

Synthesis of Composite Graphene/ Fe₃O₄ by Electrophoretic Deposition Using Pulse Direct Current

Ervina Rumpakwakra¹, Hariyati Purwaningsih², Widiyastuti¹ and Heru Setyawan¹

¹Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Surabaya

²Department of Material and Metallurgy, Institut Teknologi Sepuluh Nopember, Surabaya

e-mail: sheru@chem-eng.its.ac.id

Abstrak—Composites Graphene/Fe₃O₄ have been successfully synthesized by the electrophoretic deposition method using pulse direct current (PDC) on a nickel foam substrate. In this study, we synthesized graphene and Fe₃O₄ separately before the two materials were composited. We synthesize graphene from coconut shell charcoal and synthesize Fe₃O₄ from pure iron. Graphene and Fe₃O₄ which have been formed, are dissolved with demineralized water as a dispersing medium so that a solution of 1.5 mg / mL is obtained which is then compiled layer by layer on the surface of the substrate with variations in deposition time of 10 to 30 minutes at room temperature. This aims to determine the effect of deposition time on the formation of graphene/Fe₃O₄ composites. The results showed that the use of PDC was able to precipitate graphene/Fe₃O₄ composites on the surface of the substrate. The use of longer deposition time, results in more graphene/Fe₃O₄ composites which adhere to the substrate surface. This result is also supported by XRD testing which shows the longer the deposition time, the diffraction peaks appear sharper.

Kata Kunci—Graphene, Electrophoretic Deposition, Pulse Direct Current, Coconut Shell Charcoal.

I. INTRODUCTION

GRAPHENE is a carbon allotropic material with 2D structures arranged hexagonally. Graphene is very interesting to study because it has a unique structure, good mechanical and electrical properties, high specific surface area, and excellent electrochemistry performance [1]. In addition, magnetite (Fe₃O₄) is also an important magnetic material and is widely used in industry. In recent years, nanoparticles Fe₃O₄ have attracted many attentions due to their good biocompatibility, strong superparamagnetic properties, low toxicity, and easy preparation[2-3]. The advantages possessed by individual graphene and Fe₃O₄ can be synergized to obtain specifically designed functional material by combining the graphene/Fe₃O₄ to be composite material. The graphene/Fe₃O₄ composite has been widely applied in various fields, including catalyst support for Lithium air-battery [4], adsorbent for removal of arsenic metals [5] and methylene blue [6] in the water.

Several methods have been proposed to prepare graphene/Fe₃O₄ composites such as solvothermal, co-precipitation, and hydrothermal methods. However, the methods typically require high temperature and time-consuming, and use relatively expensive chemicals such as hexamethylene-tetramine (HTMA), polyethylene glycol

(PEG,) sodium acetate trihydrate and hydrazine hydrate. In addition, the composites obtained still contained impurities that must be washed with demineralized water and ethanol.

In this research, we investigated the process of graphene/Fe₃O₄ synthesis by electrophoresis deposition method using pulse direct current based on variations in deposition time to determine its effect on the formation of graphene/Fe₃O₄. The synthesis process of graphene/Fe₃O₄ composites is carried out in 2 steps, that is: (1) synthesis of graphene from coconut shell charcoal by modification of the hummers method and synthesis of Fe₃O₄ from pure iron by electrolysis method, and (2) synthesis of graphene/Fe₃O₄ composites by using electrophoretic deposition methods using pulse direct current on the nickel foam substrate, demineralized water electrolytes. The electrophoresis method produces a thin layer of nanocomposites which will be optimized for phase, and microstructure.

II. METHOD

A. Materials

The materials to be used in this research are coconut shell charcoal, scrap metal, demineralized water, Sodium Hydroxide (NaOH), Lewatit M-500 anion resin, Sodium Nitrate (NaNO₃) (SAP, distributor of UD. SIP), Sulfuric Acid Solution (H₂SO₄) 20% (98%, Mallinckordt, distributor of Darmstadt Germany), Potassium Permanganate (KMnO₄) (SAP, distributor of UD. SIP), Citric Acid (SAP, distributor of UD. SIP), Hydrochloric Acid Solution (HCl) 10% (37%, Mallinckordt, distributor of Darmstadt Germany), ice, Peroxide Acid Solution (H₂O₂) (30%, Merck, Darmstadt Germany distributor), Ammonium Hydroxide (NH₄OH) solution, and Nitrogen gas (PT. Aneka Gas).

B. Experimental

1) Synthesis of Graphene

a. Activation of coconut shell charcoal

Coconut shell charcoal was crushed and sieved to 120 mesh. The resulting charcoal powder was activated with KOH using a weight ratio of charcoal to KOH of 4: 1. The mixture was heated in a tubular furnace with the nitrogen gas flow at a temperature of 400°C for 1 h and 800°C for 3 h. Then, it was washed with 25 mL of 20% H₂SO₄ under stirring using a magnetic stirrer for 1 h. The mixture was then transferred to a centrifuge tube and washed with

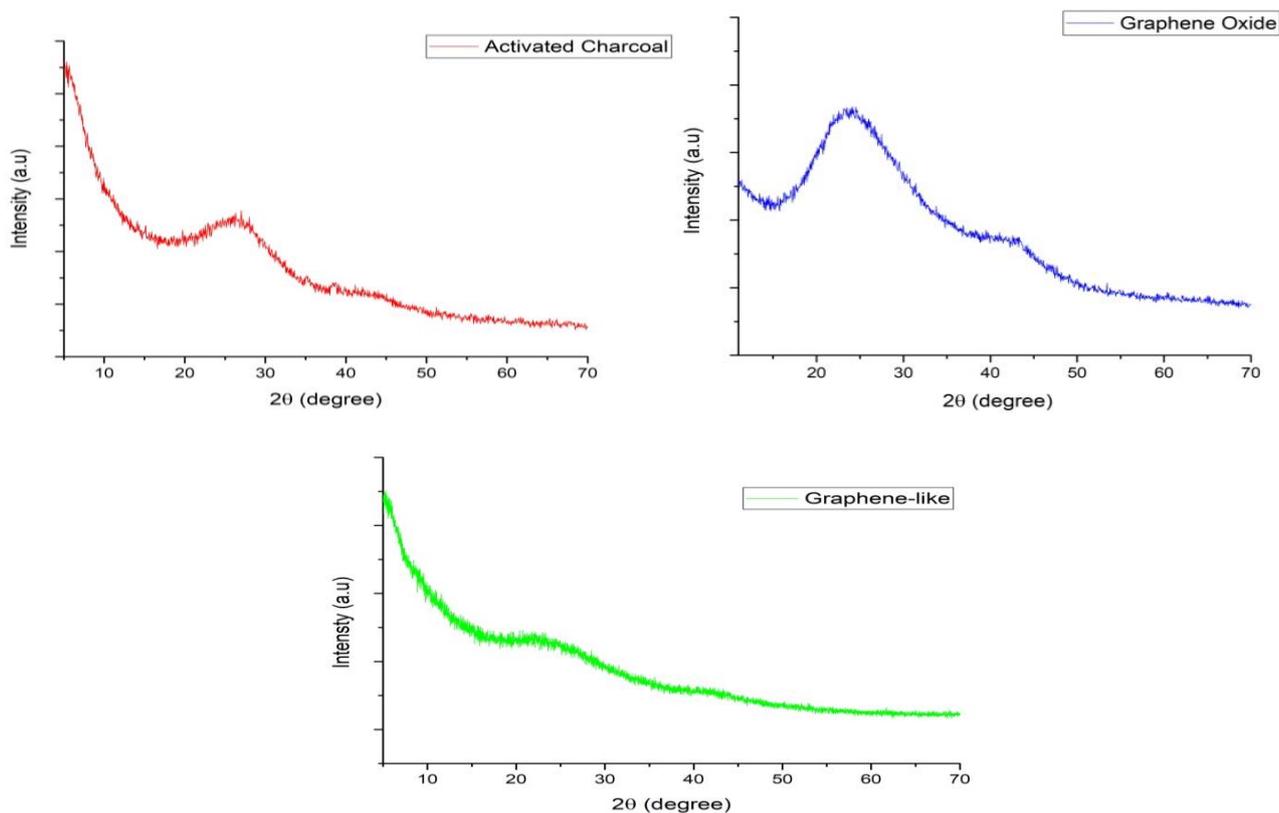


Figure 1. XRD results of (a) activated charcoal, (b) graphene oxide, and (c) graphene-like

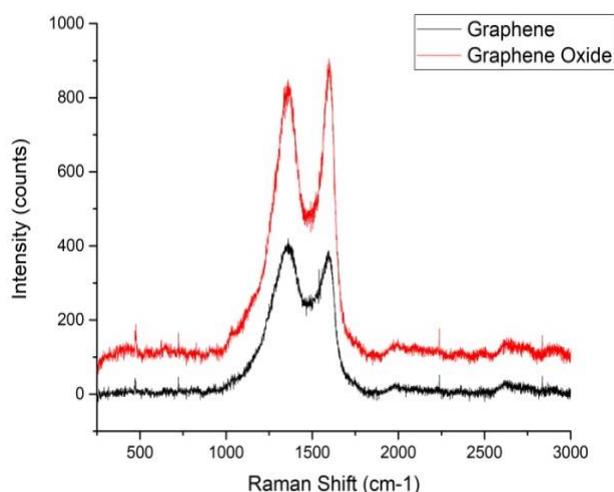


Figure 2. Raman Spectroscopy graphene oxide and graphene-like.

demineralized water to neutral pH and dried at 80°C in an oven for 1 h.

b. Synthesis of graphene oxide

2 g of activated charcoal were mixed with 80 mL of 98% H₂SO₄ in an ice bath at temperature of 5°C under stirring for 2 h. Then, 10 g KMnO₄ and 4 g NaNO₃ were added drop by drop for 1 h while continuing the stirring. The mixture was moved into a water bath at 40°C and allowed at that condition for 20 h. 80 mL of demineralized water was added into the mixture and it was stirred for one hour at a temperature of 5°C in an ice bath. It then was transferred into a water bath and allowed in it for 1 h at a constant temperature of 80°C. It was returned to the ice bath at 5°C and 200 mL of demineralized water was added slowly while stirring for one hour. Then, 20

mL of 30% H₂O₂ was added drop by drop under stirring for 30 min. 100 mL of 10% HCl was added for 30 min. The precipitate obtained was separated by centrifugation, washed with demineralized water until neutral pH, and dried at 80°C for 12 h.

c. Reduction of graphene oxide.

Reduction of graphene oxide is done by dissolving 0.15 g of graphene oxide to 60 mL of demineralized water, adding NH₄OH 1 M with drops to pH 9 and adding 12 g of citric acid. Then mixture was placed in a muffle furnace with a temperature maintained at 95°C for 120 min. Then, it was washed with demineralized water to neutral pH and dry 80°C for 12 h.

2) Synthesis of magnetite

The synthesis of Fe₃O₄ nanoparticles follows the procedure developed by Nurlilasari et al. [2]. Briefly, iron anodes were electro-oxidized in alkaline solution where the 4-pair electrodes were arranged in an alternating monopolar configuration. The voltage and pH of the electrolyte were set constant, respectively, at 25 V and 9. The electro-oxidation was conducted for 3 h at room temperature. The black precipitates were separated from the solution, washed with demineralized water, and dried in an oven at 80°C for 12 h.

3) Synthesis of graphene/Fe₃O₄ composite film by electrophoretic deposition

The electrophoretic deposition was carried out using pulsed direct current on the nickel foam substrate. The nickel foam used has a size of 5 x 2 cm with a thickness of 0.115 cm, the distance between the electrodes is 2 cm. The initial step

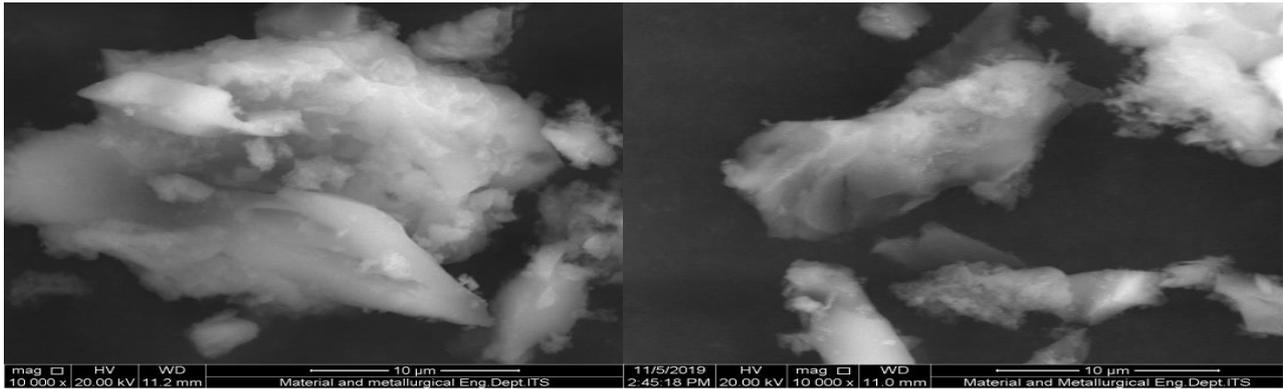


Figure 3. The morphology of (a) graphene oxide and (b) graphene-like.

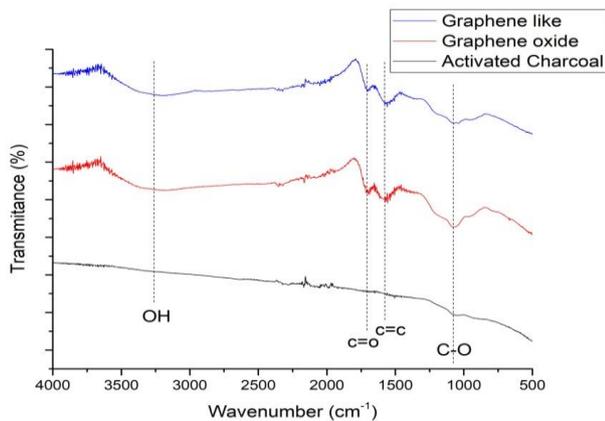


Figure 4. FTIR analysis from activated carbon, graphene oxide and graphene-like.

of composite synthesis is to make a solution of graphene and Fe_3O_4 with a concentration of 1.5 mg/mL which is carried out alternately by weighing as much as 0.15 g and adding 100 mL of demineralized water to graphene and Fe_3O_4 respectively, then sonicated during 30 min. The next step is the composite synthesis process where graphene is first deposited on the surface of the nickel foam for 10 min, after that Fe_3O_4 particles are deposited on the graphene surface with the same time also 10 min at room temperature. Then the graphene/ Fe_3O_4 composite formed is dried at 50 °C for 30 min using a sonicator. The same process is carried out for all time variations. Variable that used a 70% duty cycle, a frequency of 80 Hz, an amplitude of 10 V and a deposition time of 10, 15, 20, 25, and 30 min.

III. RESULT AND DISCUSSION

A. Graphene Properties

Graphene was synthesized from coconut shell charcoal through several stages: activation by KOH, oxidation by the modified-Hummer method, and reduction using citric acid. Figure 1 shows the XRD patterns of the samples after activation (activated charcoal), oxidation (graphene oxide; GO), and reduction (graphene-like). Activated (Figure 1a) charcoal has characteristic peaks at $2\theta = 26.26^\circ$ and 43.26° . The characteristic peaks matched well those of the standard pattern of graphite (ICDD 00-056-0159). However, the peaks are wide indicating the material is dominated by an amorphous structure. After the oxidation process, in addition

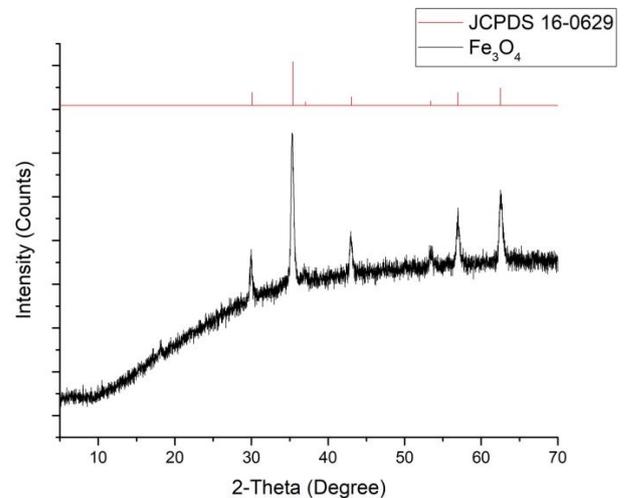


Figure 5. XRD Fe_3O_4 .

to the previous peaks, another peak appears at $2\theta = 23.94^\circ$ and 43.22° . This peak may be caused by the addition of a hydroxyl group that typically exist in graphene oxide (Figure 1b). Graphene oxide reduction results in graphene-like (Figure 1c) with the shift of peaks to $2\theta = 23.75^\circ$ and 43.41° and they are wider than the previous peaks. The results obtained in this study are similar to the results obtained from research conducted by Kartick, et al. [7] which shows the graphene diffraction pattern $2\theta = 24^\circ$, and another peak appears at $2\theta = 43.5^\circ$. So, it can be said that the diffraction patterns produced in this study are close to diffraction patterns such as graphene.

The formation of graphene produced was also analyzed using spectroscopy. Figure 2 shows an increase in the I_D/I_G ratio from graphene oxide ($I_D/I_G = 0.95$) to graphene-like ($I_D/I_G = 1.019$). This is due to the process of reducing graphene oxide to graphene-like which breaks the hydrogen and oxygen bonds randomly, so that the process of rearranging the hexagonal graphene-like bond becomes unequal and defects[8].

The graphene-like morphology was observed using SEM. Figure 3 (a) shows the SEM image of graphene oxide having a thick size in the presence of formed pores. For graphene-like in Figure 3 (b) shows a thinner size compared to graphene oxide, but still not evenly distributed. These results show the reduction process carried out is only able to reduce a portion of the layer of graphene oxide.

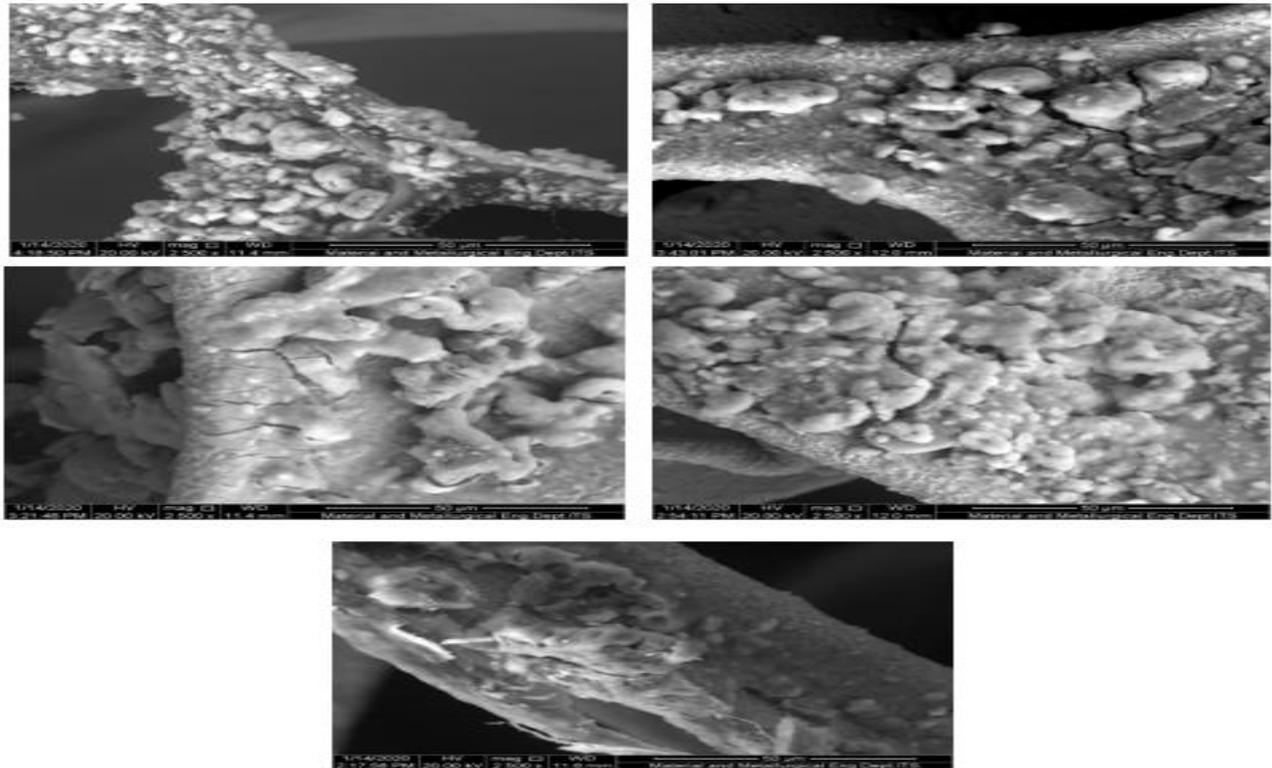


Figure 7. Morphology of composite graphene-like/Fe₃O₄ with time variations of 10, 15, 20, 25, and 30 min.

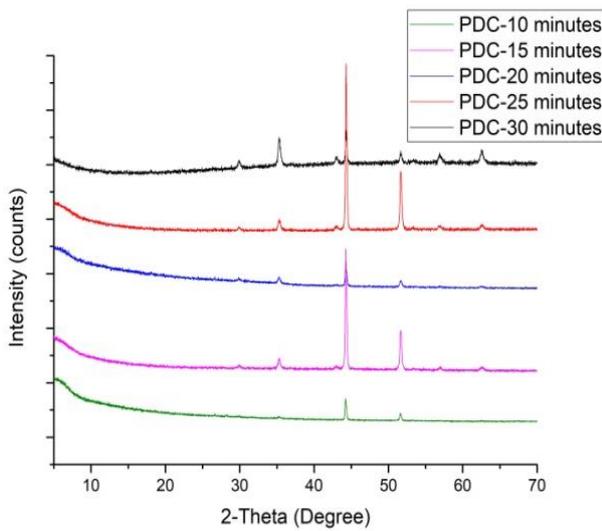


Figure 6. The results of XRD analysis of graphene-like/ Fe₃O₄ composites with time variations of 10, 15, 20, 25, and 30 min.

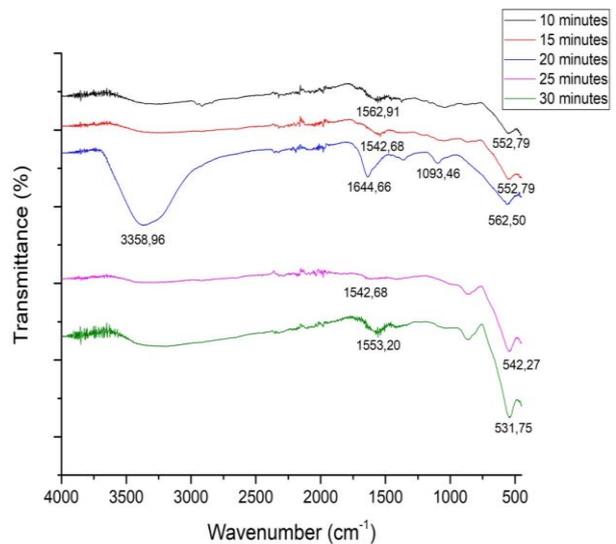


Figure 8. Results of graphene-like/Fe₃O₄ composite FTIR analysis with variations of deposition time of 10, 15, 20, 25 and 30 min.

Based on Figure 4, shows a short peak at a wavelength of 1073.23 cm⁻¹ which is a C-O functional group. These results indicate that the activation process using KOH has removed volatile compounds in the coconut shell charcoal, so that more carbon is produced. In the graphene oxide sample, 4 peaks appeared at wavelengths of 3257.78 (OH), 1695.65 (C = O), 1583.15 (C = C), and 1062.72 (C-O). There are additional OH, C = O and C = C functional groups in graphene oxide samples, which indicate the oxidation process has taken place. In the graphene-like sample 3 main peaks were found, namely 3247.26 (OH), 1553.20 (C = C) and 1040.85 (C-O). The reduced C = O bond indicates that graphene oxide has through a process of reduction to graphene-like.

B. Fe₃O₄ Properties

The synthesis of Fe₃O₄ was carried out using the electrochemical method. In Figure 5 that shows the XRD pattern of samples produced by the electrochemical method, seven characteristic peaks appear at $2\theta = 30.1^\circ; 35.35^\circ; 37.27^\circ; 43.15^\circ; 53.4^\circ; 56.98^\circ; \text{ and } 62.50^\circ$. The peaks match well with the standard pattern of Fe₃O₄ (JCPDS No. 19-0629). The use of alternating monopolar configurations can produce Fe₃O₄ with high crystallinity, and there are no intermediate product reactions in the form of FeOOH compounds found [2].

C. Graphene-like/Fe₃O₄ Composites

Synthesis of graphene-like/Fe₃O₄ composites was carried

out by electrodeposition method using PDC. Figure 6 shows the XRD observations for each variation of deposition time. Overall XRD results for each deposition period showed a peak of $2\theta = 30.13; 35.32; 43.11; 44.29; 51.53; 56.98; \text{ and } 62.54$. The peak that appears is more dominated by the peak of Fe_3O_4 . While the graphene peaks (previously known at $2\theta = 23.75 \text{ and } 43.41$) tend to be more sloping, because the surface of graphene has been covered by Fe_3O_4 particles. Besides the peak of graphene and Fe_3O_4 , other peaks appear at $2\theta = 44.29 \text{ and } 51.53$ which is the peak of the nickel foam that was followed during the analysis.

Graphene-like/ Fe_3O_4 composites were also analyzed morphologically using Scanning Electron Microscopy (SEM) to determine the surface shape of the composite and its distribution. Overall based on Figure 7, it can be seen that on the surface of the nickel substrate a graphene/ Fe_3O_4 composite has been attached. Figure 7 (a) shows a spherical Fe_3O_4 particle attached to the surface of graphene and spread evenly on a nickel foam substrate. In Figure 7 (b) - (e) it can be seen that the particle begins to allate with the particle size becoming large and thick.

The success of composites was also analyzed using FTIR, to determine the functional groups contained in the composite. Based on Figure 8 at minutes 10, 15, 20, and 30 functional groups that appear in OH, C=C and Fe-O. The functional groups that appear respectively represent graphene-like and Fe_3O_4 functional groups. The appearance of the Fe-O peak indicates that the EPD process using PDC has successfully deposited Fe_3O_4 particles on a graphene-like surface. At the 25 minute there is an OH functional group with a sharp peak, C=O, C-O, C=C and Fe-O. Differences in functional groups at min 25 due to the drying process that has not been maximized so that there is still a lot of water that

sticks to the surface of graphene-like/ Fe_3O_4 composites.

IV. CONCLUSION

Based on the research that has been done, it can be concluded that the use of PDC is able to deposit graphene-like/ Fe_3O_4 composites, this is supported by the results of SEM, XRD, and FTIR. As for the variation of deposition time, the longer the deposition time the particles tend to have agglomeration.

REFERENCES

- [1] M. Kim, H. M. Hwang, G. H. Park, and H. Lee, "Graphene-based composite electrodes for electrochemical energy storage devices: Recent progress and challenges," *FlatChem*, vol. 6, pp. 48–76, 2017.
- [2] P. Nurlilasari, W. Widiyastuti, H. Setyawan, F. Faizal, M. Wada, and I. Wuled Lenggoro, "High-throughput production of magnetite nanoparticles prepared by the monopolar arrangement of iron electrodes in water," *Chem. Eng. Sci.*, pp. 112–120, 2019.
- [3] F. Fajaroh, H. Setyawan, W. Widiyastuti, and S. Winardi, "Synthesis of magnetite nanoparticles by surfactant-free electrochemical method in an aqueous system," *Adv. Powder Technol.*, vol. 23, no. 3, pp. 328–333, 2012.
- [4] H. Lv, R. Jiang, X. Zhang, J. Wang, and Y. Li, "A Novel litchi-like Fe_3O_4 /graphene Composite Catalyst for the Lithium – Air Battery," *Int. J. Electrochem. Sci.*, vol. 10, pp. 7622–7630, 2015.
- [5] V. Chandra, J. Park, Y. Chun, J. W. Lee, I. Hwang, and K. S. Kim, "Water-Dispersible Magnetite-Reduced Graphene Oxide Composites for Arsenic Removal," *ACS Nano*, vol. 4, no. 7, pp. 3979–3986, 2010.
- [6] H. Tju *et al.*, "The Role of graphene in Fe_3O_4 /graphene Composites on the Adsorption of Methylene Blue and Their Kinetic Study The Role of graphene in Fe_3O_4 /graphene Composites on the Adsorption of Methylene Blue and Their Kinetic Study."
- [7] B. Kartick, S. K. Srivastava, and I. Srivastava, "Green synthesis of graphene," *J. Nanosci. Nanotechnol.*, vol. 13, no. 6, pp. 4320–4324, 2013.
- [8] A. Romero and J. L. Valverde, "Comparative study of different scalable routes to synthesize graphene oxide and reduced graphene oxide," *Mater. Chem. Phys.*, 2017.