Journal of Electroanalytical Chemistry 797 (2017) 78–88

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

A facile sonochemical assisted synthesis of α-$MnMoO_4$/PANI nanocomposite electrode for supercapacitor applications

J. Yesuraj[a,*], Viswanathan Elumalai[b], Muthuraaman Bhagavathiachari[a], Austin Suthanthiraraj Samuel[a], Elanthamilan Elaiyappillai[c], Princy Merlin Johnson[c]

[a] Department of Energy, University of Madras, Guindy Campus, Chennai 600 025, India
[b] Department of Chemistry, Chevron Science Center, University of Pittsburgh, Pittsburgh, PA 1526, United States
[c] PG and Research Department of Chemistry, Bishop Heber College, Tiruchirapalli 620 017, India

ARTICLE INFO

Keywords:
Sonochemical
α-$MnMoO_4$/PANI
Nanorods
Charge/discharge
Supercapacitors

ABSTRACT

One-dimensional porous α-$MnMoO_4$ nanorods and polyaniline (PANI) wrapped α-$MnMoO_4$ based hybrid (α-$MnMoO_4$/polyaniline as inorganic/organic) nanocomposite electrode materials were prepared by sonochemical and in-situ oxidative polymerization techniques, respectively. The compositional and structural details of α-$MnMoO_4$ phase were confirmed using X-ray diffraction (XRD analysis), confocal Raman spectroscopy and Fourier transform infrared spectroscopy. The formation of nanostructured morphology has been elucidated through field emission scanning electron microscopy (FE-SEM), and high resolution transmission electron microscopy (HR-TEM). The electrochemical properties have been examined using cyclic voltammetry (CV), galvanostatic charge-discharge, cycling stability and electrochemical impedance spectroscopy. The X-ray diffraction pattern of α-$MnMoO_4$/PANI nanocomposite electrode material showed the feasibility of reduction of α-$MnMoO_4$ crystallinity by the addition of 0.3 ml of aniline monomer wrapped over α-$MnMoO_4$ nanorods. Morphological images of newly prepared bare α-$MnMoO_4$ and α-$MnMoO_4$/PANI nanocomposites formed with the addition of various amounts (0.1 ml, 0.2 ml & 0.3 ml) of aniline monomer exhibit a rod like structure with porous nature and also depict the variation of polyaniline wrapping over α-$MnMoO_4$ nanorods. The α-$MnMoO_4$/PANI nanocomposite material obtained upon addition of 0.3 ml of aniline monomer exhibits a high specific capacitance value of 396 F/g at a scan rate of 5 mV/s and good cyclic stability up to 500 cycles at 100 mV/s. All the experimental results revealed that newly prepared hybrid α-$MnMoO_4$/PANI nanocomposite with the addition of 0.3 ml of aniline monomer acts as a promising electrode material for high performance supercapacitors. An attempt also has been made to explain the enhancement of electrochemical property of α-$MnMoO_4$ through density functional theory calculation and preliminary results are appropriately presented.

1. Introduction

In recent years, environment-friendly, low-cost and high-electrochemical performance coupled with quicker charge/discharge rates of energy storage devices have attracted 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 various renewable energy resources due to the rapid depletion of fossil fuels and increasing environmental issues [2–4]. Among the various renewable energy resources, supercapacitors (SCs) also known as electrochemical capacitors, have attracted as a best power sources for all portable electronic devices, electric vehicles, instant switches, backup power supply, motor starter, 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 may be classified into two types such as electric double-layer capacitors (EDLCs) which follow the non-faradaic process and pseudocapacitors that follow the reversible faradaic process [8]. Interestingly, ruthenium oxide (RuO_2) is widely accepted as the best electrode material for pseudocapacitors because of its high specific capacitance, high conductivity and good environmental stability. Though, it is expensive, low abundance and toxic natures have limited its utilization for 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] and MoO_3 [13] exhibiting excellent electrochemical behaviors and intensively investigated as alternative electrode materials for supercapacitors.

* Corresponding author.
E-mail address: yesurajjerald@gmail.com (J. Yesuraj).

http://dx.doi.org/10.1016/j.jelechem.2017.05.019
Received 22 November 2016; Received in revised form 9 March 2017; Accepted 15 May 2017
Available online 16 May 2017
1572-6657/

Recently, mixed binary/ternary transition metal oxides with multiple oxidation states have attracted intense interest for their potential application rather than single component oxides, due to the feasibility of multiple redox reactions, which may facilitate to improve the electrochemical performance [14]. Among them, $MnMoO_4$ possessing an appreciably high specific capacitance value has attracted to be a promising electrode material for high performance supercapacitors due to its better electrochemical performance arising from enhanced electrochemical activity of manganese ions apart from low-cost, low-toxicity and easily abundance [15–18]. On the other hand, it has a poor electrical conductivity, which may limit the electrochemical performance and power density [19]. In order to overcome the aforementioned issues, various approaches have been tried to improve the electrochemical performance, electrical conductivity, cyclic stability of $MnMoO_4$ transition metal oxides by wrapping with conducting polymers (polyaniline, polypyrole and polythiophene) as well as carbon based materials (activated carbon, carbon nanotubes and graphene) [20]. Since $MnMoO_4$ has been shown keen interest towards design of supercapacitors in the recent past, it is important to break bottle neck research challenges through relevant laboratory research endeavours. On contrary to supercapacitor application, $MnMoO_4$ has also been explored as a multiferroic material, since it exhibits the coexistence of ferroelectric and magnetic ordering features. It has been reported that the coupling between magnetic and ferroelectric properties may be week [21]. The new approach of hybrid composite from PANI and $MnMoO_4$ makes cumbersome the issue related to magnetic and non-magnetic domains and associated exchange interactions. Considering their fundamental and technological importance, it is essential to understand the low lying mechanism which drives the charge transport. The theoretical approach would be beneficial to explore the origin of major driving force responsible for conduction.

Among the variety of aforementioned conducting polymers, polyaniline is known to be an interesting conductive polymer for supercapacitor applications due to its high conductivity, high storage ability, good thermal and environmental stability apart from high redox activity and capacitive current. Nevertheless, polyaniline has contain drawbacks such as poor cycling stability, since redox sites of the polymer backbone get collapsed during charge/discharge cycles thereby limiting the number of cycles [22–24]. Das et al. [25] reported that polyaniline-wrapped one-dimensional $CoMoO_4$ electrode material presented a high specific capacitance of 380 F/g at the current density of 1 A/g. Furthermore, many reports are also available involving transition metal oxides hybridized with a suitable conducting polymer for supercapacitor applications [26–28].

Nowadays, ultrasound has become an efficient and important tool for the synthesis of various novel materials with many tailor-made properties and hence it could yield smaller and higher surface area nanomaterials than those reported earlier based on other methods such as

sol-gel, hydrothermal, combustion, solid-state reactions and co-precipitation methodologies [29]. Due to its distinctive reaction effects, ultrasound is widely considered as an efficient source, in the fields of organic, inorganic and nanotechnology for the design and fabrication of different types of nanostructured materials [30–32].

To date, there are limited reports on the development of one dimensional (1-D) porous pure α-$MnMoO_4$ nanorods and nanocomposite α-$MnMoO_4$/PANI electrode materials by means of sonochemical and in-situ oxidative polymerization techniques. Hence, the authors are motivated to develop porous pure α-$MnMoO_4$ and different concentrations of polyaniline wrapped α-$MnMoO_4$/PANI nanocomposite electrode materials for supercapacitor applications. The physical and electrochemical properties of pure α-$MnMoO_4$ nanorods and composite α-$MnMoO_4$/PANI electrode materials have been studied in detail. In addition to experimental studies, an attempt has also been made to correlate the effect of polyaniline addition through local density approximation (LDA) based theoretical studies and the relevant results are presented and discussed.

2. Experimental

2.1. Materials

Aniline monomer (99.5% purity) and analar grade ammonium persulphate ($NH_4S_2O_8$) were directly procured from Merck whereas sodium molybdate dihydrate ($Na_2MoO_4{\cdot}2H_2O$), manganese acetate tetrahydrate ($MnC_2H_6O_4{\cdot}4H_2O$) and ethanol were purchased from SRL (India). Carbon black, polyvinylidine difluoride (PVdF), *N*-methyl-2-pyrrolidone (NMP), nickel foil (0.025 mm thickness) and sodium sulfate (Na_2SO_4) salt were obtained from Sigma Aldrich and used as procured for electrode fabrication.

2.2. Preparation methods

2.2.1. Synthesis of α-$MnMoO_4$ nanorods

One-dimensional α-$MnMoO_4$ nanorods were prepared by sonochemical method via the reaction mechanisms of manganese acetate and sodium molybdate with the aid of ultrasound irradiation [33]. In the typical synthesis process, firstly, 0.3 M of manganese acetate tetrahydate and 0.3 M of sodium molybdate dihydrate were dissolved separately in 30 ml of ethanol and de-ionized (DI) water under constant stirring for 20 min at room temperature. Later, the clear solution of sodium molybdate was added slowly into the homogenous manganese acetate solution under constant stirring at room temperature. The resultant mixed solution was subjected to the ultrasonic irradiation with the aid of a digital ultrasonication bath for 0.5 h at a constant temperature of 60 °C. After the reaction, the obtained grey-colored precipitates were collected by centrifugation and washed 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 annealed at 500 °C for 3 h in air atmosphere so as to obtain pure α-$MnMoO_4$ nanorods.

2.2.2. Synthesis of α-$MnMoO_4$/PANI nanocomposites

The set of three different composites of polyaniline (PANI) wrapped α-$MnMoO_4$/PANI nanocomposite electrode materials were prepared by in-situ oxidative polymerization technique with the addition of varying amounts of 0.1 ml, 0.2 ml and 0.3 ml of aniline monomer, respectively. The complete synthesis process of α-$MnMoO_4$/PANI nanocomposites may be outlined as follows: At first, freshly prepared 0.1 g of α-$MnMoO_4$ nanorods were fully dispersed in 20 ml of DI water by using ultrasonicator bath for 0.5 h at room temperature, and then transferred to an ice bath (< 5 °C). Later, various amounts of 0.1 ml, 0.2 ml and 0.3 ml of aniline monomer, were added separately into the α-$MnMoO_4$ nanorods suspension under constant stirring for 0.5 h. Subsequently, 0.4 g of ammonium peroxy disulfate (APS) was dissolved in 10 ml of DI water separately, and added drop by drop into the above mentioned mixed solutions under vigorous stirring for 5 min. The resultant mixed solutions were allowed to perform the polymerization process in a refrigerator for 24 h. Finally, the obtained black-colored solutions were suction-filtered using DI water, and dried at 60 °C in a hot air vacuum oven for 12 h to obtain the appropriate α-$MnMoO_4$/PANI nanocomposite materials. For the sake of clarity, the set of three different concentrations of polyaniline wrapped nanocomposite α-$MnMoO_4$/*x* PANI, (*x* = 0.1, 0.2 and 0.3 ml) materials were labeled as MMPA-1, MMPA-2, and MMPA-3, respectively. Similarly, pure polyaniline polymer was also prepared following the same procedure by the addition of 0.3 ml of aniline monomer.

2.3. Characterization techniques

The powder X-ray diffraction patterns of all the freshly-prepared pure α-$MnMoO_4$, PANI and α-$MnMoO_4$/PANI nanocomposite materials were recorded from 2θ = 10 to 80° using PANalytical X-pert PRO diffractometer with Cu-Kα radiation (λ = 0.154060 nm, 40 kV and 30 mA) at a step size of 0.07° s^{-1}. The average crystallite sizes of all the