

Synthesis of polyaniline-intercalated graphite oxide and their electrochemical properties

Sunhye Yang^a, Ick Jun Kim, Min Je Jeon, Seong In Moon and Hyun Soo Kim

Korea Electrotechnology Research Institute, 28-1 Sungju-dong, Changwon 641-120, Korea

Abstract

Several papers have been published on the synthesis and properties of the polymer-intercalated layered materials such as graphite oxide, metal phosphates, iron oxychloride, molybdenum disulfide, etc. These intercalation compounds are expected to show new function such as optics, catalyst, charge storage and so on. Graphite oxide(GO) has been reported to possess C-H and epoxide functional group. Because of these groups, graphite oxide can easily absorb polar molecules and polar polymer to form nanocomposites of intercalated graphite oxide. In this study, polyaniline(PA)-intercalated Graphite oxide(GO) composite was synthesized by the delamination/ reassembling method in N-methyl-2-pyrrolidone(NMP) solvent, and was characterized by XRD, DSC, TGA, and SEM. These intercalation compound of GO were synthesized by the reaction between exfoliated GO layer and polymer. The X-ray diffraction peaks of GO appeared at around $2\theta=15^\circ$, and those of PA /GO composite shifted to lower angles(around $2\theta=9^\circ$). The thermal analysis demonstrated that the presence of GO enhances the char residue of the nanocomposite. The electrochemical properties of PA-intercalated GO composite as an electrode material for EDLC were also examined.

Introduction

Recently graphite/polymer nanocomposites have been studied and these intercalation compounds are expected to show superior physical and chemical properties that are dramatically different from their bulk counterparts such as electrical property [1], mechanical property [2], thermal behavior [3], surface and interfacial properties [4], and so on. Graphite oxide(GO) have strong covalent bonding within the layers. Some functional group, such as hydroxyl, carboxyl, and other group, bound to carbon sheets in GO lamellae make graphite oxide hydrophilic and give rise to rich intercalation chemistry. These groups make graphite oxide easily absorb polar molecules and polar polymer by different means and react with them to form graphite oxide intercalated nanocomposites or exfoliated nanocomposites [5]. And the insertion of electrically conductive polymers into graphite oxide is interest in battery electrode or energy storage due to properties such as enhanced mechanical strength and increased electrical conductivity.

In this study, polyaniline-intercalated graphite oxide nanocomposite was investigated in detail, based on the results of thermal decomposition products and *in situ* X-ray diffraction measurements were analyzed by SEM and X-ray diffraction measurement. And the polyaniline-intercalated graphite oxide was taken heat treatment at 500°C for 12hours under vacuum. The pyrolyzed polyaniline-intercalated graphite oxide was used electrode for EDLC and their electrochemical properties were measured.

Experimental

Needle coke derived from coal tar pitch and calcinated at 1100°C was supplied by Nippon Steel Chemical Co. Ltd. For the oxidation of needle cokes, needle cokes (5g) and sodium chlorate with the range 12.5 to 50g were put in dilute nitric acid (150ml), and then stirred at room temperature during 24 hrs. After oxidation or activation, needle cokes were thoroughly washed with distilled water and dried under vacuum at 100°C.

The electrodes were composed of the oxidized coke, carbon black as an electric conductor and polytetrafluoroethylene (PTFE). A mixture containing the oxidized coke, carbon black with 10 wt.% and PTFE with 10 wt.% was mixed with water. A paste obtained by drying the mixture was repeatedly roll-pressed for the modification of the sheet type electrode. The cell capacitors were constructed with an electrolyte impregnated the separator sandwiched between the electrodes, whose size was 2×2cm². These assemblies were housed in Al-laminated film cells. After an organic electrolyte solution of 1.2M Et₄NBF₄ in AcN. was poured, the cell capacitors were sealed taking out the leads.

Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the GO, polyaniline-intercalated GO composite and polyaniline, respectively. The strongest peak at $2\theta=13^\circ$ corresponds to the (001) diffraction peak of GO, which is a typical layered material (see Fig. 1, trace a). The 2θ value corresponds to an interlayer spacing (I_c) of 6.8Å. Upon intercalation, the (001) diffraction peak for polyaniline-intercalated GO composite shifts to a lower angle, and the I_c of polyaniline-intercalated GO increased to 9.8Å from 6.8Å of GO (fig. 1, trace b). The 3.0Å interlayer expansion is the result of inserting a single layer of polyaniline.

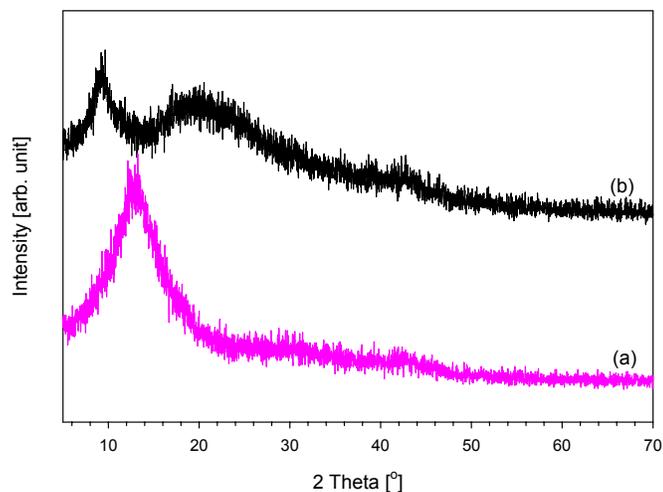


Figure 1. X-ray diffraction of graphite oxide (a), the polyaniline-intercalated GO composite (b)

The XRD result also indicates that the chain of polyaniline with extended-chain conformation exist in a dimensionally confined environment (9.8Å), thus polyaniline-intercalated graphite oxide is a GO/nano-polyaniline composite. We suggest that the extended-chain conformation should be hydrogen bond formation between -NH and -N- groups of polyaniline and the oxygen functional groups of the GO layers.

TGA curves of the GO, the polyaniline-intercalated GO composite, and polyaniline are given in Fig. 2. Fig. 2 is shown that the GO and the GO and the polyaniline-intercalated GO composite have different weight loss. The weight loss of GO up to 150°C is 8%, which is attributed to the removal of water from the GO. However, the weight loss of polyaniline-intercalated GO composite up to ca. 150°C is only 4%, which could be due to adsorbed co-intercalated NMP. This indicates that the intercalation of polyaniline has decreased the water content between the GO layers. The weight loss around 200°C owes to the decomposition of the oxygen functional groups in the GO layer. In this stage, GO loses 24% of its weight, and the polyaniline-intercalated GO composite only 17%. It implies that the intercalation of the polyaniline has improved the thermal stability of GO. In the last weight loss stage, the weight loss of GO can be attributed to the combustion of its carbon skeleton. However, the weight loss of polyaniline-intercalated GO composite above 500°C should be due to the decomposition of polyaniline, as shown in Fig. 2, trace c.

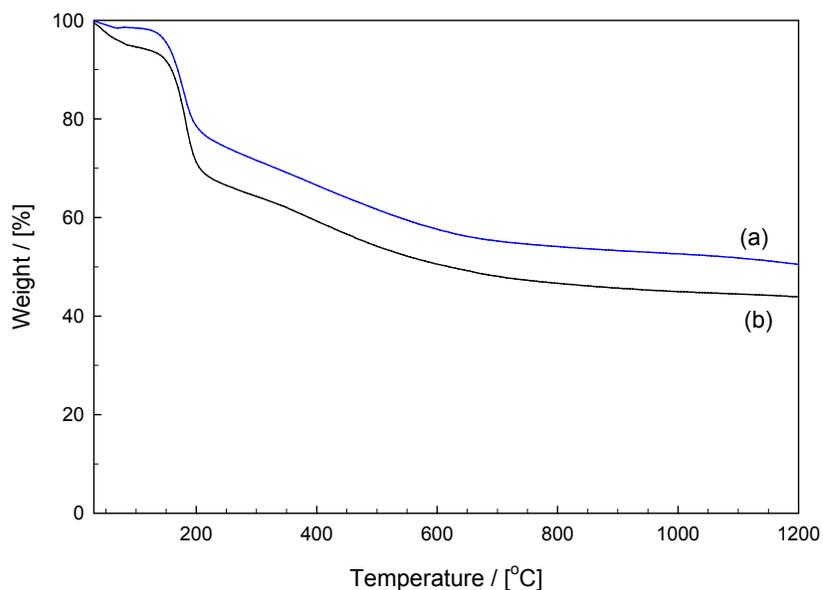


Figure 2. TGA curves of (a) GO, (b) polyaniline-intercalated GO composite

Fig. 3 show the charge-discharge curve of polyaniline-intercalated GO composite electrode in the potential range of 0 to 2.5V with Maccor test system. The charge-discharge voltage profiles of cell capacitors is fabricated with electrodes, in which composition is polyaniline-intercalated GO composite : ketjen black : PTFE = 80 : 10 : 10 wt.%, attached with the electric conductive adhesive, in which composition is carbon black : CMC = 70 : 30 wt.%. This result indicates a typical behavior of capacitive electrode. The calculation of cell capacitance was based on the following equation by assuming the discharge profiles were perfectly linear.

$$C = i\Delta t / \Delta V$$

Where Δt is the time period, ΔV the voltage charge and I the constant discharge current. As a result, polyaniline-intercalated GO electrode have exhibited large capacitance weight and volume of 26.64F/g and 26.53F/cc at the two electrode system respectively.

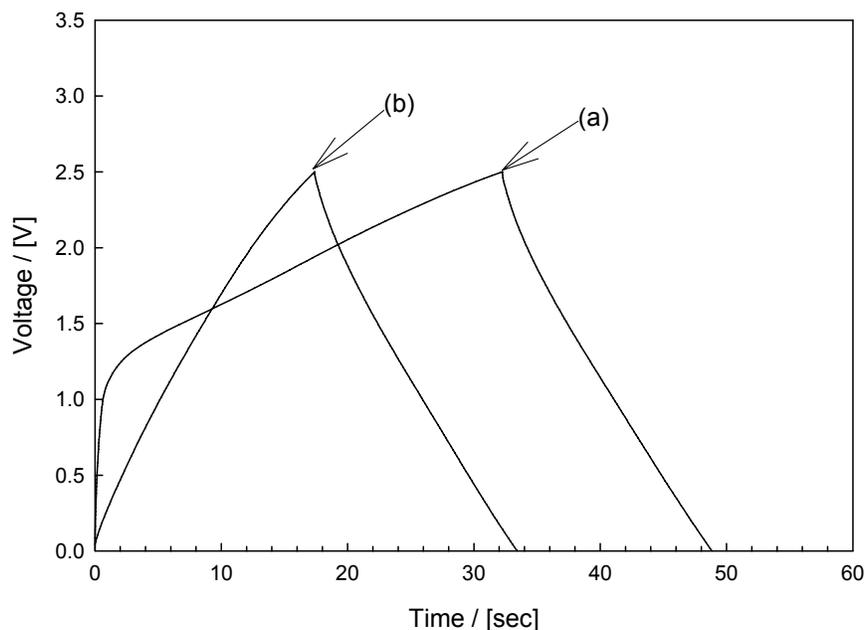


Figure 3. Charge-discharge profiles of EDLC cells prepared with polyaniline-intercalated GO. Electrolyte : 1.2M Et₄NBF₄ in AcN. (a) 1st cycle, (b) 2nd cycle

Conclusion

- 1) The (001) diffraction peak for polyaniline-intercalated GO composite shifts to a lower angle, and the I_c of polyaniline-intercalated GO increased to 9.8Å from 6.8Å of GO.
- 2) The polyaniline-intercalated GO has improved the thermal stability of GO.
- 3) The capacitor cell with polyaniline-intercalated GO electrodes has exhibited large capacitance weight and volume of 26.64F/g and 26.53F/cc. at the two electrode system respectively.

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