

Preparation and Electrochemical Characteristics of CNFs/DAAQ Electrode for Energy Storage

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Abstract - A new type of supercapacitor was constructed by using carbon nanofibers (CNFs) and DAAQ (1,5-diaminoanthraquinone) oligomer. DAAQ was deposited on the carbon nanofibers by chemical polymerization with ammonium peroxodisulfate ((NH₄)₂S₂O₈) as oxidant in the 0.1 M H₂SO₄. Polymerization reaction was carried out with constant sonication. From the analysis, it is clear that surface of carbon nanofibers was quite uniformly coated with DAAQ. The performance characteristics of the supercapacitors have been evaluated using Cyclic Voltammetry. CNFs/DAAQ based composite electrode showed relatively good electrochemical behaviors in acidic electrolyte system. CNFs/DAAQ composite electrode showed relatively good capacitance (7 Ah/kg) compared to conventional capacitors in the range of -0.4 ~ 0.4 V.

Keywords: Supercapacitor, carbon nanofibers, 1,5-diaminoanthraquinone, composite electrode

1. Introduction

Supercapacitor is being increasingly discussed not only for backup power which is an established application to electronic equipments and computers[1, 2], but also for high power applications in pulsed lasers and electric vehicles[3, 4]. In the latter cases, it is envisaged that supercapacitors will provide bursts of power during acceleration and be used in conjunction with high energy density lithium batteries.

S. Suematsu and K. Naoi have made an attempt to design polymeric or oligomeric new materials with even higher specific capacity and higher cycleability[5]. They used aniline moiety to build up a new category of the material because of its relatively high specific capacity, its high electrocatalytic activity, and electrochemical durability. Furthermore, to increase specific capacity, they have focused on 3-electron π -conjugated system by hybridizing polyaniline backbones with other redox organic moieties of even higher specific capacity than the host matrices.

The modification of carbon nanotube by electrochemical polymerization is a feasible way to enhance capacitance[6, 7]. Q. Xiao reported the electrochemical performance of a carbon nanotubes-polypyrrole composite-carbon nanotubes-poly (3-methyl-thiophene) composite based supercapacitor [8]. Currently, carbon nanofibers have been noted as feasible materials for various fields such as hydrogen storage media and semi-fuel cell application etc[3].

Carbon nano-materials of which are on the nanometer

scale, like carbon nanotubes (CNTs) and carbon nanofibers (CNFs), are novel material in next generation and exhibits an excellent mechanical, electrically selective and height efficient hydrogen storage properties etc. So it can be applied in many field such as aerospace[9], environmental energy[10], materials industry[11], medicine science[12], electronic computer[13], security and safety[14]. However, CNF is difficult to apply supercapacitor use due to their poor cycle ability. It is necessary to modify their surface for increasing their duration. Fibers of amorphous conductive polymer, such as polyaniline and polypyrrole are electrochemically synthesized in either porous template membranes or with electrode surface defects[8]. CNFs can be highly ordered as those derived from carbon arc[15] or highly disordered as the materials obtained from gas-phase pyrolysis[16, 17]. Electrochemical synthesis of elemental carbon is, in principle, accomplished either by anodic oxidation or cathodic reduction[18]. Electrochemical synthesis provides good control over material composition. In this study, we prepared new composite electrode. The aim of the present report is to discuss and explain on the synthesis of carbon nanofiber coated by pDAAQ and its application as active material for supercapacitor.

2. Experimental

Nanostructured CNFs was used as an active material for electrode according to previous work[19, 20]. And ammonium peroxodisulfate ((NH₄)₂S₂O₈, Aldrich), 1,5-diaminoanthraquinone (C₁₄H₁₀N₂O₂, TCI), sulfuric acid (H₂SO₄, 97 % Assay, Tokyo Ohka Kogyo) and potassium hydroxide (KOH, 85 % assay, Tokyo Ohka Kogyo) were

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Received May 12, 2005 Accepted July 23, 2005

used as received. Reagent-grade N-methyl-2-pyrrolidone (NMP) was used as solvent. Chemically synthesized DAAQ coated CNFs was used as a cathode material for electrochemical supercapacitor.

In order to form uniform and thin DAAQ oligomer film, selectively onto CNFs, we adopted three experimental step. First is to disperse CNFs as much as possible by electrostatic repulsion. The second is to promote mass transfer of the DAAQ monomers to CNF surface, and the third is to demonstrate the selective polymerization upon CNF surface by use of anionic oxidants. After dispersing CNFs (100 wt. %) in the polymerization solution including DAAQ monomers (rates : 100 wt. %, 200 wt. %, 300 wt. %, 400 wt. %, 500 wt. %), are well known to be adsorbed onto basal plane of graphite. In order to form the DAAQ oligomer film on CNF as uniform as possible, mass transfer of the DAAQ monomer was enhanced by cavitation micro-jet stream generated by ultrasonic sound. During ultrasonic irradiation (48 h), ammonium peroxodisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) as the oxidizing agent was dropped into the polymerization solution. The oxidant anion is considered to be adsorbed electrostatically onto the CNFs surface, then, the adsorbed anions can oxidize the adsorbed DAAQ monomers.

Then, the oxidized monomers are subjected to polymerization into DAAQ oligomer selectively onto CNF surface, leading to the formation of CNFs/DAAQ composite. To prepare CNFs/DAAQ composite films, DAAQ coated CNF was dispersed in NMP solution and stirred for 24 h. The resultant solution was cast on carbon plate and dried under vacuum for 12 h at 60 °C to give rise to composite film.

For morphological observation of as-prepared and hot nitric acid treated CNFs, SEM (LEO-1530FE) measurements were carried out. Thermogravimetric analysis (TA4100, MDSC2910) was performed to comment 10 °C/min and nitrogen purge gas of 110 mL/min. And XRD patterns were collected using a SCINTAG DMS2000 equipped. Cyclic voltammetric measurement was performed with a WBCS 3000 battery cyler system computer controlled potentiostat-galvanostat.

Electrochemical measurements were conducted using a conventional three-electrode configuration. CNFs/DAAQ on carbon plate electrode was used as the working electrode. A Pt wire and KCl-saturated Ag/AgCl were used as the counter and reference electrodes, respectively. 4 M H_2SO_4 solution was used as the electrolyte. The non-coated carbon plate was cleaned by sonication in acetone for 5 and 10 min, respectively. This plate was dried in vacuum oven for one day. Dissolved electrode active material in NMP solution has been drop-coated on carbon plate of current collector. Cyclic voltammetry was tasted on ranges of -400 ~ 400 mV. Scan rate was 50 mV/s and it was shown after

3th cycle. All the measurements were taken at room temperature and under nitrogen atmosphere.

3. Result and Discussion

3.1 Characteristics of Structure analysis for composite materials

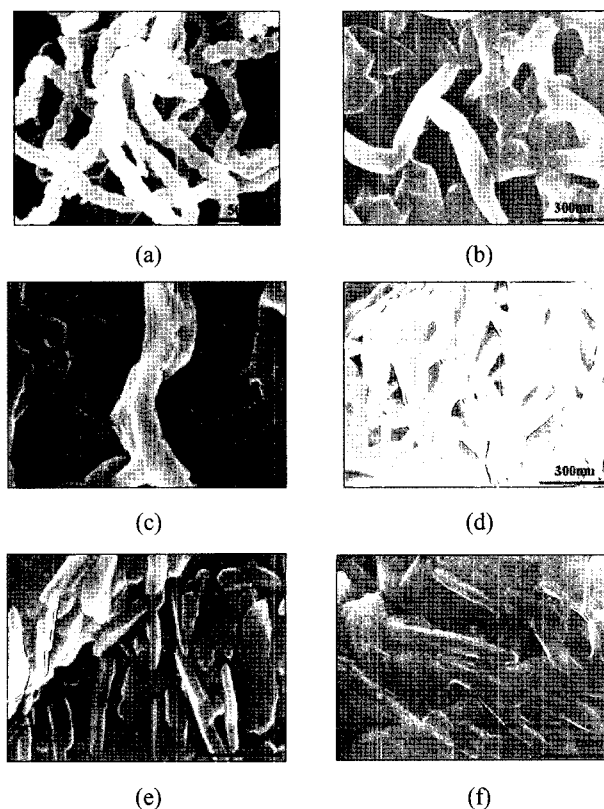


Fig. 1 SEM images of CNFs/DAAQ materials different wt. % rates: (a) CNFs, CNFs : DAAQ wt. % rates (b) 1:1 (c) 1:2 (d) 1:3, (e) 1:4, (f) 1:5

Changes in morphology after CNFs coated by DAAQ oligomer were evaluated by SEM measurements. Figs. 1 represents the SEM images of CNFs/DAAQ composite materials in different weight %. As-prepared CNFs were observed for same sizes (length and diameter) of typical spiral type CNFs in Fig. 1 (a). The shapes of these samples were classified as a part of a straight form with a thick outer diameter and the rest as a curved style with a narrow outer diameter. The SEM image of CNFs/DAAQ composite material was different to that of the result in Fig. 1 (b) ~ (e). The above results, indicates the formation of CNFs/DAAQ composite material. The oxidant anion is considered to be adsorbed electrostatically onto the CNFs surface. Then the adsorbed anions can oxidize the adsorbed DAAQ monomers. And increase a thick outer diameter of increasing insertion weight in DAAQ monomer.

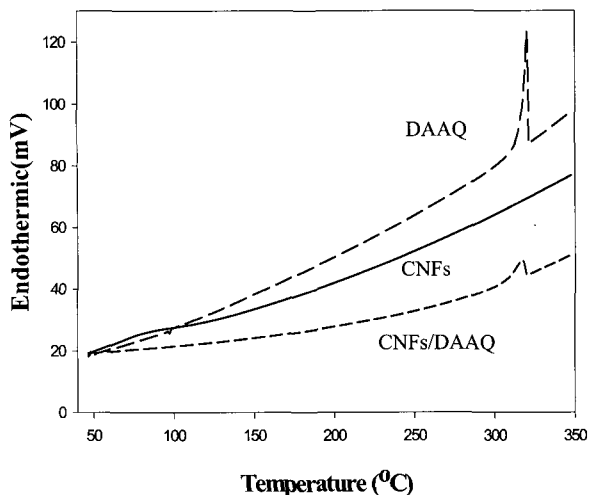


Fig. 2 DSC thermograms of purified CNFs, DAAQ and CNFs/DAAQ.

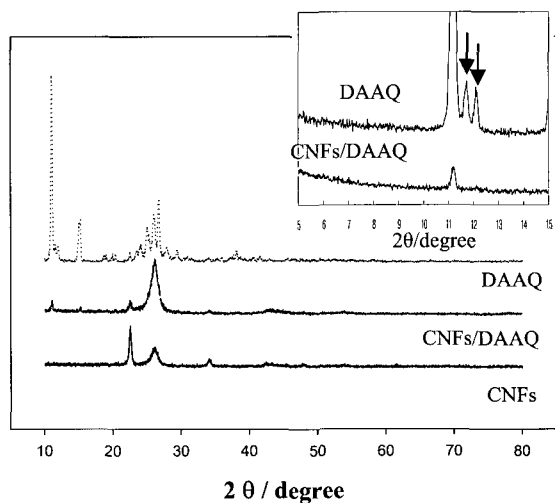
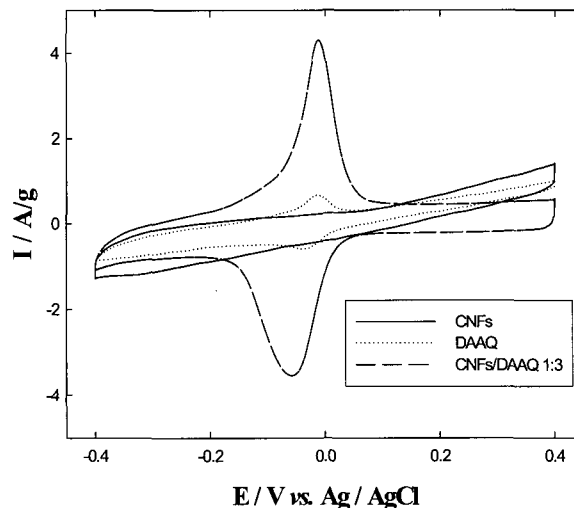


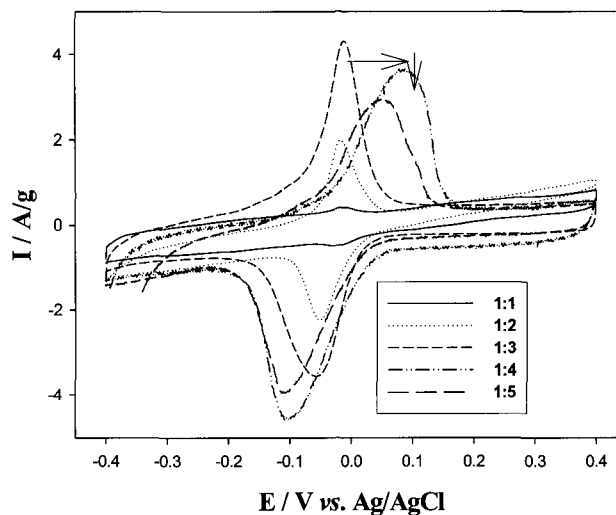
Fig. 3 XRD patterns of purified CNFs, DAAQ and CNFs/DAAQ.

Fig. 2 and Fig. 3 shows the obtained DSC thermograms and XRD patterns of DAAQ monomer, CNFs and DAAQ oligomer state. In the spectrum of the DAAQ monomer, a major peak is observed at $2\theta = 11.06$ and side peak. The appearance of the peak in Fig. 3 DAAQ and CNFs/DAAQ in major peak and side peak suggests that DAAQ maintains its crystal structure even after oligomerization and that the interstitial distance of monomer-monomer stacking extends. Fig. 2 shows structural changes of as-prepared CNFs and DAAQ in each 80 and 220 °C, but CNFs/DAAQ composite similar to as-prepared DAAQ monomer about 220 °C. The results obtained from SEM images, DSC thermograms and XRD patterns, indicates that DAAQ monomer is electrostatically coated onto the CNFs in oligomer states.

3.2 Electrochemical Characteristics



(a) cyclic voltammograms



(b) cyclic voltammograms of different wt% ratio

Fig. 4 Cyclic voltammograms of CNFs, DAAQ and CNFs/DAAQ electrodes.

Fig. 4 shows the cyclic voltammograms of DAAQ and CNF, respectively. In order to determine a good composition ratio of CNFs/DAAQ electrode, the capacitance with different ratios of active material were measured in 4 M H_2SO_4 aqueous solution. The voltammogram shows a single redox peak in +0.05 and -0.05. The DAAQ coated CNFs composite shows current increased compared to those of DAAQ and CNFs as shown in Fig. 4 (a). The anomalous increase in the current was due to enhancement in the electronic and/or ionic transfer across two layers (CNFs/DAAQ) of the nano-composite.

With increasing of conducting material content ratio, the capacitance was increased on account of improvement in CNFs inner resistance. When DAAQ conducting polymer material amount was poor, double layer capacitance was

only shown without pseudocapacitance. On the contrary, not only double layer capacitance but also pseudocapacitance was shown in higher DAAQ conducting polymer material content ratio, considering the presence of pseudo-plateau in the cyclic curve. Furthermore, it kept the higher capacity than the electrode with weight rate 400 % as shown in Fig. 4 (b) and Table 1. Therefore, in this work, electrochemical measurements were carried out based on CNFs 100 wt. %, DAAQ 400wt. %.

Table 1 Specific capacity of various materials by 4 M H₂SO₄

Active material	DAAQ	CNFs	CNFs/DAAQ (1:1)	CNFs/DAAQ (1:2)	CNFs/DAAQ (1:3)	CNFs/DAAQ (1:4)	CNFs/DAAQ (1:5)
Specific capacity (Ah/kg)	1.4	2.1	1.5	2.6	3.5	7	5.9

We compared electrochemical behavior of CNFs/DAAQ electrode in 4 M H₂SO₄ aqueous solution with that in different weight %. Table 1 shows the specific capacitance of the CNFs/DAAQ composite materials. The result is that CNFs/DAAQ composite electrode showed relatively good capacitance (7 Ah/kg) compared to different weight %. in 1 and 4 system.

Cyclic voltammogram shows reaction mechanism of faradaic reaction in 4 M H₂SO₄ aqueous solution. In the potential range from -0.1 to 0.1 V, the DAAQ oligomer exchanges two electrons by quinone/hydroquinone (Q/HQ) redox reaction, while two protons with hydrate water are exchanged. In the potential range from -0.1 to 0.1 V, the redox of the π -conjugated system occurs to exchange one electron and two anions hydrated with two molecules of water.

4. Conclusion

CNFs are covered by very thin DAAQ oligomers. The results obtained from SEM, DSC and XRD indicates that DAAQ is electrostatically coated on carbon nanofibers in oligomer state. Cyclic voltammograms indicates faradaic type of reaction mechanism with two electron exchange process. Furthermore, CNFs/DAAQ composite electrodes showed relatively good electrochemical behaviors in acidic electrolyte system and composite exhibits relatively good capacitance (7 Ah/kg) compared to conventional capacitors.

Acknowledgements

This research was supported by the Program for the Training of Graduate Students in Regional Innovation

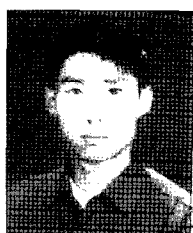
which was conducted by the Ministry of Commerce Industry and Energy of the Korean Government.

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