$_{0.9}$Sr$_{0.1}$MnO$_3$, (d) La$_{0.85}$Sr$_{0.15}$MnO$_3$, and (e) La$_{0.8}$Sr$_{0.2}$MnO$_3$; (f,g) TEM image and selected area electron diffraction images of LaMnO$_3$; (h,i) TEM image and selected area electron diffraction patterns of La$_{0.85}$Sr$_{0.15}$MnO$_3$.

The surface area and pore size distribution of La$_{1-x}$Sr$_x$MnO$_3$ (x = 0.0, 0.05, 0.1, 0.15, and 0.2) nanoparticles were measured using a N$_2$ adsorption–desorption physisorption analyzer. Figure 3a,b depicts the isotherm description and orifice size distribution curve. Investigations revealed that the isothermal curves of the La$_{1-x}$Sr$_x$MnO$_3$ (x = 0.0, 0.05, 0.1, 0.15, and 0.2)
and 0.2) samples were a type IV hysteresis coil, indicating the mesoporous region of the synthesized samples [31]. Figure 3 shows the specific surface area and average pore diameters of La\(_{1-x}\)Sr\(_x\)MnO\(_3\). The specific surface area of the La\(_{0.95}\)Sr\(_{0.05}\)MnO\(_3\), La\(_{0.9}\)Sr\(_{0.1}\)MnO\(_3\), La\(_{0.85}\)Sr\(_{0.15}\)MnO\(_3\), and La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\) sample was 24.82, 29.61, 31.56, and 44.33 \(\text{m}^2\ \text{g}^{-1}\), respectively, which is larger than that of the LaMnO\(_3\) sample (22.25 \(\text{m}^2\ \text{g}^{-1}\)). The average pore diameters of the LaMnO\(_3\), La\(_{0.95}\)Sr\(_{0.05}\)MnO\(_3\), La\(_{0.9}\)Sr\(_{0.1}\)MnO\(_3\), La\(_{0.85}\)Sr\(_{0.15}\)MnO\(_3\), and La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\) samples were 2.81, 2.03, 2.04, 3.05, and 3.14 nm, respectively. Note that the La\(_{0.85}\)Sr\(_{0.15}\)MnO\(_3\) sample had a larger specific surface area.

Figure 3. (a) N\(_2\) adsorption–desorption isotherms of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) (x = 0.0, 0.05, 0.1, 0.15, and 0.2) nanoparticles, (b) BJH pore size distributions of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) (x = 0.0, 0.05, 0.1, 0.15, and 0.2) nanoparticles, (c) The specific surface area and average pore diameters of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) (x = 0.0, 0.05, 0.1, 0.15, and 0.2).

Figure 4 shows the oxidation states and composition of the La\(_{1-x}\)Sr\(_x\)MnO\(_3\) (x = 0.0, 0.05, 0.1, 0.15, and 0.2) specimens. In particular, Figure 4a reveals the XPS survey scan, which indicated that the prepared samples included La, Sr, Mn, and O. However, Figure 4b displays the La 3d XPS spectra, with the peaks at 834.4 and 838 eV being the spin–orbit peaks of La 3d\(_{5/2}\) and including extra peaks at 850.8 and 855.4 eV representing that of La 3d\(_{3/2}\) [32]. These results indicate that La in La\(_{1-x}\)Sr\(_x\)MnO\(_3\) was present in the +3 valence state, which is identical to the results reported by Zhang et al. [33]. On the other hand, the Mn 2p spectra of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) illustrated a wide outflow line width and a unique top range, confirming the existence of Mn in various oxidation conditions [34]. Accordingly, studies have widely utilized a simple tip-differential examination of Mn 2p to determine the manganese oxidation status of manganese with combined valences [22,24,35]. Investigations also revealed that while the features of the peaks at 641.2 eV and 652.3 eV related to Mn\(_{2+}\), those at 642.3 and 653.9 eV related to Mn\(_{3+}\), and those at 644.0 and 655.5 eV related to Mn\(_{4+}\) [22]. Conversely, Figure 4d shows oxygen’s high-resolution XPS spectra. The results illustrate that the three spikes adjusted to the greater fields in the O 1s part at 529.29, 530.9, and 533.1 eV correlated with O\(_1\), O\(_2\), and O\(_3\) [32], where O\(_1\) correlated with lattice oxygen (O\(^{2-}\)), O\(_2\) correlated with the exterior extracted oxygen (O\(^{-}\), O\(^{2-}\), and O\(^{2-}\)), and O\(_3\) correlated with the oxygen-holding groups (OH). The proportional amounts of the three oxygen models are shown in Table 1. The oxygen molecules of the electrode items were inextricably connected with the conductivity, as well as the increased content of the O\(_2\) types; the chemical absorption possibility of OH\(^-\) became smoother, proposing that this connection optimized the activity of outward redox processes and their electrochemical qualities [36]. Furthermore, while the chemical oxygen vacancy of O\(^{2-}\) or O\(^-\) corresponded with oxygen deficiency, the density of oxygen vacancy was represented by the ratio of the area. The outside O\(_2\)/O\(_1\) molar proportion reduced in the following arrangement: La\(_{0.85}\)Sr\(_{0.15}\)MnO\(_3\) (1.34) > La\(_{0.9}\)Sr\(_{0.2}\)MnO\(_3\) (1.3) > La\(_{0.8}\)Sr\(_{0.1}\)MnO\(_3\) (1.16) >
La$_{0.95}$Sr$_{0.05}$MnO$_3$ (1.08) > LaMnO$_3$ (1.06), illustrating that La$_{0.85}$Sr$_{0.15}$MnO$_3$ had the highest electrochemical efficiency among the supercapacitors [37]. Finally, Figure 4e demonstrates the high-resolution XPS spectrum of Sr 3d, which revealed that the spike features at 131.08 and 132.8 eV correlated with the 3d$_{3/2}$ and 3d$_{5/2}$ spin–orbit peaks, confirming that the sample chemical valence state of Sr was +2 [38].

![XPS spectra](image)

**Figure 4.** (a) XPS survey spectrum of La$_{1-x}$Sr$_x$MnO$_3$ (x = 0.0, 0.05, 0.1, 0.15, and 0.2); high-resolution spectrum of (b) La3d, (c) Mn2p, (d) O1s, and (e) Sr3d.

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<th>La$<em>{0.95}$Sr$</em>{0.05}$MnO$_3$</th>
<th>La$_{0.9}$Sr$_0.1$MnO$_3$</th>
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### 3.2. Electrochemical Properties

Figure 5 illustrates the CV curves of La$_{1-x}$Sr$_x$MnO$_3$ (x = 0.0, 0.05, 0.1, 0.15, and 0.2) electrodes at various testing voltage situations using 3 M KOH as the electrolyte. As the scan rate rose, the CV curves remained the same, suggesting great reversibility. However, the CV curves revealed a typical pseudocapacitor behavior, indicating a relationship between the maximum redox at 0.15 V and a shift in the valence state of manganese ions from trivalent to divalent [22,24], respectively. Therefore, as per the anion insertion pathway, the redox reactions of LaMnO$_3$ during charging and discharging trials were illustrated as follows [24]:

\[
\text{La}[^{2+}/^{3+}; \text{Mn}^{3+/2+}]_1 \text{O}_{3-\delta} + 2\delta\text{OH}^- \leftrightarrow \text{LaMn}^{3+} \text{O}_3 + 2\delta\text{e}^- + \delta\text{H}_2\text{O} \quad (2)
\]

\[
\text{LaMn}^{3+} \text{O}_3 + 2\delta\text{OH}^- \leftrightarrow \text{La}[^{4+}/^{3+}; \text{Mn}^{3+/2+}]_1 \text{O}_{3+\delta} + 2\delta\text{e}^- + \delta\text{H}_2\text{O} \quad (3)
\]
The oxygen intercalation process in LaMnO$_3$ samples: First, La$\left[\text{Mn}^{2+};\text{Mn}^{3+}_{\delta}\right]$O$_3$$_{\delta}$ extracts OH$^-$ from the electrolyte to create O$^{2-}$ and H$_2$O. Then, O$^{2-}$ is pushed into the perovskite lattice, thereby diffusing from the borders of the O$_2$ octahedron and finally filling oxygen openings in the composition. As a result, the required Mn$^{2+}$ changes to Mn$^{3+}$ and finally creates a neutral LaMn$^{3+}$O$_3$. Second, manganese arises from the center of the oxygen octahedron, after which excessive oxygen is incorporated into the exterior, thus causing the generation of La$\left[\text{Mn}^{4+};\text{Mn}^{3+}_{\delta}\right]$O$_{3+\delta}$ [18]. Consequently, the divalent component (Sr$^{2+}$) replaces a part of La$^{3+}$ in the A site due to the presence of extra oxygen vacancies. The reaction then changes to the following:

$$\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3; (\delta = 0.05) \xrightarrow{\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}} \text{La}_{0.95}\text{Sr}_{0.05}\text{MnO}_3;$$

and 4.4

For the La$_{0.85}$Sr$_{0.15}$MnO$_3$ samples, the oxidation process from Mn$^{2+}$ to Mn$^{3+}$ was similar to that of Mefford et al. [18], where the oxygen vacancy was filled by O$^{2-}$ intercalation. Although all Mn$^{2+}$ were oxidized to Mn$^{3+}$, La$_{0.85}$Sr$_{0.15}$Mn$^{3+}$O$_{2.925}$ remained hypoxic. Therefore, two stages were identified in the process of Mn$^{3+}$ oxidation to Mn$^{4+}$. In the first stage, when $\delta \leq 0.075$, Mn$^{3+}$ was oxidized to Mn$^{4+}$ by constantly extracting O$^{2-}$ to occupy the residual oxygen vacancies. As a result, many oxygen vacancies moved to the material surface to form La$_{0.85}$Sr$_{0.15}$[Mn$^{4+}$; Mn$^{3+}_{\delta}$]O$_{3+\delta}$ ($\delta = 0.075$). The second stage is similar to that in LaMnO$_3$, in which the oxidation of Mn$^{3+}$ to Mn$^{4+}$ caused the formation of La$_{0.85}$Sr$_{0.15}$[Mn$^{4+}$; Mn$^{3+}_{\delta}$]O$_{2.925+\delta}$.

Figure 5 shows that the La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.0, 0.05, 0.1, 0.15,$ and $0.2$) electrodes had a large voltage window ($-0.5$ to $0.5$ V). As the Sr content rose, the closed area of the CV curves developed and eventually declined at the same scanning speed. La$_{0.85}$Sr$_{0.15}$MnO$_3$ had the largest closed region. However, when the sample was doped with Sr, the oxygen vacancies increased, in addition to the pseudocapacitance of the oxide, thereby increasing the specific capacitance value. The specific capacitance rose and dropped with increasing Sr doping levels due to the ion exchange process; the results are shown in Figure 5f. The process of oxygen admission may illustrate this capacity trend by raising Sr doping. As Sr doping increased, the concentrations of oxygen vacancies in the samples of Table 1 increased.
and then decreased. This changing trend was consistent with the specific capacitance. Furthermore, while the different radii of Sr2+ and La3+ resulted in lattice mismatch, which decreased the tolerance factor, t, it also affected the perovskite structure, indicating that excessive Sr doping could result in the lattice distortion of La1−xSrₓMnO3 because oxygen ions were not transported through the oxygen vacancies, which reduces the charge storage efficiency and specific capacitance [24]. Hence, increasing the specific surface area is useful for improving electrochemical performance.

Figure 6 shows the constant current charge–discharge (GCD) curves for the La1−xSrₓMnO3 (x = 0.0, 0.05, 0.1, 0.15, and 0.2) electrodes at diverse current concentrations. Results revealed that the samples discharged faster as the charge–discharge current density rose. This finding was due to the fact that the specific capacitance decreased as the internal resistance rose with increasing current density. Consequently, the discharge time will be lowered. Alterations in the curve slope were also proposed to result from the alterations in the valence state from Mn2+ to Mn3+. The specific capacitances of synthesized La1−xSrₓMnO3 at a current density of 0.5 A/g are 67, 97, 115, 185.5, and 137.5 F/g, respectively. Figure 6f displays the specific capacitance of La1−xSrₓMnO3 (x = 0.0, 0.05, 0.1, 0.15, and 0.2) as a function of current density. Due to the ion-exchange process, particular capacitance values fell as the current density rose, indicating that the trend of specific capacitance corresponded to the density of oxygen vacancies in the mechanism. These results also demonstrate that the capacitance of La1−xSrₓMnO3 (x = 0.0, 0.05, 0.1, 0.15, and 0.2) specimens could be elevated by a La site exchange.

Figure 6. Charge–discharge curves of La1−xSrₓMnO3 (x = 0.0, 0.05, 0.1, 0.15, and 0.2): (a) LaMnO3; (b) La0.95Sr0.05MnO3; (c) La0.9Sr0.1MnO3; (d) La0.85Sr0.15MnO3; (e) La0.8Sr0.2MnO3; and (f) specific current against the specific capacitance of La1−xSrₓMnO3.

Figure 7 shows the Nyquist plots of the La1−xSrₓMnO3 (x = 0.0, 0.05, 0.1, 0.15, and 0.2) electrodes measured by EIS within the frequency variety of 100 kHz to 0.01 Hz. Generally, while impedance diagrams were divided into linear and semicircular parts, the semicircular curve region was in the AC impedance’s high-frequency region, indicating that a redox reaction occurred on the electrode surface. Investigations also revealed that the straight-line region was in the low-frequency region of AC impedance, which shows the capacitive resistance generated at the electrode surface. Subsequently, the resistive range was adjusted to a circuit (displayed in the inset), usually containing an equivalent series resistance (Rₑ), charge transfer resistance (Rct), Warburg element (Wₚ), and constant phase element (CPE). Rₑ is a combination of the electrolyte ionic resistance, the intrinsic resistance of active material, and the contact resistance between the active material and the current collector. According to the Nyquist plot, the Rct values were 0.49, 0.47, 0.41, 0.38, and
4.4 Ω (as shown in Figure 7b), respectively, with the La0.85Sr0.15MnO3 sample having a minimal charge transfer impedance, demonstrating excellent electrochemical features. Moreover, La1−xSrₓMnO3 (x = 0.05, 0.1, 0.15, and 0.2), which had extra oxygen vacancies, was better for the insertion of oxygen than LaMnO3, thus resulting in a smaller impedance to ion diffusion. Hence, these electrochemical records confirmed that the La0.85Sr0.15MnO3 nanoparticles were favorable negative electrode materials for supercapacitors.

Figure 7. (a) The impedance comparison diagram of La1−xSrₓMnO3 (x = 0.0, 0.05, 0.1, 0.15, and 0.2) electrodes; (b) The Rct of La1−xSrₓMnO3 (x = 0.0, 0.05, 0.1, 0.15, and 0.2) electrodes.

4. Conclusions

La1−xSrₓMnO3 (x = 0.0, 0.05, 0.1, 0.15, and 0.2) nanoparticles were successfully synthesized using the sol–gel approach. As the Sr doping content increased, the grain size decreased, the specific surface area increased, and the density of oxygen vacancy in the LaMnO3 regulation initially rose and then reduced, indicating that the particular capacitance of the La1−xSrₓMnO3 nanoparticles followed a similar trend. Investigations also revealed that the La0.85Sr0.15MnO3 nanoparticles with additional intrinsic oxygen vacancies demonstrated a maximum specific capacitance (185.5 F/g). This finding demonstrated that a particular capacitance of the LaMnO3 system can be enhanced by La site substitution. As a result, this study successfully developed a potential electrode material for supercapacitor applications.

Author Contributions: Conceptualization and data curation, X.Y.; methodology and formal analysis, X.J.; investigation, J.W.; investigation, L.W.; writing—original draft preparation, S.D.; writing—review and editing, Y.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Grant No. 51702132) and the Postgraduate Research & Practice Innovation Program of Jiangsu Province (Grant No. KYCX20_3132).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors acknowledge financial support from the National Natural Science Foundation of China (51702132). Song-Tao Dong acknowledges the open project of the National Laboratory of Solid State Microstructures at Nanjing University. Jun-Lin Wei acknowledges financial support from the Postgraduate Research & Practice Innovation Program of Jiangsu Province (Grant No. KYCX20_3132).

Conflicts of Interest: The authors declare that they have no conflict of interest.
References


11. Hussain, S.; Javed, M.S.; Ullah, N.; Shaheen, A.; Aslam, N.; Ashraf, I.; Abbas, Y.; Wang, M.; Liu, G.; Qiao, G. Unique hierarchical mesoporous LaCo0.95Ni0.05O3 perovskite oxides for highly efficient electrochemical energy storage applications. *J. Power Sources* 2008, 179, 435–440. [CrossRef]


