Synthesis of LaMnO₃-reduced graphene oxide or Sr composite and their application in electrochemical properties

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Abstract
Perovskite structural metal oxides as electrode materials present promising and potential properties due to excellent storage characteristics. Herein, series of perovskite type LaMnO₃ nanopowders were synthesized by the ‘sol-gel’ method with a heat treatment at different temperatures (700 °C–900 °C) for different times. The morphology characterization, structures and electrochemical performances were investigated. The preferable sample for electrochemical energy storage device can be obtained at 900 °C with 2 h annealing. Furthermore, to improve the properties of the electrode materials, the samples were combined and rectified with reduced graphene oxide (rGO) and strontium (Sr), respectively. The results indicate that the rGO/Sr-doped LaMnO₃ oxide materials have excellent electrochemical properties. These findings are beneficial for the selection and preparation of electrode materials.

1. Introduction
With the exhaustion of conventional energy resources, the demands of the energy storage with friendly environment and high performance are urgent for scientists to find effective energy storage devices [1]. Recently, due to the short charging times, high power density and long cycle life, supercapacitors have attracted more extensive attention in energy storage field than batteries. The energy storage performances of supercapacitors mainly depend on the electrode materials [1, 2]. In generally, three categories electrode materials are carbon materials, transition-metal oxide and conducting polymers respectively [2–5]. Carbon material is one of the important electrode materials due to their high electrical conductivity and stability. However, the energy density in carbon materials is very low. Transition-metal oxides materials are widely applied as supercapacitor electrode materials due to their good thermal stability, high energy density, and the low cost [5–11].

As a new class of metal oxides, Perovskites have excellent thermal stabilities, oxygen storage and outstanding ionic conductivities. As typical perovskite metal oxides, LaMnO₃, has been reported as supercapacitor electrode materials. Mefford firstly investigated the mechanism of oxygen-vacancy-mediated redox pseudocapacitance [1, 12, 13]. Due to the super electronic and ionic conductivity properties, La₀.₈₅Sr₀.₁₅MnO₃ have been discussed as supercapacitor electrodes using the solgel method [2, 14–17]. However, the effect of the calcination temperature and time in the fabricating samples as electrode materials of supercapacitors is blurry [3, 5, 17, 18]. To improve the properties of electrochemical energy storage device, In addition, rGO is a two-dimensional carbon nanostructure with excellent electrical conductivity and physicochemical stability. The combinations of different chemical compositions can be designed [19–22]. The properties are desired to combine LaMnO₃ and rGO as electrode materials of electrochemical energy storage device [15].

In this work, we discussed the morphologies and electrochemical performances as electrodes for electrochemical energy storage device with different temperature and time. Firstly, LaMnO₃ powder was prepared by solgel method, and the influences of different calcination temperature and time on the electrochemical properties of LaMnO₃ Oxide were investigated. Secondly, LaMnO₃ composites rGO or Sr were prepared to improve the electrochemical properties for electrochemical energy storage device. By comparing with doped/undoped LaMnO₃ Oxide samples, the difference of the surface morphology and structure of the
series samples are obtained. The results show that LaMnO₃ doped rGO or Sr have higher specific capacitance than undoped and have larger specific surface area than the pure LaMnO₃, and the electrochemical properties tested in electrochemical testing, which is beneficial for explore a good electrode material for electrochemical energy storage device.

2. Experimental procedure

2.1. Materials preparation
Experimental materials: La(NO₃)₁₂ · 6H₂O, Mn(NO₃)₂ solution, n-n-dimethyl formamide, polyvinylpyrrolidone (PVP), graphite, Sr(NO₃)₂, teflon (PTFE), concentrated sulfuric acid, conductive carbon black, etc.

2.2. Synthesis of LaMnO₃
Inorganic salt is used as raw material, ‘PVP’ as template and ‘DMF’ as solvent. 1 mol La(NO₃)₁₂ · 6H₂O (0.866 g) and the concentration of 50% Mn(NO₃)₂(0.362 g) solution mixed evenly, and then added 50 ml N-N-dimethyl formamide and transferred them to a beaker, put the beaker into the temperature control electromagnetic stirrer, stirring for 1 h, then weighted 0.9 g PVP and added to the beaker, magnetic stirrer temperature control device can be set to 100 °C, heating and stirring until the colloidal sample materials is formed inside the beaker. After transferring them to specific crucible, prepared samples respectively, afterwards put labelled samples into the calciner, set the calcine temperature respectively to 900 °C, 800 °C, 700 °C, the calcination time is set to 2 h, 3 h and 4 h, taked out the samples after calcination temperature cooled down to room temperature and grinded the samples into uniform powders in the mortar, so made LaMnO₃ perovskite oxide powders samples.

2.3. Synthesis of LaMnO₃/rGO(Sr)
Samples of the LaMnO₃ powders and rGO/Sr which has been prepared previously recombined respectively with 10:1, 6:1, 2:1 and 1:2 mixed, and then grinded adequately in the mortar, then transferred the mixtures to different crucible, Put them together in the calciner, set the furnace temperature to 600 °C for 1 h, at the same time protective gas was applied to protect the sample from oxidation.

2.4. Characterization
The structure of the as-obtained samples are identified by x-ray diffractometer (XRD), adopting Bruker D8 Advance diffractometer using Cu Kα radiation. The morphology has been examined using field-emission scanning electron microscopy (FESEM; Quanta 250 FEG).

2.5. Electrochemical test
The working electrode is prepared by mixing the prepared samples powder, conductive carbon black (BP 2000, CABOT, USA), and polytetra-fluoro-ethylene (PTFE) binder together in a mass ratio of 8 : 1 : 1. Here a little isopropyl alcohol was added to the mixture to produce homogeneous paste. The getting paste was coated onto the surface of Ni foam, and then both of them were pressed together (about 0.1 mm thick). Then the electrode was dried at 80 °C for 10 h in a vacuum oven to remove solvent. The mass of the active material on nickel foam was about 2.8 mg by calculating and weighing. The electrochemical measurements of cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were conducted on a RST electrochemical workstation with a typical three-electrode system in 2 M KOH solution.

3. Results and discussing
The structure of LaMnO₃ and LaMnO₃ doped rGO/Sr were characterized by XRD. In figure 1(a), it can be seen from the XRD pattern that there are mainly 8 diffraction peaks of LaMnO₃ samples. 2θ is 23°, 32.8°, 40.1°, 46.9°, 52.7°, 58.1°, 67.9° and 77.4°, respectively, corresponding crystal planes are (012), (104), (202), (024), (116), (214), (220) and (134). The main characteristic diffraction peaks of the three diffraction spectra of LaMnO₃ samples at different calcination temperatures are consistent with the characteristic diffraction peaks corresponding to the standard phase card PDF #50–0299 (LaMnO₃.15, r-3c (167)). In addition, the strongest diffraction peak occurs around 2θ 32°, which is the typical diffraction peak of LaMnO₃ on the crystal plane (104). The sharp peak shape and narrow distribution indicate that the crystalline of LaMnO₃ oxide sample is relatively high pure. By comparing three diffraction spectra of 700 °C, 800 °C and 900 °C, it is clear that 900 °C corresponds to a spectrum line of 32.8° in 2θ, and the diffraction peak of crystal surface (104) is the sharpest with the rise of temperature, and the peak also increases the highest. This indicates that LaMnO₃ sample crystallinity
is the best performance at 900 °C. After LaMnO₃ sample is fully doped with rGO/Sr, it can be seen that the characteristic diffraction peak of the doped sample basically corresponds to the diffraction peak of LaMnO₃, and there is no diffraction peak of heterophase (La₂O₃ or SrO, Mn₂O₃/Mn₃O₄, etc), which proves that the doped samples LaMnO₃/rGO and LaMnO₃/Sr have pure phase perovskite structure. In addition, the intensity of the diffraction peak after doping is slightly larger than that before doping, and the half-peak width is smaller. Contrasting eight characteristic diffraction peak of LaMnO₃ sample, one new diffraction peak appears in 2θ 75.4° in LaMnO₃/rGO sample, the crystal face is corresponding (021), the diffraction peak and the element characteristics of diffraction peak corresponding to element ‘C’ with ICDD/JCPD elemental phase CARDS. In the diffraction pattern of LaMnO₃/Sr sample, there is also a weak diffraction peak at 2θ = 45.2°, crystal plane (104), which is consistent with the characteristic diffraction peak of element ‘Sr’.

The morphology and microstructure will affect the electrochemical performance of supercapacitors. To demonstrate the specific surface area of LaMnO₃ materials obtained at different annealing temperature and time, using N₂ adsorption–desorption measurements we characterized the BET surface areas of the LaMnO₃ samples as shown in figure 1(b). The characteristic type-IV isotherm of LaMnO₃ presents a hysteresis loop indicating the existence of mesoporous structures in the materials. From the BET results, we can obtain that the LaMnO₃ sample with 900 °C annealing temperature and 2 h presents a greater specific surface area due to greater volume change.

The SEM images of LaMnO₃ at different calcination temperatures shown in figure 2 present porous structures and loose aggregates. It can be seen that the size of the loose and porous structures are various at different annealing temperature. The morphology gradually changes from a small flake in figure 2(b) to a block in figure 2(c). Comparing different annealing temperature, the large specific surface area at the annealing temperature 900 °C is beneficial for supercapacitor.

It can be contrasted between figures 2(b), (d) and (e). With the annealing time decreases, the morphology of the sample material changes from a particle with diameter of about 5 μm to a block with diameter of more than 20 μm. The specific surface area of the sample with 2 h annealing time is larger than the other two. The figure 2(f)–(g) show the comparison SEM images of LaMnO₃ doped rGO/Sr sample with the same annealing condition. From figures 2(b) to (f)–(g), the porous structure can be seen in LaMnO₃ doped rGO or Sr, which are agreement with the specific area features of the alone samples. Here, rGO in diameter is about 1 μm, thus the electrolyte ions can transfer efficiently. It can be inferred that rGO usually wrapped on the sample or the sample dispersed on graphene. Therefore it can be estimated that the doped LaMnO₃ samples present larger specific surface area, which should increase the reaction sites of active substances and cause higher electrical conductivity.

To study the electrochemical performance of the samples, the CV curves of LaMnO₃ samples at different annealing temperature with the same annealing time are shown in figure 3(a). The apparent redox peaks can be found in the CV curves at the scan rate of 50 mV s⁻¹, which show a characteristic redox capacitance behavior. All LaMnO₃ electrode materials at different annealing temperature for 2 h were measured in 2 M KOH aqueous solution. Compare the CV curves of the three samples, it can be seen that the CV curve at 900 °C has largest area and higher redox peaks than the other two. It reveals that the LaMnO₃ at 900 °C has the better specific capacitance value. According to this results, the result can be obtained by the formula: \( C_v = \frac{\Delta Q}{\Delta V} \). Here \( C_v \)
(mAh/g) is the specific capacitance, I (mA) represents the response discharge current, Δt (s) is the discharge time, m (g) is the mass of the active material [3, 5, 23]. Figure 3(b) illustrates the specific capacitance of LaMnO₃ electrode as a function of current density. The current density is 0.5 A·g⁻¹, 0.8 A·g⁻¹, 1 A·g⁻¹, 2 A·g⁻¹, 5 A·g⁻¹ and 8 A·g⁻¹ respectively. The specific capacitance gradually decreases with current density increases.

Figure 3(c) shows the changes of the GCD curves about LaMnO₃ electrode with different current density at annealing temperature of 900 °C and annealing time of 2 h. Discharge curves can be considered as two regions due to different slopes, a sudden potential drop and a slow potential decay. At the beginning of the drop is due to
internal resistance of the electrode. The potential attenuation is attributed to continuous discharge of faradaic processes in redox peaks process.

The GCD diagram of the samples was obtained at the current density of 0.5 A g\(^{-1}\) with the maximum capacitance, as shown in Figure 4. The curve consists of the potential drop and the slow potential decay. The longer time of the charging and discharging time present that the corresponding specific capacitance is largest than the other two. According to formula of the specific capacitance, we can get 
\[ C = 19.32 \text{ mAh g}^{-1} \text{ at } 900 \degree C, \]
\[ C = 11.04 \text{ mAh g}^{-1} \text{ at } 800 \degree C, \]
\[ C = 7.59 \text{ mAh g}^{-1} \text{ at } 700 \degree C. \]
Obviously, the sample electrode of annealing 900 °C has the largest specific capacitance.

To investigate the further electrochemical performance, EIS tests were carried out at different temperature. The Nyquist plot indicates the impedance behavior as a function of frequency, consisted of two parts: a semicircle corresponding to the Faradaic reactions in the high-frequency range, together with a straight line in the low-frequency range. Figure 5 mainly shows the impedance diagram in the high-frequency region. As shown in the Nyquist plots in the high-frequency region, the intersection of the curve at the real axis represents the internal resistance (Rs), which containing the resistance of aqueous KOH solution, the resistance of intrinsic active material, as well as the contact resistance at the interfaces between active materials. By comparison, it can be concluded that the Rs of sample electrode becomes smaller and smaller with the increase of temperature, indicates that the sample electrode has the best electrical conductivity at 900 °C, pointing out it is an excellent material option for making the electrode of electrochemical energy storage device.

Figure 4. GCD curves of LaMnO\(_3\) for 2 h at different temperature.

Figure 5. Nyquist plots of LaMnO\(_3\) electrodes prepared samples for 2 h at different temperature.
Figure 6 shows that the three CV curves of the LaMnO₃ sample electrode all have obvious redox peaks. The same reason is because the prepared LaMnO₃ samples have a large number of porous structures, which leads to obvious redox peaks in the electrode curves of the three samples. It can be found that area enclosed by CV curve becomes larger and larger with apparent redox peaks. Furthermore, the redox peak of sample is the most obvious at the annealing time of 2 h (900 °C). In figure 7, it can be seen that the charge curve and discharge curve of the electrode, which indicates that the electric potential does not show a linear relationship with time. The ‘2 h’ annealing curve in the figure 7 shows that the end of the charge-discharge to the time axis because the compact layer has been saturated and the same charges repel each other.

According to the calculation formula of specific capacitance, we can get: the specific capacitance is 19.32 mAh g⁻¹ when the annealing time is 2 h; the specific capacitance is 11.04 mAh g⁻¹ when annealing time is 3 h; the specific capacitance is 6.9 mAh g⁻¹ when annealing time is 4 h. It can be concluded that, when the annealing time is 2 h, the discharge time of sample material electrode is the longest and the specific capacitance is the largest. It can be seen from figure 8 that sample electrodes with the annealing time 2 h presents the straight line in the low frequency range, more parallel to the imaginary axis than that of other electrodes, standing a lower Warburg impedance and charge transfer resistance (Rct), determine the rate of charge and discharge of the electrochemical energy storage device. Through comparison, it can be concluded that the resistance of sample...
electrode decreases with the decrease of annealing time, indicating that the sample electrode has the best conductivity at the annealing time of 2 h.

By comprehensively comparing the CV curves, GCD and EIS of LaMnO₃ samples under the above two annealing conditions, it can be concluded that the LaMnO₃ samples possess the strongest conductivity and the best electrochemical performance under the annealing condition of 900 °C for 2 h.

Figure 9 shows the CV curves of LaMnO₃ sample doped/undoped with rGO/Sr, the three samples under certain annealing condition of 900 °C for 2 h. It can be seen from the figure that all three CV curves of the sample electrodes have obvious redox peaks. The reason is due to the structure of the doped LaMnO₃ sample materials contains large number of porous structures. At the same time, it is found that the redox peak of LaMnO₃ samples doped with rGO/Sr is more obvious, and have more excellent electrochemical properties, due to the increasingly prominent electrochemical polarization and concentration difference polarization.

Figure 10 shows that the GCD curves of the undoped LaMnO₃ sample, under certain annealing condition of 900 °C for 2 h, comparison of sample doped with rGO/Sr (current density is 0.5 A g⁻¹). It can be seen from the figure that the charge-discharge curves of the electrode in different degrees, indicating the potential. Due to the saturation of the compact layer and the exclusion of the same charges, the end of the charge-discharge curve of sample electrodes doped with Sr is to the time axis. According to the calculation formula of specific capacitance, the specific capacitance is 19.32 mAh g⁻¹ when LaMnO₃ sample is not doped; When doped with rGO, the specific capacitance is 57.34 mAh g⁻¹; When doped with Sr, the specific capacitance is 54.86 mAh g⁻¹. Comparing with other composite electrodes, such as Ca doped perovskite lanthanum manganites (La₁₋ₓCaₓMnO₃) with the specific capacitance 13 F g⁻¹ at current density of 0.5 A g⁻¹ [4], the specific capacitance of
LaMnO₃ doped with rGO is higher. It can be concluded that the specific capacitance performance of sample electrode is greatly improved when LaMnO₃ electrode materials is doped with rGO/Sr.

To obtain further insight into the electrochemical performance, EIS tests were also carried out at open circuit potential to estimate the interface resistance of the prepared samples. Figure 11 shows the EIS diagram of the undoped LaMnO₃ sample and the doped rGO/Sr LaMnO₃ sample. As shown in the Nyquist plots in the high-frequency region, the intersection of the curve at the real axis represents the Rs, which containing the resistance of aqueous KOH solution, the resistance of intrinsic active material, as well as the contact resistance at the interfaces between active materials. The Rs of the LaMnO₃ doped rGO electrode estimated to 0.6 Ω is the lowest, then the Rs of the LaMnO₃ doped Sr is lower than that of the LaMnO₃ electrode. The lower Rs is corresponding its higher diffusion ability. In high-frequency region the diameter of the semicircle indicated that the Rct in the redox reaction, which affect the rate of charge and discharge of the electrochemical energy storage device [24–26]. The LaMnO₃ doped rGO or Sr electrodes possessing higher Rct than that of LaMnO₃ electrode, meaning the electrochemical reaction of the doped LaMnO₃ is a little difficult to occur than that of LaMnO₃ [2].

Based on the above XRD, SEM analysis and electrochemical workstation testing, varying the condition of annealing temperature and time, when the annealing temperature is 900 °C meanwhile the annealing time is 2 h, the crystal structure of LaMnO₃ samples is the closest to that of pure perovskite, the samples under the certain annealing condition have the strongest conductivity and the best electrochemical performance. Under the same annealing condition of 900 °C for 2 h, the LaMnO₃/rGO(LaMnO₃/Sr) perovskite composite oxide
materials significantly improves the specific surface area, specific capacitance and indexes other electrochemical performance comparison with the undoped sample materials.

4. Conclusion

The LaMnO₃/rGO and LaMnO₃/Sr composite samples have been fabricated using ‘sol-gel’ method. The morphology and structure of the samples are characterized and analyzed by means of SEM and XRD. The electrochemical workstation is used to test the electrochemical properties of electrodes prepared from different sample materials. The CV curves, GCD and EIS characterization present that LaMnO₃ samples obtained at 900 °C with 2 h has the highest specific capacitance, maximum charging-discharging power, and the most superior cyclic charging-discharging characteristics. Compared with the pure LaMnO₃, LaMnO₃/rGO and LaMnO₃/Sr composite materials specific surface area and specific capacitance increase significantly. The perovskite composite materials such as LaMnO₃/rGO(LaMnO₃/Sr) through the experiments can be applied to the preparation of electrode materials for electrochemical energy storage device, which is expected to provide a practical and feasible path for the selection and preparation of electrochemical energy storage device.

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