Synthesis and characterization Fe₃O₄/GOnanocomposites as lithium-ion battery anodes (LIBA)

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Abstract. The Nanocomposite based on magnetite-graphene oxide Fe₃O₄/GO for Lithium-Ion Battery Anodes (LIBA) has been successfully synthesized by co-precipitation method. First, GO was synthesized by Hummer's Method and Nanoparticles Fe₃O₄ were synthesized by co-precipitation method and coated with PEG 6000. Then the results were characterized by XRD and SEM. From the results obtained, graphite has become graphene oxide indicated by a shift of 2θ from 26.18° to 11.7°. Nanoparticles Fe₃O₄ have also been successfully demonstrated with corresponding results. As well as Nanocomposite Fe₃O₄/GO which match the characteristics. I-V Meter results showed that nanocomposites have good electrical properties.

Keyword: Co-Preipitation Method, Graphene oxide, Hummer’s Method, Nanoparticles Fe₃O₄

1. Introduction
The development of nanocomposite technology in particular is currently very rapid. Lots of materials are used and combined with other materials in order to obtain new materials to improve quality in various applications. One material that is at the center of research today is graphene [1]. Graphene is a material composed of carbon atoms that has a hexagonal lattice arrangement with a thickness of one atom. Two-dimensional structure and covalent bonding in graphene make it has interesting physical properties such as electrical, optical and mechanical properties [2-3]. Graphene has superior properties and wide application potential in areas such as nanoelectrics, sensors, nanocomposites, batteries, supercapacitors, and transparent electrodes [4-5]. Graphene is a promising material for energy storage because of its superior electronic conductivity, good thermal stability, exceptional structural flexibility, and high specific surface area [6]. With a thickness of about one carbon atom, graphene has optical transparency of up to 97.7%. Although very thin, the strength of graphene exceeds steel. Strong carbon-to-carbon covalent bonds make graphene difficult to stretch, so it has a Young modulus of up to 1.1 TPa. Structures consisting of layers make graphene highly conductive with charge carrier mobility of up to 200,000 cm²V⁻¹s⁻¹ and thermal conductivity of up to 5,300 Wm⁻¹K⁻¹ [7]. Graphene Oxide (GO) is an allotrope of carbon contains a random distribution of oxygen-containing functional groups which are combined with the carbon atoms retain sp² hybridization. GO is cheaper and easier to manufacture than graphene and can be easily reduced to Graphene-like sheets by removing the oxygen-containing groups leads to easily to be mixed with different polymers and other materials and enhance properties like conductivity, elasticity, tensile strength and more in solid form for composite [8]. GO is very attractive because of its low cost, easy access, and broad ability to be converted into graphene. Scalability is an important factor for graphene synthesis and one of the most
The Hummers method is a method used to oxidize graphite by reacting graphite with potassium permanganate (KMnO₄) and sodium nitrate (NaNO₃) in a solution of sulfuric acid (H₂SO₄). This method is commonly used because the material is easy to get and not too dangerous like other methods [11]. As research develops using graphene material, the Hummers method becomes an interesting study for further development.

To increase the targeting ability, graphene should be combined with some magnetic nanoparticles, such as Fe₃O₄ to form nanoparticle/graphene oxide. In a magnetic field, the GO could migrate directly to the target position [12]. Fe₃O₄ nanoparticles is low cost, non-toxicity, eco-friendly and facile preparation methods. Moreover, Fe₃O₄ nanoparticles exhibit remarkable magnetic, electrical, optical and chemical properties which enhance their response to the external magnetic field and therefore greatly facilitate the treatment of the particles in practical uses. Anodes and cathodes have an important role in the performance of lithium batteries. The material that has been developed as a lithium battery anode is Fe₃O₄, because it has a high theoretical capacity of 924 mA.h.g⁻¹, low cost, and environmentally friendly [13].

2. Experimental

2.1. Material
All the chemical reagents which was used in this study were of analytical grade and were used without further purification.

2.2. Preparation of GO
The first step in this process is to insert 2 gr of graphite into the beaker glass. Then added 1 gr of NaNO₃. This mixture was dissolved in 46 ml of 97% H₂SO₄ and stirred on a magnetic stirrer at temperature conditions below 20°C. After 1 hour of stirring, add 6 gr of KMnO₄ slowly while continuing to stir. After 1 hour then the solution is stirred at 40°C and continue to stir for 3 hours. The solution is keep in room temperature for a night. Then, add 100 ml of H₂O slowly. After that the solution is heated at 50°C and stirred for one hour. Then add another 150 ml H₂O. At this stage the solution will turn brown. Then add 10 ml of H₂O₂30%and stirring for 30 minutes. The solution will turn yellow. To obtain deposits, remove the remaining water slowly so that no sediment is wasted. Wash the sediment continuously until the pH is neutral. Maybe we have 3-4 days to make the solution neutral. The filtering results are sonicated for 30 minutes, a graphite oxide is produced in dispersed water. Then it was heated at 100°C for 5 hours. And we have a powder of graphene oxide.

2.3. Preparation of Nanoparticles Fe₃O₄
This nanoparticles is synthesis with coating PEG (polyethylene glycol) 6000 with co-precipitation method. 25 gr iron sand was stirred in 200 ml H₂SO₄ 97% for 90 minutes at 70°C and 450 rpm. Then filtered using paper filter and 1 mmol of PEG 6000 was added and stirred for 90 minutes. Two glasses of 100 ml 6.5 M NH₃ 25% Solution prepared by stirring with 350 rpm at 70°C. Until co-precipitation appeared at the bottom of both glasses. The precipitate materialthen was separated from the solution, washed with distilled water until its pH has reached 7, heated at100°C for 5 hours, until Fe₃O₄ nanoparticles powder were obtained.

2.4. Preparation of Nanocomposites Fe₃O₄/GO
This synthesis is using co-precipitation method. 1 gr of GO was dispersed in 50 ml sterile water and sonicated for 10 minutes. After that 5 gr of Fe₃O₄ was added and still sonicated for 30 minutes. The solution is heated at 100°C for 5 hours.
2.5. Electrochemical Measurement

I-V Meter can characterize electrical components, such as resistors, diodes, zener diodes and light emitting diodes (LEDs). This tool is able to measure currents from 100 pA to 14 mA. Besides being easy to use, this tool is also equipped with RS 232 for communication with computers. Electrical properties in the form of voltage and current from the sample are tested with this I-V Meter.

3. Result and Discussion

3.1. XRD Analysis

Results of XRD plot of the GO, Nanoparticles Fe₃O₄, and Nanocomposites Fe₃O₄ were shown in Figure 1. From the plot of GO, we can see that the XRD spectra of GO shows a sharp diffraction peak at \( \theta = 11.7^\circ \) with an interlayer distance of 7.5 Å. The high distance of this interlayer distance is due to the introduction of the various functional groups that have been introduced by the oxidation of the GO such as phenol groups, epoxy groups, ketone groups, carboxyl groups, and carbonyl groups. The addition of H₂O molecules and oxygen groups also causes graphene oxide to have wider d-spacing. However, there is still graphite at index (002) with \( \theta = 26.66^\circ \), some impurities such as Sulfur (S) at index (002) with \( \theta = 20.8^\circ \), Nitrogen (N) at index (011) with \( \theta = 23.44^\circ \). This might be due to a less than optimal synthesis process or impurities used [14]. Besides that, Oxygen (O) has appeared in index (201) with \( \theta = 29.1^\circ \) which proves that oxidation has taken place.

The XRD pattern of Fe₃O₄ nanoparticles shows six characteristic peaks for \( \theta \) values of 30.26°, 35.74°, 43.22°, 53.32°, 57.24° and 62.8° corresponding to (220), (311), (400), (422), (511) and (440) Bragg reflections of face-centered cubic spinel Fe₃O₄ structure, respectively (JCPDS file, No. 19-0629) which shows that the magnetite diffraction peaks appeared at the same locations with the crystallize size is 67.33 nm. The absence of the peak at \( \theta = 11^\circ \) which is typical for GO structure suggests the complete exfoliation and intercalation of Fe₃O₄ within the GO layers. But, there is a new peak at \( \theta = 33.13^\circ \) with index (100) which is an impurity namely Hydrogen (H). These particles come from H₂O which is used as a solvent. However, overall nanocomposites Fe₃O₄/GO have been successfully synthesized.

![Figure 1. XRD plot of GO, Nanoparticles Fe₃O₄, and Nanocomposites Fe₃O₄](image-url)
3.2. SEM Analysis
The samples were analysed by using SEM to investigate the morphology and size details of the nanocomposites and the results were shown in Fig. 2. From the SEM images we can see that the GO structure is a 2D sheet. Fe$_3$O$_4$ nanoparticles were seen attached to the GO sheet. From the figure, one can notice that the graphene sheets were dispersed between the loosely packed Fe$_3$O$_4$ and that of a big extent of void spaces formed on the material. Furthermore, the graphene sheets distributed between the Fe$_3$O$_4$ can avoid the aggregation of Fe$_3$O$_4$ to a certain extent, which can be of great benefit to reactions.

![Figure 2. SEM Result of GO and Fe$_3$O$_4$/GO Nanocomposites](image)

3.3. Electrochemical Properties
The I-V Meter test results show the relationship between the applied voltage and the measured current, shown in Figure 3. From the figure we can see that there has been an oxidation and reduction process. The resulting graph looks linear between the increase in voltage and the increase in the current of the nanocomposite. The reduction process looks very good which indicates that the nanocomposite has worked well in flowing current.

![Figure 3. Result of I-V Meter](image)

4. Conclusion
The Fe$_3$O$_4$/GO Nanocomposite has been successfully synthesized by the coprecipitation method. Then Nanocomposites Fe$_3$O$_4$/GO were characterized by XRD. The diffraction peaks of Fe$_3$O$_4$/GONanocomposites were in good agreement with the face-centered cubic spinal structure and showed no structural changes in comparison with Fe$_3$O$_4$ nanoparticles. From the SEM result, we can see
that the GO structure is a 2D sheet. Fe$_3$O$_4$ nanoparticles were seen attached to the GO sheet. I-V Meter results showed that nanocomposites have good electrical properties.

References

[1] Nene A G, Takahashi M, Somani P R, Aryal H R, Wakita K, & Umeno M. (2015). Synthesis And Characterization of Graphene-Fe$_3$O$_4$ Nanocomposite. Carbon - Science and Technology, 8(1), 13-24.

[2] Refitasari Y, Suhendar H, Imani N, and Luciana F. (2016). Sintesis Graphene Oxide dan Reduced Graphene Oxide. Prosiding Seminar Fisika V, 95-98.

[3] Simamora, P., Manullang, M., Munthe, J., and Rajagukguk, J. (2018). The Structural and Morphology Properties of Fe3O4/Ppy Nanocomposite. In Journal of Physics: Conference Series (Vol. 1120, No. 1, p. 012063). IOP Publishing.

[4] Simamora, P., Saragih, C. S., Hasibuan, D. P., and Rajagukguk, J. (2018). Synthesis of nanoparticles Fe3O4/PEG/PPy-based on natural iron sand. Materials Today: Proceedings, 5(7), 14970-14974.

[5] Lesmana D, Pranata G, Nurlina R, Aprilia A, Syakir N, & Fitrilawati. (2016). Karakteristik Transaparansi Film Tipis Oksida Grafena Tereduksi (R-GO) Untuk Elektroda Transparan. Jurnal Material dan Energi Indonesia, 01(2016), 15-19.

[6] Liu Y, Siddique A H, Huang H, Fang Q, Deng W...Liu Z. (2017). In Situ Preparation of Fe$_3$O$_4$ in a Carbon Hybrid of Graphene Nanoscrolls and Carbon Nanotubes as High Performance Anode Material for Lithium-ion Batteries. Journal Nanotechnology.

[7] Perkasa M B, Maryati Y, Nurlina R, Syakir N, & Fitrilawati. (2016). Pengaruh Proses Reduksi Termal Terhadap Struktur Oksida Grafena. Prosiding Seminar Nasional Fisika dan Aplikasinya, Universitas Padjadjaran.

[8] Kamakshi T, Sundari G S, Erothu E, & Rao T P. (2018). Synthesis and Characterization of Graphene Based Iron Oxide (Fe$_3$O$_4$) Nanocomposite. 11(3), 1113-1119.

[9] Alam S M, Sharma N, & Kumar L. (2017). Synthesis of Graphene Oxide (GO) by Modified Hummers Method and Its Thermal Reduction to Obtain Reduced Graphene Oxide (rGO). Scientific Research Publishing Inc. 6, 1-18.

[10] Najib A A, Amri A, & Olivia M. (2018). Pengaruh Konsentrasi Grafena Oksida dan Curing Temperature Pada Sintesis Mortar Geopolimer Berbasis Limbah Palm Oil Fly Ash (POFA). Jom FTEKNIK. 5(2), 1-5.

[11] Syakir N, Nurlina R., Anam S, Aprilia A, Hidayat S, & Fitrilawati. (2015). Kajian Pembuatan Oksida Grafit untuk Produksi Oksida Grafena dalam Jumlah Besar. Jurnal Fisika Indonesia, 19(55), 26-29.

[12] Fu R & Zhu M. (2016). Synthesis And Characterization Of Structure Of Fe$_3$O$_4$@Graphene Oxide Nanocomposites. Advanced Composites Letters, 25(6), 143-146.

[13] Bock, D. C., Pelliccione, C. J., Zhang, W., Timoshenko, J., Knehr, KW, Marschilok, A. C. (2017). Size dependent behavior of Fe$_3$O$_4$ crystals during electrochemical (de)lithiation: an in situ X-ray diffraction, ex situ X-ray absorption spectroscopy, transmission electron microscopy and theoretical investigation. Phys.Chem.Chem.Phys. 2017(19), 20867-20880.

[14] Hanh, N.T., Xuyen, N.T. and Thuy, T.T.T., 2018. Synthesis and characterization of Fe3O4/GO nanocomposite for drug carrier. Vietnam Journal of Chemistry, 56(5), 642-646.