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Formation Process of $FeCl_3$-$NiCl_2$-Graphite Intercalation Compounds

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The intercalation reaction of $NiCl_2$ from the mixture of $FeCl_3$ and $NiCl_2$ has been studied by using natural graphite at a wide range of residence times from 1 to 24 h. The microstructure changes of reaction products were investigated by XRD, SEM, and EDS, and the formation of ternary $FeCl_3$-$NiCl_2$-GICs was confirmed. In the process $FeCl_3$ was found to be intercalated preferentially at the initial stage of the intercalation, and set up the framework of the stage domain of GICs. Then $NiCl_2$ intercalated along the channels cut by $FeCl_3$. The diffusion rate and distribution uniformity of $NiCl_2$ controlled the rate of the intercalation reaction and the ternary grade of the $FeCl_3$-$NiCl_2$-GICs.

Keywords $FeCl_3$, graphite intercalation compounds, molten-salt method, $NiCl_2$

1. Introduction

Graphite intercalation compounds (GICs) were formed by the insertion of atomic or molecular layers of a different chemical species called the intercalant between the layers in a graphite host material (Ref 1). Many applications took advantages of the remarkable properties of GICs, such as especial chemical properties, interesting electrical and magnetic properties, etc. (Ref 2-5). Moreover, the chemical reduction of GICs gave rise to 2D metal clusters also evenly distributed throughout the graphite matrix. The reduction products of GICs are potential microwave absorption materials (Ref 6, 7) and potential catalysts for the reduction of oxygen in polymer electrolyte fuel cells (Ref 8). GICs have been prepared by different methods, such as two-zone vapor transport technique, liquid intercalation method, electrochemical method, and molten-salt method, etc. (Ref 1, 9). Among these preparations, the molten-salt method, which has been proposed by Inagaki and Wang (Ref 10), allows the rapid preparation of large quantities of homogeneous binary and ternary MCl_x-GICs at relatively low temperature without pollution, and the equipment for the fabrication is very simple. The influences of the host structure, reaction temperature, molten-salt composition, and reaction duration on the structure evolutions of the products have been investigated (Ref 11, 12). Inagaki has studied the formation process of $CuCl_2$-$NiCl_2$-GICs in detail. Their results indicated that the intercalation of $NiCl_2$ seemed to proceed by direct insertion into free graphite space and also by the replacement of the intercalated $CuCl_2$ (Ref 13). These studies on the $CoCl_2$-NaCl-GICs showed that evolution of the guest species, and the transport and adsorption of the guest species to the sample surface did not occur (Ref 14). The detailed investigations on the kinetics and mechanism of intercalation reactions of ternary GICs and also on the structure of GICs formed are still few, but necessary.

In the present work, the reaction of graphite with a mixture of $FeCl_3$ and $NiCl_2$ was researched to explore the intercalation mechanism.

2. Experimental

Natural graphite powder with particle size range of 165-300 μm was used as host graphite. Graphite, anhydrous $FeCl_3$ and anhydrous $NiCl_2$, in a mole ratio of 60:7:3 were mixed in a stainless steel pot and then sealed off. In this system, the dosage of $FeCl_3$ is excessive so that the dissociation of some $FeCl_3$ into chlorine gas and $FeCl_2$ would take place. The partial pressure of chlorine is about 8300 Torr, which is estimated based on the theoretical calculations on the amount of chlorine released by the dissociation reaction and the comparison with the saturated decomposition pressure. Based on the systematica investigations on the effect of temperature on the reactants, the optimal reaction temperature was established to be 450 °C. Therefore, in this study the mixture was heated at 450 °C at a wide range of residence times from 1 to 24 h. After reaction, the products were washed repeatedly with diluted HCl solution and distilled water to remove residual chlorides.

The microstructures of the $FeCl_3$-$NiCl_2$-GICs prepared at different reaction times were studied by XRD (D5000) with Cu K_α radiation. The separation of peak overlap within 2θ range 25-30° in the XRD patterns and the determination of the full widths at half maximum (FWHM) were confirmed by MDI Jade 5.0. The surface microstructures were observed by SEM (JSM-6700FII. The elemental average atom percentage and the distribution of Cl, Fe, and Ni elements in different flakes of GICs were determined by EDS (Oxford Inca). EDS electron impact depth is determined as follows:

$$Z_m = 0.033\left(E_i^{1.7} - E_k^{1.7}\right) \times m_a/\rho Z$$

where Z_m is x-ray emission depth (μm), E_i is the energy of the incidence electron (keV), E_k is critical excited energy

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(keV), m_a is the average atomic weight of the irradiation area, ρ is the mass density of the irradiation area (g/cm^3), and Z is the average atomic number of the irradiation, which is calculated by the expression:

$$Z = \sum_i c_i z_i$$

where z_i is atomic number of the element i, c_i is weight percent (wt.%) of the element i of the irradiation area. For flakes of $FeCl_3$-$NiCl_2$-GICs in this experiment, the thickness is about 5-10 μm, and the Z_m is about 4-7 μm when E_i is 20 keV. Therefore, the data measured by EDS can characterize the elemental average atom percentage of analytic area.

3. Results and Discussion

3.1 Characterization of $FeCl_3$-$NiCl_2$-GICs

3.1.1 Stage Structures of the Synthesized GICs. The XRD patterns of $FeCl_3$-$NiCl_2$-GICs prepared at different reaction times are shown in Fig. 1, which reveals that the product prepared for 1 h is composed of a lot of graphite, some stage 2 GIC, and a little of transition stage GICs. When the reaction time was prolonged to 3 h, component ratio in reactive system has altered, in which the intensity of the (004) reflection for stage 2 GIC (for short 2(004)) was enhanced remarkably, while that of the graphite (002) reflection (for short G(002)) became lower, and the transition stages still existed. When reaction time was prolonged to 7 h, the intensity of the G(002) reflection and the transition stage was further weakened. Moreover, increasing the heating time to 9 h, the transition stages ultimately disappeared, and the 2(004) reflection peak became very sharp. As the reaction time was longer than 9 h, the XRD patterns of the products showed no more change.

Table 1 displays the interplanar distances (for short d) of the 2(004) crystal face and the stage domain size of the stage 2 GIC prepared at different reaction time. The size of stage domain was calculated in terms of FWHM values of the 2(004) reflection peak by Scherrer formula. The results from XRD show that with increasing the reaction time from 1 to 7 h, the d value of 2(004) decreases from 3.215 to 3.191 Å. After that, however, it gradually increases to 3.202 Å. It is well known that the theoretical value of d for $FeCl_3$-$NiCl_2$-GIC 2(004) reflection is 3.202 Å, and that of $FeCl_3$-GIC is 3.184 Å.

Table 1 The interplanar distance of 2(004) of GICs prepared for different heating times

Reaction time (h)	Interplanar spacing (Å)	The size of stage domain of GICs (nm)
1	3.205	11.1
3	3.204	25.3
7	3.191	23.5
9	3.197	24.6
12	3.195	24.0
24	3.202	32.8

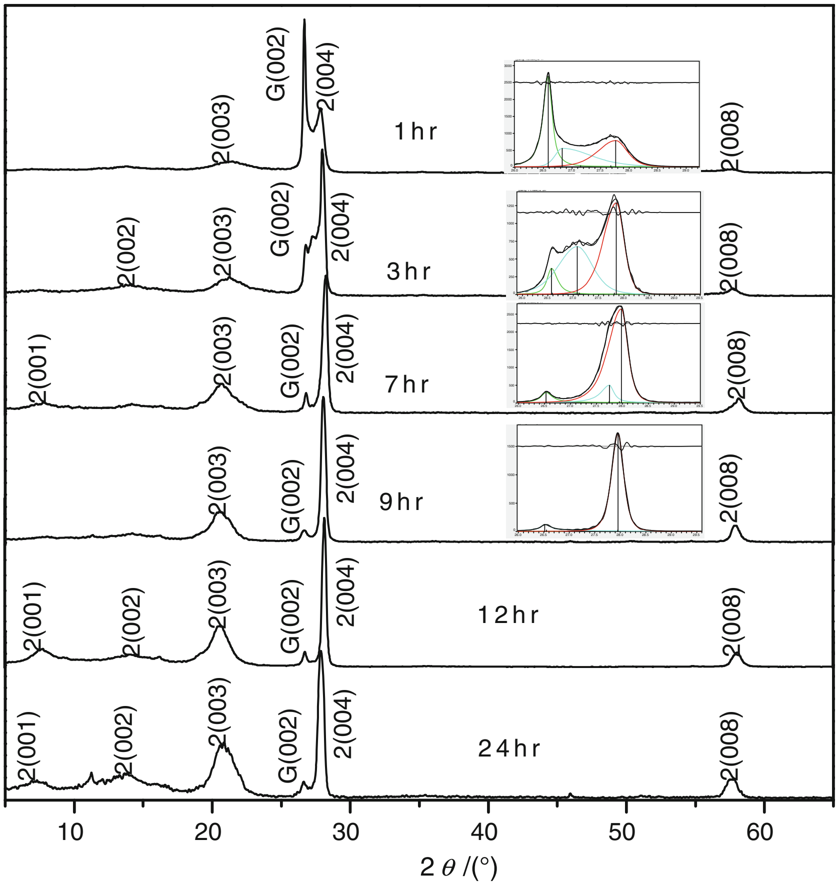

Fig. 1 The x-ray diffraction diagrams of the stage 2 $FeCl_3$-$NiCl_2$-GICs prepared for different heating times

Obviously, the *d* values of the products prepared for the shorter reaction time in present study are larger than the theoretical values of both the binary and ternary GICs. The reason relates to that there are many defects in the stage domain at the initial stages of intercalation, such as insertion accumulating, atom voids, etc. With increasing the reaction time, the insertion gradually diffused into the center of the graphite flakes, and the insertion accumulation disappeared gradually, which led to the decrease of *d* value. The *d* of 2(004) for the sample prepared for 7 h was near to the theoretical value of the stage 2 $FeCl_3$-GIC. It probably resulted in the formation of the products with microstructure being mainly composed by $FeCl_3$-GICs because $FeCl_3$ diffuses faster than $NiCl_2$. When the heating time was longer than 7 h, however, the *d* value gradually increased, and was close to the theoretical *d* value of 2(004) of $FeCl_3$-$NiCl_2$-GIC. This is possibly caused by $NiCl_2$ intercalating and diffusing largely. The stage domain size of GICs was remarkably aggrandized from 1 to 3 h, and then did not change significantly till 12 h. After that, the size further grew up. The comparison of *d* and stage domain size indicates that the slow growth of the stage domain during 3-12 h is because of $NiCl_2$ diffusion between the layers of graphite, and that this intercalation causes the structure changing from binary $FeCl_3$-GICs to ternary $FeCl_3$-$NiCl_2$-GICs. The above conclusions are proved by the results of EDS in 3.1.2.

3.1.2 Diffusion of the Intercalated $NiCl_2$. In order to investigate the diffusion of $NiCl_{2,}$ many single flakes of GICs prepared at the same condition were detected by EDS. The results show that the element distribution of the different GICs flakes prepared at the same condition is similar. Hence, we used the element distributions for nine points in a discretional single flake to compare, which size is about 200 μm. Figure 2 shows the element distribution of Cl, Fe, and Ni in the radial direction of a single flake prepared for different times, and the position of the points being detected by EDS, i.e., every flake was divided into equidistant nine points along the radial direction. Table 2 summarizes the average atomic percent of Cl, Fe, and Ni and the standard variance (σ) of Ni in the samples prepared for different times. The EDS results indicate that Ni was not found in the sample prepared at 1 h, which proved that $FeCl_3$ intercalated into the layers of graphite earlier than $NiCl_2$, and that the diffusing speed of $FeCl_3$ was very fast. This intercalation procedure was established by the results from XRD. $NiCl_2$ did not insert into the layers of graphite along the road cut by $FeCl_3$ until the distribution of $FeCl_3$ was relatively uniform in every flake of graphite. On the other hand, the curves in Fig. 2 indicate that $NiCl_2$ enters the flakes from their edges, and gradually diffuses into the center of the flakes in the radial direction with increasing the heating times. After being heated for 12 h, Ni diffused throughout the flakes, but the concentration of Ni near the edges was higher than that of center. The distribution of Ni became uniform slightly from 12 to 24 h. In Table 2, the standard variance of Ni from 1.69 to 1.55 with the heating times increasing from 12 to 24 h also indicated this gradual uniform procedure of Ni element, which acted as the main diffusion step. At the same time, the average atomic percent of Ni in the products increased slowly. Hence, the concentration of Ni in the product prepared for 12 h was closed to saturation, and the energy should be used for diffusion of Ni in a minor range.

The reviews about the intercalation process of $FeCl_3$-GICs indicate that after the formation of GICs, the intercalant forms clusters as in the form of islands (Ref 11). This phenomenon possibly happened in the system of ternary $FeCl_3$-$NiCl_2$-GICs, because $FeCl_3$-GICs was formed at the initial stage of the intercalation reaction and built up the frame of GICs. The third component $NiCl_2$ inserted into the layers along the roads between the islands, and then gradually inserted into the stage domains to form $FeCl_3$-$NiCl_2$-GICs. After the content of Ni was close to saturation, the energy was mainly used for even diffusion of Ni, which resulted in the microstructure of the ternary GICs.

3.1.3 Evolution of the Guest Species. The evolution of the guest species is an important stage in the process of intercalation. The SEM micrographs of GICs prepared at different times are shown in Fig. 3. The micrographs show that there are many small particles adhering to the surface of the flakes prepared for 1 h even if the synthesized products have been washed by diluted hydrochloric acid and distilled water. The results from EDS indicate that there is not Ni among the particles at this stage, so the composition of the particles is $FeCl_3$. When the reaction time is 7 h, the adhesion becomes floccules. As the reaction time is prolonged continuously, the edges of flakes become clear and no apparent adhesion can be observed. Furthermore, there are many channels in these samples and the flakes have been expanded. When the reaction time is prolonged to 24 h, the edges become indented and the layers become clear.

The evolution process of insertion can be probably concluded from the above phenomena. For the system of $FeCl_3$ and $NiCl_2$, first, the salts melted and a part of $FeCl_3$ was decomposed into $FeCl_2$ and chlorine gas, which is essential to initiate the intercalation of chloride into graphite in the molten-salt method. Then, $FeCl_3$ was first absorbed at the surface of flakes due to the lower absorption energy of $FeCl_3$ than that of $NiCl_2$.

It has been proved by the results from XRD and EDS that $FeCl_3$ first intercalated into layers of graphite. $NiCl_2$ began to intercalate together with $FeCl_3$ until the concentration of $FeCl_3$ near the edge of the flakes was close to saturation and the diffusion was relatively uniform. Hence, the floccules in Fig. 3(b) are probably $NiFe_2Cl_8$ according to the EDS results and the $NiCl_2$-$FeCl_3$ diagram, which was obtained from soft of FactSage 6—the integrated thermodynamic databank system. With increasing the reaction time, the concentration of $FeCl_3$ reached saturation in the flakes. Then, $NiCl_2$ inserted into the layers alone, and the composition of the surface on the product of 9 h was maybe $NiCl_2$, which needed be further proved. For the ternary system of $FeCl_3$, $NiCl_2$, and graphite, however, the absorption and diffusion of the $FeCl_3$ and $NiCl_2$ take on orderly.

3.2 Formation Process of $FeCl_3$-$NiCl_2$-GICs

According to Axdal (Ref 15), the intercalation process can be broken up into several steps:

(1) evolution of the guest species;
(2) transport of the guest species to the surface of the sample;
(3) adsorption of the guest species onto the surface of the sample;
(4) surface reaction and insertion of the guest species into the sample;

and

(5) stage reaction.

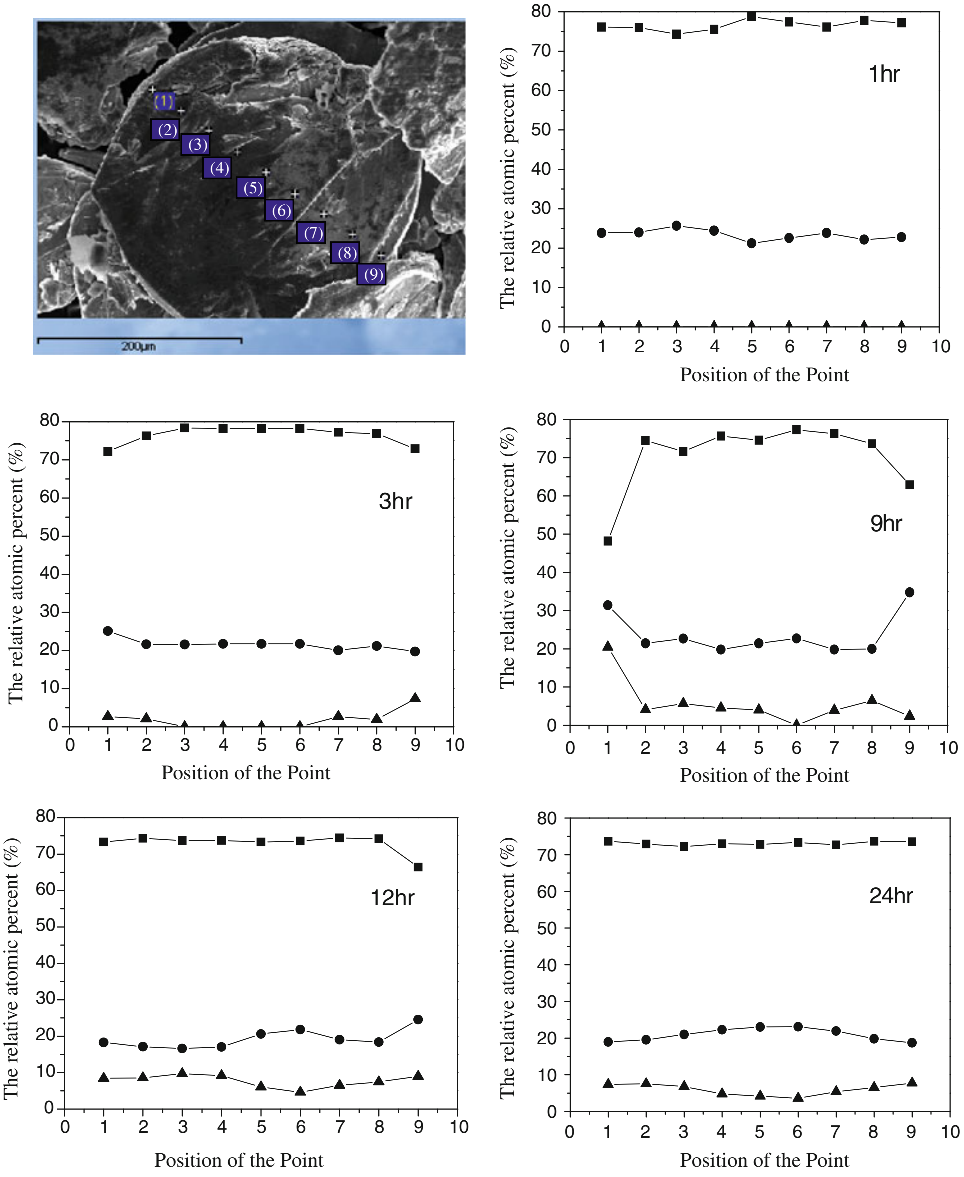

Fig. 2 The element distribution of Cl, Fe, and Ni in the radial direction of a single particle after heating for different times ■—Cl, ●—Fe, and ▲—Ni

Table 2 The elemental atom percent and the standard variance of Ni of stage 2 $FeCl_3$-$NiCl_2$-GIC prepared for different heating times

		Average atom percent of the elemental, %		
Reaction time (h)	**The standard variance of Ni**	**Cl**	**Fe**	**Ni**
1	···	72.04	27.96	0
3	2.38	69.53	26.59	3.88
7	3.46	67.72	28.04	4.24
9	5.82	72.33	22.26	5.40
12	1.69	68.95	24.40	6.66
24	1.55	71.77	21.28	6.95

The Tilquin's result (Ref 14) indicates that in the case of $CoCl_2$-NaCl molten salts, the initial three steps do not occur. However, in this system of $FeCl_3$-$NiCl_2$ molten salts, we can see that the evolution and absorption of the chlorides is divided into three steps. First, $FeCl_3$ is selectively absorbed. Following, $FeCl_3$ and $NiCl_2$ are absorbed together. Finally, $NiCl_2$ is absorbed and diffuses alone. Because of the selective absorption, the stage formation of $FeCl_3$-$NiCl_2$-GICs passes through two phases. $FeCl_3$ first intercalates into the layers of graphite and forms the stage domain of $FeCl_3$-GICs rapidly, which is the framework of $FeCl_3$-$NiCl_2$-GICs. Then, $NiCl_2$ intercalates into the stage domain of $FeCl_3$-GICs with $FeCl_3$ or alone without

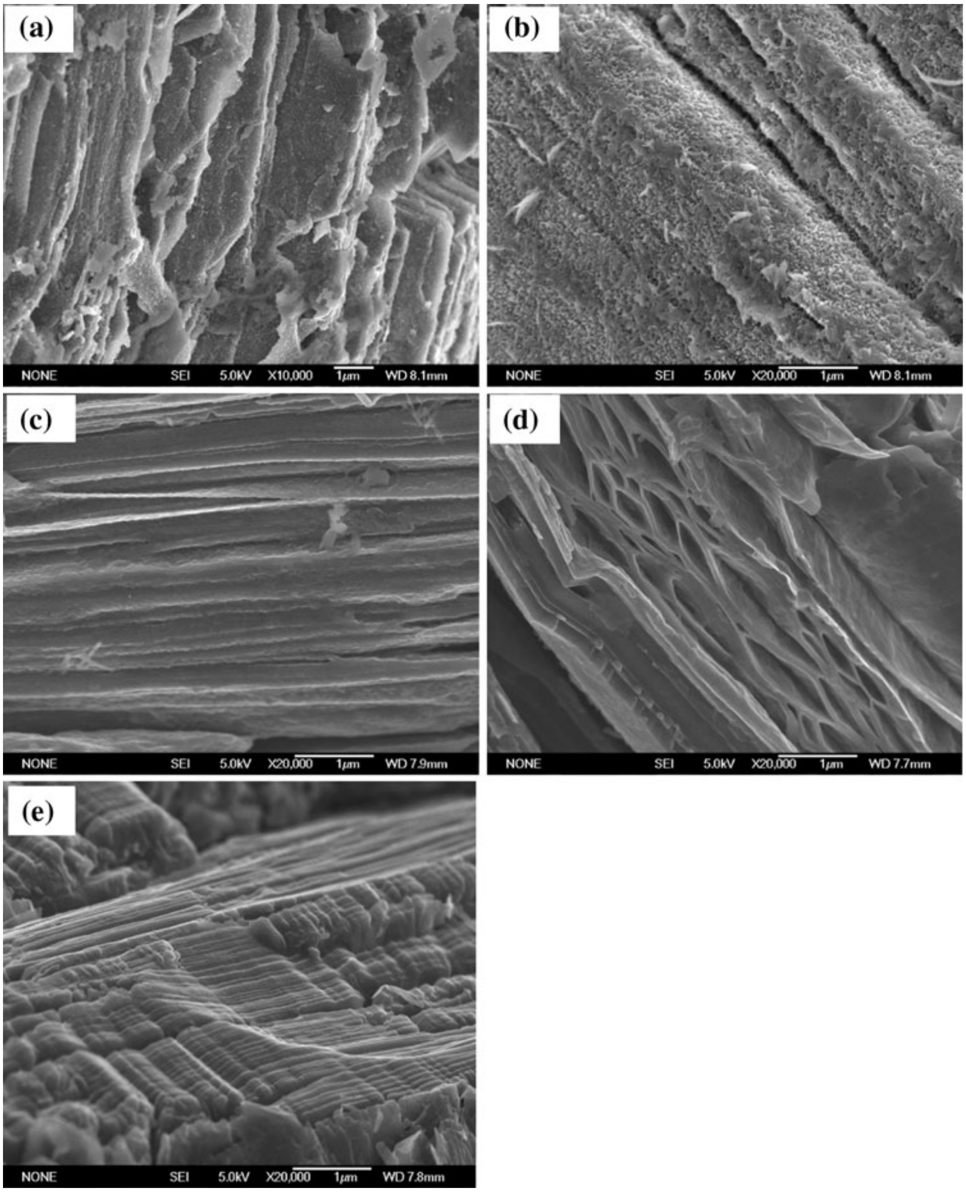

Fig. 3 SEM micrographs of GICs prepared for different heating times (a) 1, (b) 7, (c) 9, (d) 12, and (e) 24 h

changing the graphite and $FeCl_3$ stacking. The above results indicate that the diffusion of $NiCl_2$ is very slow. It needs at least 24 h to make the distribution of $NiCl_2$ be relatively uniform. For the ternary GICs, the concentration and uniform degree of the third component determines the ternary degree. Thus, in the case of $FeCl_3$-$NiCl_2$-GICs, the diffusion of $NiCl_2$ is the critical step in the process of intercalation.

4. Conclusions

The formation process of ternary $FeCl_3$-$NiCl_2$-GICs on the basis of our results is summarized as follows:

(1) At the initial stage of the intercalation of the $FeCl_3$-$NiCl_2$ molten salts, $FeCl_3$ is selectively adsorbed by graphite. Then, $FeCl_3$ intercalate rapidly and build the frame of the GICs.

(2) After the formation of $FeCl_3$-GICs with the stage 2 structure, $NiCl_2$ begins to intercalate along the roads cut by $FeCl_3$.

(3) The diffusion of $NiCl_2$ is the control step in the process of intercalation.

Acknowledgments

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