Electrochemical Performance of Graphene blended $NiFe_2O_4$ Composite

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***Abstract:** Graphene was blended with Nickel ferrite in the form of nanocomposite, which was prepared by solid state synthesis using tartaric acid as an activating agent. The nanocomposite was characterized by XRD, SEM, FTIR and UV Visible spectroscopy. Unlike the other composite materials, the Graphene – Nickel ferrite composite (GNFC) showed high specific reversible capacity, which has been studied by the cyclic voltammeter. The electrochemical impedance studies of GNFC proved that such material can be useful for the anode material of the Li-ion batteries. The fast charge-discharge property may be due to the heteroarchitechure of the GNFC..*

***Keywords :** Graphene, Nickel ferrite nanoparticles, electrochemical performance.*

I. INTRODUCTION

Graphene could be best material for the applications of battery anode material, as it has been explored for the extensive applications in the field of modern electrochemical cells [1]. Graphene has been extensively studied for the batteries, due to its unique features, such as good conductivity and sustainable to the high temperature applications. Often batteries get heated up during the charge and discharge processes. Besides, graphene utilization could make the battery very light and durable for a prolonged period and applicable for high capacity energy storage purposes and expected to reduce the duration of charge interval. Therefore, graphene is always the material of choice for exploration in the area of energy storage battery materials [1]. Unlike the graphite - which naturally available in abundant-, graphene is having excellent conducting property and that supported to make the composite of graphene with different metal nanoparticles and metal oxides [1]. To enhance the conductivity of the graphene, one of the best ways is to make the composite materials with the metal or metal oxides, which can bind to the graphene through metal – π bond interaction, which generate new band gap material depending on the percentage of metal associated with it [2]. Furthermore, the surface area plays the major role in batteries, because the charge and discharge cycle mostly rely on the number of active sites, and the active sites increases with the increasing surface area [2]. In a similar way, when the electrodes are made up of graphene materials, the addition of carbon black is not necessary for the electrode preparation. This will reflect in the reduction of weight of the electrode, which becomes lighter, when the graphene or graphene composite has been used as the electrode material. Such graphene-metal composites could be prepared by the solution phase chemical synthesis [3]. However, solution phase chemical synthesis is time consuming and involves multi step synthesis. Therefore, we are interested to synthesize the similar graphene-metal oxides composites using Nickel ferrite material for blending purposes. There are several advantages of ferrites, as they have remarkable electrical and magnetic properties and also it was used in MRI image enhancement and high density information storage media. Besides, ferrites are popular for its typical ferrimagnetic properties and for high electrochemical stability, which allowed us to make the Graphene – Nickel Ferrite Composite (GNFC). As expected, the solid state synthesis may provide an easy access to the attachment of nickel ferrite nanoparticles over graphene sheets. Furthermore, we also investigated the electrochemical activity of GNFC material to understand the fundamental significance of electrochemical conductivity and examined the suitability of this material for the Li-ion batteries. For example, Hui Lv et al have demonstrated the principle of graphene blended Fe_3O_4 nanoparticles, which functioned as electro-catalyst in Lithium Air batteries [4]. More particularly, the high temperature annealing process is expected to improve the carbon bed quality for the conductivity of the graphene and optimization of the interface of graphene-nanoparticles [5]. Among the various processes of making GNFC, nanoparticles embedded graphene is a new approach to prepare the electrodes for batteries [6]. When the nickel ferrites are calcined at high temperature and those materials displayed excellent electrochemical reversibility and cycling capacity [7]. On the other hand, Bocheng Qiu et al explored the cobalt ferrite - graphene aerogel composite material's electrochemical property and found to have good cyclic performance [8]. Besides, the morphology of Nickel ferrite nanoparticles also found to be important, because that also influenced the charge discharge capacity of the graphene - nickel ferrite nanocomposite [9]. Furthermore, the plasma treated grapheme can enhance its specific capacitance and power density [10].

These factors influenced us to explore a novel graphene / Nickel ferrite composite by the solid state synthesis method. The graphene-nickel ferrite electrochemical properties are studied by cyclic voltammetry and other characterization of composite was performed by

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X-ray diffraction (XRD), UV Visible spectroscopy.

II. Experimental Section

GNFC was prepared by Graphene / $NiFe_2O_4$ composite structure can be fabricated by incorporating nanostructured $NiFe_2O_4$material with Graphene. Graphene / $NiFe_2O_4$ composite structure was prepared by solid state synthesis. Graphene was synthesized by modified Hummers method. Nickel ferrite was synthesized by chemical co precipitation method. The electrodes were prepared by dispersing a mixture of the prepared graphene/Nickel ferrite composites), and a polystyrene binder (mass ratios: 5:1:4) dissolved in toluene onto a Cu foil current collector.

A. Synthesis of Nickelferrite (NiFe2O4) Nanoparticles

$NiCl_2.6H_2O$ (0.3 M, 100 mL) and $FeCl_2.6H_2O$ (0.5 M, 100 mL) were mixed and to that sodium hydroxide (8 M, 100 mL) was added to the mixture of Nickel chloride and ferrous chloride and it was heated with stirring at 80 ^{0}C for 1 h. This rendered the precipitate, which was filtered and annealed and calcined at 550 ^{0}C for 5 h, which was cooled and collected the reddish nickel ferrite product.

B. Synthesis of Graphene/NiFe2O4 Composite :

Graphene (1 g), nickel ferrite nanoparticles (0.05 g) and tartaric acid (0.5 g) were grinded in a mortar and heated at 600 ^{0}C for 4 h in a muffle furnace. The product became dark red color, which was cooled and characterized by SEM.

III. Results and Discussions

GNFC has been synthesized in many different pathways. However, we have used the solid state synthesis, which has not been explored until now. Here, nickel ferrite and the graphene has been grinded to become a homogeneous mixture and further mixed with tartaric acid, an activator for the synthesis of GNFC. This was kept in the crucible and heated at 600 ^{0}C in a muffle furnace to get the GNFC in the form of brick red color powder. This GNFC has been characterized by SEM, FTIR, XRD to understand the composite nature of the material. Among the various methods that has been utilized for the synthesis of GNFC, our method is less time consuming and followed the simple protocol to facilitate the synthesis of GNFC in a large scale for the battery applications. $NiFe_2O_4$ appeared as homogeneously dispersed graphene sheets and irregular nonorods as observed by the SEM images. This solid state synthesis makes the attachment of nickel ferrite into the graphene base material non-uniformly, which reflect mostly in the performance of the material, when examined by the impedance and cyclic voltammeter studies. Being the carbon material, graphene has unique conductivity property, which can be modulated by making the composite of it with different metal sources and that will reduce the hydrophobicity of the material, which can help to improve the conductivity of the material. This is the hypothesis, which has been examined by this study.

Graphene embedded $NiFe_2O_4$ nanoparticles helped the graphene sheets to get separated into different shapes and formats and that improved the conductivity of the composite material. Many of the previous studies proved that the composite of graphene with nickel ferrite gets the high mechanical strength of graphene, which can also support integration of the composite material to function as a single sourced material [1]. We observed. Often quality of the graphene helps to enhance performance in terms of energy density and longer cycle life in Li-ion batteries.

XRD analysis of GNFC

The XRD results support the formation of nickel ferrite composite material; in which we observed the peaks emerged from the graphene and the nickel ferrite [3]. The peak at 2θ = 26^0 is (002) belongs to the graphene materials. The other diffraction values of 2θ = 21.83^0, 32.97°, 35.42°, 37.89^0, 44.19°, 54.40° could be attributed to the hkl values ((111), (220), (311), (222), (400), (422)) of nickel ferrite nanoparticles respectively, which is in agreement with JCPDS card no 10-0325 [11,12].

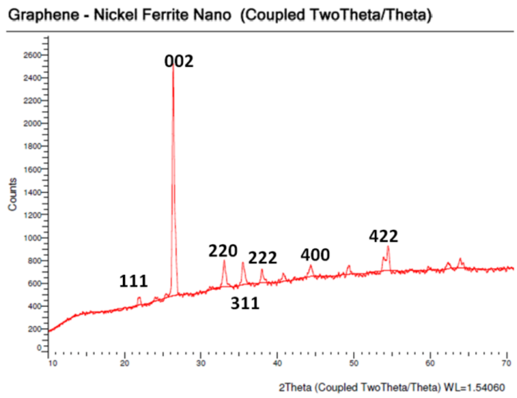

Figure 1. XRD of Graphene Nickel ferrite nanocomposite

FTIR Analysis of GNFC

The FTIR analysis of the GNFC also supports the formation of graphene-nickel ferrite composite material as the peaks of Fe–O stretching vibration appeared at 585 – 578 cm^{-1}, which previously has been assigned to the stretching vibrations of the tetrahedral M-Oxygen bond. Besides, the band at 422 – 421 cm^{-1} attributes to the M - Oxygen vibrations – octahedral sites. Although the OH peaks are very weak, due to the presence of metal oxides and they appeared at 3672 cm^{-1}. Furthermore, a weak peak at 991 cm^{-1} could be assigned to the presence of C=C-H bending vibrations from the graphene materials.

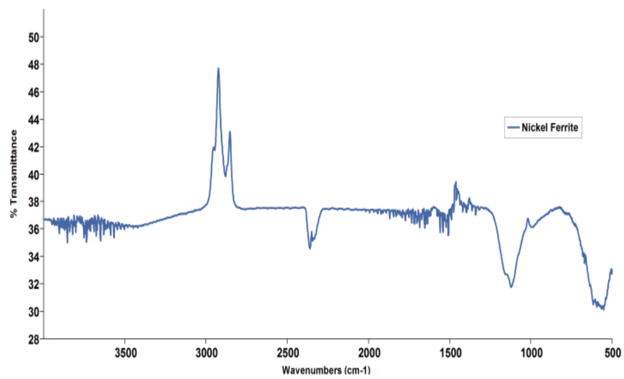

Figure 2. FTIR of the GNFC, performed with KBr pallet

We also measured the UV-vis spectroscopy for GNFC, which gave the red shifted peaks at 290 nm and the absorption peaks at 347 nm attributed to the presence of nickel ferrite nanomaterials.

SEM analysis of GNFC

The morphology and structure of GNFC nanocomposite has been examined by SEM. As shown in Fig. 4. graphene materials appeared in different forms that include sheets and rolled sheets [14]. There are many nickel ferrite nanoparticles appeared as in different forms and they are also embedded on the graphene sheets. We have also observed the intercalated nickel ferrite nanoparticles in between the graphene sheets.

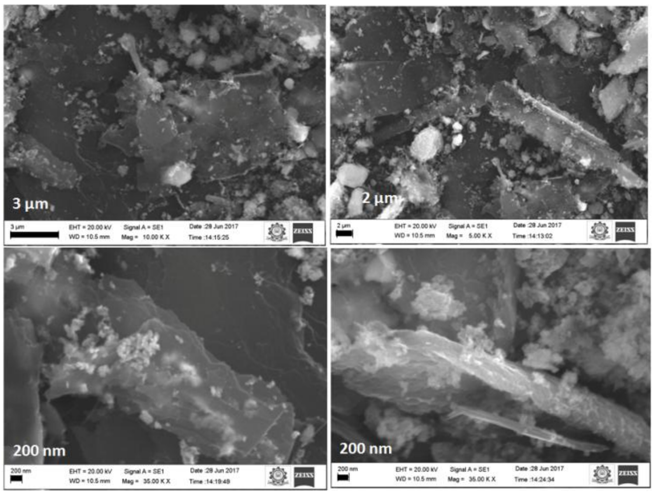

Fig. 4.SEM images of GNFC materials in different magnifications

Electrochemical performance of GNFC

The electrochemical conductivity studies revealed the enhanced electrochemical performance due to the presence of graphene and nickel ferrite in the form of composite [15,16]. The presence of graphene could reduce the mechanical stress during charging discharging cycles. A good electrochemical performance of this material could be due to the strong annealing and good blending nature of nickel ferrite with the graphene and possible due to the good intercalation of the nickel ferrite into the sheets of graphene. We have used the three-electrode system using 1 M NaCl aqueous solution as electrolyte. Platinum electrode and Ag/AgCl electrode are used as reference and counter electrodes. The working electrode was prepared using the composite and polystyrene dispersed in toluene. We performed the cyclic voltammetry (CV) curves of the GNFC at the scan rate of 50 mV/s and 100 mV/s between -1.5 V to 0.5 V. As shown in the Table 1., GNFC showed a high electrochemical activity. The area of the CV curve was quite large and appeared in rectangular shape of the CV curve, which is not regular, because of the complex capacitance offered by the materials. The electrochemical behavior of the GNFC followed the property of the pseudo capacitor like material, which might be due to the double layer capcity of the [13].

Specific capacitance = Area of the CV curve / (mass of the sample*scan rate*potential window)

$Csp = \int Idv/vm\Delta V$

Specific capacitance was calculated and found to be 10.65 Fg^{-1} for 50 mVs^{-1} scan and 8.1 Fg^{-1} for 100 mVs^{-1} scan.

Table 1: Specific capacitance of GNFC

Scan rate mV/s.	*Specific capacitance Fg^{-1}*
50	*10.65*
100	*8.1*

The electrochemical impedance spectroscopy (EIS) curve of GNFC has shown in fig. 5.. The EIS provides the information of the charge storage capacity and the electron transfer capacity of the material. EIS was performed in the frequency range of 1 Hz to 0.1 MHz. GNFC displayed a straight line in the high frequency region, which confirms the ideal capacitive behavior of the composite materials. The equivalent circuit has three resistances of R_1, R_2 and R_3 with values 6Ω, 31Ω and 300Ω and two capacitances.

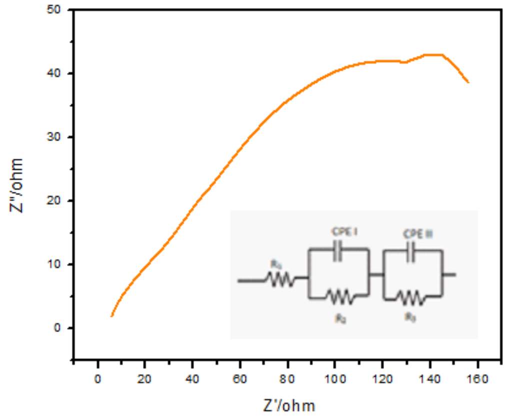

Fig. 5. Nyquist plot of Graphene Nickel ferrite nanocomposite

IV. CONCLUSION

GNFC has been prepared successfully by the solid state synthetic method from the sources of graphene and nickel ferrite, which formed the composite material and that having the dual property of graphene and the metal oxides. This composite material was characterized by the XRD, SEM, FTIR and UV-Vis spectroscopy. From the analyses of cyclic voltammetry and electrochemical Impedance spectroscopy revealed that the GNFC could be a best alternative to be used in the anode material of Li-ion batteries as they displayed a good electrochemical performance and further applications in this direction is in progress.

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