Manganese Oxide and Temperature Induced on Microstructure and Electrical Properties of Graphene-(Mn$_2$O$_3$)$_x$-ZnO/Ni Foam

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Abstract. A supercapacitor is a new device of energy storage which shares similar properties with conventional capacitors and batteries. To optimize the energy storage as well as energy release cycling, we should observe in detail the one face electrode before use in the manufacture as a supercapacitor. An interesting materials’ properties from various studies of supercapacitor are graphene, Mn$_2$O$_3$, and ZnO. It could be more intriguing when those materials deposited on nickel foam substrate. The manganese oxide Mn$_2$O$_3$ exhibits remarkable potential as a supercapacitor electrode because it has low cost, abundant and high specific theoretical capacitances. So far, many carbon-based materials have been studied as supercapacitor material electrodes, but still, show a low volumetric capacity and hamper several physical limitations. More practical and long-term use of high-performance supercapacitors is hard to find in the literature on ZnO, G, Mn$_2$O$_3$ system supercapacitors. The Mn$_2$O$_3$ nanoparticle has been synthesized using chemical co-precipitation methods. The film of supercapacitor ZnO-G-Mn$_2$O$_3$ /Ni foam system was characterized using SEM-EDX, XRD, and LCR meter. It was found that the increase of manganese oxide gives rise to increase the capacitance, specific capacitance as well as dielectric constant. The behavior of its dielectric constant as a function of temperature is not a simple relationship.

Keywords: Supercapacitor, Mn$_2$O$_3$, ZnO, Graphene, nickel foam substrate, temperature

1. Introduction
Today the development of natural-based energy storage is desirable to industry and academic attention. Consumption of fossil fuels and increasing environmental problems have triggered a search for more sustainable energy sources and more effective energy storage techniques [1]. The development of energy storage is currently focused on battery based. Batteries as a storage of energy, are now inseparable from modern power systems. Although the battery does not produce energy, its function as energy storage is essential in system planning and operations in everyday life. Batteries store electrical energy in the form
of chemical energy. However, the lithium-ion based (LIBs) material used in batteries so far is a question of environmentally friendly.

The LIBs show high capacitance and energy density (3,600 Ah/kg, and 100-250 Wh/kg) so that they play an essential role in meeting the demands of increasing energy needs, which stem from rapid developments in the electronic world. We still to overcome low power density, limited life cycles, safety problems, high costs and limited availability of lithium resources [2]. Capacitor and more precisely, supercapacitors are one of the alternatives for energy storage technology.

Supercapacitors have attracted considerable attention as renewable energy storage devices because they have high density, faster charging and long lifetime (>100,000 times) [3–5]. From a technical point of view, supercapacitors show potential for a large number of cycles, high energy density, simple and easy construction. Besides, supercapacitors can reduce the risk of environmental damage because they do not contain corrosive ingredients, fewer toxic materials, and environmentally friendly [3,6–8].

The use of transition metal has been widely investigated as an electrode material because it has high redox, low cost and abundant presence in the environment, including RuO2, MnO2, Mn3O4, NiO, CoO, MoO3 and TiO2 [9]. Among these transition metals, MnO is a promising material as a supercapacitor electrode material, due to its diverse structure, low toxicity and environmentally friendly. One of the manganese oxide materials namely Mn3O4 shows tremendous potential as a supercapacitor electrode because it has a low cost, abundance, and high specific theoretical capacitance, i.e., 1229 F/g [9].

So far there are many studies related to carbon-based materials as electrodes of the supercapacitor. A poor volumetric capacity and inhibit more practical use in the long term are among the problems. It is also rarely informed from the literature regarding ZnO, G, Mn3O4; supercapacitors system [3]. Nickel foam with its electrical conductivity and exceptional mechanical flexibility to have many advantages used as a substrate [10]. Nickel foam shows better stability, including excellent resistance to corrosion and oxidation [11]. The addition of Mn3O4 nanoparticles in the ZnO nanorods-Mn3O4-Graphene proposed to enhance the performance of supercapacitors [12].

2. Methods
Manganese acetate [(CH3COO)2Mn.4H2O], Sodium hydroxide Pellets (NaOH), Hydrochloric acid (HCl), Poly-Vinyl Pyrrolidone (PVP), Zinc Acetate Dihydrate, and Graphene are among the materials used in this work. The nanomaterials of ZnO, as well as Mn3O4, were prepared in this study to follow the previous works [6,13,14] with typical modification. A detail of ZnO nanoparticles is described as follow.

2 grams Zinc Acetate Dihydrate was firstly dissolved in 10 mL DI water with 600 rpm speed stirring. We added a 3M solution of NaOH as much as 5 mL at a temperature of 27 °C to form a milky suspension. The solution was kept at 90 °C. The ZnO NPs could be obtained after heated at a temperature of 100 °C.

The Mn3O4 nanoparticles were prepared using chemical coprecipitation briefly described as follow. We started by mixing 0.1M NaOH with 1.5 wt% PVP into 50 mL into water under constant stirring. At the same time, we also prepare other solution of 0.1M manganese acetate dissolved into DI water under a continuous rotation until the color changes from bright yellow to dark brown and then dissolve for 24 hours. The final product of Mn3O4 nanoparticles was obtained after calcining at a temperature of 550 °C. Furthermore, the Ni foam substrate was prepared using the following techniques. We firstly cut each of nickel foam substrate as of 1×2 cm2 and subsequently washing it using 6M HCl for 30 minutes under sonication assistance to remove the NiO layer foam. Before being used, the cut of Ni foam was rinsed by using DI water and ethanol several times.

The mixing process of ZnO-G-Mn3O4 is by using the blending method. The ZnO-G-Mn3O4 solution is put into a glass beaker and then mixed in toluene solution. The solution was then stirred using a magnetic stirrer for 2 hours at room temperature at 500 rpm until a homogeneous solution was reached. The fabrication of ZnO-G-Mn3O4 composite was deposited onto Ni-foam substrate by using a spin coating with 3000 rpm for 30 seconds. In this work, We characterized the samples using a laboratory X-ray diffractometer (XRD) and Scanning electron microscopy (SEM) to obtain crystallographic as well as morphological data for further analysis. We also measure their capacitance at various temperature.
3. Results and Discussion
The diffraction patterns of ZnO, graphene and Mn$_2$O$_3$ nanocomposites are depicted in Figure 1 for different Mn$_2$O$_3$.

![Figure 1](image)

Figure 1. The X-RD patterns of ZnO-G-Mn$_2$O$_3$ for various Mn$_2$O$_3$ as (a) 0, (b) 0.008, (c) 0.012, (d) 0.016 and (e) 0.02 g.

We found that all phases exist in the patterns are the composite of ZnO, Mn$_2$O$_3$ and the substrate. There is no peak of graphene or at least very weak. It is confirmed that there is no chemical interaction during the deposition. Further analysis of the XRD pattern by employing Rietica and the use of a crystallographic database of COD No. 9004178 and COD No. 1514106. The output of the crystal structure analysis is listed in Table 1.

| Mn$_2$O$_3$ (g) | $R_p$ | $wRp$ | $\chi^2$ |
|----------------|-------|-------|----------|
| 0              | 21.71 | 28.47 | 1.69     |
| 0.008          | 22.81 | 29.64 | 1.45     |
| 0.012          | 22.12 | 29.68 | 1.48     |
| 0.016          | 23.69 | 32.09 | 1.32     |
| 0.020          | 22.60 | 30.45 | 1.40     |

The particle size of ZnO-G-Mn$_2$O$_3$ nanocomposites were 44.13, 42.75, 31.35, 39.55 and 44.13 nm, for the films with Mn$_2$O$_3$ as 0, 0.008, 0.012, 0.016, and 0.02 respectively. Based on phase analysis, the peak of Mn$_2$O$_3$ exists at 2θ, namely 33°, 38°, 43°, 55°, and 66°, which showed (hkl) planes of (222), (004), (024), (044) and (020). Whereas for ZnO appear at 2θ of 32°, 34°, 36°, 57°, 63°, and 68°, associated to (010), (002), (011), (334), (145), and (112) Bragg’s plane. We found there is no visible peak of amorphous graphene or the fraction just too small. Figure 1 reveals that the substrate of the nickel foam appears in the crystalline state. The crystallinity of Mn$_2$O$_3$ is very small compared to the ZnO peak, so Mn$_2$O$_3$ does not look significantly in the ZnO-G-Mn$_2$O$_3$ diffraction patterns.
Figure 2. SEM images of ZnO-G-Mn$_2$O$_3$ nanocomposites with Mn$_2$O$_3$ of (a) 0, (b) 0.008, (c) 0.012, (d) 0.016, (e) 0.02 g. (f) Elemental mapping of nano ZnO-G-Mn$_2$O$_3$ film.

Figure 2 shows the ZnO-G-Mn$_2$O$_3$ nanofilm composite having a spherical and morphological shape with an uneven distribution that has pores. Although it shares the similar porous media, the Ni foam-based supercapacitors are higher density and also show different structure from the Cellulose acetate/PET supercapacitors [6]. The porosity of the ZnO-G-Mn$_2$O$_3$ nanofilm can be determined using Origin software. The nanoporosity of ZnO-G-Mn$_2$O$_3$ can be seen in Table 2. In Figure 1f Mn$_2$O$_3$ spreads on the surface of the ZnO-G-Mn$_2$O$_3$ nanofilm. The porosity of nano ZnO-G-Mn$_2$O$_3$ can be calculated using Equation 1.

\[
\text{porosity} = \frac{V_{\text{porous}}}{V_{\text{total}}} 
\]  

(1)
Table 2. The porosity of the ZnO-G-Mn$_2$O$_3$/Ni foam.

| Mn$_2$O$_3$ (g) | Pore size (μm) |
|----------------|----------------|
| 0              | 0.7            |
| 0.008          | 0.6            |
| 0.012          | 0.7            |
| 0.016          | 0.7            |
| 0.020          | 0.6            |

Figure 3. Particle size distribution of ZnO-G-Mn$_2$O$_3$ for various Mn$_2$O$_3$ of (a) 0, (b) 0.008, (c) 0.012, (d) 0.016, and (e) 0.02 g.

Particle size distribution from SEM images which were analyzed using software Image J is shown in Figure 3. The average of particle size for ZnO-G-Mn$_2$O$_3$ is 44.27, 55.80, 24.27, 56.08, and 31.10 nm for the associate Mn$_2$O$_3$ fraction of 0.0, 0.008, 0.012, 0.016, and (e) 0.02 g respectively. From the addition of mass Mn$_2$O$_3$ results that at the addition of 0.02 grams and 0.012 grams shows the best value of some
mass addition of Mn$_2$O$_3$. Figure 4 shows an increase in the measurement temperature in the 0.02 g Mn$_2$O$_3$ sample resulting in an increased dielectric constellation. The dielectric constant is calculated using Equation 2. The dielectric constant for all samples is shown in Figure 4.

$$\varepsilon_r = \frac{C \cdot d}{\varepsilon_0 \cdot A}$$  \hspace{1cm} (2)

where $\varepsilon_r$ and $\varepsilon_0$ are relative and vacuum permittivity $\approx 8.854 \times 10^{-12}$ C$^2$/Nm$^2$. Whereas $A$, $d$, and $C$ is the area, thickness, and the capacitance the sample.

![Figure 4](image)

**Figure 4.** The dielectric constant of ZnO-G-Mn$_2$O$_3$/Ni foam for various Mn$_2$O$_3$ and temperature.

From Figure 4, we further detail analyzed the behavior of the sample as a function of temperature. The first group is the decrease due to an increase in temperature. The second group has an optimum value, the dielectric constant increases to a certain temperature and decreases at higher temperatures. A sample showed the third group with 0.02 Mn$_2$O$_3$ which was linear with increasing temperature. The trend of the dielectric constant is also similar to its specific capacitance. When compared with the variations of Mn$_2$O$_3$ of 0.0, 0.016, 0.008 and 0.012 grams, the sample with 0.02 grams has the best particular capacitance at various temperature. This feature is not available from the previous report [6,12].

4. Conclusion
Manganese III oxide (Mn$_2$O$_3$) and ZnO has been successfully synthesized by means of coprecipitation method. The average grain size obtained from XRD patterns fall to 44.13, 42.75, 32.35, 39.55, dan 44.13 nm respectively for Mn$_2$O$_3$ of 0.0, 0.008, 0.012, 0.016, and 0.20. The best dielectric constant shows by 0.012 and while 0.020 show a great performance for temperature dependence of specific capacitance.

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