Synthesis And Characterization Of Manganese Molybdate For Super Capacitor Applications

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Abstract:

One-dimensional á-$MnMoO_4$ nanorods were prepared by one-step facile precipitation technique. The obtained powder was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) for analyzing structural and morphological features. The capacitive behaviour was investigated by cyclic voltammetry (CV), charge- discharge (CD) cycling and electrochemical impedance spectroscopy (EIS) studies using 2 M NaOH electrolyte at ambient atmosphere. From the cyclic voltammogram it was identified that the pseudocapacitance arises through the reversible faradic reactions of $Mn^{3+/}Mn^{2+}$ ionic species. The á-MnMoO4 electrode exhibited a capacitance of 145 F/g at a constant discharge current density of 1.0 A/g. The a-MnMoO4 shows capacitance retention of about **90.5**% of its initial capacitance suggesting the good cyclability of the prepared material for supercapacitor applications.

Keywords: Precipitation technique; á-$MnMoO_4$; Nanorods; Charge/discharge; Supercapacitors.

1. Introduction

In recent years, environmentally friendly, low-cost and high-electrochemical performance with quicker charge/discharge rates of energy storage devices have been attracted and substantial attention to meet the next-generation growing demands in the modern society for various applications [1]. Therefore, intense research has been carried out to develop the various renewable energy resources due to the rapid depletion of fossil fuels and increasing environmental issues [2-4]. Among the available renewable energy resources, supercapacitors (SCs) also known as electrochemical capacitor, have attracted as a best power sources for all portable electronic devices, electric vehicles, instant switches, backup power supply, motorstarter, industrial power and energy management, etc., because of their higher specific capacitance, high power density, faster charge/ discharge rate, longer life time, low-maintenance compared with conventional batteries and traditional dielectric capacitors [5-7]. On the basis of energy storage mechanism, SCs can be classified into two types such as electric double-layer capacitors (EDLC's) and pseudocapacitors. Generally, an EDLC's follows the non-faradaic process, which commonly uses high surface area carbonaceous materials as electrode. Whereas, pseudocapacitors follows the reversible faradaic process in the redox active transition metal oxides and conducting polymers as electrode materials [8]. As we know, ruthenium oxide (RuO_2) is widely accepted as best electrode material for pseudocapacitors because of its high specific capacitance, high conductivity and good environmentally stability. Though, it is expensive, low abundance and toxic nature has limited its utilization of commercial applications. Therefore, many efforts have been employed to develop various transition metal oxides such as MnO_2 [9-10], CoO_3 [11], NiO [12], MoO_3 [13] with excellent electrochemical behaviors are intensively investigated as alternative electrode materials forsupercapacitors.

Recently, the mixed binary/ternary transition metal oxides, such as $NiMoO_4$ [14], $CoMoO_4$ [15], $MnMoO_4$ [16], with multiple oxidation states have attracted intense interest for their potential application

than single component oxides, due to the multiple redox reactions, which may facilitate to improve the higher electrochemical performances. Furthermore, $MnMoO_4$/$CoMoO_4$ complex nanomaterials and $CoMoO_4$-$NiMoO_4.xH_2O$ bundles have been reported to exhibit an enhanced level of supercapacitor activities [17, 18]. Among them, $MnMoO_4$ possess high specific capacitance has been attracted to be a promising electrode material for high performance supercapacitors because of its better electrochemical performances arising from high electrochemical activity of the manganese ions, low-cost, low-toxicity and easily abundance[16].

In this work, we have prepared á-MnMoO4 using a simple precipitation technique. The major objective of this work is to attain improved capacitance through the use of a simple but novel synthetic procedure for manganese molybdate. Among the range of reported synthetic methods for MnMoO4, including solid-state reaction [19], hydrothermal [20-24], liquid phase [24] and combustion syntheses [25, 26], precipitation is one of the most simple, low-cost, and environmental friendly methods. The physicochemical and electrochemical (capacitive) properties of precipitated á-MnMoO4 are reportedhere.

2. Experimental

2.1. Materials

Sodium molybadate dihydrate [$Na_2MoO_4.2H_2O$], manganese nitrate tetrahydrate [$Mn(NO_3)_2.4H_2O$] sodium hydroxide [NaOH] and ethanol [C_2H_5OH] were received from Merck. Carbon block, polyvinylidine difluoride (PVdF) and N-methyl-2-pyrrolidone (NMP) were received from Sigma Aldrich and used for electrode fabrication.

2.2. Synthesis of á-$MnMoO_4$nanorods

á-$MnMoO_4$nanorods were synthesized by a simple one-step facile precipitation technique. In the typical synthesis process, 0.01mol of $Mn(NO_3)_2.4H_2O$ and 0.01mol of $Na_2MoO_4.2H_2O$ were dissolved separately in 50 ml of ethanol and DI water under constant stirring for 30 min at room temperature. Later, the clear solution of sodium molybdate was added slowly into the homogenous manganese nitrate solution under constant stirring at room temperature. After stirring for an hour, grey-colored precipitates were collected by filtration with DI water and ethanol for several times, and dried in hot air oven at 60 °C for 24 h. Finally, the dried powder was calcined at 500 °C for 5 h in air atmosphere to obtain á- $MnMoO_4$ nanorods.

2.3. Characterizationtechniques

Powder X-ray diffraction (XRD) patterns are recorded using X'pert PRO MPD, PANalytical X-ray powder diffractometer employing Cu Ká radiation (ë =0.15406 nm), angles ranging from 15^O to 80^O with step size 0.02. The average crystallite size of prepared sample is calculated by using Scherrer's formula. The surface morphological images of the prepared samples were taken by a field-emission scanning electron microscope (FE-SEM, Hitachi SU6600) with an accelerating voltage of 15 kV.

2.4. Electrochemicalmeasurement

The electrochemical behaviour of the MnMoO4 electrode was characterized by cyclic voltammetry, galvanostatic charge-discharge tests and electrochemical impedence performed at PARSTAT MC Multi-Channel Electrochemical workstation. A three-electrode system consisting of a working electrode, platinum wire and Ag/AgCl as counter and reference electrodes were used. The working electrode was prepared by mixing a-MnMoO4 powder, carbon black as a conducting agent and polyvinylidine difluoride (PVDF) as a binder with the mass ratio of 80:15:5. Then this mixture was grinded homogeneously with NMP and coated on the Ni foam substrate (1 x 1 cm^2) current collector and dried at 80^oC for overnight. The mass loading of the material on single electrode was about 2.43 mg. All the electrochemical measurements were carried out in 2 M sodium hydroxide electrolyte at room temperature.

3. Results andDiscussion

3.1 XRD

The XRD pattern of á-$MnMoO_4$ synthesized by simple one-step facile precipitation technique and calcined at 500^oC for 5 h is shown in figure 1. The observed diffraction peaks are in good agreement with the standard monoclinic á-$MnMoO_4$ (JCPDS card No. 01-072-0285). The calculated lattice parameters, a = 10.5479 ± 0.0215 Å, b = 9.5480 ± 0.002 Å, c = 7.1346 ± 0.0054 Å, â = 106.3 ±

0.046° are consistent with the reported values [27] confirmed the formation of pure monoclinic á-$MnMoO_4$ phase with no detectable impurities. Moreover, the presence of the major (220) reflection in the X-ray diffractogram indicates the presence of á-phase.

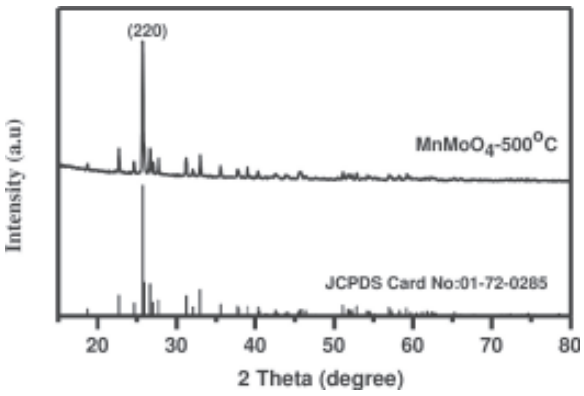
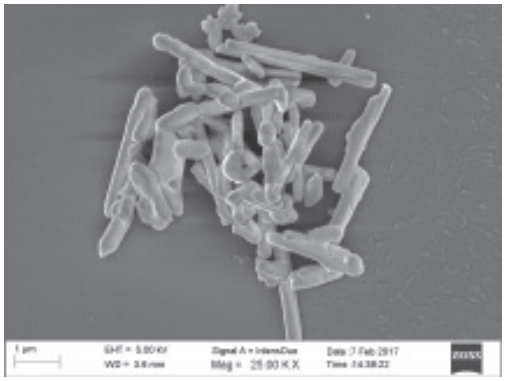
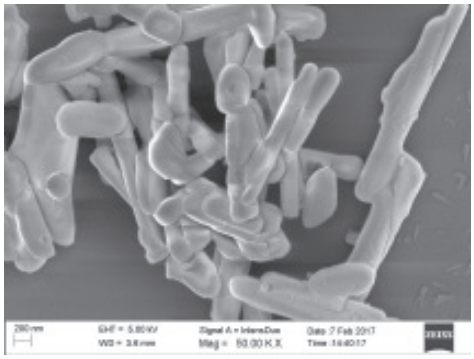


Figure 1: XRD pattern of á-$MnMoO_4$ powder calcined at 500°C for 5 h in air atmosphere

3.2 SEM

The surface morphology of the synthesized MnMoO4 is examined using field emission scanning electron microscopy (FE-SEM) and is shown in Fig. 2. The FE-SEM micrographs revealed the presence of nanorods in the range of 100 to 400 nm in diameter and 1mm inlength.





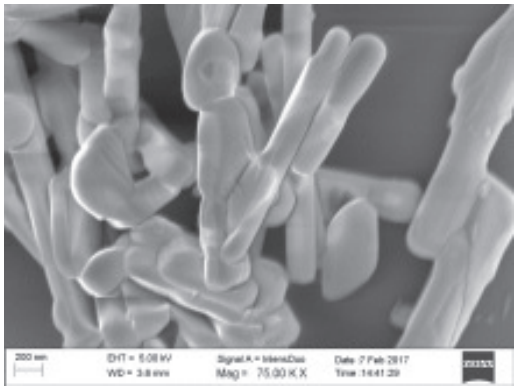


Figure 2: FESEM images of á-$MnMoO_4$ powder at 500°C for 5 h in air atmosphere

3.3. Electrochemical properties of á-$MnMoO_4$

In order to evaluate the electrochemical properties of the prepared a-MnMoO4, at first, we have studied the cyclic voltammetric (CV) analysis using 2 M NaOH electrolyte in the potential range of 0 – 0.6 V. Fig. 3(a) shows the CV curves of MnMoO4 at different scan rates from 5 mVs^{-1} to 100 mVs^{-1}. The CV curves shows the presence of a pair of redox peak which is attributed to the transition of Mn(ÀÀ)/ Mn(ÀÀI) [17]. This evidences the pseudocapacitive nature of the a-MnMoO4. With an increase in scan rate, the voltammetric current gradually increases which suggests that the kinetics of the interfacial faradaic redox reactions and the rates of electronic and ionic transport are rapid enough in the presentscan

[17].

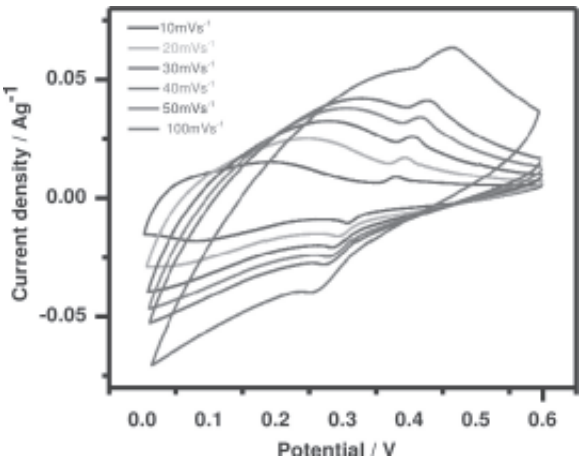
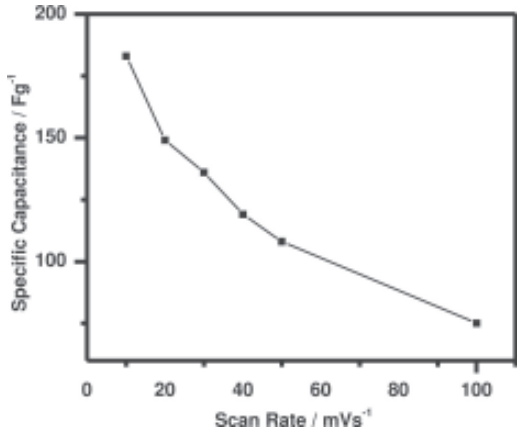


Figure 3 (a): CV curves of $MnMoO_4$ electrode at different scan rate from 10 to 100 mVs^{-}

The specific capacitances (Csp) of the a-MnMoO4 nanorods were calculated from the CV curve using the given equation [1].

$$Csp = \int(i \, . \, dv) / (S \, . \, Ov.m) \quad (1)$$

Where, C_{sp} is the specific capacitance, $\int$ i.dv is the integral area of the CV curve, S is scan rate (mV s^{-1}), OV is the potential window, m (g) is the loaded mass of the activematerial.



Scan Rate / mVs^{-1}

Figure 3 (b): Variation of specific capacitance with respect to the scan rate

Fig. 3(b) shows the variation of specific capacitance with respect to the scan rate.A specific capacitance of about 183 Fg-1 was achieved for a-MnMoO4 nanorods at a lower scan rate of about 5mVs^{-1}.With an increase in scan rate, the specific capacitance is decreased which is due to the fact that at higher scan rates, the electrolyte ions are not able to utilize the active material completely[28].

Fig. 4(a) illustrates that the galvanostatic discharge curves of the synthesized MnMoO4 at the various current densities. The observed quasi-symmetric charge-discharge profile suggests that the pseudo capacitive behaviour of the material. The specific capacitances were calculated using the equation [2].

$$Cs = (I \, Ot) / (mOV) \quad (2)$$

Where, OV is the potential window, m (g) is the loaded mass of the active material, I (A) is the discharge current densities and "t (s) is the discharge time.

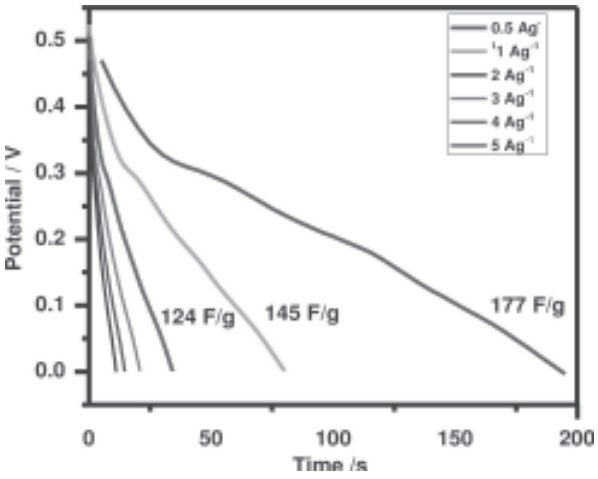


Fig. 4. (a) Galvanostatic discharge curves of a-MnMoO4 with differentdischarge currentdensities.

The Variation of specific capacitance with respect to discharge current densities are shown in fig. 4 (b). The observed quasi-symmetric charge-discharge profile again demonstrates the pseudocapacitive behavior. The calculated SC is 177, 145, 124, 113, 106 and 100F/g at current densities of 0.5, 1, 2, 3, 4 and 5 A/g respectively.

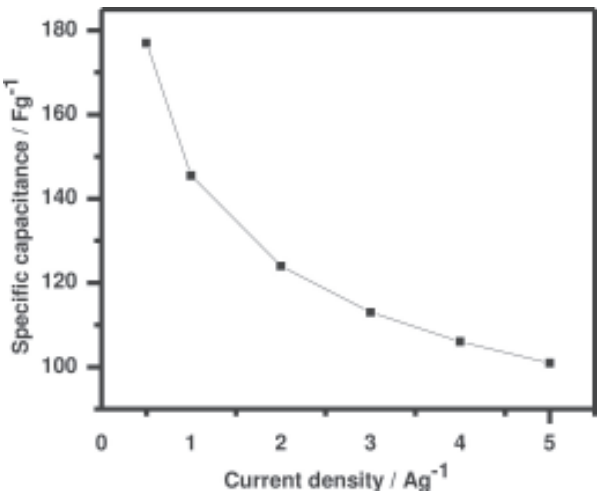


Fig. 4. (b) Variation of specific capacitance with respect to discharge current density..

With an increase in current density, the SCs of individual electrode decreases due to an increase in ohmic drop (ionic resistivity) and incomplete material utilization [21, 35, 36]. The observed capacitance is high when compare with the reported $MnMoO_4$ (9.7 F/g at 1 A/g) nanocomposite [10]. In general, the electrochemical capacitive performance of materials

is largely influenced by its crystal structure, size, shape, morphology, surface area, porosity and electronic conductivity [29-33]. It is well documented that different structural phases yield different specific capacitances [29, 30]. In the present study we have prepared pure single phase á-$MnMoO_4$. It is certainly possible that the observed better capacitance performance relative could be attributed to the purity of the phase. As well as the highly crystalline nature of the synthesizedá-$MnMoO_4$ (calcinedat 500^oC for 5h) may enhance the charge carrier mobility, which would in turn enhance the capacitance [29, 32]. In addition, we have observed the well defined reversible peaks, which is well matched with the CV curves of combustion synthesized $MnMoO_4$ [21]. Similar type of redox peaks were observed for other metal molybdates also [11, 19-21].

In order to understand the charge storage mechanism in a MnMoO4 nanorods, the EIS study has been performed in the frequency range from 0.01 Hz to 10 kHz and is resented as Nyquist plot as shown in Fig. 5. It shows the presence of a semi-circle at the higher frequency range, which is due to the capacitance in parallel with the ionic charge transfer resistance (Rct = 4.3ϕi). In addition to this, the presence of linear part at the low frequency region or the slope of the 45^o portion is called as Warburg resistance (Zw) is also observed which is due to the frequency dependent ion diffusion or transport in the electrolyte to the electrode surface [34].

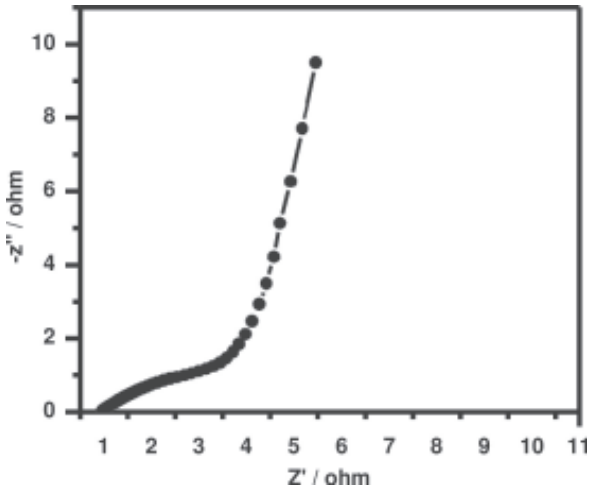


Fig. 5. Electrochemical impedance spectroscopy of MnMoO4 electrodes represented as Nyquist plot.

The long-term cyclic stability of electrode material is an important criterion for supercapacitor applications [34]. The cyclic stability test of synthesized a-MnMoO4 usingGCD

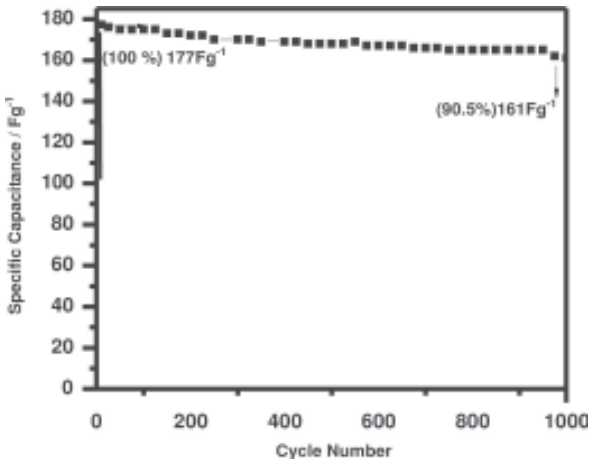


Fig 6. The specific capacitance retentions with respect to number of cycles.

measurement (at a current density of 1 Ag^1) for 1000 cycles. Fig. 6 showed the specific capacitance retentions with respect to number of cycles. About 90.5% of initial capacitance was retained even after 1000 cycles which demonstrates that the good cyclic stability of synthesizeda-MnMoO4.

4. Conclusions

In conclusion, a facile approach for the preparation of a-MnMoO4 nanorods has been demonstrated. The XRD analysis revealed the high crystallinity of the prepared a-MnMoO4 nanorods. The electrochemical studies using CV and EIS measurements suggested the pseudocapacitive nature of the a-MnMoO4 nanorods. A maximum specific capacitance value of 177 $Fg^{-1}$was obtained from the galvanostatic charge-discharge analysis at the current density of 0.5 Ag^{-1}. The a-MnMoO4 shows capacitance retention of about 90.5% of its initial capacitance after 1000 cycles at the current density of 1 Ag^{-1} suggesting the good cyclability of the prepared material for supercapacitor applications. The overall results suggested that the synthesized a-MnMoO4 is a promising electrode material for supercapacitor applications

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