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Synthesis of polyaniline-intercalated layered materials *via* exchange reaction

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Polyaniline (PANI)-intercalated graphite oxides (GOs) or FeOCl were synthesized *via* exchange reaction of *n*-hexadecylamine-intercalated graphite oxides or FeOCl by PANI in an organic solvent. PANI-intercalated GOs with interlayer spacings (I_c values) of 1.14–1.68 nm and compositions of $(PANI)_{1.1-5.0}GO$ were obtained, depending on the amine contents in the starting materials. On the other hand, only one type of intercalation compound was successfully obtained for FeOCl with the composition $(PANI)_{0.42}FeOCl$ without excess PANI particles deposited on the surface. A structure model for the intercalated PANI chains in $(PANI)_{5.0}GO$ with $I_c = 1.68$ nm has been proposed: a double layer of PANI chains with their benzene rings parallel to the GO layer.

Introduction

Conducting polymer-intercalated layered materials are candidates for the cathode materials of lithium secondary batteries.[1–6] They show higher reversibility than that of the host layered materials without polymer. These intercalation compounds have been synthesized in four ways. (1) Oxidative polymerization of monomer in the interlayer spacing of the layered host.[7–13] In this case, the host material should possess a redox couple such as Fe^{3+}/Fe^{2+}, V^{5+}/V^{4+}, *etc.* in its framework in order to polymerize the aniline monomer. (2) Polymerization of aniline monomer or anilinium ion in the interlayer spacing by an oxidation reagent or electrochemical method.[14–20] (3) *In situ* polymerization of monomer in the presence of single layers.[21,22] In these three methods it is difficult to control the polymerization degree of PANI. (4) Reprecipitation of single layers in the presence of polymer in a liquid medium.[23–25] In the last method, for example, lithium or potassium ions in the interlayer spaces of Li_xMoS_2 or $K_{2x}M_{1-x}PS_3$ (M = Cd, Mn) are replaced by PANI during the reprecipitation process.[23,24] The introduction of high molecular weight PANI would make the intercalation compounds more stable, which is favorable for the active material of a lithium battery.

In this context, we have recently succeeded in the intercalation of polyaniline into GO through the previous intercalation of octadecyltrimethylammonium.[26,27] This method is similar to method (4) and surfactant ions with hydrophobic alkyl groups were used instead of lithium or potassium ions. The obtained PANI–GO intercalation compounds were $(PANI)_{1.8}(C_8O_{3.3}H_{2.0})$, $(PANI)_{1.5}(C_8O_{6.6}H_{4.1})$, $(PANI)_{1.8}(C_8O_{8.3}H_{4.9})$, depending on the preparation method of GO. They showed large reversible capacities when used as cathodes in a lithium battery, and it was suggested that an increase in the PANI contents might increase the reversible capacity.[27] However, it was difficult to control the PANI contents in GO because the saturated amount of trimethylammonium ion was only 0.79 mol per GO unit because of the three bulky methyl groups bonded to the nitrogen atoms. Larger amounts of an alkylamine without methyl groups bonded to nitrogen atoms would intercalate into GO. As the result, *n*-hexadecylamine-intercalated GO[28] would provide intercalation compounds with higher PANI contents *via* exchange reaction, which might improve the electrochemical properties of the products. Moreover, the merit of this method using alkylamines is that it is possible to avoid reactions in aqueous solution throughout the synthetic process. For example, homogeneous alkylamine-intercalated FeOCl was obtained by solid–solid reaction, while an inhomogeneous product was obtained in aqueous solution containing ammonium ions.[29] This means that it would be possible to prepare PANI-intercalated FeOCl by this method when alkylamine-intercalated FeOCl is used as a starting material.

Therefore, in this study, intercalation of polyaniline into GO and FeOCl through the previous intercalation of *n*-hexadecylamine was performed and the products were characterized.

Experimental

2-1 Preparation of PANI-intercalated GO

Graphite oxide was prepared from natural graphite by Hummers' method.[30] Graphite (2 g) was oxidized by potassium permanganate (6 g) in 98% sulfuric acid (46 ml) containing sodium nitrate (1 g) at 0 °C for 1 h and then the resulting solution was kept at room temperature for 20 h. The intermediate intercalation compound was hydrolyzed by putting the solution in 400 ml of water. The GO formed was filtrated and dried at 60 °C. From the X-ray measurements and elemental analysis of hydrogen and carbon, the I_c value and composition of GO were calculated to be 0.76 nm and $C_8O_{8.3}H_{4.9}$ (C: 41.1%, H: 2.1%, O: balance), respectively. All the reagents except PANI were obtained from Nacalai Tesque. Polyaniline ($M_w > 15\,000$, emeraldine salt) was purchased from Aldrich. These reagents were used as received.

Hexadecylamine-intercalated graphite oxide[28] was prepared by the solid–solid reaction of *n*-hexadecylamine (105–536 mg) and graphite oxide (100 mg). The ratios of *n*-hexadecylamine/GO unit ($C_8O_{8.3}H_{4.9}$) in the intercalation compounds were between 0.73 and 3.9. PANI-intercalated GOs were prepared *via* exchange reaction of the amine in the above intercalation compounds by PANI in *N*-methyl-2-pyrrolidone (NMP). This method is basically the same as that employed for the preparation of PANI-intercalated GO by using trimethylalkylammonium ion-intercalated GO as a starting material.[26,27]

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Hexadecylamine-intercalated GOs (50 mg) were put in 20 ml of NMP and sonicated for 30 min, which provided a homogeneous solution. NMP solution (20 ml) of PANI (25–150 mg) was mixed with the resulting colloidal solution and then stirred for 6 h. The precipitate was filtered off, and the products were dried at 60 °C overnight.

2-2 Preparation of PANI-intercalated FeOCl

FeOCl (Iron(III) oxide chloride) was prepared by reaction of Fe_2O_3 with excess of $FeCl_3$ (mole ratio of 1 : 1.3) in a sealed pyrex tube at 350 °C for 2 days. Intercalation with *n*-hexadecylamine was performed by direct reaction of FeOCl and amine.[31] After mixing FeOCl and *n*-hexadecylamine well, the mixture was kept at 60 °C overnight. When the *n*-hexadecylamine : FeOCl ratio was less than 0.5 : 1, unreacted FeOCl remained as an impurity. Intercalation of PANI into FeOCl was conducted in the same way as described in the previous section. PANI (20–50 mg) was added into 100 ml of NMP solution containing 100 mg of *n*-hexadecylamine-intercalated FeOCl and stirred for 1 day. After the reaction the resulting solution was centrifuged at 3000 rpm for 30 min in order to obtain solid products.

The intercalation compounds obtained were analyzed by X-ray diffractometry using RIGAKU Rint-2100, scanning electron microscopy (JEOL JSM-5600) and FT-IR (Nicolet Avatar 360, KBr pellets were used.). The tentative compositions of the obtained intercalation compounds were calculated from the weight change during reaction, assuming that all the amine was replaced by PANI.

Results and discussion

3-1 Preparation of PANI-intercalated GOs

Fig. 1 shows the *n*-hexadecylamine-intercalated GOs with various amine : GO ratios used as starting materials. When the amine : GO ratio was 0.73 : 1, diffraction peaks at 2θ = 3.16 and 2.50° were observed, suggesting the intercalation of amine into the GO layer. These diffraction peaks shifted to 2θ = 1.85° for the sample with higher amine contents. These results indicated that three types of intercalation compounds were obtained with I_c values of 2.8, 3.5 and 4.8 nm. Considering the size of *n*-hexadecylamine, these values suggested that the alkyl chains of the amine molecules were intercalated almost perpendicular to the GO layer and located as a single and a double layer, for the samples with I_c values of 2.8 and 4.8 nm, respectively and as a paraffin type bilayer for that with I_c = 3.5 nm.

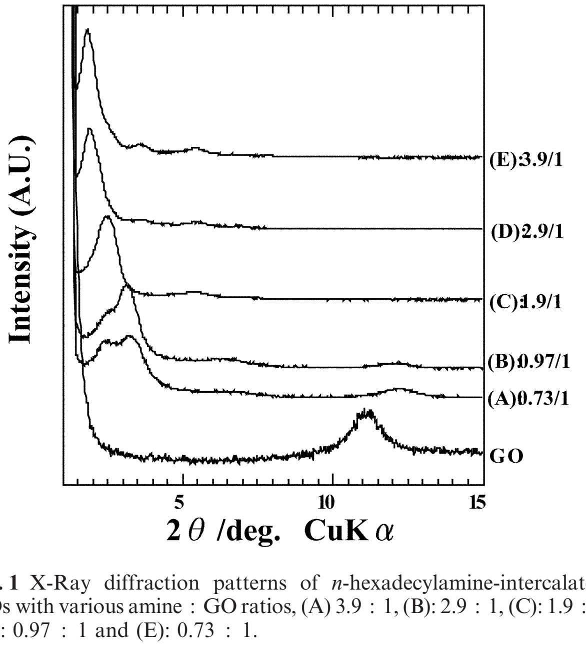

Fig. 1 X-Ray diffraction patterns of *n*-hexadecylamine-intercalated GOs with various amine : GO ratios, (A) 3.9 : 1, (B): 2.9 : 1, (C): 1.9 : 1, (D): 0.97 : 1 and (E): 0.73 : 1.

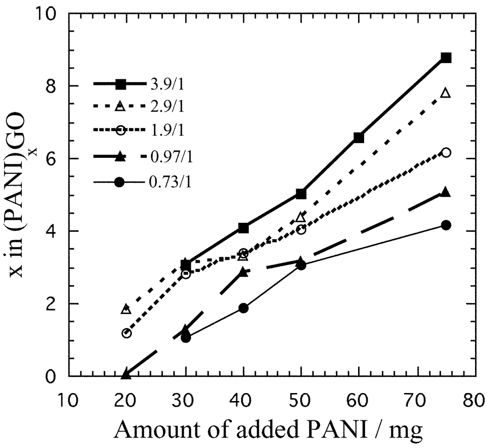

Fig. 2 Relationship between composition of PANI–GO composites (x in $(PANI)_x$GO) and the amounts of added PANI when various *n*-hexadecylamine–GOs were used as starting materials.

Fig. 2 shows the tentative compositions of the products calculated from the weight change during reaction between amine-intercalated GO with various amine : GO ratios and PANI, assuming that amine was completely replaced by PANI and the composition of GO was the same before and after the reaction. When the amount of PANI added increased, the PANI content in the products also increased. However, a small plateau was observed at 30–50 mg of added PANI.

Fig. 3 shows the IR spectra of the products with various PANI contents when (*n*-hexadecylamine)$_{2.9}$GO was used as a starting material. In the spectrum of the starting material (Fig. 3 (A)), the absorption peak at 2900 cm^{-1} due to the amine -CH_2- groups was strongly observed. When 40 mg of PANI was added, the absorption peaks at 800, 1150, 1500 and 1600 cm^{-1} due to PANI appeared as shown in Fig. 3 (B). The absorption peak at 2900 cm^{-1} became smaller and almost disappeared with increasing amounts of added PANI, which indicated that the amine molecules were completely replaced by PANI. Almost identical spectra to that of PANI in Fig. 3 (F) were obtained when the amount of added PANI was larger than 50 mg.

Fig. 4 shows the SEM images of the same samples as those in Fig. 3, together with that of (*n*-hexadecylamine)$_{3.9}$GO and PANI. The surface morphology of the samples with smaller

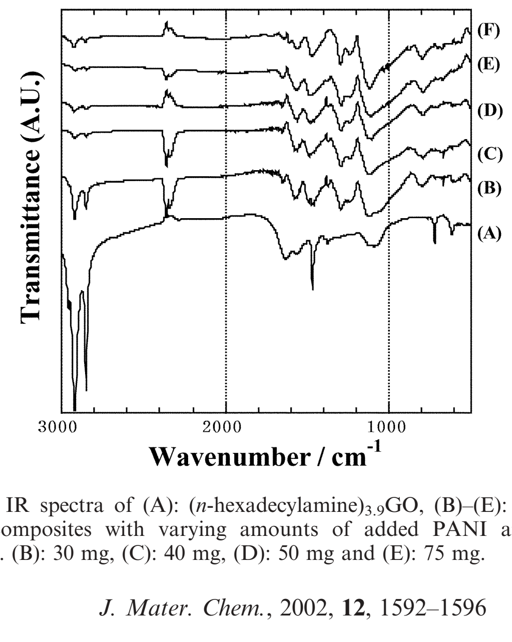

Fig. 3 IR spectra of (A): (*n*-hexadecylamine)$_{3.9}$GO, (B)–(E): PANI–GO composites with varying amounts of added PANI and (F): PANI. (B): 30 mg, (C): 40 mg, (D): 50 mg and (E): 75 mg.

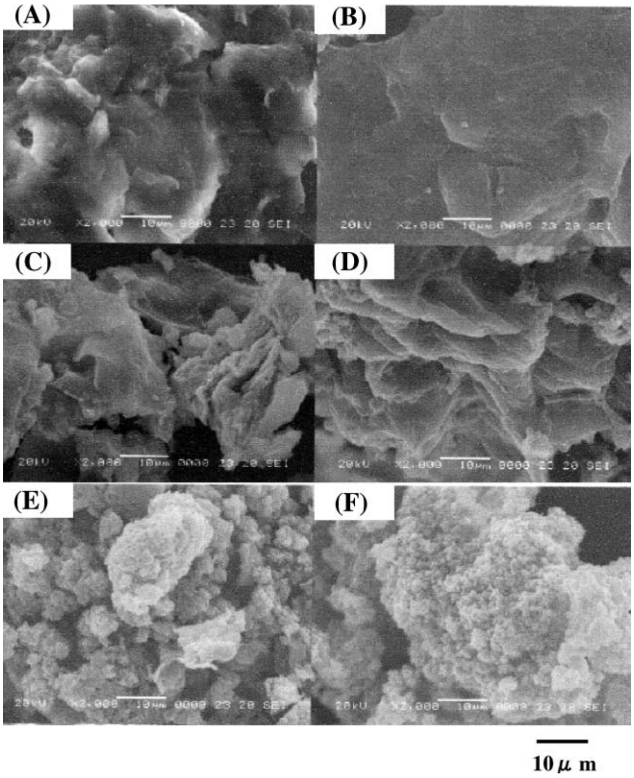

Fig. 4 SEM images of (A): (*n*-hexadecylamine)$_{3.9}$GO, (B)–(E): PANI–GO composites with various amount of added PANI and (F): PANI. (B): 30 mg, (C): 40 mg, (D): 50 mg and (E): 75 mg.

amounts of added PANI was similar to that of (*n*-hexadecylamine)$_{3.9}$GO as shown in Fig. 4 (B) and (C), though the diameters of the layer particles appeared to be smaller. This suggested that the *n*-hexadecylamine molecules were replaced by PANI chains during the restacking process of the GO layers. However, when the amount of PANI added was larger than 60 mg, smaller particles which possessed similar morphology to those of PANI in Fig. 4 (F) were observed on the edge of crystals with relatively flat surfaces (Fig. 4 (D)). Then, the surface of the sample was almost completely covered with PANI-like particles with higher PANI content as shown in Fig. 4 (E). This indicated that excess PANI particles were deposited on the surface of layered materials.

Based on these results, the reaction between PANI and *n*-hexadecylamine-intercalated GO appeared to be very similar to that between PANI and octadecyltrimethylammonium ion-intercalated GO reported in our previous studies.[26,27] The *n*-hexadecylamine molecules were replaced by PANI and once the interlayer spacing of GO was saturated by PANI, excess PANI was deposited on the surface of PANI-intercalated GOs. In TG/DTA measurements of PANI-intercalated GO prepared from (*n*-hexadecylamine)$_{3.9}$GO, a 5% weight decrease was observed below 100 °C, which could be due to adsorbed water or co-intercalated NMP. Then the GO framework decomposed into CO or CO_2 and residual carbon containing PANI at around 200 °C. This behavior made it difficult to know the amount of remaining *n*-hexadecylamine and adsorbed PANI on the surface. Therefore, the composition of the PANI-intercalated GO was determined to be (PANI)$_{5.0}$GO, assuming that it was without excess PANI and free from residual amine or co-intercalated solvent. The compositions of PANI-intercalated GOs prepared from the other *n*-hexadecylamine–GO composites were determined in this way and (PANI)$_{1.1–5.0}$GO were obtained. The complete substitution of amine by PANI was accomplished when 30–50 mg of PANI per starting material was added. Fig. 5 shows the X-ray diffraction patterns of PANI-intercalated GOs prepared using *n*-hexadecylamine-intercalated GOs with various amine contents and free from unreacted precursor or excess PANI particles. In all the diffractograms, one broad diffraction peak at around $2\theta = 5–7°$ was observed and this peak shifted to lower angles when the amine contents in the starting materials became larger. The I_c values of these PANI-intercalated GO with various PANI contents were calculated from the X-ray diffraction peaks and are summarized in Table 1, together with the composition and preparation conditions. The I_c values of the intercalation compounds increased when their PANI contents increased from 1.17 nm to 1.68 nm. The PANI : GO ratios in the intercalation compounds were almost half of those expected from the results for PANI-intercalated GOs prepared from octadecyltrimethylammonium ion-intercalated GOs.[27] However, as expected from the large amine content in the starting materials, PANI-intercalated GOs containing a large amount of PANI were successfully prepared.

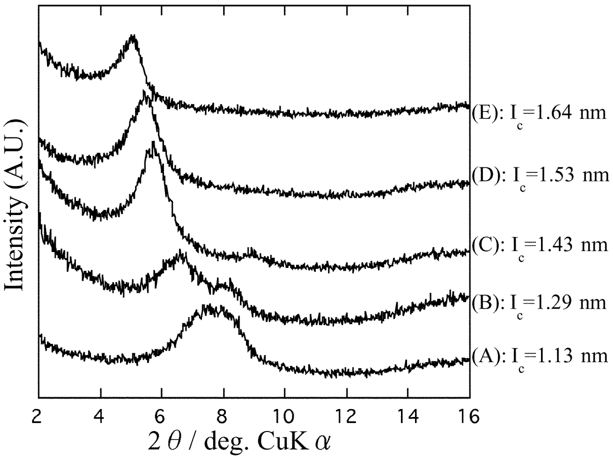

Fig. 5 X-Ray diffraction patterns of PANI-intercalated GOs prepared from amine-intercalated GOs with various amine : GO ratios; (A): (PANI)$_{1.1}$GO from (*n*-hexadecylamine)$_{0.73}$GO with I_c = 1.99 and 3.53 nm, (B): (PANI)$_{1.3}$GO from (*n*-hexadecylamine)$_{0.97}$GO with I_c = 1.99 and 3.53 nm, (C): (PANI)$_{2.8}$GO from (*n*-hexadecylamine)$_{1.9}$GO with I_c = 3.53 nm, (D): (PANI)$_{3.3}$GO from (*n*-hexadecylamine)$_{2.9}$GO with I_c = 4.96 nm and (E): (PANI)$_{5.0}$GO from (*n*-hexadecylamine)$_{3.9}$GO with I_c = 4.96 nm.

3-2 Preparation of PANI-intercalated FeOCl

Fig. 6 shows the X-ray diffraction patterns of FeOCl, (*n*-hexadecylamine)$_{0.5}$FeOCl, and PANI–FeOCl composites with the initial PANI–*n*-hexadecylamine-intercalated FeOCl weight ratio of 0.3 : 1. After the reaction between (*n*-hexadecylamine)$_{0.5}$FeOCl and PANI in NMP, the diffraction peaks at 2θ = 2.0, 3.9, 5.8, 7.8, 9.7 and 11.2° due to (*n*-hexadecylamine)$_{0.5}$FeOCl completely disappeared and new peaks at 2θ = 7.0 and 14.0° were observed as shown in Fig. 6 (C) when 30 mg of PANI was added. In the FT-IR spectrum of this sample, the absorption peak around 2900 cm^{-1} due to the amine -CH_2- groups almost disappeared and SEM observation showed that no excess PANI particles were

Table 1 Preparation conditions, composition and I_c values of PANI-intercalated GOs

$C_{16}H_{33}NH_2$: GO ratio	Amount of added PANI/mg per 50 mg $C_{16}H_{33}NH_2$–GO	Composition	I_c value/nm
0.73	30	(PANI)$_{1.1}$GO	1.17
0.97	30	(PANI)$_{1.3}$GO	1.33
1.9	30	(PANI)$_{2.8}$GO	1.47
2.9	40	(PANI)$_{3.3}$GO	1.57
3.9	50	(PANI)$_{5.0}$GO	1.68

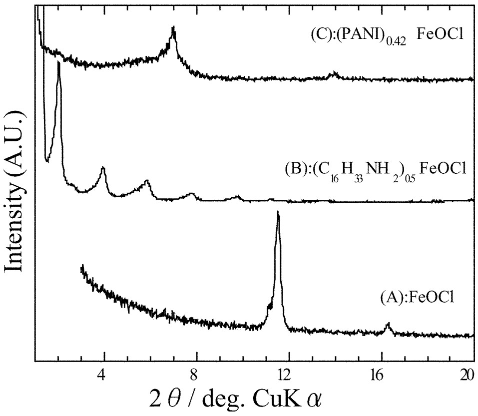

Fig. 6 X-Ray diffraction patterns of FeOCl, (n-hexadecylamine)$_{0.5}$-FeOCl, and PANI–FeOCl composites with a nominal PANI–n-hexadecylamine-intercalated FeOCl weight ratio of 0.3 : 1.

deposited on the surface area. These facts indicated that the exchange reaction of amine by PANI had occurred, providing PANI-intercalated FeOCl as was observed for the reaction between amine-intercalated GO and PANI presented in the previous section. When the amount of added PANI was smaller or larger than 30 mg, either the diffraction peak at 2.0° due to unreacted amine-intercalated FeOCl in the X-ray diffraction pattern or the absorption peak around 2900 cm^{-1} due to amine -CH$_2$- groups in the FT-IR spectrum was observed. The composition of PANI-intercalated FeOCl calculated from the weight change during reaction was (PANI)$_{0.42}$FeOCl. The increase of interlayer spacing as the result of intercalation of PANI into FeOCl was 0.49 nm (I_c = 1.28 nm). Comparing the product prepared in this study with PANI-intercalated FeOCl ((PANI)$_{0.16-0.28}$FeOCl, I_c = 1.39–1.45 nm) prepared by *in situ* polymerization,[8,10] the I_c value was slightly smaller and the PANI content was larger, which indicates that the density of PANI in the interlayer spacing was considerably larger.

On the other hand, when (n-hexadecylamine)$_{1.0}$FeOCl with higher amine content was used as a starting material, the I_c value of the obtained intercalation compound was 1.38 nm, slightly larger than that obtained above. However, a large amount of PANI (150 mg per 100 mg of starting material) was needed in order to accomplish complete substitution of amine by PANI and excess PANI deposited on the sample was inevitable, which made it impossible to determine the composition of the product.

3-3 Structure of PANI-intercalated GOs and FeOCl

Various sizes (0.34–1.2 nm) for the intercalated PANI in layered materials have been reported.[7–25] In PANI-intercalated materials except for copper carboxyethylphosphate, MoS$_2$, Mn$_{0.86}$PS$_3$ and V$_2$O$_5$ hydrogels,[7–13,23] they were 0.49–0.68 nm, which indicated that the benzene rings of PANI were arranged in a zigzag conformation and located perpendicular to the layer. On the other hand, in MoS$_2$ and montmorillonite, it was only 0.34–0.42 nm, suggesting that the benzene ring of PANI was lying flat.[15,24] Based on the reported structural analyses of PANI,[32,33] the former would possess a similar structure to that of the ES-I phase and the latter to that of the ES-II phase. The interlayer spacings of PANI-intercalated copper carboxyethylphosphate,[13] Cd$_{0.73}$PS$_3$[23] or V$_2$O$_5$ hydrogels[12] were extremely large: 1.02, 1.015 and 1.2 nm, which were almost twice the former values. The authors suggested that the PANI chains lie as a double layer in the interlayer spacing of the host lattice.

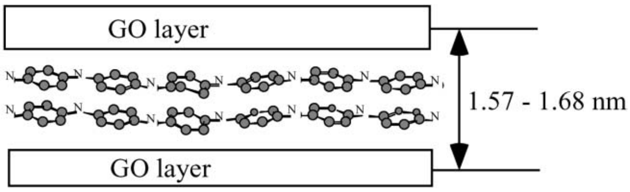

Fig. 7 Structure model for PANI-intercalated GOs with double planar PANI chains.

The increase of the interlayer spacing in PANI-intercalated GOs appeared to increase almost linearly without an apparent plateau, however, based on the above reports, the sizes of PANI in the GO and FeOCl layer might be classified into three, 0.37 nm, 0.49–0.67 nm and 0.77–0.88 nm. The former two sizes are almost the same as those of the other PANI-intercalated layered materials reported in the literature. Therefore, PANI chains would lie in the GO gallery as planar ones with their benzene rings parallel to the layer and zigzag ones, respectively. Here, the PANI content; 1.1 benzene ring per GO unit, seems too much when the benzene rings of PANI lie parallel to the GO layer. As discussed in section 3-1, this would be because the adsorbed PANI on the surface and co-intercalated NMP were neglected and the PANI contents in the samples were overestimated. The above two arrangements of PANI chains were observed for ES-II and ES-I type emeraldine salts of PANI. On the other hand, 0.77–0.88 nm for the size of intercalated PANI chains was almost twice that for PANI chains with their benzene rings lying flat. Considering the large PANI contents in these products, PANI might lie as a double layer with their benzene rings parallel to the GO layer (ES-II type). The structure model for this phase is schematically illustrated in Fig. 7.

The reason for the wide variety of PANI-intercalated GO would be as follows.

The structure of GO has not been determined yet,[34–36] however, it is known that GO has various functional groups such as hydroxy, ether and carbonyl groups.[37] The amine molecules are bonded to these groups *via* hydrogen bonding, therefore, slightly different interactions between these groups and amine molecules would lead to various amine-intercalated GO free from unreacted GO and with different compositions, and as the result, various PANI-intercalated GOs were obtained.

Conclusions

Various PANI-intercalated GOs and FeOCl were synthesized *via* exchange reaction between n-hexadecylamine-intercalated precursors and PANI in an organic solution. By changing the amine contents in the starting materials, the composition and I_c value of PANI-intercalated GOs varied in a wide range; (PANI)$_{1.1}$GO–(PANI)$_{5.0}$GO and 1.14–1.68 nm, respectively. Both the PANI content and I_c values increased with the increase of amine contents in the starting materials. On the other hand, only one type of PANI-intercalated FeOCl with the composition of (PANI)$_{0.42}$FeOCl and I_c value of 1.26 nm was obtained without excess PANI particles. For (PANI)$_{5.0}$GO, a new structure model was proposed in which PANI chains with their benzene ring parallel to the GO layer lie as a double layer. The increase of amine content in the starting material caused the deposition of excess PANI particles on the surface of PANI-intercalated FeOCl. These PANI-intercalated materials obtained in this study are expected to show good electrochemical performance as a cathode in a lithium battery. Finally, the authors believe that the present synthetic method to replace previously intercalated amine with PANI would be widely available for obtaining PANI-intercalated layered materials.

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