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# Sol gel thermolysis process for the synthesis of nano $ZnMn_2O_4$ by using PVA with combustion fuel and their electrochemical properties

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ABSTRACT

In this paper we are demonstrating the synthesis of mixed transitional metal oxide $ZnMn_2O_4$ nano powder carried out by Sol-gel thermolysis process. The mixture of metal nitrates, PVA and urea have been used for $ZnMn_2O_4$ synthesis process. The obtained powder was characterized by XRD, PSA, and FE-SEM. The X-ray diffraction analysis revealed that the $ZnMn_2O_4$ nano powder has pure phase and tetragonal structure. Crystallite size was calculated by using Debye-Sherrer's and Williamson-Hall equations. The average crystallite size was around 14 nm. A particle size of 28 nm was obtained with particle size analyzer. The FESEM morphology studies indicate that $ZnMn_2O_4$ nano particles were coagulated with some amount of porosity. The electrochemical analysis of the synthesized $ZnMn_2O_4$ electrode showed specific capacity upto 603 mAh/g at 5 mV/s.



## 1. Introduction

Increase in smart phones, electric vehicles and hybrid electric vehicles with rapid growth in the world population and reduction in cost expansion have led to the search for new energy storage based electrode material for lithium ion batteries (LIB's) and Supercapacitors (SC's) applications. In recent years, mixed transition metal oxides (MTMOs) based electrode material have been intensively studied for electrochemical storage technology [1–6]. As electrochemical energy-storage devices, lithium ion batteries and Supercapacitors have received wide attention in portable electronics to electronic automotive industry such as electric vehicles hybrid electric vehicles and plug-in hybrid electric vehicles [7,8]. Several people reported on Co and Ni based mixed transitional metal oxides such as $ZnCo_2O_4$ [9] $NiCo_2O_4$ [10–13], $CuCo_2O_4$ [14], $MnCo_2O_4$ [15] and $FeCo_2O4$ [16] compared to Co and Ni species. Manganese (Mn) based mixed transitional metal oxide showed better electrochemical properties. The advantage of Mn based electrode material is in higher specific capacity, more eco-friendliness and environmentally compatible. Till date, many synthesis methods reported on $ZnMn_2O_4$ electrode material. T.H et al. [17] have reported on hierarchical porous $ZnMn_2O_4$ nanostructured electrode materials that were successfully synthesized by sucrose-assisted combustion method. They achieved specific capacitance up to 416.96 F/g in 6 M KOH electrolyte at a scan rate of 5 mV/s. After that, Y.L.Wang [18] also developed micro-size Cd-doped $ZnMn_2O_4$ sphere were prepared by hydrothermal method. The Cd-doped $ZnMn_2O_4$ microsphere electrodes which showed specific capacitance of 364 F/g in 2 M KOH electrolyte at a scan rate of 2 mV/s. For improving specific capacitance we are demonstrating $ZnMn_2O_4$ nanostructured electrode materials, which have been successfully synthesized by Sol-gel thermolysis method with the help of PVA and combustion fuel (urea). In this process, PVA is controlling the particle size and morphology of nano crystalline powder. Here, without further heat treatment $ZnMn_2O_4$ pure phase formation occurred. The obtained nano powder were studied by electrochemical analysis in 1 M LiOH [19–22] electrolyte solution.

## 2. Experimental methods

### 2.1. Materials

To prepare the $ZnMn_2O_4$ nano particles required to Zinc nitrate Zn $(NO_3)_2$ .$6H_2O$ Manganese nitrate Mn $(NO_3)_2$ .$4H_2O$, PVA and Urea. Similar synthesis procedure has been used by Subramania et. al [23,24]. All the analytical grade reagents were received form Merck Pvt. Ltd without further purification used for $ZnMn_2O_4$ nanoparticles.

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### 2.2. Synthesis procedure

$ZnMn_2O_4$ nano particles synthesis process has been briefly explained in Fig. 1. A stoichiometric ratio (1:2) of Zn $(NO_3)_2$ .$6H_2O$ and of Mn $(NO_3)_2$ .$4H_2O$ 1 M of zinc nitrate and 2 M of manganese nitrate was dissolved in double distilled water then stirred for 20 min at room temperature and 0.005 mml of urea was added and further stirred for 10 min. After that, the Zn/Mn – urea mixture was added into 0.1 g of PVA solution. The total solution was stirred again at 80 °C for 1 h. After one hour, the solution converted into a gel. The obtained polymeric gel precursors was then transferred to 20 ml ceramic crucible. The crucible was placed in air atmosphere at 400 °C for 1 hThe resultant product was collected and underwent physical and electrochemical characterizations.

## 3. Results and discussions

### 3.1. X-ray diffraction analysis

The XRD pattern of the $ZnMn_2O_4$ powder is studied with the diffraction angle 10°−80°. All the diffraction peaks phase matching with the $ZnMn_2O_4$ tetragonal phase of standard JCPDS No. 00-024-1133, and it is shown in Fig. 2. There was no other impurities peaks which also confirm that the obtained powder is in pure phase. The reflection peaks were indexed to the different (*hkl*) planes (1 0 1) (1 1 2) (2 0 0) (1 0 3) (2 1 1) (0 0 4) (2 2 0) (2 0 4) (3 1 2) (3 0 3) (3 2 1) (2 2 4) and (4 0 0) observed 2θ at 18.22, 29.29, 31.25, 33.12, 36.40, 38.93, 44.98, 50.71, 54.43, 56.68, 59.22 60.84 and 65.21. As the width of full width-half maxima increases the size of particle decreases which indicated the nano size of the present material [25] The average crystallite size of the $ZnMn_2O_4$ powder is around 14 nm estimated by Scherrer's Eq. (1) [26–28].

$$\text{Crystallite size } (D) = \frac{0.9 * \lambda}{\beta.\text{Cos}\theta} \quad (1)$$

Where D is the average of the crystallite size, λ is the wavelength of the X-ray radiations (Cu Kα radiation = 1.5418 Å), θ is the diffraction angle and β is the full width half maximum (FWHM).The Williamson Hall Eq. (2) is

$$\beta.\text{Cos}\theta = K\lambda/D + 2\varepsilon\ \text{Sin}\theta \quad (2)$$

Where β is the full width half maxima of the X ray diffraction peaks, K is the Sherrer's constant, λ is the wavelength of the X ray radiations, D is the crystallite size, ε lattice strain and θ is the diffraction angle, 2ε Sinθ is plotted against β.Cos along x and y axis as shown in Fig. 2(b). From the linear fit of the plot, crystallite size value is obtained from the intercept whereas the strain is obtained from the slope. The average crystallite size was found to be 14 nm and a strain of 0.285 strain was calculated by W-H plot equation. A particle size of 28 nm was obtained with particle size analyzer (Fig. 3a). The average crystallite size decreased with increase in strain due to the mechanical surface free energy of the metastable nanoparticles. Fig. 3(b and c) reveals the field emission scanning electron microscopy images of $ZnMn_2O_4$ nano particles which were coagulating with each other with some amount of porosity.

### 3.2. Electrochemical analysis

Fig. 4 shows the cyclic voltammetry of synthesized $ZnMn_2O_4$ electrode material. The cyclic voltammetry measurements of $ZnMn_2O_4$ porous material grown on copper substrate were done. The coated copper foil was tested in three electrode system with a

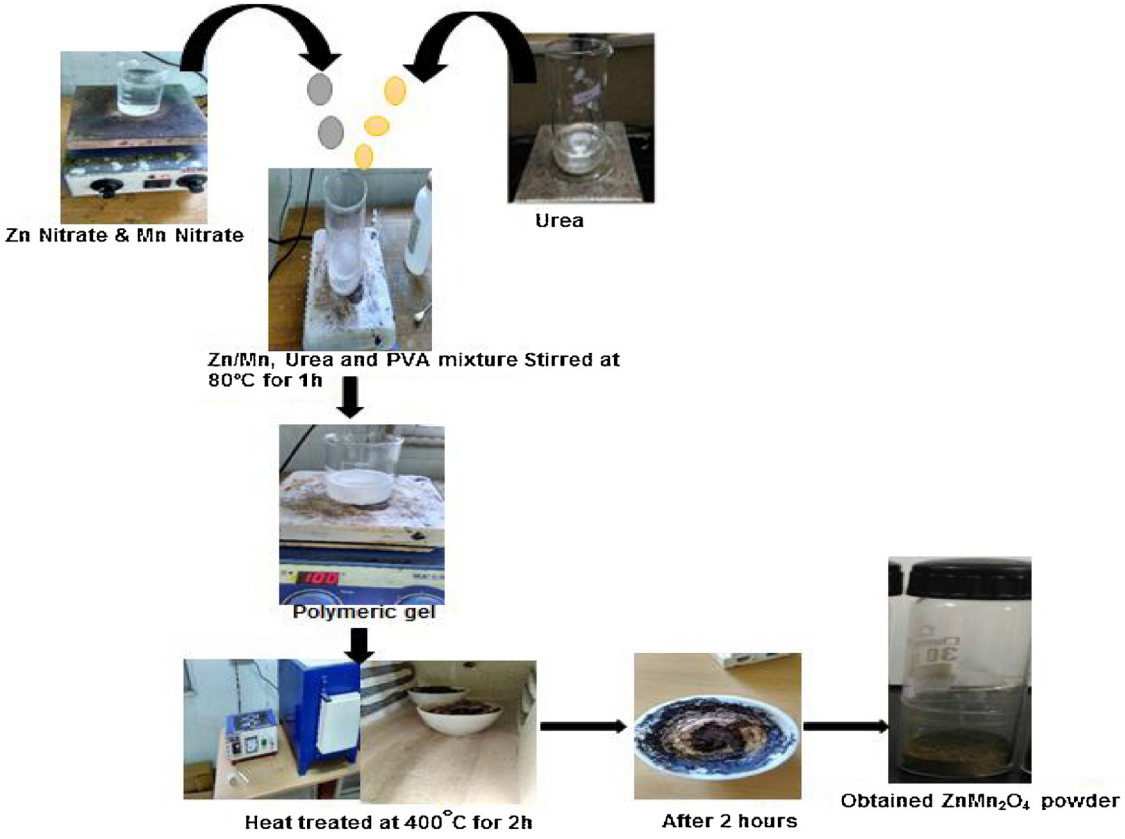


**Fig. 1.** Scheme for the preparation of $ZnMn_2O_4$ by sol gel thermolysis process using PVA urea.