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Effects of processing parameters on the structure and amount of intercalation of copper chloride-graphite intercalation compounds

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Natural graphite powders were intercalated with copper chloride using gas phase reaction in this study. The effects of intercalation temperature, time, and the amount of intercalants on the structure and the amount of intercalation were investigated. An electron probe x-ray microanalyzer (EPMA) was used to quantitatively measure the copper concentration in copper chloride-graphite intercalation compounds. Only stage 1 and stage 2 structures were found in the present processing conditions and the stage structure is mainly determined by the reaction temperature. Results of EPMA quantitative measurement indicated that the amount of intercalation increased with increasing intercalation temperature. However, the amount of intercalation was independent of the reaction time due to the small particle size of graphite host materials. © *2001 Kluwer Academic Publishers*

1. Introduction

Weak van der Waals bonding between graphite basal planes makes it possible for many atoms or molecules to be inserted between the basal planes to form graphite intercalation compounds (GICs). A number of chemical species, ranging from a simple metal to large organic molecules, have been found to form GICs when using different synthesis processes [1, 2]. With their special structure and properties, GICs have potential for many different applications [3–5]. One of the remarkable properties of GICs is the high electrical conductivity, which may allow the application of GICs in the field of electrical engineering. As high as 50 times increase in conductivity has been reported for vapor grown carbon fibers heat treated up to 3300°C and intercalated with AsF_5 [6]. The resulting intercalated fibers had conductivity better than copper.

For the purpose of practical application, we must solve several different problems in science and technology including the development of suitable host materials, establishment of high reproducibility of the physical properties, development of practical synthesis processes and high stability under various conditions. However, in spite of the excellent enhancement of conductivity, the high reactivity of GICs against water and humidity prevents these compounds from wide practical applications.

Promising ambient stability behavior has been reported for some GICs of transition metal halides, in particular of copper chloride [7–9]. The GICs of copper chloride and other metal chlorides have received great attention because they possess relatively high electrical conductivity and are rather stable in air [8–11]. Many studies have been made in terms of synthesis [12, 13], structure [14], and physical properties [9, 10, 15, 16] of GICs of copper chloride, and could be found in the open literature. However, little work has been done concerning the relationship between the amount of intercalation and the processing parameters. In this study, GICs of copper chloride will be produced by vapor process under different reaction parameters. An electron probe x-ray microanalyzer (EPMA) was used to quantitatively measure the copper concentration in $CuCl_2$-GICs. The effects of intercalation temperature, time, and the amount of intercalants on the structure of GICs and the amount of intercalation will be investigated.

2. Experimental

2.1. Sample preparation

Natural graphite powders with an average particle size of 15.2 μm were used as host materials for intercalation. $CuCl_2$-GICs were synthesized using a gas phase reaction. Cupric chloride powders were dried by heating in an oven to 120°C for 24 hours before intercalation reaction. A suitable amount of copper chloride intercalant and graphite host materials were put into a Pyrex glass tube, then the glass tube was sealed at one end. The other end of the tube was also sealed after the complete evacuation of air inside the tube. Three

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TABLE I The experimental runs

Sample ID	T250	T360	T420	T480	T540	H3	H12	H24	H36	H60	H72	C5	C15	C20
Temperature (°C)	250	360	420	480	540	480	480	480	480	480	480	480	480	480
Time (hours)	48	48	48	48	48	3	12	24	36	60	72	48	48	48
Weight of $CuCl_2$(g)	10	10	10	10	10	10	10	10	10	10	10	5	15	20
Weight of graphite host (g)	5	5	5	5	5	5	5	5	5	5	5	5	5	3

processing parameters, intercalation temperature, time, and weight ratio of $CuCl_2$/graphite, varied in this study. Table I shows the experimental runs.

2.2. Characterization

X-ray diffraction (XRD) was used to analyze the structure of GICs using powder samples. A Siemens diffractometer was used in the analysis with Cu K_α radiation and a graphite monochromator. The operating power was 40 kV and 20 mA. Step scanning was used with an interval of 0.015° (2θ) and a residence time of 2 seconds.

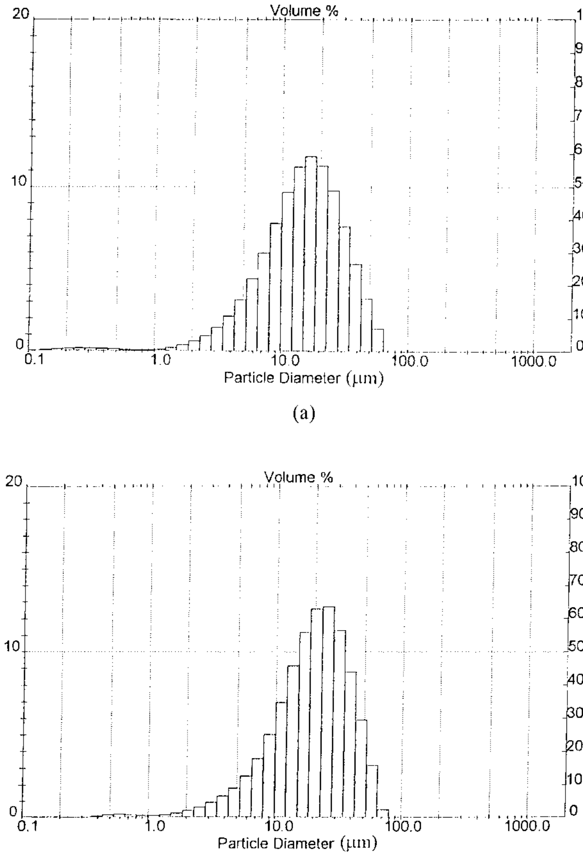
For the quantitative measurement of intercalant amount inside the graphite host materials, an electron probe x-ray microanalyzer (EPMA) was used. The model was JOEL JXA-8800M. A circular disk sample with a diameter of 11 mm was uniaxially pressed in a steel die. An electron beam with a diameter of 200 μm was used in the analysis of the graphite disk sample. Five measurements were taken for each sample.

Particle size distribution of the graphite powders before and after intercalation was measured using laser particle size analyzer (Model Malvern Mse02sm).

3. Results and discussion

3.1. Effect of intercalation temperature

In this study, the $CuCl_2$-GICs were synthesized using a gas phase reaction as described in Section 2.1. Natural graphite powders were used as host materials and Fig. 1 shows the particle size distribution of as-received (Fig. 1a) and intercalated (Fig. 1b) graphite powders. The intercalated powders were prepared at 480°C for 48 hours. As shown in Fig. 1, the particle size became larger after intercalation and the average particle size was increased from 15.2 μm to 20.2 μm. Fig. 2 shows the x-ray diffraction patterns of $CuCl_2$-GICs prepared at different temperatures for 48 hours. In Fig. 2, the intensity of the strong (002) peaks was cut to 1/8 of the original peak intensity in order to show clearly the other peaks of graphite and the peaks of stage structure. Fig. 2a shows the x-ray diffraction pattern of graphite particles before intercalation. There is small portion of rhombohedral phase as indicated by the symbol ▼ coexisting with hexagonal graphite. It is known that the rhombohedral phase, which always occurs together with the hexagonal phase and can be induced by grinding, is thermodynamically less stable at normal temperature and pressure than the hexagonal phase [17, 18]. At low intercalation temperature (250°C), no stage structure was found as shown in Fig. 2b, which could be caused by the low vapor pressure of $CuCl_2$ at 250°C for intercalation reaction to occur [19]. It is noted that the small portion of rhombohedral phase in the hexagonal graphite remained unchanged. However, when comparing the XRD patterns between Fig. 2a and 2b, it was found that the (00ℓ) peaks of as-received graphite powders were sharper than that of graphite powders intercalated at 250°C. Also, the other peaks of hexagonal graphite and the peaks of the rhombohedral phase of unintercalated graphite powders can be identified more clearly than that of intercalated samples. EPMA data as will be presented in Fig. 4 indicated a small amount of copper (~5 wt%) present in graphite powders intercalated at 250°C. Above evidences seem to suggest that small amount of intercalants were inserted into the graphite host, but they did not form the GICs at low intercalation temperature of 250°C. The insertion of intercalants distorts some graphite crystals, which leads to a less sharp XRD pattern. When the reaction temperature was raised to 360°C, weak and broad peaks of stage 2 structure appeared (Fig. 2c). As shown in Fig. 2c, a strong and sharp (002) peak of graphite can be found, indicating that only a small portion of the



(a)

(b)

Figure 1 Particle size distribution of natural graphite powders: (a) as-received and (b) intercalated at 480°C for 48 hours.

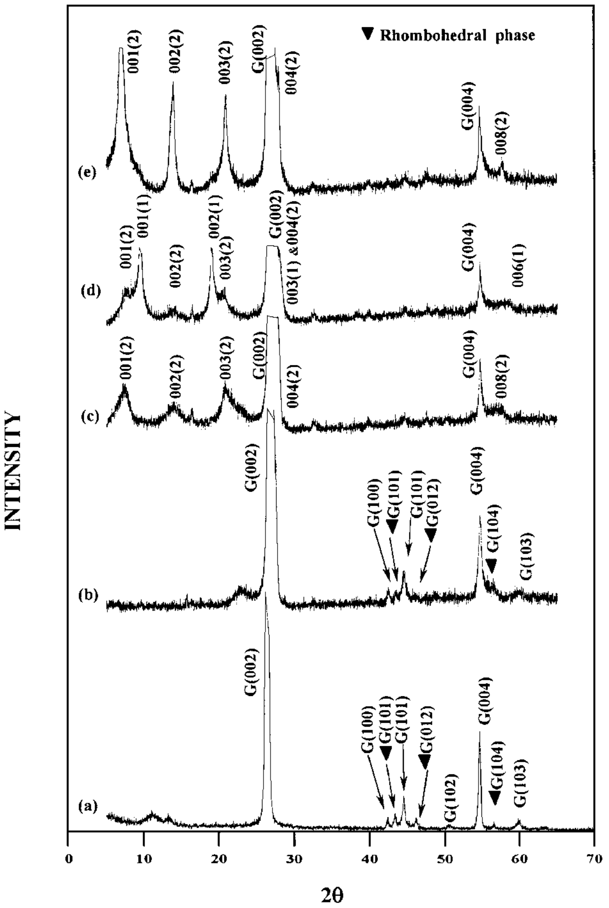


Figure 2 X-ray diffraction patterns of $CuCl_2$-GICs prepared at different intercalation temperatures for 48 hours: (a) before intercalation, (b) 250°C, (c) 360°C, (d) 420°C, and (e) 540°C.

graphite particles form GICs. It is also noted that after intercalation the graphite peaks other than (00ℓ) were almost vanished. Both the stage 1 and stage 2 structures were found at the intercalation temperature of 420°C (Fig. 2d). However, the peak intensity of stage 1 structure is much stronger than that of stage 2. This phenomenon was found in all the other samples with mixed stage 1 and stage 2 structure. The calculated identity period for stage 1 $CuCl_2$-GIC is 9.31 Å, which is consistent with the value reported in the literature [20]. The x-ray diffraction pattern for $CuCl_2$-GICs prepared at 480°C was similar to that at 420°C and was not shown in Fig. 2.

When the reaction temperature was raised to 540°C, some powders in the reaction tube were agglomerated and others remained in powder form after intercalation. The agglomerate powders tended to stick with one another even after being segregated, washed with water and dried. Both the agglomerate and powder samples were examined by XRD and EPMA. Unlike the weak peaks of stage 2 in other samples, we found strong and sharp peaks of stage 2 and only stage 2 structure was observed in both the agglomerate (Fig. 3a) and powder samples (Figs 2e and 3b). In other words, a well-crystallized stage 2 structure was obtained. However, the intensity of the peaks of stage 2 structure relative to that of graphite (002) in the agglomerate sample is stronger than that in the powder sample, but the absolute intensity was lower in the agglomerate sample. As will be shown in the EPMA data in Fig. 4, there is no significant change of weight percentage of copper in powder samples synthesized at 540°C when compared with the samples intercalated at 420°C and 480°C, but a significant increase in copper concentration in the agglomerate sample was found. From the results of XRD and EPMA, we suggest that there is more $CuCl_2$ insertion into graphite layer planes in the agglomerate sample, but these intercalants form a discontinuous stage 2 structure, thus lowering peak intensity of both stage 2 structure and graphite (002).

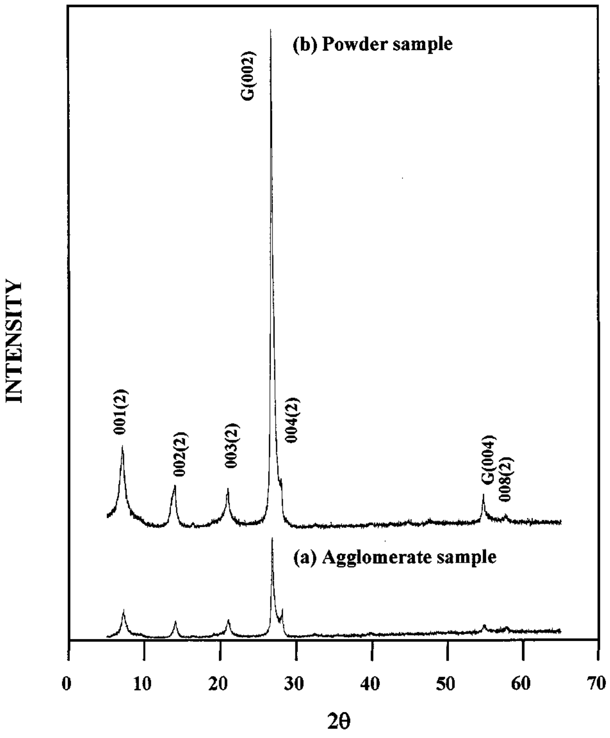


Figure 3 X-ray diffraction patterns of $CuCl_2$-GICs prepared at 540°C for 48 hours: (a) agglomerate sample and (b) powder sample.

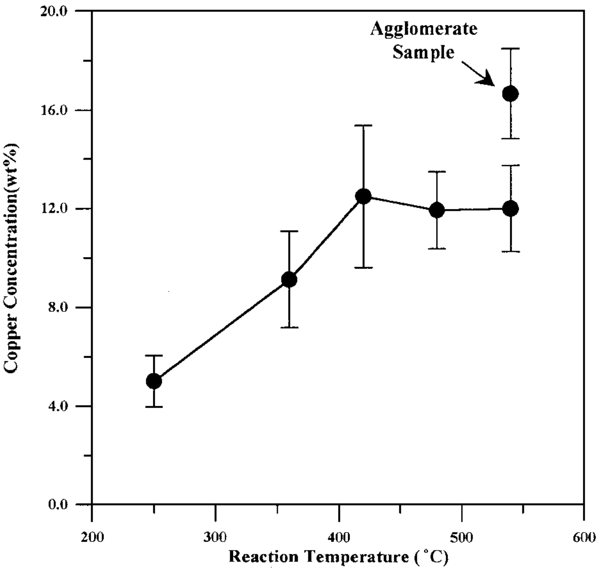


Figure 4 Copper concentration (wt%) in the $CuCl_2$-GICs as a function of reaction temperature.

Fig. 4 shows the copper concentration (wt%) in the GICs as a function of intercalation temperature. The copper concentration was measured using EPMA as described in Section 2.2. As shown in Fig. 4, the copper concentration increases with rising temperature up to 420°C, then the concentration remains relatively constant. It was reported [10] that the humidity stability of GICs is controlled by the diffusion of water into the graphite lattice. Rüdorff [21] explained the relatively high stability of $FeCl_3$-graphite flakes based on the assumption that the intercalant near the edges of the flakes deintercalates and the empty galleries collapse in the periphery. The intercalated flakes were then sealed by themselves and the interior was protected from a further attack by water molecules. In this study, the copper concentration in the GIC samples was measured after the sample was washed in water and dried in the oven. The intercalant at the surface of GIC particles can be washed out easily during the washing process. As a result, the concentration measured represents the remaining stable concentration after washing, not the original intercalation concentration. Since the graphite particles used as the host materials have only a mean particle size of 15 μm, they can be fully intercalated easily. On the other hand, since the particle size is small, the portion of intercalants which will be washed out is more appreciably than that for larger particles. Consequently, despite the fact that the amount of intercalation at the higher temperature should be larger, the intercalants tend to be washed out and a relatively constant copper concentration remains inside the sample. The effect of particle size on the intercalation was also reported by Inagaki and Wang [12]. They synthesized $CuCl_2$-GICs by the molten salt method. By the process of washing out the unreacted molten salts by water, they found that the amount of the coexisting graphite in the GICs increased, very remarkably in the graphite with small particle size (46 μm) but not appreciably in that with larger particle size (400 μm size powder and kish graphite). Another factor which is attributed to the constant copper concentration for the intercalation temperature above 420°C is the amount of intercalants added. As will be shown later from the EPMA data in Fig. 6, copper concentration in the GICs can be increased at the reaction temperature of 480°C if the weight ratio of $CuCl_2$/Graphite added increases. Therefore, at higher intercalation temperature, there is not sufficient intercalants to intercalate into the graphite host, resulting in the constant copper concentration.

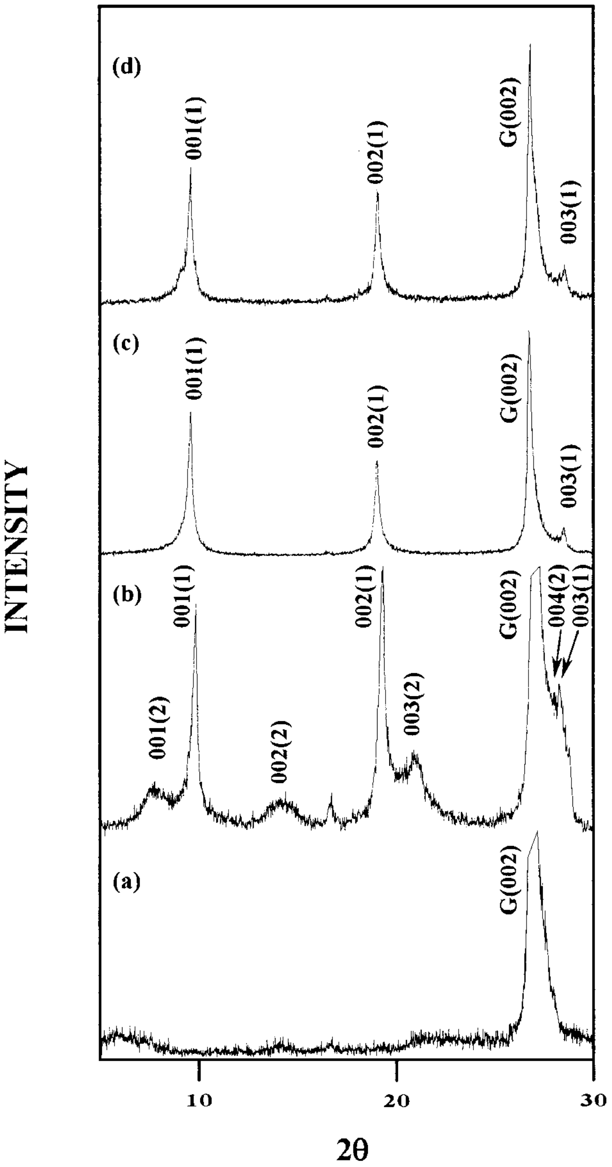


Figure 5 X-ray diffraction patterns of $CuCl_2$-GICs prepared using different weight ratios of $CuCl_2$/graphite: (a) weight ratio = 1, (b) weight ratio = 2, (c) weight ratio = 3, and (d) weight ratio = 6.7. The GICs were synthesized at 480°C for 48 hours.

3.2. Effect of amount of intercalants

Fig. 5 shows the x-ray diffraction patterns of $CuCl_2$-GICs prepared at 480°C for 48 hours using different weight ratio of $CuCl_2$/Graphite. It needs to be mentioned that the intensity of the strong (002) peak in Fig. 5a and 5b was cut to 1/3 of the original peak intensity in order to show clearly the weaker peaks of stage structure. As shown in Fig. 5a, when the weight ratio of $CuCl_2$/Graphite is 1 (5 g $CuCl_2$ and 5 g graphite), only very weak stage 2 peaks were observed. A mixed stage 1 and stage 2 structure with much stronger stage 1 peaks was found when using 10 g $CuCl_2$ and 5 g graphite (Fig. 5b). When the amount of $CuCl_2$ was increased to 15 g (weight ratio = 3), a well-crystallized stage 1 compound was obtained (Fig. 5c). Although the intensity of graphite (002) is still high, the intensity ratio between (002) and stage peaks is greatly reduced as compared with samples having lower weight ratio of $CuCl_2$/Graphite. However, a further increase of weight ratio (20 g $CuCl_2$ and 3 g graphite) did not seem to change the x-ray diffraction pattern (Fig. 5d). The EPMA quantitative analysis of copper concentration as shown in Fig. 6 shows a consistent result. The copper concentration increases with increasing $CuCl_2$/graphite weight ratio. However, when the ratio was greater than 3, the copper concentration remains relatively constant. As previously mentioned, since the graphite particles used as the host materials have only a mean particle size of 15 μm, they can be fully intercalated easily. As a result, more intercalants could not increase the amount of intercalation after the graphite hosts were fully intercalated.

3.3. Effect of intercalation time

Fig. 7 shows the EPMA measurement results of copper concentration as a function of intercalation time.

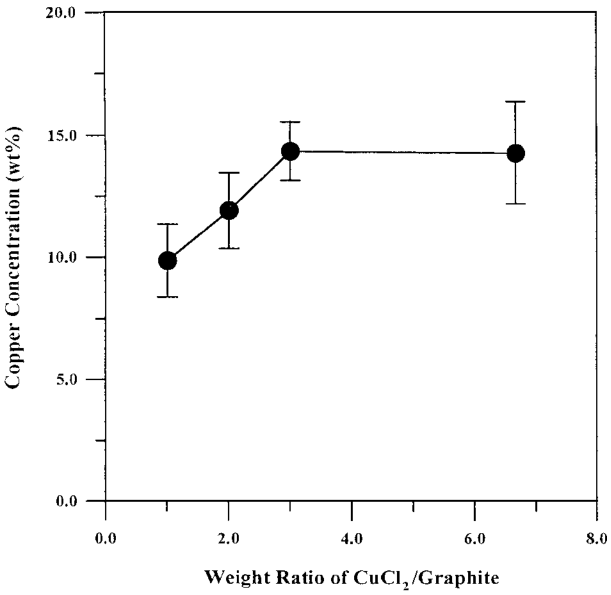


Figure 6 Copper concentration (wt%) in the $CuCl_2$-GICs as a function of weight ratio of $CuCl_2$/Graphite. The GICs were synthesized at 480°C for 48 hours.

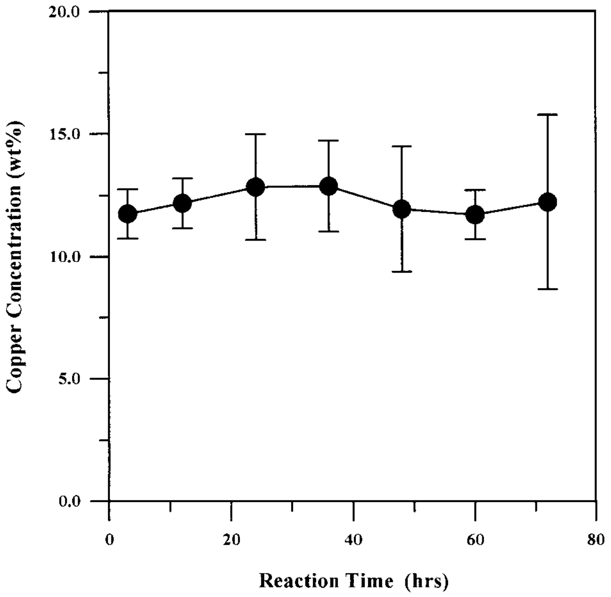


Figure 7 Copper concentration (wt%) in the $CuCl_2$-GICs as a function of reaction time. The GICs were synthesized at 480°C.

The intercalation reaction was carried out at 480°C. As shown in Fig. 7, although some data show larger standard deviation, relatively constant copper concentration was obtained regardless of the difference of intercalation time. As in previous discussion, the mean size of graphite particles used was so small that they could be easily fully intercalated. Also, since the particle size was small, a large portion of the intercalants will be washed out. As a result, the long period of intercalation reaction did not seem to have an effect on the final stable amount of intercalation. The larger data scatter could be partly attributed to a wide distribution of particle size as shown in Fig. 1. X-ray diffraction results show that the GICs have a structure of mixed stage 1 and stage 2 with much stronger stage 1 peaks for intercalation time less than 48 hrs. However, for intercalation time of 60 and 72 hrs, we found only stage 1 structure. This probably resulted from the fact that the intercalants have enough time to redistribute themselves to a more stable state.

4. Conclusions

Copper chloride-graphite intercalation compounds were synthesized using gas phase reaction in this study. The effects of three processing parameters, intercalation temperature, time, and amount of intercalants, on the structure and the amount of intercalation of copper chloride-graphite intercalation compounds were investigated. Results indicated that the stage structure is mainly determined by intercalation temperature in the present processing conditions. However, the amount of intercalation could be influenced by above three parameters, and the degree of influences is also related to the particle size of host graphite particles.

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