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Synthesis and characterization of nanostructured ternary zinc manganese oxide as novel supercapacitor material

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HIGHLIGHTS

- Novel electrode material for supercapacitor: Mn-based Ternary metal oxide.
- $ZnMn_2O_4$ is synthesized by cost effective urea combustion technique.
- Unique architecture consisting of homogeneous pores (10–30 nm) distribution.
- Homogeneous pores distribution plays vital role over surface area.
- Nano-$ZnMn_2O_4$ exhibits specific capacitance of 160 Fg^{-1}.

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ABSTRACT

Nanostructured $ZnMn_2O_4$ is prepared by easy and cost effective urea combustion method, and characterized by X-ray diffraction, field-emission scanning electron microscope, transmission electron microscope and surface area analyzer. The prepared $ZnMn_2O_4$ (ZMO) is found to be crystalline and mesoporous in nature with homogenously distributed pores. The supercapacitive properties of the synthesized materials are studied using cyclic voltammetry, galvanostatic charge–discharge cycling and electrochemical impedance spectroscopy in 2 M KOH solution employing three-electrode system. The FESEM analysis reveals nearly spherical morphology of ZMO which is found to be beneficial for improved supercapacitive performance. Cyclic voltammetry shows unsymmetrical charge–discharge curves with the capacitance value of 160 (±5) Fg^{-1}. The galvanostatic charge–discharge cycles exhibit good electrochemical stability of ZMO. The coulombic efficiency of ZMO is found to be almost 100% till 500 charge–discharge cycles. The electrochemical impedance spectroscopy studies confirm the structural stability and further complement the findings of cyclic voltammetry and galvanostatic cycling. The improved supercapacitive behavior of nano ZMO is ascribed to the unique morphology that consists of interlinked almost spherical nano particles. This interlinked assembly of ZMO nano particles with porous structure (homogeneous pores 10–30 nm) probably facilitates the ion kinetics at electrode-electrolyte interface.

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1. Introduction

Energy crises, global warming, emission of green house gases are known to be the origin of the greatest threats to the human being, so modern world have started to give considerable attention not only to produce the clean, and sustainable energy, but also to invent a sustainable energy storage device. Those devices can efficiently store energy from intermittent renewable energy sources like sun, wind, and hydro power and, can supply the same whenever it is required [1]. Supercapacitors, also known as electrochemical capacitors have been known for over fifty years and are considered as one of the potential energy storage systems in addition to the batteries. Supercapacitors may be distinguished by several criteria such as the nature of the electrode material, used electrolyte and cell design [2]. Mainly, research is being focused on development of different electrode materials. In this series,

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transition metal oxides and hydroxides are found to exhibit high supercapacitance (Theoretical > 1000 Fg^{-1}) via storage mechanism of double layer and pseudo-capacitance arising from fast and reversible faradic reaction involving motions of ions and electrons into/from the material [3–6]. Particularly, RuO_2 received considerable attention in the past. However, its commercial acceptability is hindered due to its high cost. In addition to cost, commercial viability of any material is decided by its abundance nature and most importantly its environmental compatibility. Considering this, many metal oxides (binary) in different shape and sizes have been investigated as electrode material for supercapacitor [7–12]. Recently, ternary metal oxides are emerged as novel electrode material. For example, Fe-based spinel $NiFe_2O_4$ and its composite with PEDOT were synthesized and studied as supercapacitor electrode material. The electrochemical performance of $NiFe_2O_4$ was found to be dependent on crystallite size, pore size and their distributions [13]. On the other hand, $MnFe_2O_4$ in spherical shape, prepared by solvothermal method exhibited the specific capacitance of 80 Fg^{-1}, whereas, co-precipitation routed $MnFe_2O_4$/carbon composite delivered specific capacitance in the range of 14 Fg^{-1} to 50 Fg^{-1} depending upon the calcination temperature of precursors and crystallite size of the final product [14]. From above discussion, it is clearly noticed that the supercapacitance (as a consequence of double layer storage and redox reaction) highly depends upon the nature of electrode material, its morphology, pore size and its distribution. These parameters can be tuned easily by employing different synthetic procedures. Thus, synthetic procedures become crucial to get improved electrochemical performance of any given material. Following the ongoing research trends, another ternary spinel, that may be studied as electrode material for supercapacitor is $ZnMn_2O_4$ (ZMO). ZMO may be considered as commercially viable material due to its low cost, abundance and environmental compatibility. Further, ZMO is expected to follow the similar reaction mechanism as of MnO_2 i.e. surface adsorption of electrolyte cations (K^+ in case of KOH) on surface and/or intercalation/de-intercalation of cations in the empty voids of spinel structure ZMO during redox reaction. ZMO is a promising functional material that has been widely studied as Li-ion battery electrode material. So, it is expected that ZMO nanostructures serving as promising Li-ion battery active material may also have a superior capacitive performance as compared to above discussed oxides. To the best of our knowledge, there is no information about ZMO as electrode for supercapacitor. So far, ZMO in different shapes and sizes have been synthesized by several methods, including hydrothermal, solvothermal, pyrolysis, electrospinning technique and template methods [15–17]. These methods are relatively complicated, time consuming, and involve a sophisticated instrument that results fewer yields. Therefore, a method which could be simple and less time consuming, and can be scaled up for industrial application, is highly demanding. To address this, urea combustion method may be referred to as low budget, less time consuming and mass productive method with almost identical morphology. Evolution of gas via combustion may leave behind the pores (meso) that may be beneficial for fast ion transfer from electrolytes at electrode/electrolyte interface. In the present work, ZMO is prepared by urea combustion technique. Unique microstructure of ZMO that consists of interconnected nearly spherical nanoparticles, form a porous structure with homogenous pore (10–30 nm) distribution. The ZMO is characterized as electrode material for supercapacitor and delivers the specific capacitance of 160 (±5) Fg^{-1}. The reasonably good value of capacitance and the fact that ZMO is known to be good Li-ion battery electrode material further justify its viability as a good hybrid electrode material for both energy storage devices (supercapacitor and Li-ion battery).

2. Experimental

2.1. Preparation of spinel zinc magnetite

The spinel zinc magnetite ZMO was synthesized by urea combustion technique. In the urea combustion method, metal nitrates, $Zn(NO_3)_2.6H_2O$ (0.005 mol; Merck) and $Mn(NO_3)_2.4H_2O$ (0.01 mol; Acros) were dissolved in minimum amount of distilled water and kept at 60 °C for half an hour with continuous stirring. Urea (0.045 mol; Rankem) was added to the nitrate solution and kept into preheated muffle furnace at 300 °C. The ignition initiates reaction and within 10 min smoke is evolved that leaves behind the floppy material. Later it was ground using mortar and pestle and calcined at 600 °C in air for 6 h, and then cooled to ambient temperature.

2.2. Characterization

The as prepared powder was structurally characterized by X-ray diffractometer (XRD: BRUKER D8 FOCUS) employing CuK_α radiation. Surface morphology was examined by field emission scanning electron microscope (FESEM: QUATA 200 FEG) and transmission electron microscope (TEM: TECNAI G^2 20 S-TWIN). Surface area was determined by Brunauer–Emmet–Teller (BET) method (QUANTA CHROME, ASIQWIN). For the surface area measurement, the sample was degassed for 6 h at 300 °C under a flow of nitrogen.

2.3. Electrode preparation and electrochemical characterization

For the electrochemical studies, the performance of nano-ZMO was studied using three electrode configurations where ZMO works as working electrode, Platinum wire as counter electrode, and Ag/AgCl as reference electrode. Freshly prepared 2 M KOH aqueous solution using doubled distilled water was used as the electrolyte. The working electrode was prepared using 70:15:15 wt% of ZMO, conducting carbon, and polyvinylidenefluoride (PVdF) respectively. The slurry was prepared by mixing all three constituents in N-Methyl-2-pyrrolidone (NMP) followed by stirring for 12 h. Then the slurry (Active material ~ 2.5 mg) was coated on a graphite substrate with an area of 1.5 cm^2 and the electrodes were dried at 80 °C for 12 h in air oven. The electrochemical analysis was carried out using cyclic voltammetry (CV) in the potential range of −0.45 V to 0.45 V at different voltage scan rate and galvanostatic charge/discharge (GCD) cycling in the voltage window of −0.1 V to 0.45 V at current densities of 0.16 Ag^{-1}, 0.33 Ag^{-1} and 0.5 Ag^{-1}, respectively. Electrochemical Impedance Spectroscopy (EIS) was performed using voltage signal of 5 mV in the frequency range of 1 MHz–10 mHz. All the electrochemical measurements were performed using multichannel Potentiostat/Galvanostat (AUTOLAB: MAC-80039).

3. Results and discussion

3.1. Structural and morphological properties

In the urea combustion method, nitrate ions in the metal nitrates work as oxidizer and urea (NH_2CONH_2) works as fuel. The reaction gives byproduct gases and water as per following equation.

$$Zn(NO_3)_2 + 2Mn(NO_3)_2 + 9CO(NH_2)_2 + 6\frac{1}{2}O_2 \rightarrow ZnMn_2O_4 + 18H_2O + 9CO_2 + 12N_2 \quad (1)$$

The freshly formed metal oxides will combine to form the oxide spinel. Nano $ZnMn_2O_4$ could only be formed at 600 °C. The urea in

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