



## Preparation of Fe-intercalated Graphite Based on Coal Tailings, Dimensional Structure

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**Abstract** - Intercalated graphite from coal tailings have been modified through the intercalation of iron. Coal tailings which is a byproduct of the destruction process and flakes washing results from mining coal. Intercalation of iron goal is to improve the physical properties of graphite and modifying sizes of crystal lattice structure with thermal method. Modification process begins with the carbonization of coal tailings at 500°C and activated with phosphoric acid. Activation process has done by pyrolysis at 700°C. The results of pyrolysis was soaked in mineral oil for 24 hours, then pyrolysis again with variations in temperature 800°C and 900°C for 1 hour and subsequent intercalation iron at 1% and 2%. Material before activated, after activated, and the results of pyrolysis still indicates order nano: 29, 25 and 36 nm respectively. X-ray diffraction characterization results indicate that change in the structure, the sizes crystal lattice structure of the material. The greater the concentration of iron was added, the resulting peak at  $2\theta = 33$  and 35 also will be more sharply. The results of SEM showed different morphologies from each treatment.

**Keywords:** Activation; Pyrolysis; Coal tailings; Intercalation.

### Introduction

Graphite has been studied intensively for many applications. Graphite is indispensable as a cathode material to produce a stable electron, compact with high power, but it can also be used as a catalyst because it has a wide surface area. On other hand Graphite Intercalation Compounds (GICs) have attracted considerable attention because of their superconductivity and transition temperature, such as Ca-graphite with  $T_c = 11.5$  K, which is the highest among the GICs (Matsumoto *et al.*, 2009). The structure of GICs can be intercalated with alkali metals and alkali earth metals. Among many possibilities, intercalation of K, Li recently have been considered as an alternative to intercalation for applications in electrochemical energy storage (Kumar *et al.*, 2011). The availability of carbon materials is of special importance from the application point of view. It should be noted that large scale synthesis processes usually demand the presence of a substrate wafer (Virojanadara *et al.*, 2010).

Tuning the electronic structure and carrier densities of graphite-based materials is crucial to modern day semiconductor technology. An example graphite intercalated materials, which are formed by insertion of atomic or molecular layers of different species. Intercalated metal atoms usually occupy interlayer sites above the center of the C hexagon (Emery *et al.*, 2005 and Kaloni *et al.*, 2012), leading to novel and exotic materials properties (Dresselhaus and Dresselhaus, 2002). For example, superconductivity has been observed below temperatures of  $T_c = 0.55$  K (Hannay *et al.*, 1965) and  $T_c = 0.39$  K (Pan *et al.*, 2011) in K-intercalated graphite. In addition, superconducting states of YbC<sub>6</sub> and CaC<sub>6</sub> are obtained at higher temperatures of  $T_c = 6.5$  K and  $T_c = 11.5$  K (Weller *et al.*, 2005), respectively, due to a strong electron-phonon coupling (Valla *et al.*, 2009). Previous studies have reported that graphite source derived from natural materials as graphite nano-sized materials (Mopoung, 2011 and Viswanathan, 2014). The most important issue in the synthesis of graphite one of which is the cost of production, in addition to the quality, and methods of synthesis. Coal tailings not used optimally, only accommodated in ponds deposition and after separated from the water piled up. As barrow, in terms of the commercial does not have any sale value.

This paper has fabricated graphite from coal tailings and iron intercalation. The purpose of modified the graphite of coal tailings are utilizing the byproduct of coal mines and turn it into advanced materials. Fe-Intercalated goal is to improve the physical properties of graphite and modifying sizes of crystal lattice structure with thermal method. Graphite and interactions of Fe have studied by X-ray diffraction, morphology was observed from the SEM image.

### Materials and Methods

Coal tailings were obtained from the coal mining company PT. Bukit Sunur, Bengkulu Indonesia. phosphoric acid (from Merck), Iron (II) chloride tetrahydrate (from Merck). Coal tailings was sorted from impurities and then dried in an oven at 105°C for 2 hours. The next stage is carbonization, coal tailings move into the reactor and carbonization process was carried out at 500°C for 2 hours using a muffle furnace. Carbon from carbonization subsequent activated using phosphoric acid solution with a ratio of 0.5: 1 volume per weight, activation has done for one night with stirring.

The results of activation performed by pyrolysis at 700°C for 2 hours, pyrolysis process was carried out in the same manner by carbonization steps using a muffle furnace, different temperature. The next, soaked in 2% mineral oil for 24 hours. After soaked in in 2% mineral oil were performed by pyrolysis again at 800°C and 900°C for 1 hour. Fe-Intercalated graphite has done by using the FeCl<sub>3</sub> 1% and 2%. Carbon pyrolysis process were soaked in solution FeCl<sub>3</sub> 1% and 2% by means of stirring overnight then heated at 150°C for 2 hours. Materials analyzed are carbon before activation, after activation and pyrolysis and intercalated graphite. Materials were characterized using X-ray diffraction and morphology using SEM.

The X-ray powder diffraction (XRD) analysis were performed using X-ray diffractometer (Rigaku D-MAX2200, Japan) with Cu Ka ( $\lambda = 1.5406 \text{ \AA}$ ) radiation over therange 2 $\theta$  between 0° and 70°. The morphology of the graphite was observed by SEM-type JEOL 7001 FESEM (Tokyo, Japan).

### Results and Discussion

The X-ray diffraction pattern carbon before activation, after activation and pyrolysis (Figure 1). From X-ray diffraction pattern of activated carbon in the process of carbonization, activation of chemical and physical activation is formed consisting of three peaks are at an angle 2 $\theta$  of about 19, 23 and 26°. Three diffractogram showed the same pattern, a different look in terms of the peak intensity of the angle 2 $\theta$  crystal, crystal peak intensity: pyrolysis > after activation > before activation. Diffractogram were showed that at an angle 2 $\theta$  between 35-38°, amorphous phase begins to decline. Pyrolysis diffractogram showed crystalline peaks.

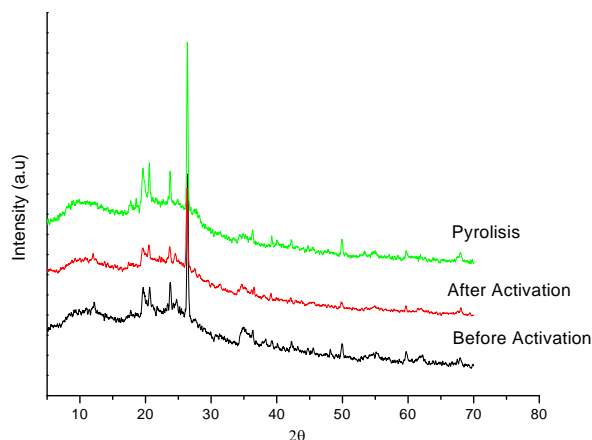


Figure 1. Diffractogram carbon before activation, after activation and pyrolysis.

This crystalline peak intensity differences as a result of the activation of chemical and physical activation influence of temperature increase. Diffractogram pattern of this study is similar to the diffractogram pattern that has been reported previously (Awasthi *et al.*, 2011), where the crystalline peaks

of  $2\theta = 26.4^\circ$  for before activation and after chemical activation at  $2\theta = 13.2^\circ$ . Previous study, according to Iqbal *et al.*, (2013) graphite has hexagonal structure (JCPDS No. 36-1451) with a sharp diffraction peak at  $2\theta = 26.07$ . Another study reported that peak at  $2\theta = 13.2^\circ$ , corresponding to the (002) plane of graphite (Schniepp *et al.* 2006). Peak at  $2\theta$  peak around  $34^\circ$  indicates chaoite or white carbon which is a mineral described as allotropes of carbon whose existence is disputed which merges with the reflection graphite gray to white (Mopoung, 2011), and having electron diffraction pattern with carbyne structures; linear, acetylenic and carbon allotropes. From this diffractogram patterns indicate that pyrolysis results showed peaks sharp crystals at  $2\theta$  between  $20-26^\circ$ .

Structurally, the size of the material before activation, after activated, and the results of pyrolysis still indicates order nano 29, 25 and 36 nm respectively based on the equation of Debye Scherrer. Differences in structural size before activation, after activated and pyrolysis results allegedly under the influence of carbonization temperature and the addition of chemical activator that causes softening effect and leaching when neutralization. Figure 2 showed Fe-intercalated graphite, iron 1% and 2% at  $800^\circ\text{C}$  and  $900^\circ\text{C}$ . The diffraction pattern showed the peaks characteristic of graphite (JCPDS No. 36-1451) similar with previous studied (Iqbal *et al.*, 2013). At concentration of 1% Fe was showed peak characteristics of graphite/Fe although the low peak. Fe was detected in the form  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ .  $\text{Fe}_2\text{O}_3$  peak (JCPDS No. 04-0755) at  $2\theta$  is 32.96 and  $\text{Fe}_3\text{O}_4$  peak (JCPDS No. 19-0629) at  $2\theta$  is 35.42). Compared with intercalated graphite 1% iron, intercalated graphite 2% showed a clear crystalline peaks at  $2\theta = 33$  and 35. The greater the concentration of iron was added, the resulting peak at  $2\theta = 33$  and 35 also will be more sharply. Structurally graphite still allotropes of carbon graphite with hexagonal structure, is one of the classic examples of the crystal as a host that can widely intercalation by some atoms, ions and molecules included in this research report is iron. Graphite with a planar structure allows for iron to the intercalated between the carbon layers. The layers of carbon to form a layer of superposition, the coordination number 3 carbon resulting layers have the distance and as if stacked with a carbon layer underneath the theoretical within  $3,35\text{\AA}$ . Carbon atoms with  $\text{sp}^3$  hybridization, and with the addition of p orbitals, which contains a single electron, perpendicular to the plane of the ring.

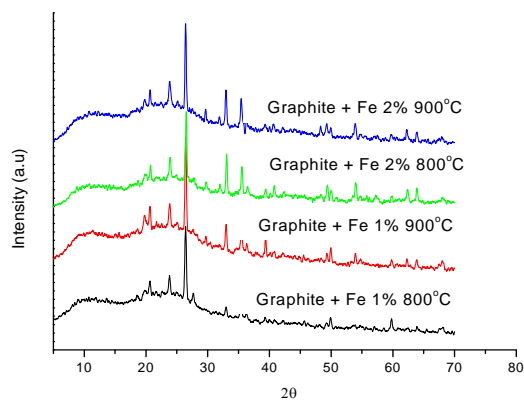


Figure 2. Diffractogram graphite + 1% Fe  $800^\circ\text{C}$ ,  $900^\circ\text{C}$  and + 2% Fe  $800^\circ\text{C}$ ,  $900^\circ\text{C}$ .

Figure 3 showed the morphology of coal tailings before activation, activated carbon and Fe-intercalated graphite. Coal tailings before activation was showed small pores and after activated have pores large enough mean diameter compared with coal tailings before activated. In addition, changes in the pores before activation was influenced by the phosphoric acid activator, because before activation has been activated using phosphoric acid. The use of phosphoric acid as an activator will open the pores of the surface of coal tailings and gone deep into the pores inside. When the physical activation the impurities will be evaporated to leave certain parts to form large pores. Morphology of physical activation showed that the more visible cavities on the surface of activated carbon. This shows that increasing the ability of activated carbon adsorption, the more surface area of activated carbon produced as well as a growing number of cavities on the surface of activated carbon.

The addition of iron showed affects the morphology of the surface structure of graphite. The greater the percentage of iron is added to the result in the morphology of graphite becomes more coarses and pores become larger. Compared with studies that have been reported (Viswanathan, 2014), which has conducted the synthesis and characterization of carbon nano-materials of Calotropis latex using iron, graphite of coal tailings produce rougher surface and uneven surfaces.

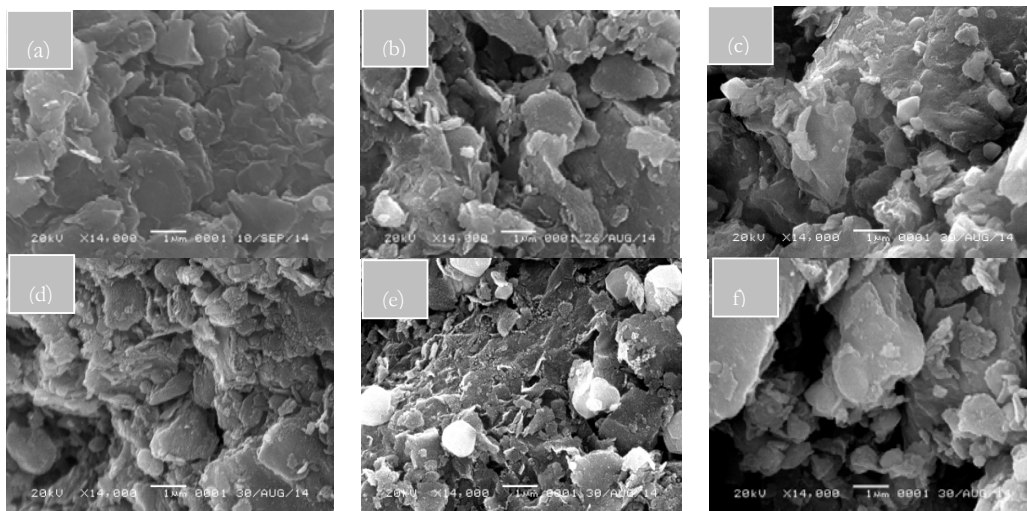


Figure 3. The morphology of coal tailings before activation, activated carbon and Fe-intercalated graphite, (a) before activation, (b) after activated at temperature 500 °C, (c) 1% Fe T 800 °C, (d) 1% Fe T 900 °C, (e) 2% Fe T 800 °C, (f) 2% Fe T 900 °C.

## Conclusions

Fe- intercalated graphite based on coal tailings have been done. X-ray diffraction pattern of activated carbon, activated chemical and activated physical were formed consisting of three peaks, namely at an angle  $2\theta$  around 19, 23 and 26 °. The greater the concentration of iron was added, the resulting peak at  $2\theta = 33$  and 35 also will be more sharply. The affects intercalation of Fe on the morphology of the surface structure of graphite showed that the greater the percentage of iron is added to the result in the morphology of graphite becomes more coarses and pores become larger. From all of treatments showed the pores, and the difference in morphology pores of each such treatment.

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