DEVELOPMENT OF TWO-DIMENSIONAL Mg DOPED ZnO NANO HYBRIDS AS ELECTRODE MATERIALS FOR ELECTROCHEMICAL SUPERCAPACITOR APPLICATIONS

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ABSTRACT

In the past two and a half decades, there has been rapid growth in the study of electrochemical supercapacitors. Zinc oxide based electrode materials are proposed for supercapacitor applications because of their less price, eco-friendliness, good electrochemical reversibility, more specific capacitance, etc. In this research work, a set of nanohybrid electrode materials with a composition of $Zn_{1-x}Mg_xO_{1-\delta}$ (where $x = 0.1, 0.2, 0.3$ and 0.4) has been prepared by a simple chemical precipitation technique. The prepared electrode materials were analyzed by XRD, FTIR, SEM and EDAX. Electrochemical studies, such as cyclic voltammetry, galvanostatic charge-discharge and impedance analysis were carried out in an aqueous electrolyte ($1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$) to understand the electrochemical characteristics of the Mg-doped ZnO nanohybrid materials. The findings show that the doping level of Mg in ZnO had an important role in understanding the capacitive behaviors of the materials. Among the four-electrode materials studied, $Zn_{0.90}Mg_{0.10}O_{1-\delta}$ electrode material exhibits a maximum specific capacitance of 26.33 Fg^{-1} at a scan rate of 10 mV and hence which may be suitable for electrochemical supercapacitor applications.

Keywords: Supercapacitors, Electrode Materials, Mg-doped ZnO, Characterization

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INTRODUCTION

Supercapacitors have shown great attention as an energy storing device in the recent past especially as a solution to the increasing world demand for efficient energy storage. Supercapacitors have significantly superior specific powers and greater life cycles compared to secondary cells such as lead-acid, nickel-cadmium, and Li-ion cells. Hence, supercapacitors have attracted considerable interest because of the ever-increasing demands of electric cars, portable electronic systems, and power devices for memory backup.¹⁻⁵ However, supercapacitors suffer from low specific capacitance ultimately which results in low energy density. These drawbacks limit their applications in the area of power storage. To overcome these limitations, scientists have taken greater efforts in developing novel electrode materials with excellent characteristics.

In recent years, metal oxides⁶⁻⁸, perovskite oxides⁹⁻¹⁰, polymer composites¹¹⁻¹² and carbon/graphene-based materials¹³⁻¹⁴ have been widely proposed as supercapacitor electrode materials. Wu et.al¹⁵ have proposed NiCo_2O_4 based materials as electrodes for supercapacitor applications that exhibit not only large power density but also high energy density up to 35 W h kg^{-1} . Vikash Sharma et.al¹⁶ have developed nanostructures of copper oxides as next-generation electrode materials for supercapacitors with improved electrochemical characteristics. They found that the ion transport channels in the materials facilitated efficient de-intercalation which results in the enhancement of cyclability and coulombic efficiency. Recently, Yin She et. al¹⁷ have prepared nickel-cobalt-molybdenum metal oxide (NCMO) nanosheets with hierarchical, porous structures by hydrothermal method. They reported that as-prepared NCMO nanosheets possessed high specific capacitance (1366 Fg^{-1} at the current density of 2 Ag^{-1}), good rate

capability (71.3% at the current density of 40 Ag^{-1}), as well as excellent cycling stability (89.75% retention after 5000 cycles). Sasirekha *et. al*¹⁸ have synthesized ZnO/C nanocomposite adapting sol-gel method. They reported that ZnO/C electrode exhibits a maximum specific capacitance of 820 Fg^{-1} at a constant specific current of 1 Ag^{-1} . It was reported that the mixed metal oxides have shown better electrochemical performance when compared to individual metal oxides as electrode materials in supercapacitors.¹⁹ However, no understandable report is available in evaluating the electrochemical characteristics of Mg-doped ZnO based electrode materials for application in supercapacitors. In this research work, we describe a simple mode of synthesizing Mg-doped ZnO ($\text{Zn}_{1-x}\text{Mg}_x\text{O}_{1-\delta}$) based nanostructured electrode particles and their electrochemical behavior towards potential application in supercapacitors.

EXPERIMENTAL

Materials

The chemicals such as zinc nitrate (99%, Fisher Scientific, India), magnesium nitrate (99%, Nice, India), sodium hydroxide (97%, Himedia, India) and ethanol (99.9%, Changshu Yangyuan, ROC) were used in the experiment. They were used as received without any further purification.

Synthesis of Mg Doped with ZnO Nanostructured Materials

The zinc nitrate, magnesium nitrate and sodium hydroxide solutions with known specific concentrations were prepared in distilled water. The precipitating solution (sodium hydroxide) was taken in a beaker with 500 ml capacity. The metal nitrate solutions were mixed well with sodium hydroxide solution in a magnetic stirrer under 1000 rpm at room temperature. The pH of the mixture was maintained above 9 by adding the required amount of NaOH pellets as reported.²⁰ The resultant metal hydroxide precipitate mixture ($\text{Zn}(\text{OH})_2 + \text{Mg}(\text{OH})_2$) was filtered off and then washed with double distilled water and ethanol (9:1 ratio) for 2 to 3 times and dried at $50 - 60^\circ\text{C}$ overnight in a hot air oven. The dried precipitate was subjected to thermal treatment at 150, 300, 450, 600 and 800°C for 2 hours each to get pure nano-crystalline Mg-doped ZnO hybrid material. The flow chart to synthesize Mg-doped ZnO hybrid materials is indicated in Fig.-1.

Fig.-1: Flow Chart to prepare Mg-doped ZnO Hybrid Materials

Reaction Mechanisms Involved

The expected chemical reactions in the synthesis of Mg doped ZnO hybrid materials and the subsequent experimentation procedure can be explained as follows:

Materials Characterization

Physical Characterization Of Materials

The thermally treated nanocrystalline materials were characterized by Shimadzu XRD6000 X-ray diffractometer using $\text{CuK}\alpha$ radiation. Shimadzu IR Prestige-21 model FTIR spectrometer was employed to record the FTIR spectra of materials in the range of $4000\text{--}400 \text{ cm}^{-1}$. The surface morphology of the materials was studied using JEOL Model JSM-6360 scanning electron microscope. EDAX analysis was also performed with JEOL Model JSM-6360 to find out the atomic weight percentage of elements present in the samples.

Electrochemical Characterization of Materials

Electrochemical studies were carried out with an electrochemical workstation (CH1700D) with a conventional three-electrode system consisting of electrode material coated on the stainless steel plate as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode. The standard electrode potential (E°) for Ag/AgCl is $0.230 \text{ V} \pm 10 \text{ mV}$. 1 M Na_2SO_4 was used as the supporting electrolyte. All the experiments were performed at room temperature.

The electro-active material (Mg-doped ZnO), conducting material (carbon powder) and binder (PVDF) were mixed in the wt. % of 90:9:1. The mixture was finely made into a paste with the help of solvent Diethyl Acetamide (DEA). The as-prepared paste was finely applied onto a stainless steel plate (having a specific area of $1 \times 1 \text{ cm}^2$) and this acts as a working electrode in the three-electrode system for electrochemical studies.

The electrochemical activity of the prepared Mg-doped ZnO nanocrystalline materials was studied using galvanostatic charge-discharge and cyclic voltammetry (CV) techniques. Electrochemical impedance spectroscopy (EIS) studies were performed in the frequency range of 1 Hz to 100 MHz under amplitude of 5 mVsec^{-1} . The Zview software was used to fit the impedance data.

RESULTS AND DISCUSSION

XRD Studies

Figure-2 (a, b, c and d) shows XRD diagrams of the $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$, $\text{Zn}_{0.80}\text{Mg}_{0.20}\text{O}_{1-\delta}$, $\text{Zn}_{0.70}\text{Mg}_{0.30}\text{O}_{1-\delta}$ and $\text{Zn}_{0.60}\text{Mg}_{0.40}\text{O}_{1-\delta}$ nanocrystalline materials prepared by chemical precipitation method. The obtained XRD patterns were compared with the reported standard JCPDS data for ZnO (JCPDS card No: 65-4596). As per the reported JCPDS data, the XRD patterns of the above nanocrystalline materials have eight similar diffraction peaks which could be indexed to the (100), (002), (101), (102), (110), (103), (200) and (112) reflection planes of cubic geometry of ZnO. There is a new phase shift found near (102) plane with an increased concentration of Mg in $\text{Zn}_{1-x}\text{Mg}_x\text{O}_{1-\delta}$. Except for this, no impurities were present in any of our samples.

Fig.-2: XRD Patterns obtained on the Nanocrystalline Materials prepared by Chemical Precipitation Method (a) $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$; (b) $\text{Zn}_{0.80}\text{Mg}_{0.20}\text{O}_{1-\delta}$; (c) $\text{Zn}_{0.70}\text{Mg}_{0.30}\text{O}_{1-\delta}$ and (d) $\text{Zn}_{0.60}\text{Mg}_{0.40}\text{O}_{1-\delta}$

FTIR Studies

Figure-3 (a, b, c and d) shows the FTIR spectra obtained on $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$, $\text{Zn}_{0.80}\text{Mg}_{0.20}\text{O}_{1-\delta}$, $\text{Zn}_{0.70}\text{Mg}_{0.30}\text{O}_{1-\delta}$ and $\text{Zn}_{0.60}\text{Mg}_{0.40}\text{O}_{1-\delta}$ nanocrystalline materials prepared by chemical precipitation method. FTIR measurements were carried out using KBr method at room temperature (RT). As seen from the analysis, the peak appeared at 440 cm^{-1} in all the samples is attributed to the presence of ZnO .²¹ The peaks that appeared at 548 cm^{-1} in Fig.-3 (c and d) are corresponding to vibration Mg-O .²² The peak found at 3400 cm^{-1} is due to the O-H vibrations of absorbed water in the samples.²²

Fig.-3: FTIR Spectra obtained on the Nanocrystalline Materials prepared by Chemical Precipitation Method (a) $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$; (b) $\text{Zn}_{0.80}\text{Mg}_{0.20}\text{O}_{1-\delta}$; (c) $\text{Zn}_{0.70}\text{Mg}_{0.30}\text{O}_{1-\delta}$ and (d) $\text{Zn}_{0.60}\text{Mg}_{0.40}\text{O}_{1-\delta}$

SEM Studies

Figure- 4 (a, b, c and d) displays the scanning electron microscope images of the nanocrystalline materials ($\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$, $\text{Zn}_{0.80}\text{Mg}_{0.20}\text{O}_{1-\delta}$, $\text{Zn}_{0.70}\text{Mg}_{0.30}\text{O}_{1-\delta}$ and $\text{Zn}_{0.60}\text{Mg}_{0.40}\text{O}_{1-\delta}$) prepared by chemical precipitation method. The SEM image confirms the presence of smaller grains ($\sim 300 - 400\text{ nm}$ size) however at increased concentration we obtained agglomerated products. Fig.-4(a) shows a perfect arrangement of cubic grains in the sample ($\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$). Fig.-4(b) shows that the sample ($\text{Zn}_{0.80}\text{Mg}_{0.20}\text{O}_{1-\delta}$) slightly started to undergo agglomeration thereby causing the structure to slightly change its conformation which revealed that the prepared material contains both micro and nano-sized grains. Fig.-4 (c) and (d) revealed that the prepared materials ($\text{Zn}_{0.70}\text{Mg}_{0.30}\text{O}_{1-\delta}$ and $\text{Zn}_{0.60}\text{Mg}_{0.40}\text{O}_{1-\delta}$) are undergoing a phase shift which is confirmed from the XRD analysis also. This phase shift does not undergo a drastic lattice overlap but a formation of a new MgO phase which starts to overlap within the ionic radius of the zinc. The larger sized grains (more than 400 nm) present in the samples (Fig.-4 (b), (c) and (d)) may be due to the agglomeration of materials during the thermal treatment process. The SEM results showed that with increasing concentration of Mg results in an increase in the grain size as well as the increase in overall grain boundary which might influence the capacitance.

Fig.-4: SEM Images obtained on the Nanocrystalline Materials prepared by Chemical Precipitation Method (a) $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$; (b) $\text{Zn}_{0.80}\text{Mg}_{0.20}\text{O}_{1-\delta}$; (c) $\text{Zn}_{0.70}\text{Mg}_{0.30}\text{O}_{1-\delta}$ and (d) $\text{Zn}_{0.60}\text{Mg}_{0.40}\text{O}_{1-\delta}$

EDAX Analysis

Figure-5 (a, b, c and d) displays the energy dispersive X-ray microanalysis (EDAX) spectra of the nanocrystalline materials ($\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$, $\text{Zn}_{0.80}\text{Mg}_{0.20}\text{O}_{1-\delta}$, $\text{Zn}_{0.70}\text{Mg}_{0.30}\text{O}_{1-\delta}$ and $\text{Zn}_{0.60}\text{Mg}_{0.40}\text{O}_{1-\delta}$) prepared by chemical precipitation method. EDAX spectra of the samples show peaks for the elements Zn, Mg and O only and not for any other impurity elements in the samples. The elemental composition data obtained on nanocrystalline materials by EDAX analysis is in line with the stoichiometric composition taken for the synthesis. Hence, the data confirmed the presence of appropriate elements in all the samples.

Fig.-5: EDAX Images obtained on the Nanocrystalline Materials prepared by Chemical Precipitation Method (a) $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$; (b) $\text{Zn}_{0.80}\text{Mg}_{0.20}\text{O}_{1-\delta}$; (c) $\text{Zn}_{0.70}\text{Mg}_{0.30}\text{O}_{1-\delta}$ and (d) $\text{Zn}_{0.60}\text{Mg}_{0.40}\text{O}_{1-\delta}$

Electrochemical Studies

The electrochemical behavior of the prepared nanocrystalline materials for electrochemical capacitors was studied by cyclic voltammetry (CV) in 1 M Na_2SO_4 aqueous solutions. The cyclic voltammetry measurements were performed at various scan rates (10, 20, 30, 40 and 50 mV/s) and results as shown in Fig.-6 (a, b, c and d). The CV studies were carried out within the potential range of -0.7 to 0.5 V vs. Ag/AgCl . As evidenced from the figure, CV curves of all the four-electrode materials are symmetrical, characteristic of ideal capacitive behavior with quasi rectangular shape exhibiting good the excellent capacitive behavior²³. From the CV curves, it can be found that the shape of CV curves remained the same at different scan rates. As the scan rate raises, the peak current also increases as reported.²⁴ Fig.-6 (e) shows the comparison CV curves obtained on the all four materials at a scan rate of 50 mV s^{-1} through which it was noticed that among the four materials, $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$ material may be of good preference as an electrode material for electrochemical capacitor applications. The specific capacitance can be calculated according to the following equation:

$$C_s = [(I \times \Delta t) / (m \Delta V)] \text{ Fg}^{-1} \quad (5)$$

Where, I is the discharge current (A), Δt is the discharge time (s), m is the mass of the electroactive material (g) and ΔV is the potential difference (V). The specific capacitance values calculated for all the four materials at different scan rates are presented in Table-1. Among the samples studied, $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$ resulted in the highest specific conductance value of 26.33 Fg^{-1} at the scan rate 10 mV . Also, it was noticed that the specific capacitance values decrease with raise in scan rate for all the electrode materials. The best sample, $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}_{1-\delta}$ was further studied by charge-discharge technique with the anodic and cathodic current varying from 1mA, 0.5mA and 0.25mA in 1M Na_2SO_4 solution at the voltage window between 0 and 0.3 V and the results are shown in Fig.-7 (a, b and c). All the obtained curves revealed a good symmetrical triangle shape which implies an ideal capacitive behavior in the electrode.

The electrochemical impedance spectral (EIS) analysis was carried out in the best electrode, $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}_{1-\delta}$ at the open circuit potential over the frequency range from 1 Hz to 100 kHz. For all the measurements,

the amplitude was kept at 5mVs^{-1} . Figure-8 shows a typical Nyquist plot obtained on nanocrystalline $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}_{1-\delta}$ electrode material. The EIS pattern can be represented by an equivalent circuit as shown in the inset of Fig.-8. Figure-8 exhibits two distinct parts including a semicircle in the high-frequency region and an inclined line in the moderate-low frequency region. The inclined line in the moderate-low frequency region corresponds to Warburg resistance of the electrolyte in the electrode material ($\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}_{1-\delta}$). The obtained Nyquist plot of the synthesized material ($\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}_{1-\delta}$), exhibits the presence of distorted semi-circle in the high-frequency region, and a straight line which is almost parallel to the imaginary components. The straight lines in the low-frequency region reveal the ideal capacitance behavior in $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}_{1-\delta}$.²⁴

Fig.-6: Cyclic Voltammograms of the Electrode Materials (a) $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$ (Sample 1); (b) $\text{Zn}_{0.80}\text{Mg}_{0.20}\text{O}_{1-\delta}$ (Sample 2); (c) $\text{Zn}_{0.70}\text{Mg}_{0.30}\text{O}_{1-\delta}$ (Sample 3) and (d) $\text{Zn}_{0.60}\text{Mg}_{0.40}\text{O}_{1-\delta}$ (Sample 4) at Various Scan Rates ranging from $10 - 50\text{ mVs}^{-1}$ in $1\text{ M Na}_2\text{SO}_4$ and (e) Cyclic Voltammetry Response of all the Four Samples at 50 mVs^{-1} Scan Rate

Fig.-7: Charge- Discharge Curves of $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$ Electrode Material at the Current Density of 0.5 A g^{-1}

Fig.-8: Nyquist Plot and Equivalent Circuit Obtained on Nanocrystalline of $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$ Electrode Material

Table-1: Specific Capacitance Data Obtained on Mg-doped ZnO Nanocrystalline Materials

Electrode Material	Specific Capacitance Values at Different Scan Rates				
	10 mV	20 mV	30 mV	40 mV	50 mV
$\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}_{1-\delta}$	26.33F/g	19.07F/g	15.96F/g	14.04F/g	12.85F/g
$\text{Zn}_{0.80}\text{Mg}_{0.20}\text{O}_{1-\delta}$	23.63F/g	18.55F/g	15.66F/g	13.66F/g	12.13F/g
$\text{Zn}_{0.70}\text{Mg}_{0.30}\text{O}_{1-\delta}$	18.95F/g	15.16F/g	12.91F/g	11.72F/g	10.73F/g
$\text{Zn}_{0.60}\text{Mg}_{0.40}\text{O}_{1-\delta}$	11.12F/g	08.47F/g	07.28F/g	06.32F/g	05.68F/g

CONCLUSION

Chemical synthesis route can be efficiently used to prepare pure Mg-doped ZnO nanoparticles for application as electrode materials in supercapacitors. The obtained XRD patterns of the Mg-doped ZnO nanoparticles were matched with the reported standard JCPDS data of ZnO and all of them indexed to cubic symmetry. FTIR spectra of all the samples exhibited the occurrence of the metal-oxygen bond which is characteristic of metallic oxide particles. The SEM results showed that with increasing concentration of Mg increases in grain size as reported in the literature. The existence of elements such as Zn, Mg and O in the samples was confirmed by energy-dispersive X-ray microanalysis (EDAX) spectra. It is concluded that the magnesium concentration of low levels is proved to be much more efficient than at higher concentrations because of the phase change observed at nearly 7:3 (70 mol% Zn and 30 mol% Mg) ratio which causes the decrease in capacitance. Among the four-electrode materials studied, $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}_{1-\delta}$ nanocrystalline materials have shown better specific capacitance of 26.33 Fg^{-1} . Optimization and observation of the phase shift concentration have to be further studied for corrosion and coating applications for future studies.

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