ATLANTIS PRESS

Advances in Engineering Research, volume 113

International Forum on Mechanical, Control and Automation (IFMCA 2016)

Towards Enhanced Electrochemical Capacitance with Preparation of La-doped MnO_2 Nanoparticles

Naying Zhao[1, a], Zhenzhong Hou[1, b], Qinghao Yang[1, c] and Xuejian Yang[2,d]

[1]College of materials science and Engineering, Xi'an University of Science and Technology, Xi'an, China, 710054

[2] College of Safety Science and Engineering, Xi'an University of Science and Technology, Xi'an, China, 710054

[a]532061434@qq.com, [b]1343941671@qq.com, [c]yangxjtu@hotmail.com, [d]yangxuejian@foxmail.com

Keywords: manganese dioxide, nanoparticles, supercapacitance, sol-gel method

Abstract. La-doped MnO_2 nanoparticles were synthesized by a facile sol-gel method. Using XRD and SEM to analyze the structure and morphology of the obtained nano-MnO_2, the results show that it exhibit α-MnO_2 crystal form with some amorphous structure and irregular granular morphology with size of 150-300 nm. Through electrochemical tests of CV and GCD, La-doped nano-MnO_2 presents enhanced electrochemical capacitance with a specific capacitance of 168.7 F g^{-1}, much higher than that of pure nano-MnO_2 prepared at the same conditions.

Introduction

As well as we know, the super-capacitor with combining the advantages of batteries and capacitors has high power density and long service life, becoming a research hotspot in the world[1-2]. In high performance battery, electrolytic manganese dioxide (MnO_2) has been a kind of indispensable raw material[3]. Recently years, many researchers have applied themselves to investigating the preparation and properties of nano-MnO_2 so as to overcome the disadvantages of the electrolytic manganese dioxide (EMD) including long production period, high energy consumption and high cost. Sol-gel method is an effective and environment-friendly approach to prepared nano-MnO_2, while avoiding the aboved disadvantages. It was reported that nano-MnO_2 as electrode materials could significantly improve the capacitance[4,5]. Wei H and colleagues[6] have prepared one-dimensional nanostructured α-MnO_2, which is a promising candidate of electrode materials for high effective supercapacitors, via facile hydrothermal synthesis. This nano-α-MnO_2 exhibits a specific capacitance of 158 F g^{-1} at current density of 4 A g^{-1} and fine cycle stability. Yu Y. et al.[7] have synthesized the ultrathin MnO_2 nanosheets with a thickness of 0.9 nm for flexible supercapacitors, which presents a specific capacitance of 98 F g^{-1} at 50 A g^{-1} and a capacitance retention after 6000 cycles of 95%. In this work, we have fabricated La-doped MnO_2 nanoparticles by sol-gel method and investigated its electrochemical capacitance.

Experiment

Synthesis. All the reagents were analytical pure and used as received. The La-doped MnO_2 nanoparticles were prepared by sol-gel method. A typical preparation process is as follows: citric acid ($C_6H_8O_7$, 5.2535g), manganous acetate [$Mn(CH_3COO)_2$, 12.2545g] and appropriate lanthanum nitrate [$La(NO_3)_3$] were firstly dissolved in deionized water to form a uniform solution. Then a small amount of ammonia water was added to adjust the pH value to 6, consequently the sol was formed at 80 ^oC via a liquid phase chemical reaction. After drying, the sol changed into a gel, which has an open skeleton structure. Finally, the products of La-doped MnO_2 nanoparticles were obtained during the high temperature calcination. In order to further improve the conductivity, La-doped MnO_2

nanoparticles were added into sulfuric acid solution for 2 h, then the as-prepared sample was filtered and washed with ethanol and deionized water for several times until the filtrate became neutral. After drying, the obtained solid powder is acid treated La-doped MnO_2 nanoparticles. As the control sample, the pure MnO_2 nanoparticles were prepared following the same method above without adding $La(NO_3)_3$.

Characterization. XRD was carried out on a D/max 2550 spectrograph with a copper target at a scan speed of 6.00 deg/min. The micro-morphology of prepared MnO_2 nanoparticles was observed by SEM (JSM-6460LV, JEOL, Japan). Electrochemical performance of the samples were evaluated by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD), which were performed on CS 350 electrochemical workstation (Corrtest Corporation, Wuhan Chian) at room temperature. All electrochemical experiments were carried out in 1 mol/L Na_2SO_4 solution using a three-electrode system, which contained a saturated calomel electrode and a platinum plate (ca. 1 cm^2) as the reference electrode and counter electrode, respectively, the obtained MnO_2 nanoparticles loaded on foam nickel (1 cm^2) as the working electrode. (Working electrodes were prepared by mixing 80 wt% as-prepared MnO_2 with 10 wt% acetylene black and 10 wt% polytetrafluoroethylene dissolved in ethanol as a binder to form a homogeneous slurry. The obtained slurry was then pressed onto a foam nickel at 10 MPa for 45 s and dried under vacuum at 60 ^oC for 24h.)

Results and Discussion

Structure and Morphology of the MnO_2 Nanoparticles.

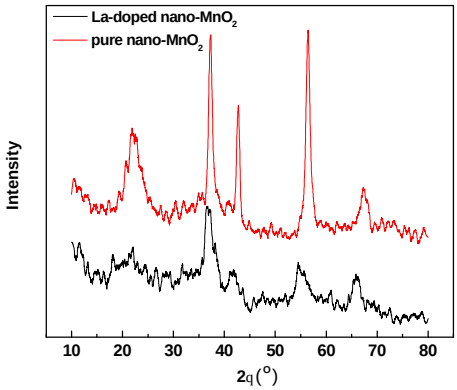

Fig. 1 XRD patterns of as-prepared MnO_2 nanoparticles. Red line is pure nano-MnO_2; black line is La-doped nano-MnO_2.

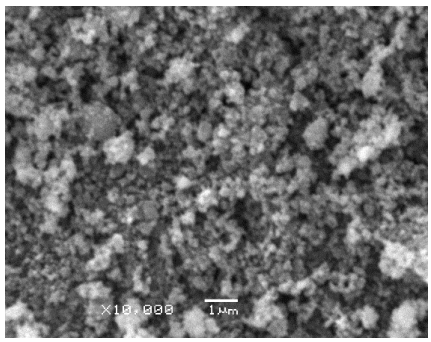

Fig. 2 SEM images of the La-doped MnO_2 nanoparticles.

Figure 1 shows the XRD patterns of as-prepared pure MnO_2 nanoparticles and La-doped MnO_2 nanoparticles. It can be found that the two patterns have the same diffraction peaks at about 22 º, 38 º, 42 º, 58 º and 68 º, which belong to the characteristic peaks of α-MnO_2 according to the PDF standard card (440141) of XRD, indicating that the two kinds of nano-MnO_2 have the same crystal, in other words, La-doping has no effect on crystal form of the obained MnO_2. In addition, comparing with the pattern of pure MnO_2 nanoparticles, the one of La-doped MnO_2 nanoparticles exhibits weaker and broader diffraction peaks, revealing more amorphous in structure. It is seen from Figure 2 that the La-doped MnO_2 nanoparticles with size of 150-300 nm gather mutually and exhibit an irregular granular morphology. As the electrode material for supercapacitor, La-doped nano-MnO_2 with some amorphous structure could provide larger specific surface area and higher porosity than bulk high-crystallized MnO_2, which allow fast ionic migration and charge storage within the material during the electrochemical reactions, favouring an improvement in electrochemical capacitance[8].

Electrochemical Capacitance of the MnO_2 Nanoparticles.

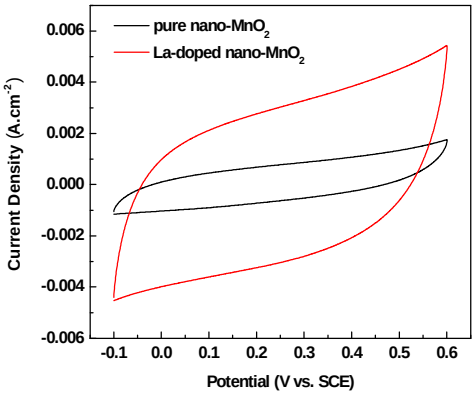

Fig. 3 CV curves of pure and La-doped nano-MnO_2 electrodes in 1 mol/L Na_2SO_4 with a sweep rate of 20 mV s^{-1} at 25 °C.

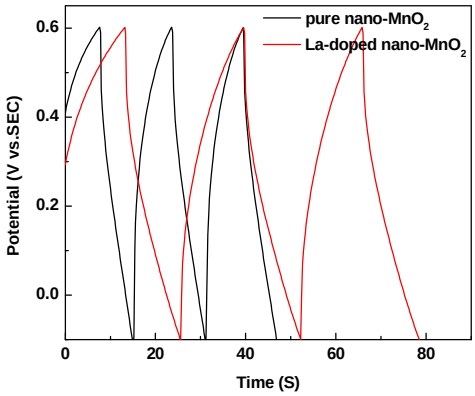

Fig. 4 GCD curves of pure and La-doped nano-MnO_2 electrodes in 1 mol/L Na_2SO_4 at a current density of 0.3 A g^{-1}.

Figure 3 depicits the CV curves of pure and La-doped nano-MnO_2 electrodes in 1 mol/L Na_2SO_4 solution at 20 mV s^{-1}. Obviously, both curves in this figure show a typical faradaic capacitance performance with symmetrical redox behavior, and the current response of La-doped nano-MnO_2 is evidently larger, suggesting its enhanced electrochemical capacitance. According to the equation of $C = \int \frac{I}{vmV} dV$ [9],Where C is the specific capacitance (F g^{-1}); I is the response current (A); m is the the mass of the electroactive material in the electrode (g); v is the potential scan rate (V s^{-1}) and V is the potential (V), the specific capacitance of La-doped nano-MnO_2 with acidification can be calculated as 168.7 F g^{-1}, more higher than that of pure nano-MnO_2 (76 F g^{-1}). The similar result is also confirmed by GCD measurements, as shown in Figure 4. The La-doped nano-MnO_2 electrode exhibit longer discharge time at the same current densities, implying its improved specific capacitance[10].

Conclusions

The La-doped MnO_2 nanoparticles have been prepared by a facile sol-gel method. The obtained nanoparticles exhibit α-MnO_2 crystal form with some amorphous structure and irregular granular morphology with size of 150-300 nm, as demonstrated by XRD and SEM, respectively. After acidification, the La-doped nano-MnO_2 delivers a much higher specific capacitance of 168.7 F g^{-1} than pure nano-MnO_2 synthesized at the same conditions. These results indicate the La-doped nano-MnO_2 possesses enhanced electrochemical performance, just being appropriate for supercapacitor application.

Acknowledgments

This work was financially supported by National Natural Science Foundation of China(21204072) and Key Scientific and Technological innovation team Program of Shaanxi Province, China (2014K CT-04).

References

[1] Largeot C, Portet C, Chmiola J, et al: Journal of the American Chemical Society. 130(2008), p. 2730.
[2] Kandalkar SG, Dhawale DS, Kim CK, et al: Synthetic Metals. 160(2010), p. 1299.
[3] Li Tongqing: Battery Bimonthly. 31(2001), p. 52.
[4] Srither SR, Karthik A, Arunmetha S, et al: Materials Chemistry and Physics. 183(2016), p. 375.

[5] Dang W, Dong C, Zhang Z, et al: Electrochimica Acta. 217(2016), p. 16.
[6] Wei H, Wang J, Yang S, et al: Physica E: Low-dimensional Systems and Nanostructures. 83(2016), p. 41.
[7] Yu Y, Zhai Y, Liu H, et al: Materials Letters. 176(2016), p. 33.
[8] Shi Y, Pan L, Liu B, et al: Journal of Materials Chemistry A. 2(2014), p. 6086.
[9] Yang QH, Hou ZZ, Huang TZ: Journal of Applied Polymer Science. 132(2015), p. 41615.
[10] Jin Y, Huang S, Zhang M, et al: Synthetic Metals. 168(2013), p. 58.