High performance of Mn₃O₄ cubes for supercapacitor applications

Yang Luo, Tianye Yang, Zhifang Li, Bingxin Xiao, Mingzhe Zhang*

State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012,

People's Republic of China.

Abstract:

High specific capacitance performance was exhibited by Mn₃O₄ cubes interlocked with each other. Galvanostatic charge–discharge and cyclic voltammetry measurements can elucidate it. And its specific capacitance is 667 Fg⁻¹ at scan rate of 1 mVs⁻¹, 583 Fg⁻¹ at a low current density of 1 Ag⁻¹. When the current density is increased by 40 times, relative high specific capacitance retention (153 Fg⁻¹) was left. These Mn₃O₄ cubes were made by simple method: dissolution evaporation and then calcination. The excellent specific capacitance suggests that it could be a promising candidate as electrode material for supercapacitors in terms of fast charge-discharge rate, high specific power and long lifespan.

Keywords: Mn₃O₄ cube; Oxidation; Energy storage and conversion; Microstructure; Electrochemical measurements

1. Introduction:

Supercapacitors store energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions (pseudocapacitors). A variety of electrode materials including transition metal oxides and conducting polymers have been developed for pseudocapacitor application [1-4]. Among transition metal oxides, manganese oxides are increasingly welcomed in supercapacitor because of their high capacitance, environment-friendly nature and low cost of

* Corresponding Author: State Key Laboratory of Superhard Materials, Jilin University, China. E-mail: zhangmz@jlu.edu.cn

manufacture [5-8]. Manganese oxides include various crystallographic structures, such as MnO, Mn₂O₃, MnO₂ and Mn₃O₄. In Mn₃O₄, Mn exhibits different oxidation states including +2 and +3 states. The Mn₃O₄ can be expressed by (Mn²⁺(Mn³⁺)₂O₄) [9-10].

Large experiments have been carried to spare no effort to fabricate materials with high specific capacitance. In order to achieve this target, the materials should provide sufficient Faradic reactions between material electrode and electrolyte. The aim of present work is to fabricate Mn₃O₄ three-dimensional (3 D) cubes with high specific capacitance.

2. Materials and methods

2.1. Materials and experimental

All the chemicals used here were of analytical grade without further purification. The procedure was in detail as follows: 1.9791 g MnCl₂·4H₂O was dissolved in 10mL deionized water, then 10mL absolute ethyl alcohol was added dropwise into above aqueous solution with constant stirring for 30 min at room-temperature. After enough stirring, the solution looked transparent pink. Then the solution was dried in an oven at 100 °C for 8 hours. The samples turned faint yellow soliquid. Finally the product was on calcination at 500 °C for 2 h. The temperature was rising at a speed of 2° min⁻¹. The calcined sample was used in the subsequent study.

2.2. Characterization

The synthesized product was characterized by field emission scanning electron microscopy (FESEM) using a FEI Magellan 400 microscope operating at 20 kV. X-ray diffraction (XRD) pattern of the sample was recorded using a Rigaku D/max-2500V X-ray powder diffraction (XRD) with Cu Kα1 radiation ($\lambda = 1.54056 \text{ \AA}$) in the range of 10–80° (2θ) at a scanning rate of 4° min⁻¹. Raman spectra were recorded on ARC-SP 2558 spectrograph (Princeton Instruments) furnished with charge

coupled detector (CCD) PyLon: 100 B. The excitation line was 532 nm from the diode pumped solid state (DPSS) laser.

2.3. Electrochemical Measurements

All electrochemical measurements were carried out on a Bio-Logic Model VMP3 16 Channel Electrochemical Workstation in a three-electrode system at room temperature. The working electrode was prepared by mixing the sample (active material), conductive acetylene black at a mass ratio of 8:1 to obtain slurry, and was dropped onto nickel foam. Then the working electrode was fully dried at 60 °C. The Pt electrode was used as the counter electrode and saturated calomel electrode was used as the reference electrode in 6 M KOH electrolyte solution. This unique 3 D structure on porous skeleton of Ni foam could supply effective electrolyte accessible channels for ion transportation and shorten the distance for ion diffusion [6]. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) were performed in the potential range from 0.4 to 1.1 V. Electrochemical impedance spectroscopy (EIS) test was carried out in frequency range from 0.1 Hz to 200,000 Hz with AC amplitude of 10 mV.

3. Results and discussion:

3.1. FESEM Analysis and XRD Analysis

Fig. 1a shows the FE-SEM images of Mn_3O_4 at two different magnifications ($\times 10000$ and $\times 100000$). The size of the three-dimensional cubes is between 2 and 10 μm as seen in fig. 1a. The average length and high is about 5 μm . From higher magnification, it can be seen more clearly that the particle edges are chiseled. The clear particle edges indicate the high conductivity of the sample. The high conductivity might due to calcination [11]. As lower magnification shows, these Mn_3O_4 cubes are interlocked with each other or aggregated. The structures provide abundant space for electrolyte infiltrating into active materials, which ensure sufficient Faradic reactions can take place.

Fig. 1b shows the XRD pattern of the sample, Mn_3O_4 cubes obtained at 500°C. The XRD peaks can be indexed to tetragonal Mn_3O_4 phase (JCPDS Card no.024-0734). It indicated high purity of the obtained sample.

3.2. TEM Analysis

Further investigation of these samples was performed by transmission electron microscopy (TEM),

selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM). The TEM image shown in Fig. 1(b I) further reveals the structure of the samples. Fig. 1(b II) shows the SAED patterns which reveal these samples are single crystal. HRTEM images supply the internal microstructure information of these Mn_3O_4 cubes (Fig. 1(b III)). It indicates that the interplanar spacing between the adjacent atomic lattice fringes is 0.497nm, which corresponds to the (101) plane of tetragonal Mn_3O_4 . The results agree with the XRD patterns.

3.3. Raman Spectroscopy Analysis

Raman spectrum of the obtained samples is exhibited by Fig. 1(b IV). Two peaks at 644.36 cm^{-1} and 352.69 cm^{-1} can be observed, similar result was found for Mn_3O_4 nanocrystals obtained at low temperature [12]. Thus, the sample is identified as Mn_3O_4 . The sharp peak is corresponding to the Mn-O breathing vibration of Mn^{2+} ions, which is found in mineral hausmannite [13]. Fig. 1(b IV) further supports the XRD result. Thus, the sample was confirmed as Mn_3O_4 .

3.4. Electrochemical Performance

The specific capacitances were calculated through formulas in the supporting information.

Fig. 2a shows the cyclic voltammetry (CV) curves of the active material at various scan rates. Fig. 2b shows corresponding specific capacitance at different scan rate. They are 667 Fg^{-1} , 525 Fg^{-1} , 416 Fg^{-1} , 338 Fg^{-1} , 294 Fg^{-1} , 261 Fg^{-1} , 228 Fg^{-1} , 173 Fg^{-1} , 116 Fg^{-1} and 86 Fg^{-1} at scan rate of 1 mVs^{-1} , 2 mVs^{-1} , 5 mVs^{-1} , 10 mVs^{-1} , 15 mVs^{-1} , 20 mVs^{-1} , 30 mVs^{-1} , 50 mVs^{-1} , 100 mVs^{-1} and 150 mVs^{-1} , respectively. It can be seen that the specific capacitance of the sample decreases with increasing scan rate. Charge transfer kinetics is the limiting step of the reaction [14]. At low scan rate, the ions from the electrolyte can not only occupy the available sites in surface of the active electrode material, but also can diffuse into the inner portion of the electrode material within enough time. Therefore, low scan rate can lead to higher capacitance.

Fig. 2c shows that the galvanostatic charge-discharge (GCD) tests carried out at different current densities. Fig. 2d shows corresponding specific capacitances at various current densities. At the current densities of 1 Ag^{-1} , 1.5 Ag^{-1} , 3 Ag^{-1} , 5 Ag^{-1} , 7 Ag^{-1} , 10 Ag^{-1} , 20 Ag^{-1} and 40 Ag^{-1} , the

corresponding specific capacitances were found to be 583 Fg^{-1} , 546 Fg^{-1} , 420 Fg^{-1} , 371 Fg^{-1} , 348 Fg^{-1} , 331 Fg^{-1} , 218 Fg^{-1} and 153 Fg^{-1} , respectively. At a high current density of 40 Ag^{-1} , the specific capacitance is relatively high, which confirms that the Mn_3O_4 cubes are promising electrode materials by processing a great potential utilization in fabrication of supercapacitors.

To further examine the cycling stability, the specific capacitance was valued through GCD test at a current density of 10 Ag^{-1} . Fig. 3a shows the capacitance retention is 71.8% after 1200 cycles, which indicates that Mn_3O_4 cubes exhibit a good electrochemical stability. At the beginning of this test, the specific capacitance dropped heavily because the test was not stable. Then the specific capacitance was increasing for this reason: the electrolyte was gradually penetrating into the electrodes which more electrode materials were activated and contributed to the raise of the specific capacitance. As the GCD test continued, the specific capacitance reduced mainly due to the abscission of the electrode samples.

Electrochemical impedance spectroscopy (EIS) is a powerful tool to examine the kinetics involved during the electrochemical process. According to Fig.3b, the Nyquist plot for the sample illustrates a small semicircle in the high frequency region and a straight line in the low frequency region. And the black line indicates the fitting line obtained by Zview software. The semicircle reflects the charge transfer resistance (R_{ct}). The insert is electrical equivalent circuit. It fits actual EIS spectroscopy well. The Nyquist plot shows the solution resistance R_s (0.3 Ω), charge transfer resistance R_{ct} (1.6 Ω) and Warburg resistance Z_w (1.3 Ω). Obviously, the low resistance also partly benefits from the acetylene black used as conductive additive. The sharp spike at low frequency region represents Warburg resistance (Z_w) and indicates fast speed of diffusion and adsorption of ions onto the electrode surface. The result is in good agreement with the corresponding specific

capacitance data.

4. Conclusions:

In conclusion, a simple method was adopted to fabricate Mn_3O_4 cubes with optimized electrochemical properties including high specific capacitance and long lifespan. The enhanced electrochemical performance of the active material electrode could have resulted from 3D hierarchical architecture with different sizes interlocked with each other and higher conductivity. Therefore, the properties will lead it to be a potential application for supercapacitor.

Acknowledgments:

This work was funded by the National Science Foundation of China, no. 11174103 and 11474124, and Specialized Research. Fund for the Doctoral Program of Higher Education of China, no. 20130061110012.

References

- [1] Miller JR, Simon P. Science 2008; 321: 651–2.
- [2] Simon P, Gogotsi Y. Nat Mater 2008; 7: 845–54.
- [3] Xiong XH, Wang ZX, Guo HJ, Li XH. Mater Lett 2015; 138: 5-8
- [4] Zhang Y, Feng H, Wu XB, Wang LZ, Zhang AQ, Xia TC, Dong HC, Li XF, Zhang LS. Int J Hydrogen Energ 2009; 34: 4889-99
- [5] Jiang JH, Kucernak A. Electrochim Acta 2002; 47: 2381-6
- [6] Li DW, Meng FH, Yan XL, Yang LS, Heng H, Zhu Y. Nanoscale Research Letters 2013; 8: 535-43
- [7] Wang B, Park J, Wang CY, Ahn HJ, Wang GX. Electrochim Acta 2010; 55: 6812-7
- [8] Nguyen VH, Tran VC, Kharismadewi D, Shim JJ. Mater Lett 2015; 147: 123-7
- [9] Bose VC, Maniammal K, Madhu G, Veenas CL, Raj ASA, Biju V. IOP Conf Ser Mater Sci Eng 2015; 73: 012084
- [10] Bose VC, Biju V. Mater Sci Semicon Proc 2015; 35: 1-9

- [11] Li YM, Li XM. RSC Adv 2013; 3: 2398-403
- [12] Yang LX, Zhu YJ, Tong H, Wang WW, Cheng GF. J Solid State Chem 2006; 179: 1225-9
- [13] Wang YL, Zhu L, Yang X, Shao EL, Deng XY, Liu N, Wu MH. J Mater Chem A 2015; 3: 2934-41
- [14] Gao Y, Mi LW, Wei WT, Cui SZ, Zheng Z, Hou HW, Chen WH. ACS Appl Mater Interf 2015; 7: 4311-9

Figures

Figure captions:

Fig. 1. (a) SEM images of Mn_3O_4 cubes at low magnification. The insert shows high magnification image of Mn_3O_4 . (b) XRD patterns of Mn_3O_4 . The inserts show the TEM image (b I), SAED patterns (b II), HRTEM image (b III) and Raman spectrum (b IV) of the obtained samples, respectively.

Fig. 2. (a) Cyclic voltammograms for Mn_3O_4 cubes at different scan rates. (b) Specific capacitance at different scan rates. (c) Galvanostatic charge/discharge curves of Mn_3O_4 cubes at different current densities. (d) Specific capacitance variation at different current densities.

Fig. 3. (a) Cycling behavior of the materials at a current density of 10Ag^{-1} . The insert represents the charge-discharge curves of the first ten cycles. (b) Electrochemical impedance spectrum and corresponding fitting line of Mn_3O_4 electrode. The insert is the electrical equivalent circuit.

Fig. 1

Fig. 2

Fig. 3

Figure 1

Figure 2

Figure 3