TEMPERATURES DEPENDENCE OF Zn-Ni-Mn HIERARCHICAL TERNARY METAL OXIDE FILMS ON NICKEL FOAM

Mya Hnin Wai Wai[1], Zin Min Tun[2], Zin Min Myat[3],Yin Maung Maung[4]

Abstract

Supercapacitors have been widely distributed in recent years and are becoming one of the promising energy storage systems. In this work, hierarchical mesoporous Zn-Ni-Mn ternary oxide (ZNMO) films were firstly prepared to ongoing the supercapacitors by a simple hydrothermal method at different annealing temperatures. Hydrothermal treatment is conducted to prepare unusual ternary metal oxide nanostructures (nanocubes and hollow spheres). The structural and morphological properties of Zn-Ni-Mn ternary metal oxide films onto the nickel foam were characterized by some analytical methods such as X-ray powder diffraction (XRD), Scanning Electron Microscopy (SEM). The XRD analysis confirmed that the crystallographic phases of samples were in good agreement with the tetragonal structure for Zn-Ni-Mn ternary metal oxide film. SEM can be shown that the presence of non-homogeneous grains and having different grain sizes were found the surface morphology of Zn-Ni-Mn ternary metal oxide film.

Keywords: Hierarchical, Zn-Ni-Mn ternary oxides, hydrothermal, XRD, SEM

Introduction

Supercapacitors have been extensively used in recent years because of their advanced properties including long cycle stability, fast charging/discharging rate, high power density and eco-friendly and is becoming one of the promising energy storage systems [S. Li, S. J. Silvers,et al, 1997]. Recently, the transition metal oxides, such as MnO_2, NiO, et al. have been wildly explored due to the advantages including easy large-scale fabrication and brilliant flexibility in morphology and structures [A. Kolodziejczak-Radzimska and T. Jesionowski, 2014]. A number of electrode materials have been examined for enhancing the capacitive performance of the SC devices including carbonaceous nanostructures, metallic species, metal/carbon hybrids, etc [G. Oxide and E. Suvaci, 2020]. Supercapacitors (SCs) have induced enormous interest due to high power density, fast charging/discharging and long service life and have found extensive scale applications from portable electronic devices to large road market [S. Komarneni,et al, 1998]. However, the SCs generally display to lower energy densities (0-10 Wh Kg^{-1}) which limit their applications at commercial scale [Y.-L. Cheng, et al, 2016]. The issue of relatively lower energy density has been approached by increasing either the capacitive performance i.e., increasing specific capacitance or by broading the operating voltage window [C. Abinaya ,et al.,2017]. The specific capacitance and operating window are dependent upon the properties and structure of the constituent materials along with several other factors. Nanotechnology has opened up new horizons with the development of novel materials and Nanostructures [C. Abinaya ,et al., 2017]. Among various electrode materials, the metal based materials have exposed promising results due to reversible Faradaic reactions happening on the metal electrode surface reporting for higher charge storage capability [G. Z. Gayda ,*et al*,2019]. Most of research induced to use hydrothermal and sol gel processes because the shape of materials that can be easily controlled, while others better precipitation method since it offers simplicity, low cost, quick preparative method, finally easily controlled of both particle size and composition [J. N. Hasnidawani, et al, 2016]. The search for nanostructured ceramic materials that result in high-performance materials has led to the development of several chemical methods on a laboratory scale [G. Vijayaprasath ,*et al.*, 2016]. Among the various methods of chemical synthesis, the effective and simple method

[1] Department of Physics, Sittway University

[2] Department of Physics, Sagaing University

[3] Department of Physics, Sagaing University

[4] Department of Physics, University of Yangon

is hydrothermal method [X. Wang, C. Yan,et al, 2013]. In this work, Nickel foam supported hierarchical mesoporous Zn-Ni-Mn ternary oxide (ZNMO) films will be firstly prepared by a hydrothermal method. The hydrothermal method is a useful and attractive technique for the preparation of nanosized particles because of its benefits: it's good to control chemical rate and the production of excellent particles with a narrow size distribution in a relatively short processing time at lower temperatures [A. R. Nanakkal and L. K. Alexander, 2017].

Materials and Method

Experimental Procedure of Zn-Ni-Mn Ternary Metal Oxide Film Materials

In this work, analytical grade of zinc chloride ($ZnCl_2$), nickel chloride ($NiCl_2.6H_2O$) and manganese chloride ($MnCl_2.4H_2O$) mixture were used as the starting materials to produce hierarchical ternary oxide by hydrothermal method. Ammonium fluoride and distilled water were used as the dissolving and cleaning factors. All chemicals and solvents were purchased from Academy chemical shop in Yangon. All reagents were commercial grade and were used without further purification.

Method

Hydrothermal synthesis relies on the forced hydrolysis of the reactants in order to produce the oxide ceramics. This is achieved at moderate temperatures (<200 °C) and high pressures by placing the reagents in a sealed container and heating the system to the reaction temperatures. Hydrothermal synthesis can generate nanomaterials which are not stable at elevated temperatures and thus that combines results of first principal calculations, elements of aqueous thermochemistry, and experimental free energies of formation.

Experimental Procedure of Zn-Ni-Mn Ternary Metal Oxide Film

ZNMO ternary metal oxide film is prepared by a simple hydrothermal treatment. In first step, 0.1 mol of zinc chloride ($ZnCl_2$), 0.1 mol of nickel chloride ($NiCl_2.6H_2O$), 0.1 mol of manganese chloride ($MnCl_2.4H_2O$), 0.3 mol of urea ($CO(NH_2)_2$) and 0.1 mol of ammonium fluoride (NH_4F) were added to the 50 ml of distilled water with continuous stirring by using magnetic stirrer for 2 h. The 1 cmx1 cm sizes of nickel foams were immersed into the precursor solution. The homogeneous mixture was kept at 130 ° C for 8 h after transferred into 100 mL Teflon-lined stainless -steel vessel. Then nickel foams were took out and washed several times with distilled water. Afterwards, the sample was dried at room temperature for 24 h. And then annealed at 300 ° C, 350 ° C, 400 ° C, 450 ° C and 500 ° C in a muffle furnace for 3 h to obtain the Zn-Ni-Mn ternary metal oxide film onto the nickel foam. The block diagram of the experimental procedure of Zn-Ni-Mn ternary metal oxide film was shown in figure 1.

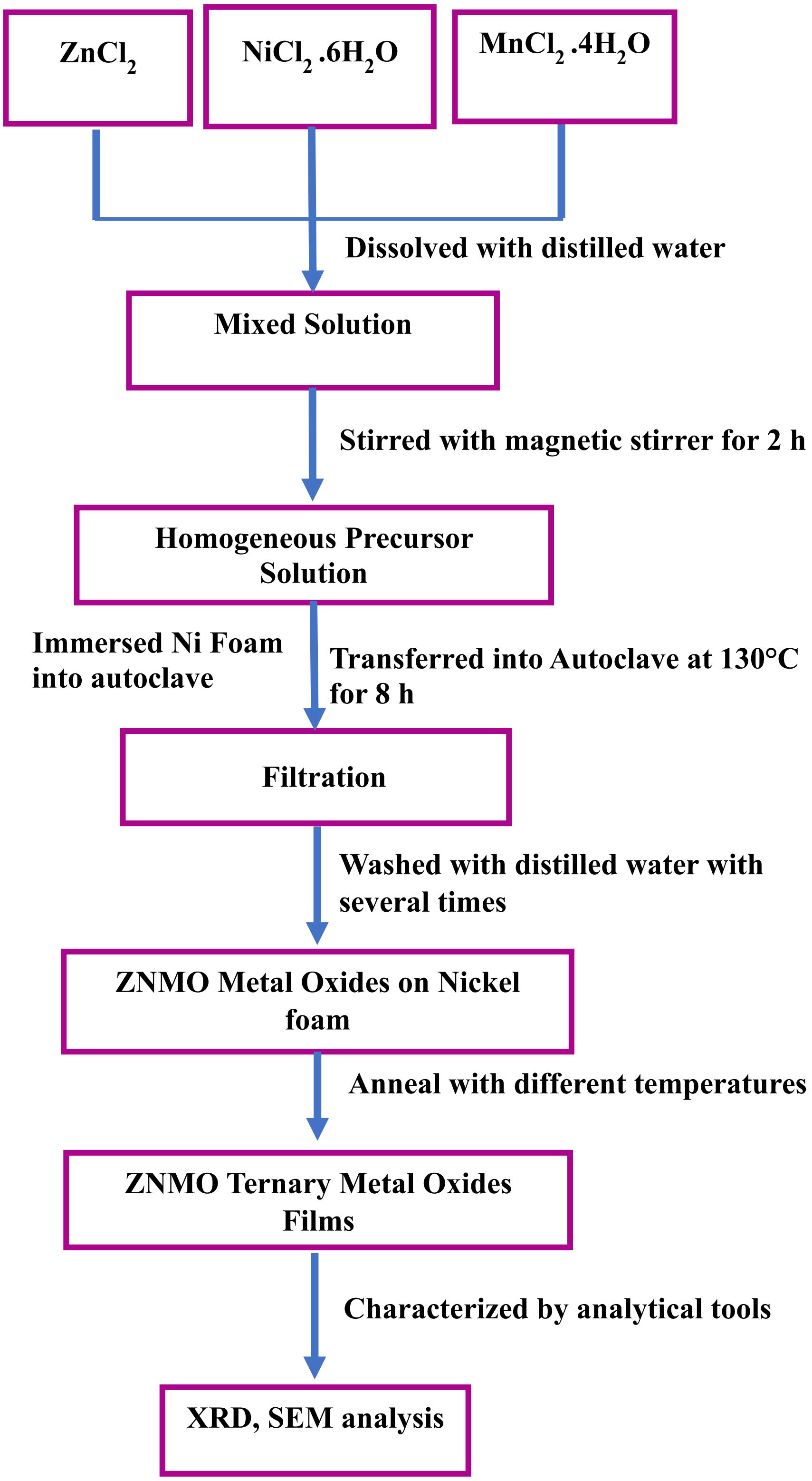

Figure 1 Block diagram of the experimental procedure of Zn-Ni-Mn ternary metal oxide films on nickel foam

Results and Discussions

Characterization of Materials

The prepared Zn-Ni-Mn hierarchical ternary metal oxide film were characterized for structural and crystal structures with X-ray Diffraction (XRD) technique (Rigaku D/max 220 i.e., X-ray Diffractometer System D/max Japan) and the grain sizes and surface morphology of prepared oxides were examined using Scanning Electron Microscopy (SEM) (Phenom Pro X).

XRD Analysis of Zn-Ni-Mn Ternary Metal Oxide Films on Nickel Foam Substrate

Structural properties of Zn-Ni-Mn ternary metal oxide films on nickel foam were examined by XRD technique. It was performed using monochromatic Cu K_α radiation (λ = 1.54056 Å) operated at 40 kV (tube voltage) and 30 mA (tube current). Sample was scanned from 20º to 70º in diffraction angle 2θ with a step-size of 0.01º. All diffracted peak of observed spectrum well match with those of standard peaks. The most dominant peaks were also occurred at (220), (222) and (151) planes for all temperature. According to the observed XRD, the Zn-Ni-Mn ternary metal oxides have tetragonal structure. The crystallographic phases of samples were in good agreement with the typical tetragonal structure. The crystallite sizes of the prepared ternary oxide were calculated using the Debye Scherrer's formula.

$$D = \frac{0.9\,\lambda}{\beta cos\theta} \quad (1)$$

where λ, θ and β are the X-ray wavelength (1.54056 Å), Bragg diffraction angle and full width at half maximum (FWHM) respectively. Table 1 described the average crystallite sizes and crystal structure of Zn-Ni-Mn ternary metal oxide films on nickel foam for different temperatures. Table 2 showed the calculated dislocation density and microstrain of Zn-Ni-Mn ternary metal oxide films. From the XRD results, when the temperature increased, the crystalized size also increased. Figure 2 showed the comparison of ZNMO/nickel foam at different temperatures.

Table 1 The average crystallite sizes and crystal structure of ZNMO/nickel foam at different temperatures

ZNMO/nickel foam					
Temperatures	300 °C	350 °C	400 °C	450 °C	500 °C
Average Crystallite sizes	44.68 nm	48.62 nm	49.27 nm	53.57 nm	57.24 nm
Crystal structure	Tetragonal structure				

Table 2 Dislocation Density and Microstrain of ZNMO/nickel foam at different temperatures

Temperature	300 °C	350 °C	400 °C	450 °C	500 °C
Average Dislocation Density	0.00050	0.00042	0.00041	0.00035	0.00031
Average Microstrain	0.2134	0.1849	0.2978	0.1855	0.1783

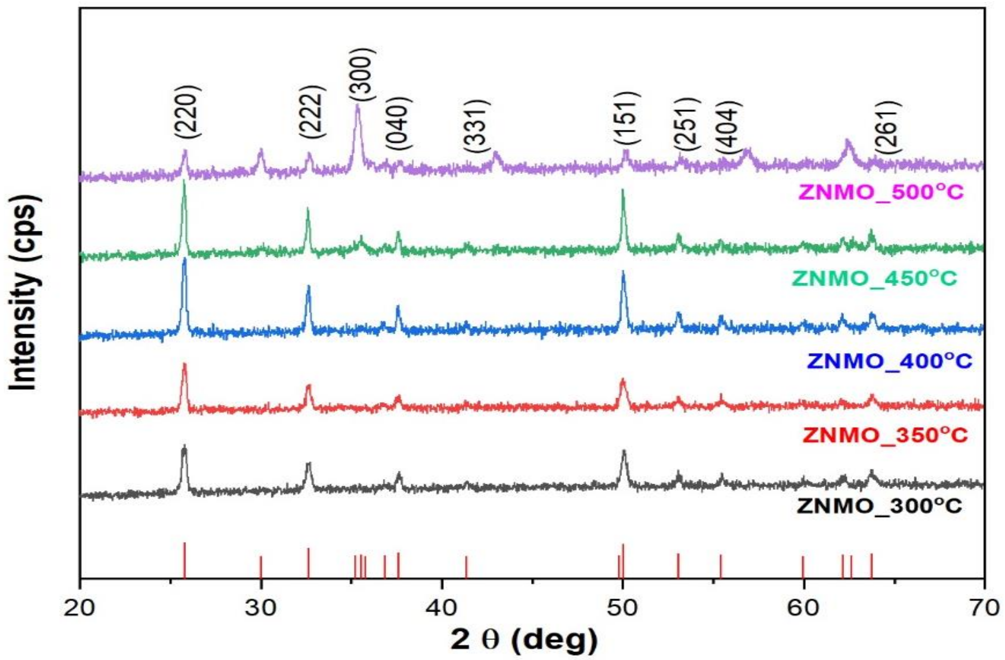

Figure 2 The XRD patterns for Zn-Ni-Mn ternary metal oxide film on nickel foam at different temperatures

SEM Analysis of Zn-Ni-Mn Ternary Metal Oxide Films on Nickel Foam

The surface morphology, microstructural properties of fabricated Zn-Ni-Mn ternary metal oxide films on nickel foam at different temperature were carried out by using the Scanning Electron Microscope (SEM) as shown in Figure 4 (a-e). From the SEM images, the Zn-Ni-Mn ternary metal oxide was well deposited on nickel foam and it has good morphology. According to SEM analysis, the morphologies ZNMO/nickel foam films were absolutely rod shapes and approach to wires phase. The well-defined nanorod shapes samples were found in Figure 6(a,b,d) and in Figure 6 (c,e), it look liked mixtures of nanorod and nanocube shapes. The diameters of these Zn-Ni-Mn ternary metal oxide films onto nickel foam were 0.170 µm (~170 nm) at 300 °C, 0.140 µm (~140 nm) at 350 °C, 0.13 µm (~130 nm) at 400 °C, 0.125 µm (~125 nm) at 450 °C and 0.113 µm (~113 nm) at 500 °C.

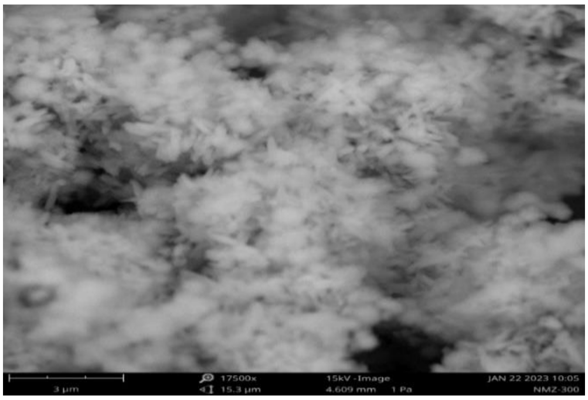

Figure 3 (a) SEM micrograph of Zn-Ni-Mn ternary metal oxide film at 300 °C

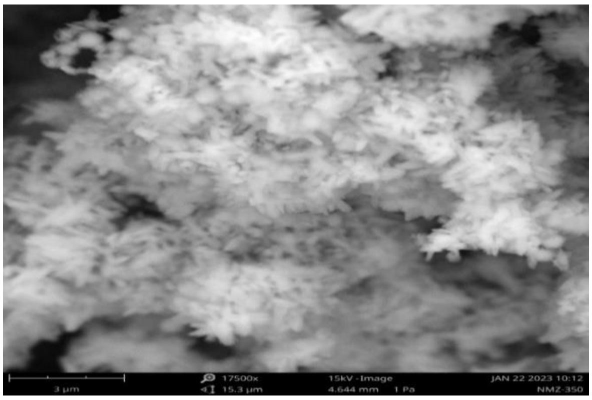

Figure 3 (b) SEM micrograph of Zn-Ni Mn ternary metal oxide film at 350 °C

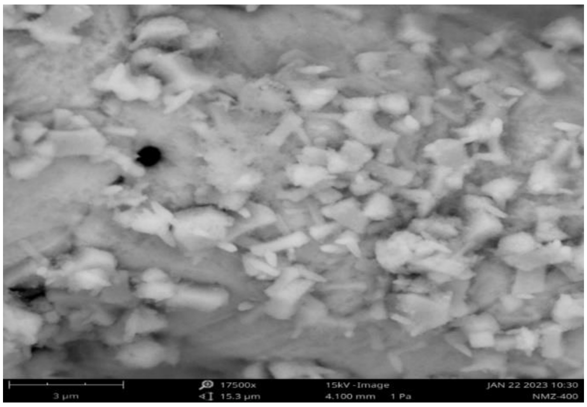

Figure 3 (c) SEM micrograph of Zn-Ni-Mn ternary metal oxide film at 400 ^{o}C

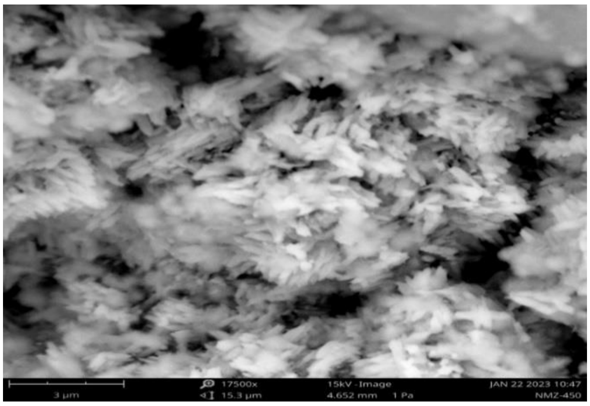

Figure 3 (d) SEM micrograph of Zn-Ni-Mn ternary metal oxide film at 450 ^{o}C

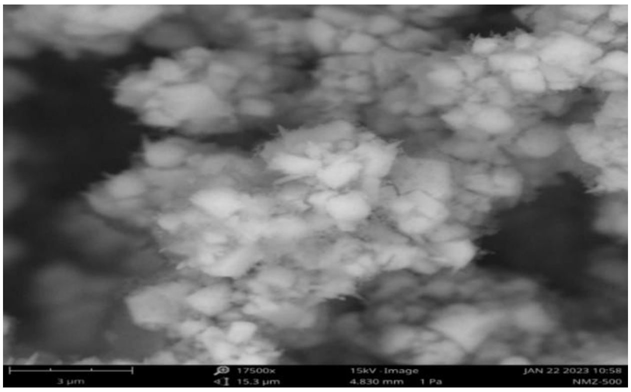

Figure 3 (e) SEM micrograph of Zn-Ni-Mn ternary metal oxide film at 500 ^{o}C

Conclusion

In this research, the controllable fabrication of highly ordered nanostructure on nickel foam substrate will be widely studied by using hydrothermal method. In his research work, hierarchical ternary metal oxide films of Zn-Ni-Mn array onto nickel foam were synthesized by a hydrothermal method. According to literature research papers, the hydrothermal routes are much more easily controlled and can produce nano arrays in a designed structure and morphology. Several general strategies for making advanced materials for supercapacitors have been developed, such as nanostructuring, nano-/microcombination, pore structure control, hierarchical design. According to XRD analysis, all the peak heights and peak positions of different temperatures were in good agreement of tetragonal structure with library file of XRD machine. According to the observed XRD, the average crystallite sizes of the Zn-Ni-Mn ternary metal oxide films were 44.68 nm, 48.62 nm, 49.27 nm, 53.57 nm and 57.24 nm at 300 °C, 350 °C, 400 °C, 450 °C and 500 °C which indicates that the crystallite size increases with the increasing temperature. From SEM images, some pores and crack growth pattern nano flowers and tube like structures were formed and it might not be cleared in shapes due to some impurity’s formation during thermal treatment. It was also found to be look liked mixtures of nanorod and nanocube shapes. This suggests that the diameter of agglomerated grain size decrease with increasing thermal decomposition temperature. The experimental finding resulted from this research work indicated that the crystal structure, phase formation and morphology of Zn-Ni-Mn ternary metal oxide films were influenced by different annealing temperatures. The resulting values were successfully represented significant progress in the development of supercapacitors.

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