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Facile preparation of graphite intercalation compounds in alkali solution

Research Article

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Abstract: Graphite intercalation compounds are often prepared by flake graphite, oxidants, inorganic acids, organic acids and intercalated ions which are usually hydrogen protons between the graphene planes. They are also known as the acid-treated graphite intercalation compounds. In this work, alkaline graphite intercalation compounds were prepared by flake graphite, $K_2Cr_2O_7$, concentrated H_2SO_4 and NaOH, and the morphology and structure were characterized by Electron microscopy and X-ray techniques. The results display that the combination of neutralisation heat and oxidation capability produced by $K_2Cr_2O_7$ can break the bonds to produce the spaces between the graphene planes and hydroxyl ions also intercalate into the graphene planes to form alkaline graphite intercalation compounds in alkali solution. The morphology and structure of alkaline graphite intercalation compounds are analogous to the ones of the acid-treated graphite intercalation compounds, but the intercalated ions and the expansion volume are different. The results show that the method is an innovation.

Keywords: *Intercalated OH^- ions in graphite • Multilayer structure • Thermal properties • Electron microscopy • X-ray techniques*

1. Introduction

The graphite crystal structure consists of stacked, two dimensional sheets of carbon [1]. Graphite intercalation compounds (GIC) are formed when hydrogen protons, acid radicals and positive ions are inserted into the spaces between the graphene planes [2,3]. GIC owns a distinct characteristic by which it is able to exfoliate to exfoliated graphite (EG) in the process of the heat expansion. Thereby, GIC is also known as expandable graphite. So far the methods to prepare GIC have included electrochemistry intercalation (anodic oxidation) [4], chemistry oxidation intercalation [5,6], and ultrasound irradiation intercalation [7,8]. All of the GICs prepared by these methods should belong to the acid-treated GIC because hydrogen protons remain between the graphene planes. Although the acid-treated GIC has been used widely in some fields [9-12], they are still confronted with the challenges in the process of the applications. Such as, the expansion volume is too big so that the wormlike structure is broken easily in the process of agitation; the acidity substances seep to erode the surface of the metal; GIC cannot be applied as a solid alkali catalyst in organic chemistry and so on. For answering the challenges, it is very necessary to prepare an alkaline GIC.

In this work, our goals were to intercalate hydroxyl ions into the graphene planes and to prepare the alkaline GIC. For carrying out the goals, the preparation of the alkaline GIC was conducted by the method of chemistry oxidation intercalation. In the process, flake graphite, $K_2Cr_2O_7$, concentrated H_2SO_4 and NaOH

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were used as the reactants. Scan electron microscope (SEM) and X-ray diffraction (XRD) were applied to characterize the morphology and structure of the alkaline GIC. Meanwhile, it had been also discovered that the supreme expansion volume of the alkaline GIC (54 mL g^{-1}) was smaller than one of the acid-treated GIC (280 mL g^{-1}), and the alkaline GIC could catalyze benzyl acetate, ethyl o-bromobenzoate, and p-nitrophenol acetate hydrolysis.

2. Experimental Procedure

2.1. Preparation of the alkaline GIC

The sketch map of the preparation process is shown in Fig. 1. According to weight ratio = 1:0.2:0.46:0.52, flake graphite (Average flake size = 320 μm mesh, Carbon content = 99 wt.%), $K_2Cr_2O_7$ (99.8 wt.%), concentrated H_2SO_4 (98.0 wt.%) and NaOH (96.0 wt.%) were added in a three-neck round bottom flask, and the thermometer, muddler and round condenser were fixed on three necks, respectively. It should be pointed out that the purposes to use the thermometer were i) to measure the temperature change and ii) to control the reaction temperature in the whole process. The temperatures of concentrated H_2SO_4 and NaOH were defined as t_1 before they were added in the flask; the temperature of the reaction system was defined as t_2 after concentrated H_2SO_4 and NaOH were added in the flask. The results exhibited that t_1 and t_2 were 20 and 30.5°C and the temperature change (Δt) was 10.5°C (t_2-t_1= 30.5-20), which should relate to the neutralisation heat on direct proportion. After 2 min of stirring the pH of the solution (pH=12) was recorded instead of the measure of alkalinity. Subsequently, the reaction system was continually stirred at 45°C. After 60 min, the synthesis was stopped while the solution color changed into sage green. Then, suitable quantity of water was added in the flask after the thermometer, muddler and round condenser on the three necks were taken down. After the mixture precipitated completely, the sage green solution was removed from the flask, and the mixture was remained in the flask and washed repeatedly until the sage green solution changed into a colorless solution, and the colorless solution appeared to the neutrality (pH=7). Last, the neutral mixture was removed from the flask and dried at 50–60°C in an Electric Blast Drying Oven. After 30 min of drying, the alkaline GIC could be obtained. 1 00 g of alkaline GIC was placed in a muffler furnace of which a given temperature was at 700°C. After 1 min of the thermal expansion, the alkaline exfoliated graphite (alkaline EG) could be obtained, and the expansion volume was 54 mL g^{-1}.

2.2. Affirmation of hydroxyl ions between the graphene planes

0.10 g of the alkaline GIC and 20 mL of distilled water were added in a 50 mL of beaker. After 24 h of marinating, the alkaline GIC and the solution were separated from each other by filtration, and the filtrate was analyzed with regard to the alkalinity (OH^- ions), SO_4^{2-} ions and dichromate ($K_2Cr_2O_7$ or $Na_2Cr_2O_7$) inserted into the spaces between the graphene planes. The results showed that the filtrate was clear and colorless, and the pH value was 11. The stirring and washing procedure were repeated two more times. After each time, the filtrate was analyzed with regard to the pH and the presence of different ions. The alkaline pH and the ions were demonstrating the intercalated species between the graphene planes. The results indicated that the pH values were 10 and 9 after second and third stirring and washing. In addition, white precipitate of $BaSO_4$ could be observed after $BaCl_2$ solution was added in the filtrate. Potassium, sodium, and chromium in the filtrate were measured by using atomic absorption spectroscopy (AAS), and the concentrations of them were lower than 10^{-8}-10^{-10} g mL^{-1}. These explained that hydroxyl ions had intercalated into the graphene planes and were able to be released slowly in aqueous solution. Meanwhile, negative ions (SO_4^{2-}) and a little of potassium, sodium, and chromium element also existed between the graphene planes.

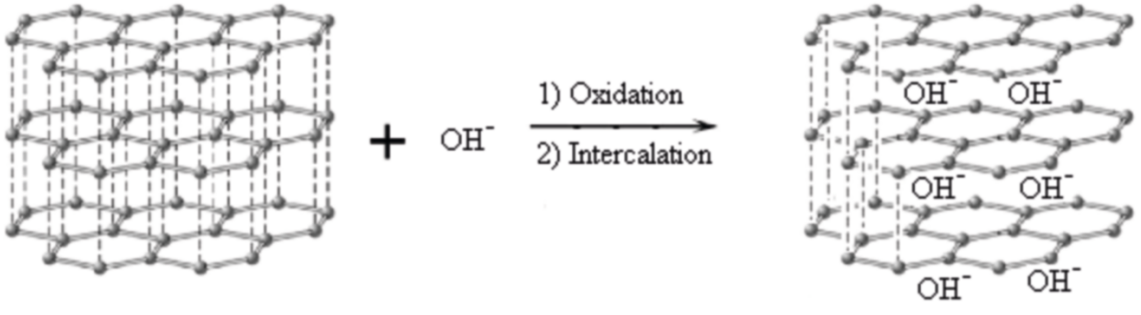

Figure1. Sketch map of the preparation process

2.3. Investigation of the action of the neutralisation

For investigating the action of the neutralisation heat, the alkaline GIC was prepared according to the above procedures. In the process of preparation, the reactants were flake graphite, $K_2Cr_2O_7$, Na_2SO_4 and NaOH saturated solution. Obviously, the neutralisation heat could not be produced in the process because of the absence of concentrated H_2SO_4. In other words, the oxidation capability produced by $K_2Cr_2O_7$ was a sole extra force to open the graphene planes in the process. The result showed that the neutral mixture dried and appeared to the neutrality (pH=7) could not be expanded to EG. In addition, when the weight ratios of flake graphite, $K_2Cr_2O_7$ and concentrated H_2SO_4 were not changed, the alkaline GIC had been also prepared after changing the weight ratio of NaOH. The results showed that the neutral mixture dried and appeared to the neutrality (pH=7) could be expanded to the alkaline EG and the expansion volume was influenced by the solution alkalinity. Apparently, these experiments explained that the neutralisation heat would be indispensable while the alkaline GIC was prepared in alkali solution. It should be pointed out that the roles of concentrated H_2SO_4 were i) to assist $K_2Cr_2O_7$ to open the graphene planes after producing the neutralisation heat and ii) to produce the intercalated ions (SO_4^{2-}).

2.4. Characterization of the alkaline GIC

Scanning electron microscope (S-570, Japan) was used to obtain the micrographs of the alkaline GIC and the alkaline EG. The morphology and the structure were characterized via observing and analyzing the micrographs. XRD measurement was conducted by using a Brucker-AXSD8 Advance vertical θ/2θ goniometer to obtain XRD patterns of the flake graphite and the alkaline GIC. The Ni-filtered Kα radiation of copper (λ=0.154178 nm) was used. The XRD patterns were collected in the θ/2θ step scanning mode with a step size of 0.02° (2θ); scanning range, 2θ=20–90°; scanning rate, 4° min^{-1}; anodic voltage, 40 kV and current, 30 mA. The multilayer structure of the alkaline GIC could be explained via analyzing XRD patterns of the flake graphite and the alkaline contrastively.

3. Results and discussion

3.1. Influence of the neutralisation heat

The data in Table 1 display that the expansion volume of the alkaline EG will be increased from 7 to 54 mL g^{-1} while the solution alkalinity enhances from 8 to 12 (pH) and the temperature change (Δt) from 5.6 to 10.5°C, and then 54 mL g^{-1} of the expansion volume will not be changed while the solution alkalinity enhances from 12 to 14 (pH) and the temperature change (Δt) does not alter. Even as Fig. 1 shows that, two distinct processes can be distinguished in the preparation process, which are known as oxidation/intercalation process. In the process of the oxidation, the bonds between the graphene planes are broken by extra forces produced by oxidation capability of oxidants, neutralisation heat or ultrasound irradiation. Meanwhile, the spaces between the graphene planes are also formed after the bonds are broken. In the process of the intercalation, hydroxyl ions and other ions intercalate into the spaces between the graphene planes via the thermal movement. Meanwhile, the alkaline GIC is formed as well. According to the preparation process, it should be a pivotal process that the bonds are broken and the spaces between the graphene planes formed. Reviewing the above preparation, visibly the bonds broken and the spaces formed should be attributed to the extra forces produced by the oxidation capability of $K_2Cr_2O_7$ and the neutralisation heat of concentrated H_2SO_4 combining with NaOH. To come to light, the oxidation capability produced by $K_2Cr_2O_7$ in alkali solution is weaker than the one in acidic solution. This namely implies that the oxidation capability can not break the bonds and form the spaces between the graphene planes without the neutralisation heat. Indeed, the action of the neutralisation heat has been investigated anteriorly and also proved that the alkaline GIC can not be prepared without concentrated H_2SO_4.

Table 1. Influences of the neutralisation heat on the expansion volume of the alkaline EG

Weight ratio (A: B: C: D)	pH	$\Delta t = t_2 - t_1$ (°C)	Expansion volume (mL g^{-1})
1:0.2:0.46:0.20	8	5.6	7
1:0.2:0.46:0.40	9	6.5	11
1:0.2:0.46:0.44	10	7.5	34
1:0.2:0.46:0.48	11	9.3	40
1:0.2:0.46:0.52	12	10.5	54
1:0.2:0.46:0.56	13	10.5	54
1:0.2:0.46:0.60	14	10.5	54

The expansion temperature is 700°C. A, B, C and D represent flake graphite, $K_2Cr_2O_7$, concentrated H_2SO_4, and NaOH, respectively

The reason for the expansion volume of the alkaline EG to be increased from 7 to 54 mL g^{-1} while the temperature change (Δt) enhances from 5.6 to 10.5°C, can be explained by the change of the neutralisation heat. This is because the oxidation capability produced by the neutralisation heat will be strengthened when the solution alkalinity enhances. Meanwhile, the extra force will be strengthened as well. Under the condition, the amounts of the bonds broken and the spaces formed between the graphene planes will be increased as well. Accordingly, the amount of the intercalated ions which intercalate into the graphene planes will be also increased. Thereby, this causes the expansion volume of the alkaline EG to be increased from 7 to 54 mL g^{-1} while the solution alkalinity enhances from 8 to 12 (pH). Of course, according to Hess law which is usually applied in physical chemistry, the neutralisation heat can be calculated by the temperature change (Δt) under standard conditions. It is a pity that the preparation reaction does not occur under standard conditions. Therefore, we have to apply the temperature change (Δt) to estimate the neutralisation heat. As for the reason, of which 54 mL g^{-1} of the expansion volume will not be changed while the solution alkalinity enhances from 12 to 14 (pH) and the temperature change (Δt) does not change, should also be able to be illuminated by the change of the neutralisation heat. This is because the oxidation capability produced by the neutralisation heat will not be strengthened after concentrated H_2SO_4 is exhausted completely. Meanwhile, the extra force produced by the neutralisation heat will not be strengthened as well. Under the condition, the oxidation capability produced by $K_2Cr_2O_7$ becomes a sole extra force. This is a weak force which can not break the bonds between the graphene planes in alkali solution. Therefore, the amounts of the bonds broken and the spaces formed between the graphene planes will not be increased continually along with enhancing the solution alkalinity. Accordingly, the amount of the intercalated ions which intercalate into the graphene planes will not increase as well. This namely causes the expansion volume of the alkaline EG to not be increased (54 mL g^{-1}) while the solution alkalinity enhances from 12 to 14 (pH).

To sum up, it is a pivotal process that the bonds are broken and the spaces formed between the graphene planes. In the process, the combination of the neutralisation heat and the oxidation capability produced by $K_2Cr_2O_7$ conducts the process jointly, and the expansion volume of the alkaline EG is chiefly influenced by the neutralisation heat.

3.2. Morphology and structure of the alkaline GIC and the alkaline EG

SEM micrographs of the alkaline GIC, flake graphite as raw materials and the alkaline EG are shown in Fig. 2. Fig. 2a shows that the alkaline GIC owns the flake morphology, Fig. 2b shows that the single slice of flake graphite as raw materials has the interbedded structure, Fig. 2c displays that the single slice of the alkaline GIC also has the interbedded structure, and Fig. 2d shows that the single particle of the alkaline EG owns the wormlike morphology [7,8]. Comparing Fig. 2b to Fig. 2c, the multilayer structure of the single slice of flake graphite arrays tidiness and tightness, and the edges of multilayer structure are very clear, and the spaces between the graphene planes do not exist. On the contrary, the multilayer structure of the single slice of the alkaline GIC range out of order and relax, and the edges of multilayer structure are not clear, and the spaces between the graphene planes exist. These results illustrate that the combination of the neutralisation heat and the oxidation capability produced $K_2Cr_2O_7$ not only break the bonds but also form the spaces between the graphene planes. Meanwhile, these also explain that the alkaline GIC slices still own the multilayer structure like flake graphite slices. Of course, the spaces between the graphene planes also supply some rooms for the intercalated ions. After the intercalated ions move into the spaces thermally, the alkaline GIC will be prepared. In addition, comparing the edges of the single slice of flake graphite with the ones of the single slice of the alkaline GIC, the edges of the graphene planes inside the single slice of flake graphite do not crinkle. In contrast, the edges of the graphene planes inside the single slice of the alkaline GIC have been crimpled. This explains that the oxidation action not only breaks the bonds to form the spaces between the graphene planes but also reduces the flake size of flake graphite as raw materials. Comparing the interlayer distances inside the single slice of flake graphite with the ones inside the single slice of the alkaline GIC, the interlayer distances inside the single slice of flake graphite are smaller than the ones inside the single slice of the alkaline GIC. This is because SEM micrographs of flake graphite (Fig. 2b) and the alkaline GIC (Fig. 2c) have the same magnification (22×15.0 k, 2.00 μm). This might explain that the interlayer distances have also been widened in the process of the oxidation, due to forming the spaces between the graphene planes. Indeed, the interlayer distance widened is only a deduction after comparing Fig. 2b to 2c. Further attesting, it will be finished in the process of XRD measurement.

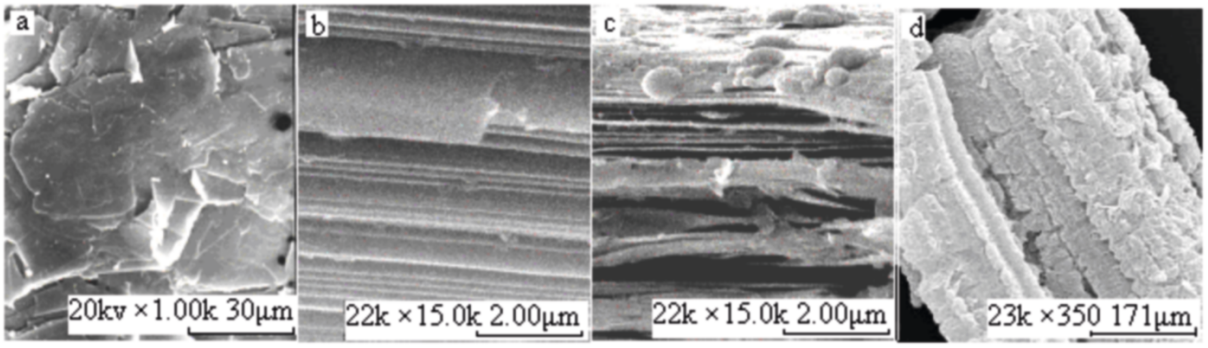

Figure 2. SEM micrographs of the (a, c) alkaline GIC, (b) flake graphite and (d) alkaline EG

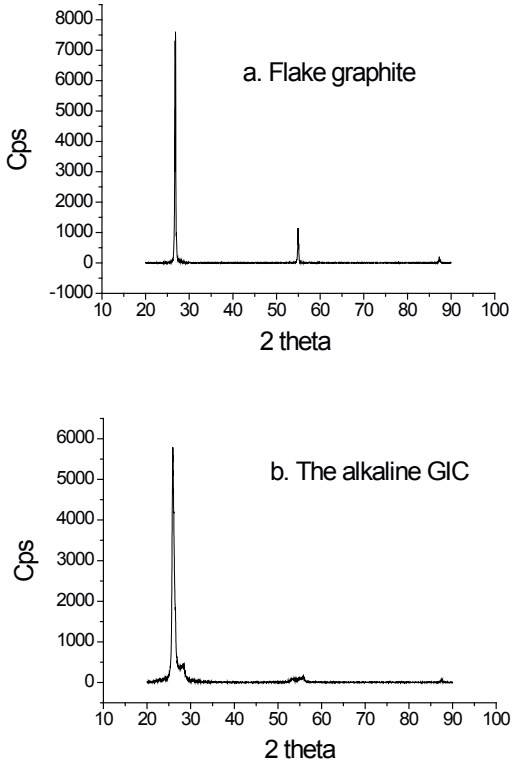

Figure 3. XRD patterns of (a) flake graphite and (b) the alkaline GIC

In conclusion, SEM micrographs illuminate clearly that the alkaline GIC owns the flake morphology like flake graphite as raw materials. Comparing the multilayer structure of the single slice of flake graphite with the one of the single slice of the alkaline GIC, it has been also confirmed that the alkaline GIC still has the same multilayer structure as flake graphite between the graphene planes, but the flake size of flake graphite has been reduced and the interlayer distance might be changed. In addition, the alkaline EG still owns the wormlike morphology like the EG [7,8].

3.3. Analysis of the multilayer structure of the alkaline GIC

In order to confirm the multilayer structure still exists and the interlayer distance has been widened inside the alkaline GIC, X-ray diffraction patterns of the flake graphite and the alkaline GIC were measured and are shown in Fig.3.

Fig. 3a shows that two groups of diffraction peaks appear at near 2θ=26.2° and 55.0°. Considering the multilayer structure of flake graphite has been displayed in Fig. 2b, two groups of diffraction peaks are determined as characteristic diffraction peaks. Meanwhile, the location and the intensity of the characteristic diffraction peaks should relate to the multilayer structure and the interlayer distance. Comparing Fig. 3a to Fig. 3b, although the characteristic diffraction peaks which appear at near 2θ=26.2° and 55.0° inside XRD pattern of the alkaline GIC can be found as well, the intensities of the characteristic diffraction peaks have been weakened. These indicate that the multilayer structure still exists inside the alkaline GIC, but the interlayer distance has been changed between the graphene planes. The reason might be attributed to the oxidation action produced by $K_2Cr_2O_7$ and the neutralisation heat in the process of the preparation. In the process, the bonds between the graphene planes are broken by the combination of the oxidation capability produced $K_2Cr_2O_7$ and the neutralisation heat, and the edges of the graphene planes are turned up, and the spaces between the graphene planes are formed. Obviously, these changes of the graphene planes might cause the arrangement of the graphene planes to change into a more open arrangement and the interlayer distance to be widened. In addition, according to Bragg equation and the method reported in [3,13], the stage indexes of the alkaline GIC are 2, 3, 4 and 5. It is bigger than the interlayer distance (3.354 Å) inside flake graphite that the average interlayer distance inside the alkaline GIC is 3.387 Å. This shows that the level of intercalation is not regular and the interlayer distance has been widened.

In conclusion, the above analyses illuminate that the alkaline GIC has the multilayer structure like flake graphite as raw materials, but that the average interlayer distance inside the alkaline GIC is wider than the one inside flake graphite.

4. Conclusions

The alkali GIC can be prepared by flake graphite, potassium dichromate, concentrated sulfur acid and sodium hydroxide in alkali solution. In the process, the combination of the neutralisation heat and the oxidation capability produced $K_2Cr_2O_7$ break the bonds and form the spaces between the graphene planes. Meanwhile, hydroxyl ions intercalate into the graphene planes to prepare the alkaline GIC. The alkaline GIC and the acid-treated GIC have the analogous morphology and structure, but the intercalated ions between the graphene planes are different. This namely suggests that the expansion volume of the alkaline GIC is influenced by the solution alkalinity instead of the solution acidity in the process of preparing the acid-treated GIC. In addition, comparing the alkaline GIC with the acid-treated GIC, the alkaline GIC owns distinct characteristics: i) the expansion volume of the alkaline GIC is smaller than the one of the acid-treated GIC; ii) the alkaline GIC can not produce the acidic erosion to metals; iii) the alkaline GIC can be applied as alkali analyst and so on.

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