A facile synthesis of novel α -ZnMoO₄ microspheres as electrode material for supercapacitor applications

B JOJI REDDY, P VICKRAMAN* and A SIMON JUSTIN

Solid State Ionics Lab, Department of Physics, The Gandhigram Rural Institute-DU, Gandhigram 624302, India

*Author for correspondence (vrvickraman@yahoo.com)

MS received 4 April 2018; accepted 24 August 2018; published online 21 February 2019

Abstract. A mixed metal oxide, α -ZnMoO₄ is prepared in a simple, lucid and facile synthesis route as an active material for supercapacitor applications. The structural and morphological information is provided by X-ray diffraction, Fourier transform infrared, Raman and scanning electron microscopy data. The as-prepared α -ZnMoO₄ microspheres are subjected to cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy studies to examine its electrochemical behaviour in 2 M KOH aqueous electrolyte. Zinc molybdate microspheres have demonstrated very good electrochemical performance with 234.75 F g⁻¹ at 0.5 A g⁻¹ with good specific capacitance retention (82%) for sustained 1600 charge/discharge cycles.

Keywords. Zinc molybdate; microspheres; cyclic voltammetry; specific capacitance; cyclic stability.

1. Introduction

The challenges of global warming and depletion of fossil fuel deposits have impelled the world to search for alternative energy sources and the use of energy storage devices. The rapid increase of the possession of consumer electronic goods and portable devices has only doubled this cause and hence the importance of energy storage devices like supercapacitors and batteries is on the rise [1]. Supercapacitors possess high power density, good mechanical stability, cyclability and environmental friendliness which make them endearing in the research and industrial sectors. Since electrode materials play a pivotal role in making supercapacitors an effective alternative in the field of energy storage devices, novel materials and materials with different morphologies have been investigated. Carbon materials, metal oxides and mixed metal oxides have proven to be effective electrode materials for electrochemical energy storage devices. Among the metal oxides, RuO₂ showed exceptional pseudocapacitive behaviour [2], but due to its high cost, more environmental friendly and inexpensive metal oxides like NiO, MnO₂ and ZnO have shown to be favoured electrode materials for supercapacitors [3]. Therefore, research is on to explore new materials to meet the energy requirements.

Mixed metal oxides have garnered tremendous interest because of improved electronic conductivity and enhanced electrochemical activity [4]. In the field of electrochemical energy storage, mixed metal oxides are preferred to single oxides as one or more oxides help in augmenting the capacitances as they tend to be complementary in their properties [5]. Their rich redox reactions involving different ions contribute to high specific capacitance beyond conventional

materials for energy storage devices [6]. NiCo₂O₄, ZnCo₂O₄ and MnCo₂O₄ are some of the examples for such a mechanism. Recently various molybdates with a general formula MMoO₄ have been tested and tried for various applications which include photocatalytic, electrocatalytic, humidity sensing, photoelectric and electrochemical energy storage applications [7–10]. NiMoO₄, CoMoO₄ and MnMoO₄ have shown great promise for energy storage devices like Li-ion batteries and supercapacitors. Peng *et al* [11] and Zhou *et al* [12] synthesized NiMoO₄ nanostructures for supercapacitors. Wang *et al* [13] reported the synthesis of CoMoO₄/MnO₂ heterostructures for asymmetric supercapacitor applications. Xia *et al* [1] prepared CoMoO₄/graphene composites for supercapacitors. Purushottaman *et al* [14] and Senthilkumar *et al* [15] prepared MnMoO₄ nanomaterials for supercapacitor applications.

ZnMoO₄ was used in Li-ion battery technology as anode material, and found to be a proven candidate for energy storage purposes. It is found to be a potential candidate for applications such as Li-ion batteries and photocatalytics. Xue *et al* [16] prepared ZnMoO₄/graphene composite for Li-ion batteries. Ramezani *et al* [17] used it for photocatalytic applications. However, until now, no attempt has been made in exploring ZnMoO₄ as an electrode material for supercapacitor applications. ZnMoO₄ structures were prepared by various methods such as the Czochralski and Kyropoulos method, hydrothermal synthesis and full-potential linear-augmented-plane-wave method [18–21]. Zinc molybdate structure, which is more complex than that of MMoO₄ (M = Co, Mn), includes monoclinic (ZnMoO₄) and triclinic (α -ZnMoO₄) structures [18,22]. As of now, there are few reports using ZnMoO₄ for supercapacitor applications. Here, we report the synthesis of

α -ZnMoO₄ microspheres by a simple and ordinary coprecipitation technique. The as-prepared sample α -ZnMoO₄ is used as an active electrode material for supercapacitor applications.

2. Materials and methods

2.1 Materials

Ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄ · 4H₂O) (81–83%) and zinc acetate dihydrate (Zn(O₂CCH₃)₂ · (H₂O)₂) (99%) were received from Alfa Aesar; ethanol and liquid ammonia from Merck, India and deionized water were of AR grade and used as received without further purification.

2.2 Synthesis of α -ZnMoO₄

α -ZnMoO₄ was prepared by dissolving Zn(O₂CCH₃)₂ · (H₂O)₂ and (NH₄)₆Mo₇O₂₄ · 4H₂O separately. 0.21 M solution of zinc acetate was prepared by using 50 ml of ethanol and the precursor salt. 0.03 M solution of (NH₄)₆Mo₇O₂₄ · 4H₂O was prepared by dissolving the precursor salt in 50 ml of DI water. The two mixtures were allowed to stir for 30 min at room temperature. The zinc solution was slowly added to the molybdate precursor solution and allowed to stir for a few minutes and the pH of the mixed solution was adjusted to 8 by adding a few drops of NH₃. The resultant mixture was kept at 95°C and stirred for 2 h. The obtained solution was allowed to cool to room temperature, washed and dried at 80°C overnight.

2.3 Structure and morphological analyses

The as-prepared mixed metal oxide zinc molybdate was studied using X-ray diffraction (XRD) technique for the structural confirmation with the help of PANalytical XPERT-PRO diffractometer in the wavelength ($\lambda = 1.54060 \text{ \AA}$) of CuK α ₁. The morphological information was provided by scanning electron microscopy (SEM) data. Fourier transform infrared (FTIR) studies were carried out to identify the various functional groups present in the samples using a Jasco 460 plus spectrometer with the resolution of 1 cm⁻¹. Raman spectra were recorded by using an STR 500 mm Focal Length Laser Raman spectrometer, Seikei, Japan.

2.4 The fabrication of working electrode

The as-prepared sample was used as the active material for the construction of the working electrode using graphite sheet as the substrate material with active material, acetylene black and PTFE mixed in a 85:10:5 ratio and prepared as slurry in 10 μ l of ethanol. The slurry was then coated on the substrate material in a 1 $\times$ 1 cm² area of cross-section and dried for 8 h at 80°C. The mass of the active material loaded on the graphite

sheet was 1 mg. It was then used as the working electrode in a three electrode system for electrochemical supercapacitor applications.

2.5 Electrochemical performance evaluation

The electrochemical performance was evaluated using the three electrode set up, with an electrochemical workstation CHI 660D. Platinum wire was used as the counter electrode and Ag/AgCl was used as the reference electrode. 2 M KOH was used as the electrolyte for all the measurements. The specific capacitance was calculated from cyclic voltammetric studies and the chronopotentiometry technique. From the cyclic voltammetry (CV) studies, the specific capacitance of the prepared samples was calculated by using the formula:

$$C = \frac{2 \times I_{av}}{m \times \Delta v} F g^{-1} \quad (1)$$

where ' I_{av} ' is the average anodic current (A), ' m ' is the mass of the active material (g) and ' Δv ' is the scanning rate. The specific capacitance from the charge–discharge studies was evaluated according to the equation:

$$C = \frac{I \times \Delta t}{m \times \Delta V} F g^{-1} \quad (2)$$

where ' I ' is the current (A), ' Δt ' is the discharge time (s) in charge–discharge curve, ' m ' is the mass of the active material (g) and ' ΔV ' is the potential window (V). The energy density and power density can be evaluated by employing the formulae:

$$E = \frac{1}{2} C V^2 \quad (3)$$

$$P = \frac{E}{t} \quad (4)$$

where ' C ' is the specific capacitance, ' V ' is the potential window and ' t ' is the discharge time obtained from charge–discharge studies. The energy density is measured in Wh kg⁻¹ and power density in W kg⁻¹.

3. Results and discussion

3.1 XRD analysis

The crystallographic information is provided by XRD technique. The diffraction pattern, as can be seen in figure 1, confirms the formation of α -ZnMoO₄ mixed metal oxide compound with lattice parameters $a = 8.3670$, $b = 9.691$ and $c = 6.964$ matched with (JCPDS no. 35-0765). The values of 2θ at 13.2, 15.8, 16.6, 19.1, 20.2, 22.7, 24.0, 26.0, 26.4, 27.4, 28.0, 28.9, 32.1, 33.1, 33.7, 35.5, 37.2, 38.5,

Figure 1. XRD pattern for α -ZnMoO₄ microspheres.

40.2, 41.5, 43.4, 46.1, 46.6, 47.6 and 49.1° are indexed with the (*hkl*) planes ($\bar{1}10$), (110), ($\bar{1}\bar{1}0$), (011), ($\bar{1}20$), ($\bar{1}21$), (120), (012), ($\bar{1}12$), (211), (031), (201), (221), (121), ($\bar{3}10$), ($\bar{2}12$), (132), (041), ($\bar{1}40$), ($\bar{3}30$), (241), (123), (103), (231) and (321) respectively. The XRD data reveal pure α -phase formation of ZnMoO₄ microspheres without any impurity.

3.2 FTIR analysis

The complexation of the system is further provided by FTIR spectroscopy studies. Figure 2 shows the FTIR spectrum of α -ZnMoO₄ spheres in the range of 3800–400 cm⁻¹. The bands at 3167 and 1613 cm⁻¹ are ascribed to OH stretching and bending vibration of water molecules. The infrared bands at 1412 and 1278 cm⁻¹ may be due to the presence of organic impurity formation [23,24]. The vibration at 918 cm⁻¹ is due to the stretching of (MoO₄)²⁻ tetrahedra [9,25] whereas the absorption band at 818 cm⁻¹ corresponds to Mo–O stretching mode [26,27]. The observed band at 485 cm⁻¹ is assigned to the stretching vibration of Zn–O bonds [28] in α -ZnMoO₄.

3.3 Raman studies

Raman spectroscopy technique is carried out on the as-synthesized α -ZnMoO₄ microspheres, shown in the figure 3 in the spectrum and the observed bands at 915 and 869 cm⁻¹ correspond to symmetric and asymmetric stretching vibrations of MoO₄ of zinc molybdate [29]. The vibrational band observed at 768 cm⁻¹ may be due to the stretching vibration in Mo–O bonds of distorted MoO₄ tetrahedral units. The characteristic peak at 311 cm⁻¹ is likely due to bending vibrations which usually lies in the region of 300–520 cm⁻¹ [30].

Figure 2. FTIR spectrum for α -ZnMoO₄.

Figure 3. Raman analysis of zinc molybdate microspheres.

3.4 SEM analysis

The micrographs of the as-prepared α -ZnMoO₄ sample via coprecipitation technique are shown in figure 4 in different magnifications. The SEM data reveal the formation of uniform microspheres spread randomly and conjoined to one another. The spheres are found to be in the range of 800 nm size.

3.5 Electrochemical analysis

The mixed metal oxide (α -ZnMoO₄) performance was evaluated by calculating the specific capacitance from CV and galvanostatic charge/discharge from equations (1 and 2) and then measuring the impedance by using AC impedance analysis. The CV curves, from figure 5a, display clearly the pseudocapacitive behaviour of the sample with oxidation

Figure 4. SEM micrographs of conjoined microspheres of zinc molybdate.

and reduction peaks. On increasing the scan rate from 5 to 100 mV s^{-1} the oxidation and reduction peaks shift in the positive and negative directions, respectively. Two anodic and two cathodic peaks are observed for the as-prepared composite. Corresponding to the oxidation peak at -0.419 V , a reduction peak is seen at -0.377 V . Similarly the second oxidation and reduction peaks are noticed at -0.012 and 0.089 V , respectively suggesting a good reversibility of the chemical reaction. By using CV, the current is measured at various voltage sweep rates in the potential window of 0.8 V , from -0.5 to 0.3 V . The specific capacitance of the sample is measured by equation (1) which is found to be 59.7, 63.9, 68.6, 88.7, 114.2 and 159.2 F g^{-1} at 100, 75, 50, 25, 10 and 5 mV s^{-1} , respectively. The value of the specific capacitance is found to be inversely proportional to the scan rate which implies that at the higher scan rate, the ions have less time to travel while at the lower scan rate, the ions have sufficient amount of time and shows improved specific capacitance. To explore further information about the appropriateness of the as-prepared sample, chronopotentiometry technique is applied to study the charge/discharge behaviour at constant current within

the potential window of 0.8 V from -0.4 to 0.4 V . The curves (shown in figure 5b) exhibit a slight deviation from the symmetry between the charge/discharge patterns indicating pseudocapacitive contribution along with the double-layer contribution. The specific capacitance value is measured by formula (2), and it is found to be 64.37, 75.5, 91.1, 120, 172.87 and 234.75 F g^{-1} at various constant currents 10, 5, 4, 3, 2, 1 and 0.5 A g^{-1} , respectively.

The electrochemical impedance spectroscopy (EIS) analysis is generally done to examine the electrochemical properties of the as-prepared electrode material. The measured impedance spectrum is analysed on the basis of the Randle's fitting circuit (shown in the inset of figure 6a). At high frequency, the X -intercept of the real part (Z') is the sum of the resistance of the electrolyte, intrinsic resistance of the current collector and the contact resistance between the active material and the current collector. The Nyquist plot, shown in figure 6a, consists of a straight line in the low frequency region and a semicircle in the high frequency region. The straight line at an angle of 45° in the low frequency region reveals the pure capacitive character of the prepared sample. The semicircle

Figure 5. (a) CV and (b) GCD curves of the active material.

at the higher frequency region gives the information regarding the charge transfer resistance while the X -intercept of the plot indicates the solution resistance (R_s). From the Nyquist plot (shown in the inset), the diameter of the semi-circle in the higher frequency region is calculated as 3.989 Ω . The EIS study reveals that the prepared sample has favourable electrochemical behaviour with low R_{ct} value of 3.989 Ω and R_s value of 1.16 Ω .

The coulombic efficiency (η) is a measure of efficiency of charge transfer in electrochemical reaction calculated by using the equation:

$$\eta = \frac{t_d}{t_c} \times 100\% \quad (5)$$

where ' η ' is the coulombic efficiency, ' t_d ' is the discharge time (s) and ' t_c ' is the charge time (s).

The material has exhibited 100% coulombic efficiency (figure 6b) even after 1600 charge/discharge cycles. The cyclic stability of the mixed metal oxide material α -ZnMoO₄ is investigated by using chronopotentiometry technique at

Figure 6. Plots of (a) impedance analysis and (b) cyclic stability, coulombic efficiency of α -ZnMoO₄ microspheres.

10 A g⁻¹. The electrode material has shown a very good retention of specific capacitance. It showed 82% of capacity retention even after the continuous 1600 charge/discharge cycles as can be seen in figure 6b. The energy density and power density are the two important parameters to evaluate the electrochemical performance of an electrode material. They are calculated according to the equations (3 and 4) and found to be 20.808 Wh kg⁻¹ and 199.44 W kg⁻¹, respectively.

4. Conclusions

A facile and lucid synthesis of α -ZnMoO₄ microspheres is attempted successfully. XRD diffraction pattern confirms the formation of α -ZnMoO₄ with good crystallinity and phase purity. The information of the well-formed conjoined microspheres of zinc molybdate is provided by SEM analysis. FTIR and Raman studies validate the results obtained by XRD. Zinc molybdate as an electrode material for supercapacitors has shown good electrochemical behaviour i.e., a specific capacitance of 234.75 F g⁻¹ at 0.5 A g⁻¹ and cyclic stability of

82% sustained for 1600 charge/discharge cycles. As a consequence, the as-prepared α -ZnMoO₄ mixed metal oxide has shown great potential as an electrode material for supercapacitor applications and it can be further explored as a composite with carbon and other metal oxides improving its stability and specific capacitance.

References

- [1] Xia X, Lei W, Hao Q, Wang W and Wang X 2013 *Electrochim. Acta* **99** 253
- [2] Vellacheri R, Pillai V K and Kurungot S 2012 *Nanoscale* **4** 890
- [3] Wang Y, Guo J, Wang T, Shao J, Wang D and Yang Y-W 2015 *Nanomaterials* **5** 1667
- [4] Xue R, Hong W, Pan Z, Jin W, Zhao H, Song Y *et al* 2016 *Electrochim. Acta* **22** 838
- [5] Jayalakshmi M and Balasubramanian K 2009 *Int. J. Electrochem. Sci.* **4** 571
- [6] Yuan C, Wu H B, Xie Y and Lou X W 2014 *Angew. Chem. Int. Ed.* **53** 1488
- [7] Xiao W, Chen J S, Li C M, Xu R and Lou X W 2010 *Chem. Mater.* **22** 746
- [8] Singh R N, Singh J P and Singh A 2008 *Int. J. Hydrogen Energy* **33** 4260
- [9] Kianpour G, Soofivand F, Badiei M, Salavati-Niasari M and Hamadani M 2016 *J. Mater. Sci.: Mater. Electron.* **27** 10244
- [10] Cherian C T, Reddy M V, Haur S C and Chowdari B V R 2013 *ACS Appl. Mater. Interfaces* **5** 918
- [11] Peng S, Li L, Wu H B, Madhavi S and Lou X W (David) 2014 *Adv. Energy Mater.* 1401171
- [12] Zhou C, Yang W, Zeng G, Lei Y, Gu L, Xi X *et al* 2015 *Chem. Asian J.* **10** 1745
- [13] Wang J, Liu S, Zhang X, Liu X, Liu X, Li N *et al* 2016 *Electrochim. Acta* **213** 663
- [14] Purushottaman K K, Cuba M and Muralidharan G 2012 *Mater. Res. Bull.* **47** 3348
- [15] Senthilkumar B, Selvan R K, Meyrick D and Minakshi M 2015 *Int. J. Electrochem. Sci.* **10** 185
- [16] Xue R, Hong W, Pan Z, Jin W, Zhao H, Song Y *et al* 2016 *Electrochim. Acta* **222** 838
- [17] Ramezani M, Hosseinpour-Mashkani S M, Sobhani-Nasab A and Ghasemi Estarki H 2015 *J. Mater. Sci.: Mater. Electron.* **26** 7588
- [18] Zhang G, Yu S, Yang Y, Jiang W, Zhang S and Huang B 2007 *J. Cryst. Growth* **312** 1866
- [19] Gironi L, Arnaboldia C, Beeman J W, Cremonesi O, Danevich F A, Degoda V Y *et al* 2010 *J. Instrum.* **5** 11007
- [20] Lv L, Tong W, Zhang Y, Su Y and Wang X 2011 *J. Nanosci. Nanotechnol.* **11** 9506
- [21] Ivleva L I, Voronina I S, Berezovskaya L Y, Lykov P A, Osiko V V and Iskhakova L D 2008 *Crystallogr. Rep.* **53** 1087
- [22] Abrahams S C 1967 *J. Chem. Phys.* **46** 2052
- [23] Liang Y, Liu P, Li H B and Yang G W 2012 *Cryst. Growth Des.* **12** 4487
- [24] Hardcastle F D and Wachs I E 1990 *J. Raman Spectrosc.* **21** 683
- [25] Bhattacharya S, Kar T, Bar A K, Roy D, Graca M P F and Valente M A 2011 *Sci. Adv. Mater.* **3** 284
- [26] Subcik J, Koudelka L, Mosner P, Montagne L, Revel B and Gregora I 2009 *J. Non-Cryst. Solids* **355** 970
- [27] Keereeta Y, Thongtem T and Thongtem S 2012 *Mater. Lett.* **68** 265
- [28] Jia R, Zhang Ch and Xu J 2013 *Adv. Mater. Res.* **624** 51
- [29] Aleksandrov L, Komatsu T, Iordanova R and Dimitriev Y 2011 *Opt. Mater.* **33** 839
- [30] Nakamoto V K 1963 *Infrared spectra of inorganic and coordination compounds* (New York, London: John Wiley & Sons, Inc.)